A chemotaxonomic study of phenolic leaf compounds in the genus *Aloe*

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ABSTRACT

This chemotaxonomic study of the leaf phenolic compounds in the genus *Aloe* is introduced by presenting a review of *Aloe* taxonomy, followed by a second review of all known leaf compounds.

A chemotaxonomic study of virtually all species of *Aloe* has made it possible to define several chemical groups in the genus of 420 species. The chemical groups are either identified by a single marker compound or by a series of unique compounds. The following groups have been identified and the chemotaxonomic value of each group is discussed:

1. An aloin / aloinoside / microdontin group, comprising 36 species, mostly of tropical origin. This group includes species not previously associated with one another.
2. An 8-*O*-methyl-7-hydroxyaloin group. Here the co-occurrence of some leaf compounds suggests that 8-*O*-methyl-7-hydroxyaloin is not homologous in the 18 species where it has been detected. Evidence is presented illustrating that 8-*O*-methyl-7-hydroxyaloin is an 'hybrid compound' which forms when two chemically divergent species (aloin- and homonataloin-containing parents) are crossed.
3. An aloenin group, comprising 16 species which are believed to be a monophyletic group.
4. A microstigmin group, indicating a taxonomic alliance between series *Purpurascentes* and series *Anguialoe*, with *A. broomii* an intermediate between the two.
5. A 10-hydroxyaloin B group, represented by series *Asperifoliae* and related species, which appears to be a drought adapted clade of tropical origin.
6. A homonataloside group, comprising 14 species, suggesting a biochemical link between the aloes of north Africa and southern Africa.
7. An aloeresin E and F group, indicating a taxonomic alignment between series *Mitriformes* and five anomalous species.
8. A plicataloside group, with its single marker compound indicating a taxonomic relationship between 20 mostly tropical east African species.
9. A flavone group. The large number of species with flavones (sections *Leptoaloe, Graminialoe, Lomatophyllum* and series *Macrifoliae*) are suggested to be basal in the genus.
10. A flavanone group. A few anomalous species produce flavanones but it is unlikely that they form a monophyletic group.

A concluding review of leaf exudate compounds (not mentioned above) is also presented which includes hypotheses on the chemotaxonomic value of chromones and anthrones in general. A chemical re-arrangement of species is presented in the form of a new 'chemical classification' for *Aloe* based on chemotypes.

These chemical groups have lead to an improved understanding of natural relationships in a genus where no satisfactory infrageneric classification has hitherto been available.

Chapter 1

Aloe taxonomy - a review

You ask me what were the secret forces which sustained me during my long fasts. Well, it was my unshakable faith in God, my simple frugal life style, and the Aloe whose benefits I discovered upon my arrival in South Africa at the end of the 19th century

Mahatma Gandhi
(In a letter to his biographer Romain Rolland)

The medicinally important *Aloe ferox* which is indigenous to South Africa (Photo: Ben-Erik van Wyk).

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CHAPTER 1

ALOE TAXONOMY - A REVIEW

> "The German Egyptologist, George Ebers (1837 - 1898) bought an ancient papyrus, now called the Ebers Papyrus, dating from the region of the Pharaoh Amen-Hotep in 1552 BC. This ancient medical treatise listing the use of plant materials as cosmetics and drugs, includes Aloes, was found between the knees of a mummy excavated near Thebes in 1858. This papyrus demonstrated the use of Aloe Vera during the preceding 2000 years and listed 12 different formulae for *Aloe* preparations".
>
> (From: *The Essential Aloe Vera*, P. Atherton, 1997)

Taxonomic interest in *Aloe* was probably initiated due to the primal use of aloes by man since early civilization. This is confirmed by inclusion of *Aloe vera* in the herbal of Dioscordes Codes Aniciae Juliana in 512 AD. This is the first illustration of any species of *Aloe*. This figure was 'borrowed' by several authors and in 1542 Fuchs published the same figure in De Historia Stirpium which was again later used by Dodonaeus in his Stiripium Historiae in 1583. This interest in *Aloe vera* heralds the start of aloe taxonomy. Although several references to *Aloe* appear since early history, the authenticity of the material is in doubt as aloes were generally confused with members of the genus *Agave,* this confusion is still prevalent today. In 1680 eight illustrations appeared in Muntingus Aloidarun of which seven were agaves.

The most important contributions to *Aloe* taxonomy are briefly discussed below and summarised in Table 1.1 at the end of Chapter 1.

In the period 1600 - 1800 various descriptions and lists of *Aloe* species were published. Initially *Gasteria* and *Haworthia* fell within the taxonomic concept of *Aloe*. Most of the work in the period was summarised by Baker in 1880 in his Synopsis of Aloineae and Yuccoideae in which he mentioned 61 species that were known up to then. In 1804 Haworth published a review of all aloeaceous taxa in the Transactions of the Linnean Society of London. Although no distinction was made between *Aloe*, *Gasteria* and *Haworthia* he commented on the differences between these three groups. In 1809 Duval suggested that *Gasteria* and *Haworthia* should be separated from *Aloe*; a move which provided more clarity in the early taxonomy of *Aloe*. This distinction as suggested by Duval was acknowledged by Haworth in his Synopsis Plantarum Succulentarum (1812) in which Haworth described 30 species of *Aloe*. The work of Schultes and Schultes (1929) in Systema Vegetabilum gave an extensive account of *Aloe* (South African and Tropical species). In 1880 Baker presented a revision of *Aloe* in Synopsis of Aloineae and Yuccoideae published in the Journal of the Linnean Society (Botany). In 1908 the most comprehensive work on *Aloe* was published in Das Pflanzenreich (Liliac.-Aloin.).

***Aloe vera*, the earliest known illustration of any species of *Aloe* (Photo: Reynolds, 1966).**

From this period up to the publishing of the benchmark publication of Reynolds in 1950, various species were described in a variety of journals. The two monumental publications by Reynolds in 1950 and 1966 laid the foundation and corner stone for the taxonomy of *Aloe*. In the Aloes of Southern Africa, Reynolds (1950) includes 132 species of *Aloe* and mostly follows the system of classification as published in Das Pflanzenreich Liac.-Aloin. in 1908. This system of classification and that adopted by Reynolds is an unitarian system and does not necessarily reflect natural relationships as morphological similarity is the only criterion used to group species. This is more obviously reflected in the treatment of the Aloes of Tropical Africa and Madagascar (Reynolds, 1966) where species were placed in several 'numerical groups'. Although this work provides a comfortable 'taxonomic handle' to get a grasp on this large and daunting genus it does not suggest any phylogenetic relationships at the infra-generic level. Since these valuable contributions by Reynolds, many new species have been published by several *Aloe* taxonomists (not included in Table 1.1). Len Newton published descriptions of numerous species, mostly from East Africa. New species from the Arabian Peninsula, Somalia and Madagascar have enjoyed the interest of succulent specialist John Lavranos. Larry Leach described numerous species from Namibia and Angola. Susan Carter-Holmes with various co-workers have recorded new species of *Aloe* and have speculated on relationships between taxa mostly in east Africa. Her interest in *Aloe* culminated in the Flora of Tropical East Africa (Aloaceae) in 1994.

The present classification system of *Aloe*

Dahlgren (1985) divided the Monocotyledons into several superorders of which the Liliflorae is the largest. The order Asparagales houses the family Asphodelaceae which is sub-divided into the *Asphodeloideae* and the *Alooideae* (Table 1.2). The Alooideae consists of six genera of which *Aloe* is the largest.

The present classification for *Aloe* is diagrammatical presented in Figure 1.1. This four-hierarchal system is based on Berger (1908) and Reynolds (1950 & 1966). In his treatment of the aloes of Southern Africa, Reynolds (1966) divided the genus into various sections, subsections and series. In his 1966 treatment he arranged the species in numerical groups based on an assemblage of morphological characters or on a single characteristic morphological feature (e.g. plants with clavate perianths). He did include cross-references where he thought species to be related to the south African species. The section dealing with the Malagasy species remain the biggest challenge as these species are simply arranged in

groups without well-defined morphological characteristics.

Table 1.2. Genera of the two sub families in the Asphodelaceae. The estimated number of species is given for each genus.

Asphodelaceae sensu Smith & Van Wyk (1998)			
Asphodeloideae		**Alooideae**	
Asphodeline	14	*Aloe*	424
Asphodelus	12	*Astroloba*	7
Bulbine	60	*Chortolirion*	1
Bulbinella	22	*Gasteria*	16
Eremurus	40	*Haworthia*	70
Jodrella	3	*Poellnitzia*	1
Kniphofia	70		
Thrachyandra	50		

The first section *Aloinella* Berger is mentioned in Reynolds (1950) . Berger (1908) created this monotypic section containing the Malagasy endemic *A. haworthioides*. Reynolds (1966) includes *A. haworthioides* in Group 1 together with 11 other 'small aloes' from Madagascar. Sections *Graminialoe* Reynolds and *Leptoaloe* Berger contain the grass-like aloes. It is not clear why Reynolds created *Graminialoe* as the distinction between these two sections seem to be vague. Groups 1 and 2 (Reynolds, 1966) corresponds to sections *Graminialoe* and *Leptoaloe* respectively. These two sections (and Groups 1 and 2) collectively contain all the grass-like aloes with linear leaves and minutely dentate margins. The grass-like aloes are mostly restricted to southern Africa. Smith (1990) created *Aloe* section *Graminialoe* Reynolds subsection *Bowieae* (Haw.) G.F. Smith to accommodate *A. bowiea*

Section *Bulbiformes* Christian contains four species of which the macro-morphology fits the grass-like aloes but the leaf bases of these aloes dilate underground forming prominent bulbs. The genus *Lomatophyllum* has recently been included in *Aloe* as *Aloe* section *Lomatophyllum* (Willdenow) Rowley sect. nov. and consists of *ca.* 20 species all characterised by the fruit which is a berry. Section *Eualoe* Berger is the largest section containing all the 'typical aloes' and consists of five subsections. The subsection *Parvae* consists of three series; series (1) *Haemanthifoliae* Berger is monotypic containing *A. haemanthifoliae.* Series (2) *Longistylae* Berger comprises four morphologically diverse species and series (3) *Aristatae* Berger is

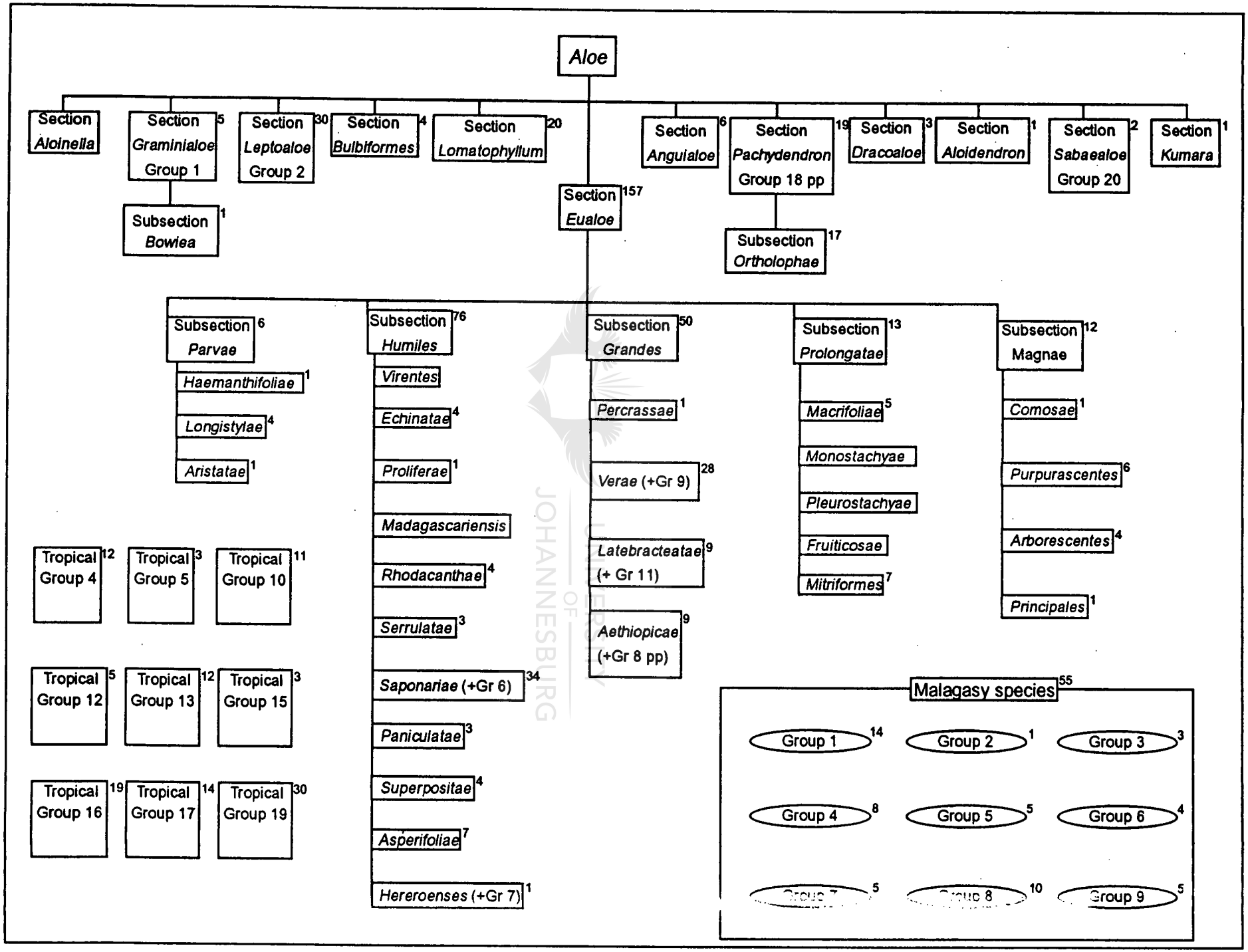


Figure 1.1: Taxonomic hierarchy for *Aloe*. All 'post-Reynolds' species have been placed in groups to which authors have expressed them to be related. The number at the top right is the total number of species in each group.

monotypic with *A. aristata*. Subsection *Humiles* is the largest consisting of 11 series. Series (4) *Virentes* Berger is represented by a single 'doubtful' species *A. virentes*. Series (5) *Echinatae* Salm-Dyck contains *Aloe humilis*, *A. krapohliana* and *A. melanacantha* with *A. erinacea* added recently (Hardy 1972). The monotypic series (6) *Proliferae* Salm-Dyck comprises *Aloe brevifolia* and its varieties. Berger created series (7) *Madagascariensis* Berger with *A. deltoideodonta* being the only representative. Series (8) *Rhodacanthae* Salm-Dyck includes four South African species; *A. pratensis*, *A. polyphylla*, *A. lineata* and *A. glauca.* Series (9) *Serrulatae* Salm-Dyck accommodates three species which more closely resemble the related genus *Gasteria*. The three species included in this group are *A. sladeniana*, *A. variegate* and *A. dinteri*. All the maculate aloes of which the perianth shows a constriction above the ovary are included in series (10) *Saponariae* Berger which also includes species in Group 6 (Reynolds, 1966). This is a large group of species of which the taxonomy at species level is problematic. The closely related series (11) *Paniculatae* Salm-Dyck consists of three species (Reynolds, 1950) bearing a strong resemblance to species in series *Saponariae*. Series (12) *Superpositae* Pole Evans comprises four species; *A. suprafoliata*, *A. thomcroftii*, *A. pretoriensis* and *A. chistianii*. Although an asperous leaf surface is a common character in *Aloe*, Reynolds included all the species from southern Africa in series (13) *Asperifoliae* Berger. Various species were later described as being related to this group. Series (14) *Hereroenses* Reynolds is monotypic containing *A. hereroensis* which is equivalent to Group 7 (Reynolds, 1966).

Subsection *Grandes* constitutes four species and includes many of the species from tropical Africa (Reynolds, 1966). Series (15) *Percrassae* Berger is monotypic containing *A. littoralis* (syn. *A. rubrolutea*). Reynolds includes no South African species in series (16) *Verae* Berger as amended. This is a large group of species (Group 9, Reynolds, 1966) with the historical important *Aloe vera* as the type. Series (17) *Latebracteatae* Berger is represented by three South African species which are morphologically very similar together with species included in Group 11 (Reynolds, 1966). It is uncertain which species belong to series (18) *Tropicales* Berger as *A. abyssinica* Lam. which is the type is included in Reynolds (1966) under species imperfectly known. Series (19) *Aethiopicae* Berger includes all species of which the perianths are trigonously indented. Species in Group 8 (Reynolds, 1966) are partially included in this series. The last series (20) *Cernuae* Berger in this subsection is represented by *Aloe capitata* from Madagascar.

The fourth subsection *Prolongatae* also consists of five series. Series (21) *Macrifoliae* Haworth

comprises all the scandent aloes which are only represented in southern Africa.

Series (22) *Monostachyae* Berger, series (23) *Pleurostachyae* Berger and series (24) *Fruiticosae* Berger were not recognised by Reynolds in his 1966 treatment and the small number of species contained in each of the three series are distributed with allied species in the various tropical groupings. The last series (25) *Mitriformes* Salm-Dyck comprises seven species mostly characterised by a long perianth and pedicel and a dense umbel. Several species have been described since Reynolds' treatment with comments relating them to this group.

Subsection *Magnae* is organised into four series of which two are monotypic. Series (26) *Comosae* Berger is represented by *A. comosa*. Series (27) *Purpurascentes* Salm-Dyck contains five South African species. Four tall shrub-like or arborescent aloes are grouped in series (28) *Arborescentes* Salm-Dyck. The last series in subsection *Magnae*, series *Principales* Berger constitutes a single species, *A. speciosa*.

Moving up in the hierarchy back to sectional level, Reynolds created section *Anguialoe* to contain the aloes with sessile and campanulate flowers. The section *Pachydendron* Haworth is divided into subsection *Ortholophae* Christian housing the aloes with oblique racemes and secund flowers. Group 14 created by Reynolds (1966) is also included in subsection *Ortholophae*. The remaining species in section *Pachydendron* are usually tall stemmed aloes with large inflorescences.

The last sections contain the majestic tree-like aloes. Three species, *A. ramosissima*, *A. dichotoma* and *A. pillansii* are included in section *Dracoaloe* Berger. Section *Aloidendron* Berger is monotypic with *A. barberae*. Section *Sabaealoe* Berger has no South African representatives and although not explicitly stated, Reynolds (1966) probably related his Group 20 (*A. sabaea* and *A. eminens*) to this section. The last monotypic section *Kumara* Medicus is represented by *Aloe plicatilis* from the south western Cape.

This concludes the discussion on the formal taxonomic arrangement of species as known today. Reynolds created various informal groups in his 1966 treatment and he was unable to correlate them to the existing classification as detailed in his 1950 treatment. He created informal groups using a single morphological character or an assemblage of various characters to define his groups. These groups are shown at the bottom left of Figure 1.1. The groups have been 'latched onto' the formal classification where his groups correlated to the existing hierarchical structure.

He followed very much the same approach with the Malagasy species. Here he created nine

groups (bottom right) based on various morphological characters. Reynolds (1966) however emphasised that he is unable to draw any taxonomic correlations between the Malagasy endemics and the aloes of the African continent.

Aloe has enjoyed the interest of many succulent hobbyists who have contributed immensely to our present understanding of the genus. The publications of various societies (e.g Excelsa, Aloe, Journal of the Cactus and Succulent Society (U.S) and British Cactus and Succulent Journal) have been the vehicles for promoting knowledge, interest and collaboration on *Aloe*.

Although previous taxonomic alignment of species have relied strongly on morphological characters, various authors have studied additional characters for taxonomic evidence. These studies are briefly summarised below.

Anatomy

Most research relating to anatomy of *Aloe* has been done on the cuticular sculpturing. In 1976 Cutler & Brandham demonstrates that the leaf surface characters are genetically controlled and speculate on the value of epidermal characters in taxonomic studies. The researchers at Kew integrated anatomical evidence with various other characters and with this multi-disciplinary approach they studied the evolution of various species. The conclusion drawn from these studies are that epidermal characters used in conjunction with other characters are of taxonomic value (for references to these studies see the cited examples under 'cytology'). Newton (1976) illustrated the use of epidermal characters in identifying 'unknown' material when compared to authentic specimens.

The internal anatomy has been studied by Beaumont, who concentrated her study on the secretory cells (Beaumont *et al.* 1985 & 1986 & Beaumont, 1986). As indicated by Cutler in 1972, the anatomy of the leaf section of *Aloe* shows little variation restricting its use as a taxonomic character. Similar conclusions were made by Steyn *et al.* (1998) on the comparative pollen morphology which seems to be of little taxonomic value. Steyn and Smith (1998) remarked on the ovule orientation and curvature in Aloaceae which is exclusively hemitropous, a character of limited value at the generic level.

Cytology

References to literature indicate that the first chromosome counts for *Aloe* (*A. striata*) were published by Müller in 1912. Riley (1959) tabulates all known chromosome counts for *Aloe*

incorporating the work of Müller (1945), Afify (1945), Mendes (1950) and Snoad (1951a and 1951b), Kondo & Megata (1943), Resende (1937a), Riley (1959), Sato (1937 & 1942), Taylor (1925a and 1925b), Johansen (1929), Fernandes (1931), Marshak (1934), Gioelli (1930). In this publication Riley (1959) gives the chromosome counts for 165 taxa of *Aloe*. Riley states that 95 % of all taxa are diploids (2n = 14) with a small number of species being polyploids. He concludes that the genus *Aloe* displays a low incidence of polyploidy and that chromosome numbers would shed little light on the evolution of *Aloe*. The karyotype of *Aloe, Gasteria* and *Haworthia* were extensively studied by Shamara and Mallick (1965). The conclusions were similar to those of Riley (1959) emphasising the homogeneity in the chromosome compliment. It was found that all aloes studied are diploid (2n = 14) with the exception of *A. ciliaris* (2n = 42) and *A. humilis* (2n = 21). The work of Brandham and co-workers have integrated cytological evidence with various other taxonomic characters (mostly morphology, anatomy and chemistry) The cytological evidence form these studies have been incorporated with results from other character sets to assess the evolutionary relationships (e.g. Cutler *et al.* 1980, Brandham *et al.* 1993, Brandham & Carter 1982 & 1990, Carter *et al.* 1984).

Chemistry

Due to the medicinal uses attributed to *Aloe*, scientists, especially chemists took an early interest in *Aloe* to unravel the chemical compounds responsible for the healing properties. Although most of this work was purely analytical, these studies paved the way for chemotaxonomic studies to be done on *Aloe*. In the period 1963 to 1965 Van Oudtshoorn published a series of papers in which the occurrence of anthraquinones in *Aloe* and related genera were reported. Although the sample size was very small, attempts were made to interpret the results in a chemotaxonomic sense (Van Oudtshoorn 1963, 1964, Van Oudtshoorn & Gerritsma 1964, 1965). Holdsworth (1970 & 1972) and McCarthy and Price (1965 & 1966) reported the presence of various chromones and anthrones in *Aloe*. Although they listed the species showing the absence and presence of various compounds, no conclusions were drawn relating to chemotaxonomy, once again the sample size was not representative of the large genus. The most comprehensive report on the distribution of leaf compounds was published by T. Reynolds. In 1985 Reynolds published a review article discussing all the compounds isolated from *Aloe*. This article is an excellent summary of relevant phytochemical work on *Aloe* and provided the foundation for his valuable publications in 1985, 1986 and 1990. In all three publications Reynolds studies the chromatographic zones

visualised on TLC after using various spraying reagents and summarises the chemical relationships between the species. Although many samples were studied and the chromatographic zones (over 90!) were carefully recorded the compounds were only assigned to a class of compound and not identified. The resolution of the data (which is true for any TLC study) restricted the interpretation of the data. Reynolds in collaboration with co-workers at Kew also incorporated his data in multi-disciplinary studies to establish possible mechanisms of evolution at infrageneric level (Brandham *et al.* 1994, Cutler *et al.* 1980, Carter *et al.* 1983). In later studies Reynolds (1994, 1996 & 1997) incorporated HPLC data with his TLC data which proved to be valuable for researchers to correlate their work to these chromatographic zones. Rauwald dedicated a research career to the chemistry of *Aloe* (see Chapter 2). Rauwald *et al.* (1991) recorded the exudate composition of 183 species but unfortunately these results were only published in a summarised poster abstract. Dagne (1996) published a comprehensive review on the chemical constituents in the leaves and roots of *Aloe*. Dagne *et al.* (1994) and Van Wyk *et al.* (1995a) discussed the chemotaxonomic value of root anthraquinones and pre-anthraquinones in *Aloe* and in *Lomatophyllum* (Van Wyk, *et al.* 1995b).

The research cited above provided the base on which this study has been designed and completed. The work of the analytical chemists provided the chemical structures of the potential chemotaxonomic markers while the chemotaxonomists provided sets of results against which this data could be tested and the patterns evaluated. The greatest challenge was to obtain authentic material from as many species as possible in order to make this the most comprehensive chemotaxonomic account for *Aloe*. Furthermore, the leaf exudate would be analysed using HPLC and diode array detection - a powerful chromatographic method tailor made to study phenolic exudate compounds characteristic of *Aloe*.

The present taxonomic status of *Aloe* is best summarised by Newton 1998:

> "Firstly the existing infra-generic classification of the genus *Aloe* is far from satisfactory, and it is in need of revision. There are several species whose affinities within the genus are obscure..." (Newton 1998).

These words have been echoed by various aloe specialists:

> "There seems to be no constancy of species, no fixation of characters, no relative stability, and nature refuses to be forced into the fetters of a man-made precise system." (Reynolds 1950).

"The relationships within the genus *Aloe* are often obscure and I have frequently experienced much difficulty in deciding upon the true affinities of certain species..." (Lavranos 1973).

"It has proved virtually impossible to arrange the species of the Flora in a sensible phylogenetic sequence. There are no characters, ..."(Susan Carter 1994).

It is against this back-drop of taxonomic disorder in *Aloe* that I embarked on this study to investigate additional characters in an attempt to make a contribution towards the improved understanding of natural relationships in *Aloe*, which may eventually lead to a phylogenetic classification system for the species.

Table 1.1: Summary of important taxonomic events in *Aloe* as discussed in preceding text.

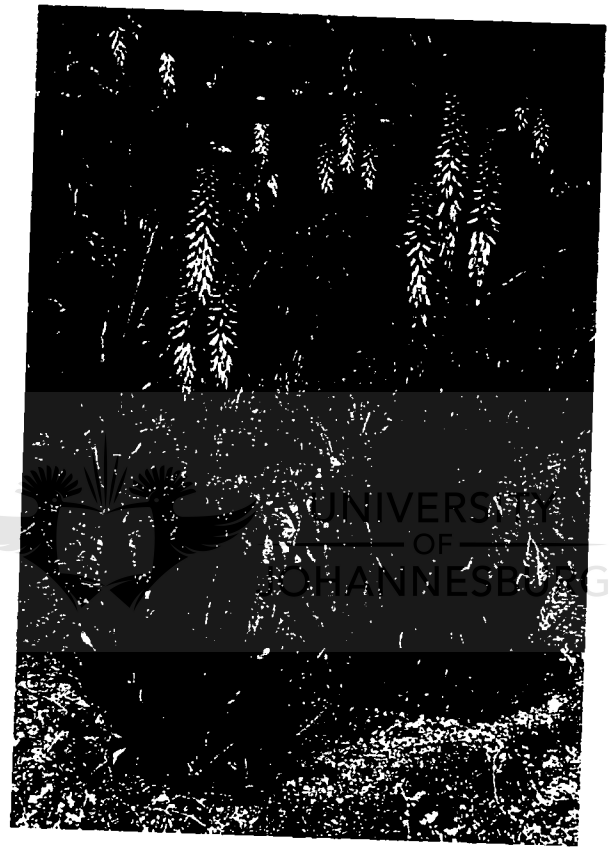
Date	Author	Reference	Comment
1583	Dodonaeus	Stirpium Historiae	Painting of *A. vera*
1680		Muntingus Aloidarum	Illustration of eight aloes (seven are agaves)
1690	Anon.	Horti Beaumontii Catalogus	Listing of seven species of *Aloe*
1697	Johan Commelin	Horti Medici Amstelodamensis	Illustration of *A. succotrina*
1701	Casper Commelin	Horti Medici Amstelodamensis Part II	Illustrates *Aloe saponaria*, *A. brevifolia* var. *postgenita* and A. *arborescens*
1703	Casper Commelin	Praeludia Botanica	Illustrations of *A. glauca*, *A. ferox*, *A. humilis*, *A. supralaevis* and *A. variegate*
1711	James Petiver	Gazo Phylacii Naturae and Artis	Contains four figures of aloes
1723	Tillius	Catalogus Plantarum Horti Pisani	Lists 30 species of *Aloe*
1727	Boerhaave		Lists 45 taxa including aloes, gasterias and haworthias
1732	Dillenius	Horthus Elthamensis	Description of *A. mitriformis* and *A. obscura* (*A. saponaria*)
1737	Weinmann	Phytanthoza Iconographa	Illustrations of eight aloes
1737	Linnaeus	Hortus Cliffortianus	Listing of various aloes
1751	Linnaeus	Philosophia Botanica	States that *Aloe* and *Agave* should be one genus
1753	Linnaeus	Species Plantarum	Introduces Binomial System
1759	Linnaeus	Flora Capensis	Mentions only one *Aloe*
1768	Miller	Gardener's Dictionary 8 ed.	Using the Binomial System lists 23 species of *Aloe*

Date	Author	Reference	Comment
1769	John Hill	Hortus Kewensis	A listing of all plants in cultivation at Kew (including 11 aloes)
1775	Weston	The English Flora	Includes 22 aloes, introduces new vernacular names
1775	Forsskål	Fl. Aegypt. Arab	Descriptions of *A. inermis*, *A. pendens*, *A. vera* & *A. vacillans*
1781	Linnaeus *f*	Supplementum Plantarum	Adds three species to those published in 1753
1783	Lamarck	Encyclopedie Methodique	Listing of 31 species of *Aloe*
1785 & 1880	Thunberg	Dissertations Vol. 1& 2	Lists 15 aloes (including haworthias and gasterias)
1786	Medicus	Theodora Speciosa	*Aloe* spit into two genera: *Catevalia* - aloes and haworthias and *Kumara* - aloes, haworthias and gasterias
1789	William Aiton	Hortus Kewensis I	Prepared a listing of all aloes cultivated in Kew
1789	Patterson	Narrative of four journeys	Four plates of *A. dichotoma* published
1794	Thunberg	Podromus Plantarum Capensium	Publishes same listing as in 1785
1797	Andrew Murray	Systema Vegetabilium	Listing of 10 aloes
1799	Willdenouw	Species Plantarum Vol II	Listing of 17 *aloes*
1804	Haworth	Transactions of the Linnean Society of London	A review of 59 taxa. No distinction is made between *Haworthia*, *Aloe* or *Gasteria* yet comments on the differences are included
1809	Duval	Plantae Succulentae in Horto Alenconio	Separates *Haworthia* and *Gasteria* from *Aloe*
1811	Aiton	Hortus Kewensis II	A catalogue of all plants in the Kew collection

Date	Author	Reference	Comment
1812	Haworth	Synopsis Plantarum Succulentarum	Acknowledges the distinction between *Haworthia*, *Aloe* and *Gasteria* as suggested by Duval. Describes 30 species of *Aloe*.
1817 - 1830	Bowie	Taylors Philosophical Magazine	Visits the Cape and sends various specimens of *Aloe* to Kew of which he described many himself
1817	Salm Dyck	Cataloque raisonné des Especes de' Aloes	Completes a cataloque of all known species of *Aloe* up to date
1819	Haworth	Supplementum Plantarum Succulentarum	A comprehensive listing of all aloes added to English Gardens since 1819
1824 - 1825	Haworth	Philosophical Magazine	A description of six new species of aloe
1829	Schultes & Schultes	Systema Vegetabilum	An extensive account of *Aloe* including new species
1836 - 1863	Salm Dyck	Monographia Generum et Mesembryanthemi	Figures 39 aloes (37 from South Africa)
1837	Bojer	Hort. Maurit.	First two aloes from Madagascar are published
1843	Kunth	Enumeratio Plantarum	Listing of various species and varieties
1878	Baker	Trans. Linn. Soc. Bot.	Descriptions of *A. palmiformis*, *A. angolensis*, *A. zebrina* and *A. littoralis*
1880	Baker	Synopsis of Aloineae and Yuccoideae in Journal of the Linnean Society Botany	Revises *Aloe* and describes several new species
1883	Baker	Journal of the Linnean Society	Describes species of *Aloe* (and *Lomatophyllum*) from Madagascar
1886 (?)	Baker	Flora Capensis (Vol. 6)	Eight species of *Aloe* are described

Date	Author	Reference	Comment
1887	Baker	Journal of the Linnean Society	*Aloe haworthioides* is described (Madagascar)
1889	Deflers	Voyageau Yemen	Mentions *A. tomentosa* and *A. officinalis*
1895	Engler	Pflanzenreich. Ost Afr.	
1895	Baker	Bot. Mag.	Paintings of *A. brachystachys* and *A. luntii.*
1899	Watson	Gard. Chron	Description of *A. somaliensis.*
1891	Scott Elliot	Journal of the Linnean Society	Describes *Aloe bakeri* from Madagascar
1895	Engler	Pflanzenwelt Ostafrikas	Mentions the following species: *A. secundiflora*, *A. lateritia*, *A. boehmii*, *A. confusa* and *A. volkensi*
1896	Dyer	Flora Capensis VI	70 aloes from South Africa are listed
1897	Baker	Hook. Ic. Pl. t.	Description and painting of *A. nuttii*
1898	Baker	Flora of Tropical Africa	Listing of various species of *Aloe*
1899	Rendle	Cataloque of African Plants collected by Dr Fredrich Welwitch	Includes six species from Angola
1903	Balfour	Nat. Hist. Sokotra	Descriptions of *A. perryi* and *A. squarrosa.*
1904	Berger	Monatsschrift f. Kakteenkunde	
1903 - 1907	Schönland	Records of the Albany Museaum	Describes ten species of *Aloe*
1905	Marloth	Englers Botanische Jahrbücher	Describes two species of *Aloe*
1906	Berger (?)	Notizblatt Berlin Bot. Gart. Museums	Synopsis of *A. dawei*, *A. candelabrum* and *A. excelsa.*
1908	Engler (Ed.)	Das Pflanzenreich	Publishes the most comprehensive work of *Aloe* up to date

Date	Author	Reference	Comment
1911	Rendle	Jour. Linn. Soc. Bot.	Contributions to the Flora of Gazaland - *A. rhodesiana* and *A. swynnertonii* are described.
1912	Poisson	Recherch Fl. Merid. Madag.	Two Malagasy aloes are described
1915 & 1917	Pole-Evans	Transactions of the Royal Society of South Africa	Describes 12 species of *Aloe*
1921	Decary	Bull. Econ. Madag.	Descriptions of aloes from Madagascar are published
1926	Perrier & De La Bathie	*Lomatophyllum* et les *Aloe* de Madagascar	
1926	Perrier	Mem. Soc. Linn. Norm.	A monograph of all aloes known from Madagascar
1933	Christian	Rhodesian Agricultural Journal Bulletin	Notes of various African species
1933 & 1934	Pillans	South African Gardening and Garden Life	Describes ten species of *Aloe*
1936 - 1940	various	various	Descriptions of 37 species are published
1938	Perrier	Fl. Madag. Liliac.	Updates his monograph published in 1926
1941	Groenewald	Aalwyne van Suid Afrika, Suidwes-Afrika, Portugees Oos-Afrika, Swaziland en Basoetoland	Systematic and Cytological study (M.Sc. thesis)
1950	Reynolds	The aloes of South Africa	Comprehensive treatment of 132 species of *Aloe*
1954	Reynolds	The aloes of Nyasaland	Treatment of the aloes of Malawi
1958	Reynolds	Les aloes de Madagascar. Revision	A revision of all 38 species of aloes endemic to Madagascar
1966	Reynolds	The Aloes of Tropical Africa and Madagascar	An extensive treatment of all known species of *Aloe* not covered in the 1950 publication



Chapter 2

Aloe leaf chemistry - a review

CHAPTER 2

ALOE LEAF CHEMISTRY - A REVIEW

Aloes have been renowned since antiquity for various phytotherapeutic purposes. In the light of this historic importance it seems obvious that the chemical investigation of aloes would also be initiated by the scientific community at an early stage in recent time. It is interesting that aloin was the first compound to be isolated in 1851 from Barbados aloe and the structure was confirmed in 1956, fairly recent considering the primal use by early civilization. Figure 2.1 shows the progress in the historical events in the isolation and characterization of *Aloe* leaf compounds since 1956. The interest in *Aloe* chemistry seems to be somewhat erratic and probably coincides with interest fluctuations in the medicinal and cosmetic markets and the rapid evolution of scientific technology. It is even more interesting to note that although the healing qualities of *Aloe* are ascribed to the leaves much of the research that followed in the 1970's was on the subterranean plant organs (Yagi, *et al.* 1974, 1977, 1978, 1983). The high number of compounds isolated in 1996 and 1997 coincides with the completion of this project where leaf compounds were selected for isolation on the basis of their chemotaxonomic importance. The immense growth in the *Aloe vera* industry has captured the enthusiasm of many chemists who are actively involved in the 'chemical treasure hunt' to isolate the compounds to which the healing properties of this mystical plant can be attributed.

As this study is restricted to the leaf compounds (and mostly the compounds contained in the leaf exudate) the discussion which follows will not deal with the other classes of compounds located in various other plant organs. The decision to restrict the study only to the leaf compounds was not only a practical consideration, but it is well known that there is a clear distinction between subterranean and above ground metabolism in *Aloe* (Van Wyk, *et al.* 1995, Dagne *et al.* 1994, Sigler *et al.* 1994[a], 1994[b],). The two classes of compounds which accumulate in the leaves of *Aloe* species are the anthrone-C-glucosyls (Figure 2.2a) and the chromones (Figure 2.2b). Other classes of compounds which are sporadically detected in the leaves include anthraquinones, pre-anthraquinones, bianthraquinoids, benzene and naphthalene derivatives, coumarins, phenyl pyrones, triterpenes and alkaloids.

All phenolic compounds known from the leaves of *Aloe* are summarised in table format at the end of the chapter. The proceeding key illustrates the interpretation to the tabulated summary. The numbers e.g. [A1] used in the following text refer to the compound in the summary.

The medicinal value attributed to *Aloe vera* initiated extensive phytochemical research on the genus *Aloe* (Photo: Ben-Erik van Wyk).

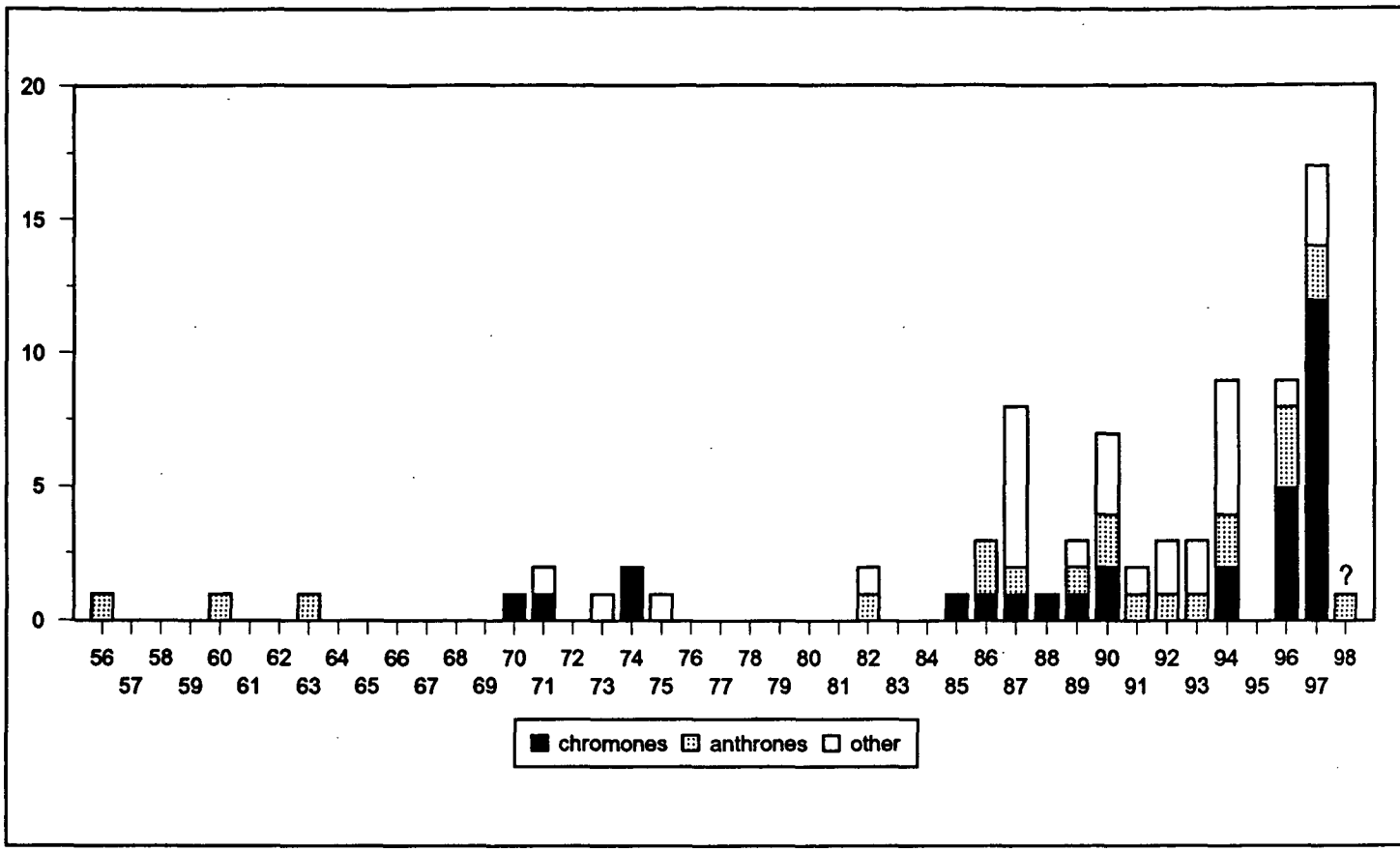


Figure 2.1: Progress in the isolation of leaf compounds from *Aloe* since 1956. (Vertical axis indicates the number of compounds identified.

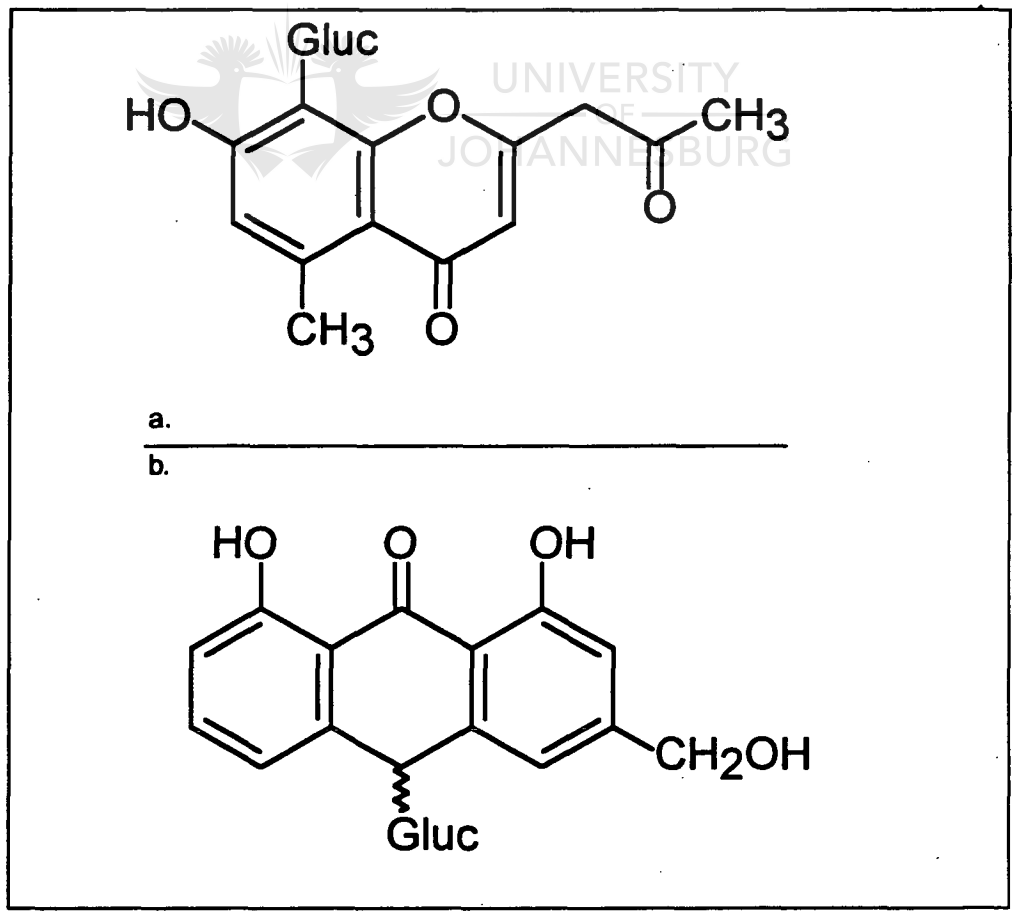


Figure 2.2: The two classes of compounds most abundant in the leaves of *Aloe*; a. an example of a chromone and b. an example of an anthrone.

Anthrones

As the anthrone-*C*-glucosyls are the 'prodrugs' responsible for the laxative effect of aloes these were the first compounds to be isolated and characterised. References to literature indicates that barbaloin (the collective name for aloin A and B) was isolated by Stenhouse from Barbados aloe in 1851. Hay and Haynes (1956) confirmed the work of Stenhouse and reported the structure of aloin [A1]. Grün *et al.* (1979) separated aloin into aloin A and aloin B and Auterhoff *et al.* (1980) demonstrated that the aloins have different configurations at the C-10 of the anthrone part. In 1990 Manitto *et al.* recorded ^{13}C-NMR spectra and corrected previous ^{1}H-NMR assignments. Biosynthetic studies on *Aloe arborescens* (Grün *et al.* 1980) showed that aloin B is actively synthesised in the plant where it is partially converted into aloin A. Graf and Alex (1980) showed the instability of aloin A and B due to pH effects, heat and presence of oxygen and that the main decomposition product is 4-hydroxyaloin. Much of this pioneering work was done on *Aloe ferox*, the commercial product Cape aloe and on *Aloe arborescens*. In 1964 Van Oudsthoorn *et al.* reported the occurrence and distribution of the anthrone aloin in other species of *Aloe*. The second anthrone to be isolated and characterised was homonataloin [A2]. Fluckiger *at al.* (1871) reported a pale yellow substance from Natal aloes which they called nataloin. In 1917 Léger claimed to have separated this yellow crystalline substance into two compounds which he called homonataloin and nataloin. The structures proposed for these compounds are now known to be incorrect. The work of Tschirch and Klaveness in 1901 resulted in the isolation of homonataloin from Natal aloes while Rosenthaler once again reported nataloin and homonataloin from the same source in 1913. Haynes *et al.* (1960) unambiguously reported the isolation and structure of homonataloin from Natal aloes. These two compounds; aloin and homonataloin are the two anthrones most frequently detected in the leaves of aloes (Rauwald *et al.* 1991). The third anthrone to be described from *Aloe* was aloinoside B [A3] from Socotra aloe (Hörhammer, 1963). This compound differs from aloin in the presence of an additional rhamnose moiety. In 1982 Rauwald described 7-hydroxyaloin [A4] from *A. barbadensis* followed by the isolation of the acetate derivatives of this compound in *Aloe succotrina* [A5 & A6]. Unfortunately no chemical data on the two latter compounds were published. The isolation was reported in the form of a poster abstract (Rauwald, 1986) and the occurrence and distribution in a single plant was reported by Sigler *et al.* (1994). In the same manner Rauwald reported the isolation of three isomer pairs of 7-hydroxyaloin derivatives [A9, A10 & A11] from *Aloe barbadensis* (Rauwald *et al.* 1990, 1991). The isolation of nataloin [A7] was reported by Conner *et al.* in 1987 from the leaves of *A.*

nyeriensis. This compound was also later isolated from *A. pulcherrima* by Dagne *et al.* (1991) and has been used as a reference sample of nataloin in this study. Conner *et al.* (1989) also reported the isolation of the first anthrone C-10 rhamnoside [A8] from *Aloe*. Farah *et al.* (1990) isolated microdontin A and B [A12] from *Aloe microdonta* and by using NMR data and mass spectral analysis he concluded that the glucose of aloin A and B is esterified in the 6'-position with a 4-hydroxycinnamic acid. This compound was also isolated from *Aloe elegans* (Viljoen *et al.* unpublished) while Dagne (1996) reported the distribution of microdontin in various Ethiopian species. In 1993 Rauwald & Beil reported the occurrence of 5-hydroxyaloin [A13] in the genus *Aloe*, yet, no literature could be found on the isolation and characterisation of this compound. In 1997 Dagne *et al.* and Holzapfel *et al.* independently reported the isolation and structural elucidation of 5-hydroxyaloin A. The initiation of a chemotaxonomic survey of the genus *Aloe* in 1994 directed the isolation of chemotaxonomic markers. This led to the isolation of three novel oxanthrones [A16, A17, A18] from *Aloe littoralis* (Dagne *et al.* 1996) and the chemotaxonomic value of these compounds were discussed by Viljoen *et al.* (1996). A fourth compound, 10-hydroxyaloin B 6'-*O*-acetate B [A20] which also occurs in *Aloe littoralis* was later isolated from *A. claviflora* (Dagne *et al.* 1998). Microstigmin [A19] from *Aloe microstigma* was selected for isolation due to its occurrence in *Aloe* series *Purpurascentes* and was described by Dagne *et al.* (1997). The first di-glucoside in *Aloe*, homonataloside B was isolated from *A. lutescens*, together with two novel chromones (Van Heerden *et al.* 1997).

Chromones

The chromones are the most abundant of the chemical compounds in the leaf exudate. In most cases only one isomeric pair of anthrone-*C*-glycosides (e.g. aloin A/B) co-occur with a series of chromone compounds. Aloesin [C1] was the first chromone to be isolated and structurally characterised from *Aloe capensis* (=*A. ferox*) (Haynes *et al.* 1970). McCarthy (1969) reported aloesin to be present in 29 species of *Aloe* and Holdsworth (1971) reported the occurrence of this compound in a further five species of *Aloe*. Holdsworth (1972) reported the aglycone of aloesin, aloesone [C2] as a minor compound in 11 species of *Aloe*. Wagner *et al.* (1970) isolated and described aloeresin A but Makino *et al.* (1974) and later Gramatica *et al.* (1982) showed the structure proposed by Wagner was incorrect. The two latter papers proved that the coumaroyl ester is attached to the 2' position of the glucose moiety and not to the 6' position as postulated by Wagner *et al.* (1970). Makino and co-workers (1974) also reported the structure of 2-*O*-feruloylaloesin [C4] from *Aloe arborescens* var. *natalensis*.

Most of the research on aloe chromones was done by Speranza and various collaborators who published a series of papers on the compounds contained in the commercial product of *Aloe ferox*, Cape aloes. It has to be stated here, that although these compounds have been included in this review they have been obtained from the aloe lump and not from the plant in its natural state. The preparation of this product is rather vigorous and accompanied by high temperatures. Although most compounds detected in the aloe lump has also been detected in the leaf exudate of *Aloe ferox* (aloesin, aloeresin C, aloeresin A, aloins A and B) the possibility exists that some of the compounds are artifacts which form during the preparation of the drug. Aloeresin C [C5] was reported as a minor constituent of Cape aloe (Speranza *et al.* 1985) and became part of a series of coumaroyl esters of aloesin to be reported from *Aloe*. Aloeresin D [C6], another 7-methoxy-5-methyl chromone (Speranza, *et al.* 1986) with a coumaroyl ester was described from Kenya aloes (obtained from the exudate of *A. ferox* and its hybrids). Iso-aloeresin A [C8] was described as minor constituent in Cape aloes (Speranza *et al.* 1988) and differed from aloeresin A at the C-2" and C-3" of the p-coumaroyl group which is cis in isoaloresin A and trans in aloeresin A. More recently two other chromones were isolated from Cape aloes; furoaloesone [C12] and 7-hydroxy-2,5-dimethyl-chromone [13] (Speranza *et al.* 1994). Mebe (1987) reported 2'-*p*-methoxycoumaroylaloeresin [C7] from *Aloe excelsa*. This compound differs from aloeresin A by the presence of the *p*-methoxy group attached to the coumaroyl ester. The work of Conner resulted in the isolation of various anthrones and chromones. The first caffeoyl chromone with the trivial name rabaichromone [C9] was isolated from *Aloe rabaiensis* (Conner *et al.* 1989). A study of the leaf exudates of *A. jacksonii* and *A. cremnophila* (Conner *et al.* 1990) yielded the 2'-*O*-tigloyl ester of aloesin [C11] in both species while 2-(carboxyethenyl)-5,7-di-hydroxychromone [C10] was only found in the exudate of *A. cremnophila*. The first two cinnamoyl chromones were isolated from *A. peglerae* (Van Heerden *et al.* 1996) and were named aloeresin E [C14] and F [C15]. Aloeresin E has an additional glucose moiety attached to the 7 position of the chromone nucleus. Unfortunately Okamura *et al.* (1996) also described a chromone from *Aloe barbadensis* and assigned the name Aloeresin E [C18] to this novel compound. This compound has a different structure to the Aloeresin E of Van Heerden *et al.* (1996) but the latter name takes precedence as it was published before the Aloeresin E of Okamura *et al.* (1996). In addition to the latter compound isoaloeresin D [C17] and 8-*C*-glucosyl-7-*O*-methyl-(*S*)-aloesol [C16] were also isolated from the leaves of *Aloe barbadensis* (Okamura *et al.* 1996). In a second publication Okamura (1997) described three new chromone derivatives from the same species.

In a comprehensive publication Holzapfel *et al.* (1997) described four new chromones from *Aloe speciosa* [C23], *Aloe africana* [C24] and *Aloe broomii* [C25 & C26]. The compound from *Aloe speciosa* was the first report of a di-*O*-*O*-coumaroyl chromone derivative in *Aloe*. Two unusual chromones were isolated from the exudate of *Aloe lutescens*; 3'6'-di-coumaroyl aloesin [C28] and 3'-*O*-coumaroyl aloesin [C29]. This was the first account of esters attached to the 3' and not the 2' position of the glucose moiety.

Other compounds (anthraquinones, pre-anthraquinones, bisanthraquinoids, benzene and naphthalene derivatives, coumarins, phenyl pyrones, triterpenes and alkaloids)

The anthrones and chromones are the two classes of compounds which are most commonly found in the leaf exudate. Various other compounds not relating to the two classes discussed above have also been reported.

Two coumarins have been isolated from *Aloe*; a dihydroiscoumarin glucoside [Co1] from *Aloe hildebrandtii* (Veitch *et al.* 1994) and feralolide [Co2] from Cape aloes (Speranza *et al.* 1993). The former compound corresponds to Reynolds' P20 zone (Reynolds, 1985) and the distribution of this compound was mentioned by Brandham *et al.* (1994).

Aloenin [P1] was the first of five phenyl pyrones which have been isolated. Aloenin was isolated from *Aloe arborescens* var. *natalensis* by Makino *et al.* (1973) who initially named this compound aloearbonaside. Suga *et al.* (1972) independently isolated the same compound and named it aloenin. Suga *et al.* (1974) re-examined the structure of aloenin and proposed a new structure which was later confirmed by Hirata *et al.* (1976) to be correct. The aglycone of aloenin [P3] was isolated from the leaves of *Aloe nyeriensis* var. *kedongensis* (Conner, *et al.* 1987) together with aloenin and a 2"-*O*-*p*-coumaroyl ester of aloenin [P4]. Speranza *et al.* (1993) reported the *O*,*O*-diglucoside analogue of Conner's compound (P4) where the additional glucose moiety is attached to the C10 of the phenyl pyrone nucleus and called this compound aloenin B [P2]. Finally, Woo *et al.* (1987) reported aloenin acetal [P5], an unusual phenyl pyrone from *Aloe arborescens*.

Two benzene derivatives; methyl p-coumaroate [B1] and protocatechuic acid [B2] have been isolated from aloe leaves. The former compound was isolated by Graf *et al.* (1982) from Cape aloes while the latter compound was isolated from *A. berhana* and characterised by Dagne *et al.* (1991). Protocatechuic acid is rarely reported from a natural source but its occurrence was confirmed by applying various extraction methods to confirm that this compound could not be considered an artifact.

All but one of a series of naphthalene derivatives have been described from Cape aloes [N1 - N6] by Speranza *et al.* (1990, 1992, 1994). Plicataloside [N7], an *O*-*O*-diglucoside naphthalene derivative was isolated from *Aloe plicatilis*, a compound only found in this one South African species and in several other species from east Africa.

Various infrageneric groups in *Aloe* showed the presence of flavonoids based on UV-Vis spectra. Williams (1977) reported the presence of various unidentified flavonoids in trace amount using paper chromatography. During my study, four flavonoids were isolated from the leaves of various species and the distribution and chemotaxonomic value of these compounds were discussed by Viljoen *et al.* (1998). Isovitexin [F2] was isolated as from *A. verecunda* and is the major flavonoid in most of the grass-like aloes. The flavanone naringenin [F3] and a dihydroflavonol [F4] was isolated from the leaves of *Aloe lineata* and was positively identified in various species belonging to *Aloe* series *Superpositae* and series *Rhodacanthae*.

Many anthraquinones have been reported from *Aloe* with the majority of these compounds occurring in the roots. The list of anthaquinones [Aq1-Aq8] and the single bisanthraquinoid [Bq1] is merely included to make the list complete for all leaf compounds from *Aloe*. The extraction procedures and analytical parameters in this study were not optimised for this group of compounds and were not used as chemical characters in this chemotaxonomic study.

Although *A. vera* and *A. ferox* have dominated the workplace in the chemistry laboratory, the other 400 species of *Aloe* are systematically being included in phytochemical studies. Many research teams are actively exploring the chemical complexity of aloes. The complete reference summary of compounds detailed in this chapter will be outdated at the time this thesis is published as new compounds are reported almost monthly from this topical genus.

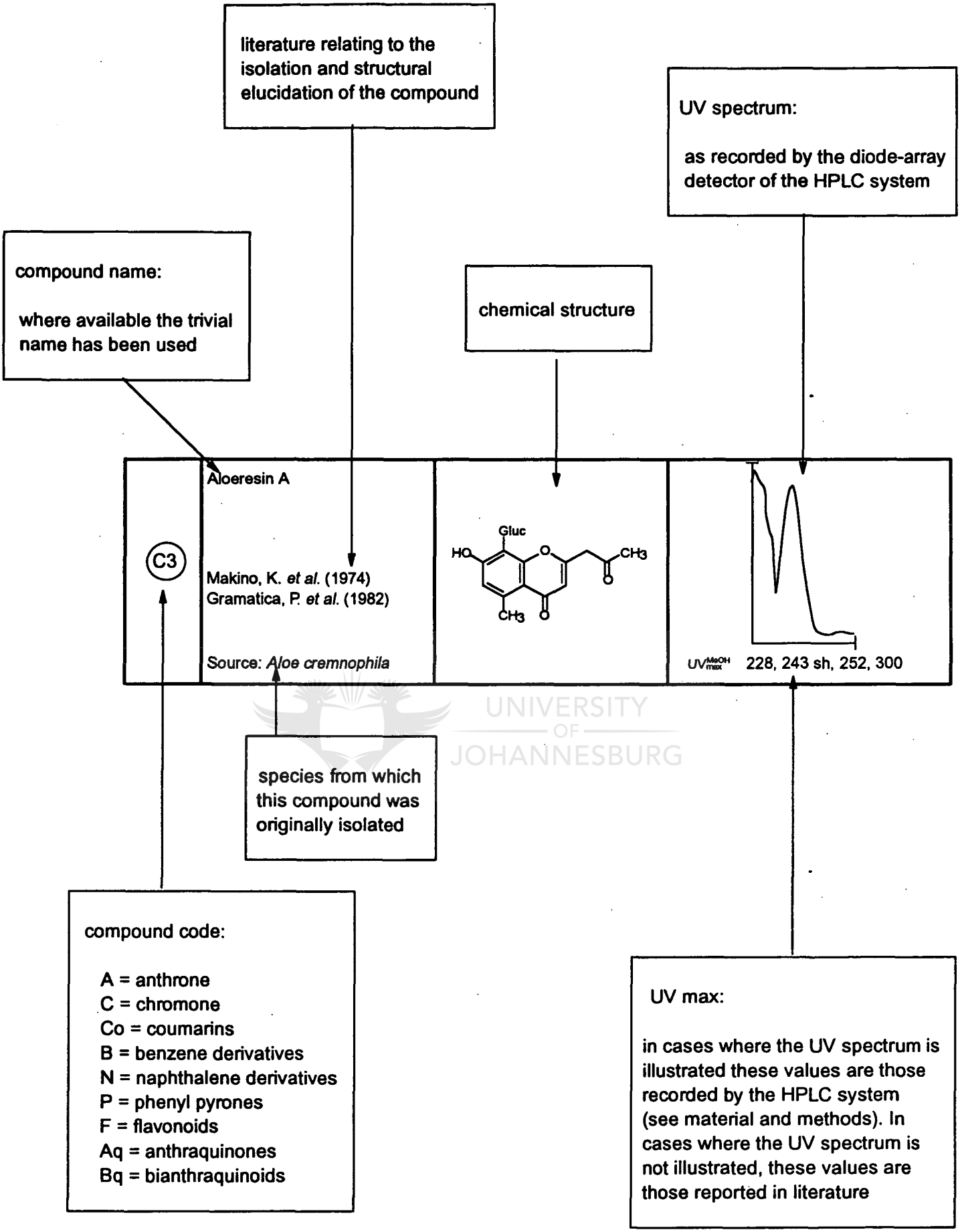
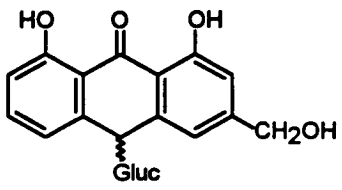
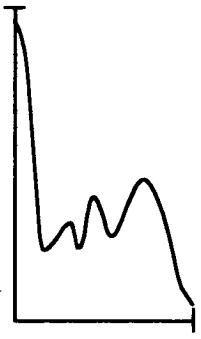
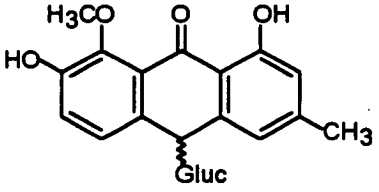
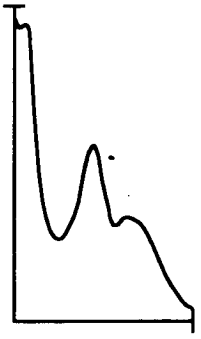
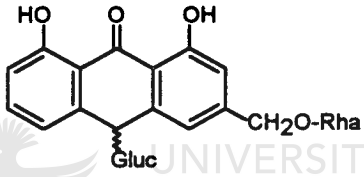
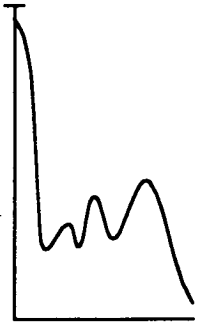
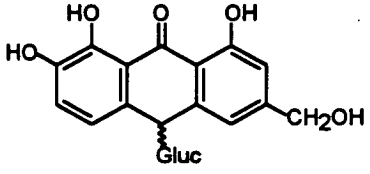
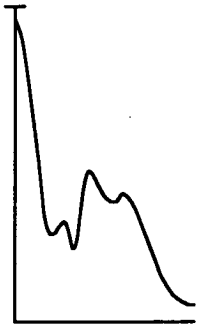
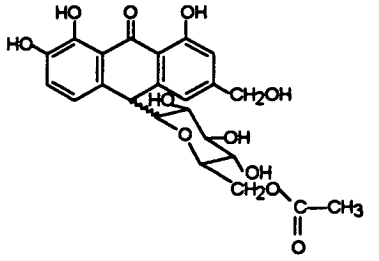
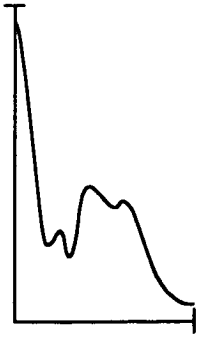
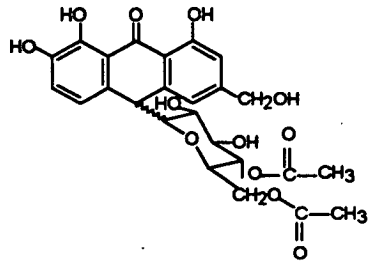
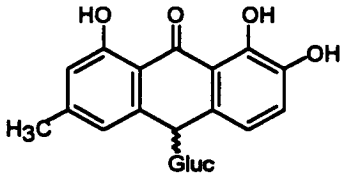
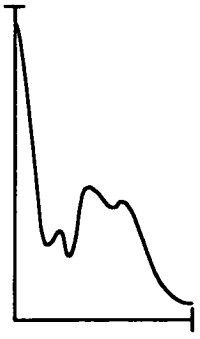
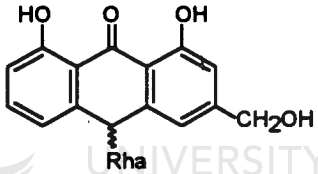
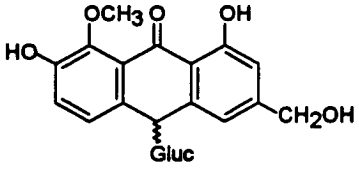
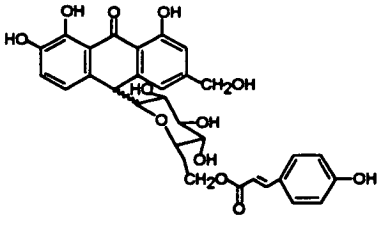
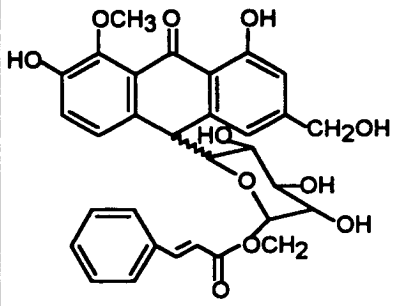
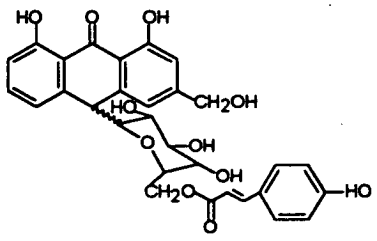
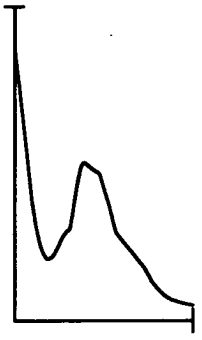
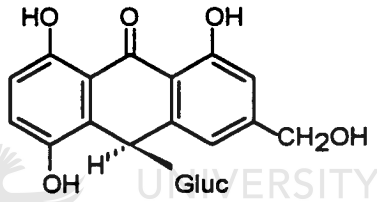
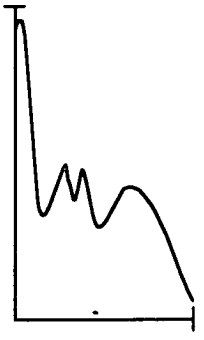
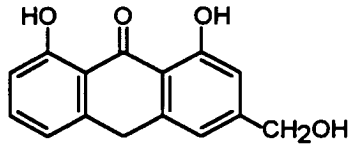
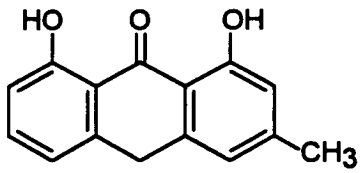
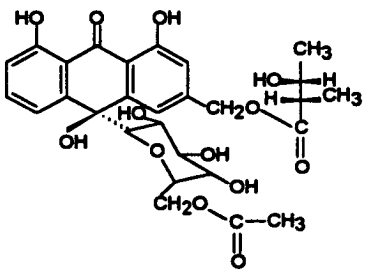
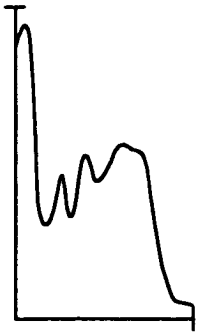
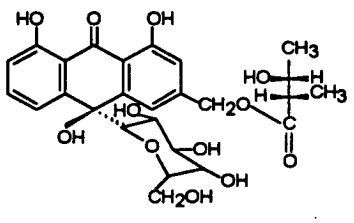
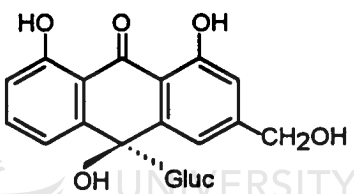
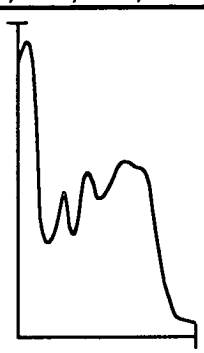
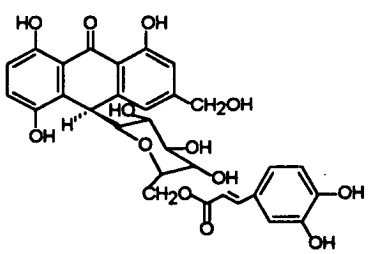
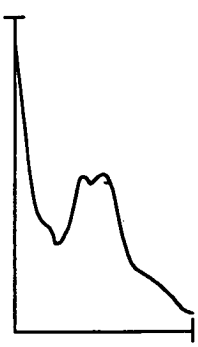
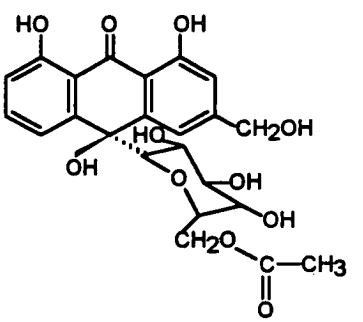


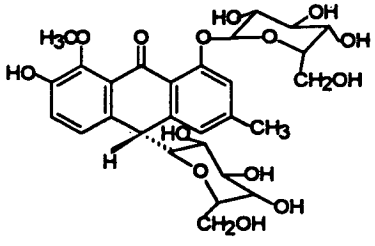
Figure 2.3: Key for the interpretation of the chemical review of leaf compounds.

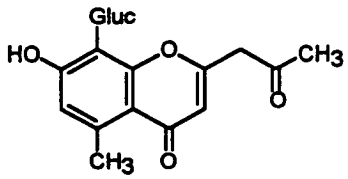
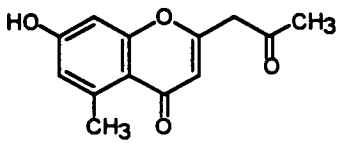
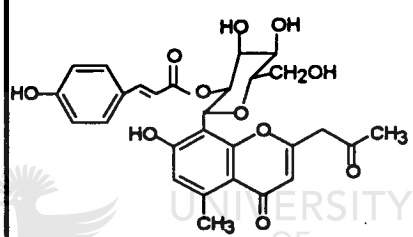
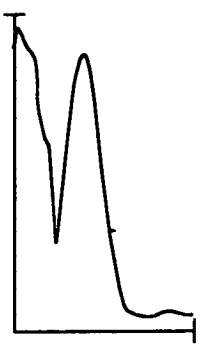
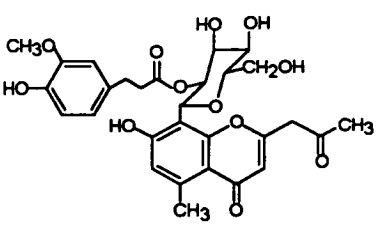
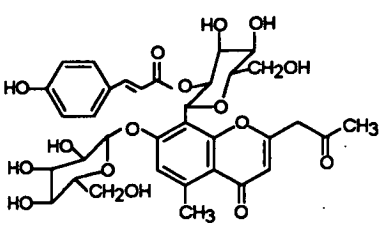
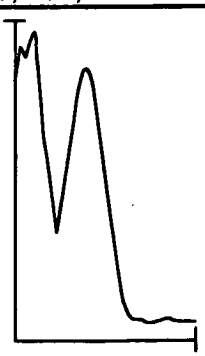
A1	Aloin A/B Hay, J.E. *et al.* (1956) Auterhoff, H. (1980) Rauwald, H.W. *et al.* (1989) Manitto, P. *et al.* (1990) Source: *Aloe*		 λUV max 268, 295, 355
A2	Homonataloin A/B Haynes, L.J. *et al.* (1960) Van Rheede van Outshoorn, M.C.B. *et al.* (1963) Conner, J.M. *et al.* (1990) Source: *Aloe*		 λUV max 218, 269, 295, 341
A3	Aloinoside A/B Hörhammer, H *et al.* (1963) Thomson, R.H. (1971) Source: *Aloe perryi*		 λUV max 268, 296, 355
A4	7-hydroxyaloin A/B Rauwald, H.W. (1982) Source: *Aloe barbadensis*		 λUV max 219, 268, 305, 351
A5	6'-*O*-acetyl-7-hydroxyaloin A/B Rauwald, H.W. *et al.* (1986, 1994) Source: *Aloe succotrina*		 λUV max 219, 268, 305, 351

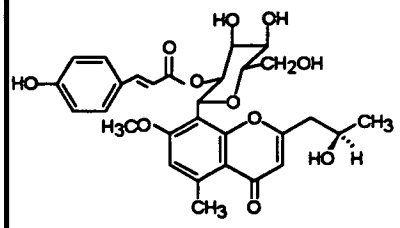
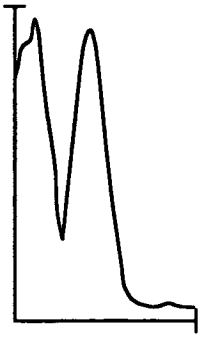
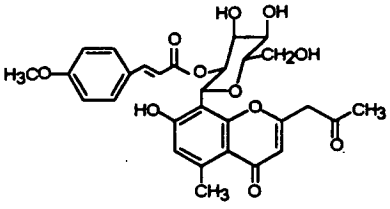
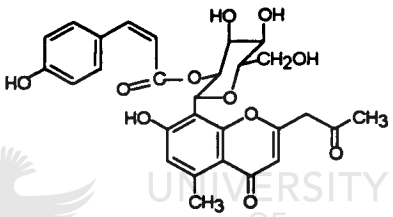
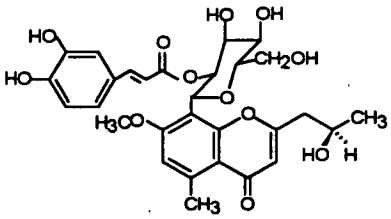
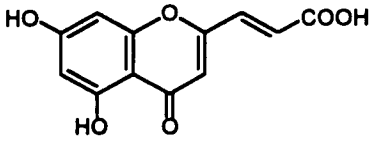
A6	4',6'-di-*O*-acetyl-7-hydroxyaloin A/B Rauwald, H.W. *et al.* (1986, 1994) Source: *Aloe succotrina*		 λUV $_{max}$ 219, 268, 305, 351
A7	Nataloin A/B Conner, J.M. *et al.* (1987) Source: *Aloe nyeriensis*		 λUV $_{max}$ 214, 272, 305, 349
A8	Aloe-emodin-10-C-rhamnoside Conner, J.M. *et al.* (1989) Source: *Aloe rabaiensis*		λUV $^{MeOH}_{max}$ 252, 260, 272, 295, 358
A9	8-*O*-methyl-7-hydroxyaloin A/B Rauwald, H.W. (1990) Source: *Aloe barbadensis*		 λUV $_{max}$ 219, 277, 294, 338
A10	6'-*O*-*p*-coumaroyl-7-hydroxy-aloin A/B Rauwald, H.W. (1990) Source: *Aloe barbadensis*		λUV $^{MeOH}_{max}$ (not published)

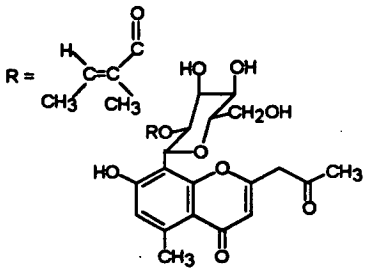
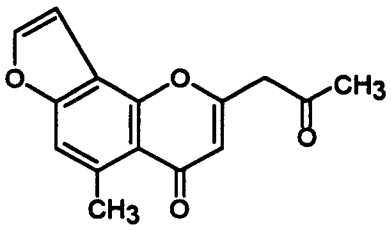
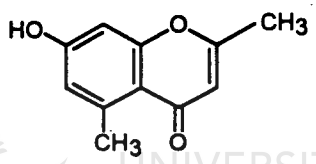
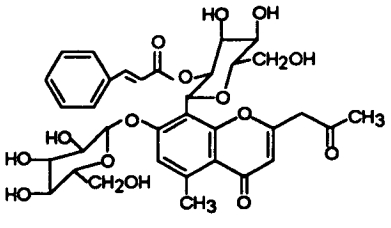
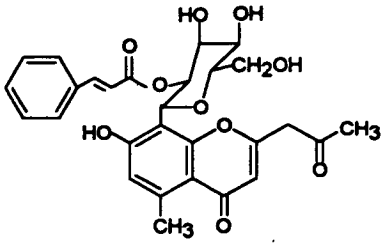
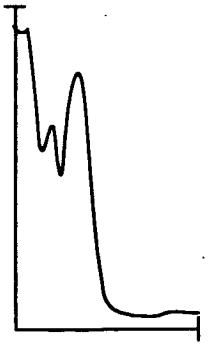
A11	6'-*O*-cinnamoyl-8-*O*-methyl-7-hydroxyaloin A/B Rauwald, H.W. *et al.* (1991) Source: *Aloe barbadensis*		λUV_{max}^{MeOH} (not published)
A12	Microdontin A/B Farah, M.H. *et al.* (1992) Source: *Aloe microdonta*		 λUV_{max} 212sh, 275, 299, 323, 350
A13	5-Hydroxyaloin B Rauwald, H.W. *et al.* (1993) Dagne, E. *et al.* (1997) Holzapfel, C.W. *et al.* (1997) Source: *Aloe spp.*		 λUV_{max} 210, 269, 297, 362
A14	Aloe-emodin anthrone Sigler, A. *et al.* (1994) Source: *Aloe spp.*		λUV_{max}^{MeOH} (not published)
A15	Chrysophanol anthrone Sigler, A. *et al.* (1994) Source: *Aloe spp.*		λUV_{max}^{MeOH} (not published)

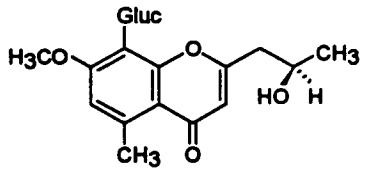
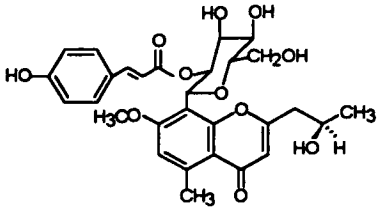
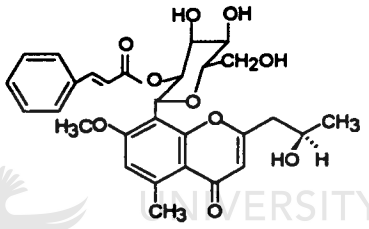
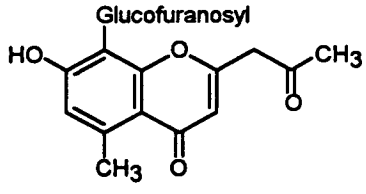
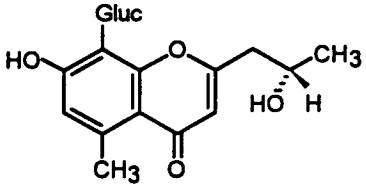
A16	Littoraloin Dagne, E. *et al.* (1996) Source: *Aloe littoralis*		 λUV max 212, 268, 300, 360
A17	Deacetyllittoraloin Dagne, E. *et al.* (1996) Source: *Aloe littoralis*		 λUV max 212, 268, 300, 360
A18	10-Hydroxyaloin B Dagne, E. *et al.* (1996) Source: *Aloe littoralis*		 λUV max 212, 268, 300, 360
A19	Microstigmin Dagne, E. *et al.* (1997) Source: *Aloe microstigma*		 λUV max 246, 298, 327
A20	6'-*O*-acetyl-10-hydroxyaloin B Dagne, E. *et al.* (1998) Source: *Aloe claviflora*		 λUV max 212, 268, 300, 360

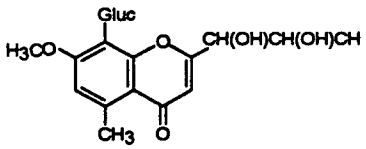
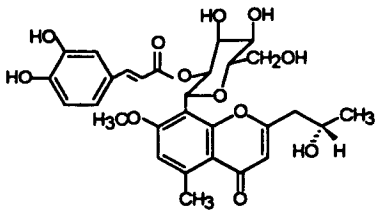
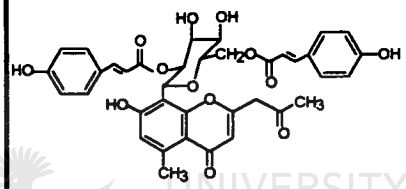
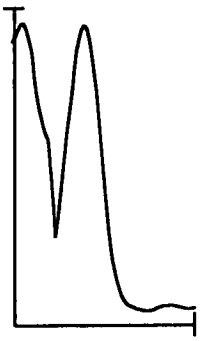
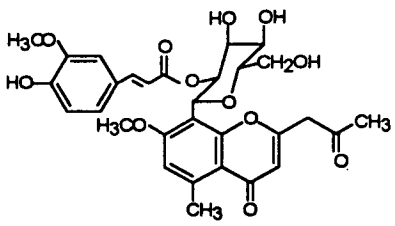
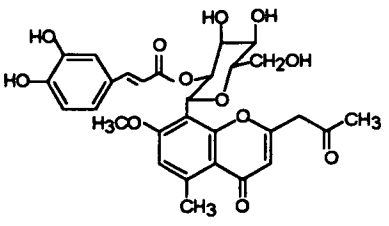
(A21)	Homonataloside B Van Heerden, F.R. *et al.* (1997) Source: *Aloe lutescens*		 λUV max 216, 292

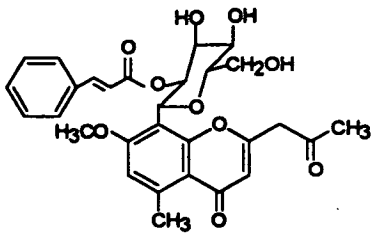
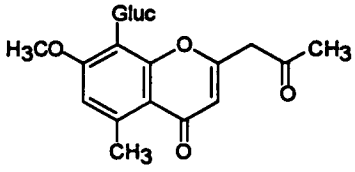
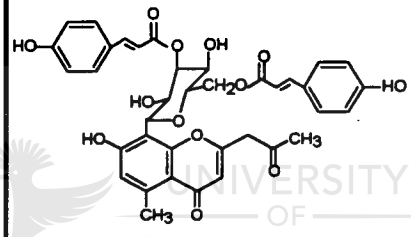
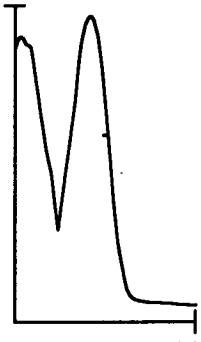
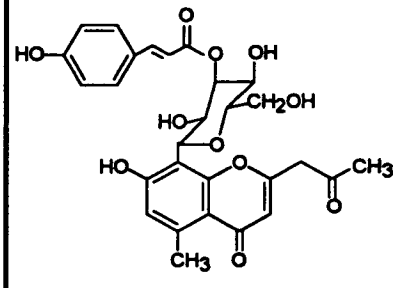
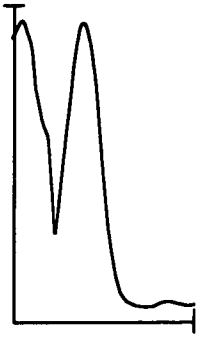
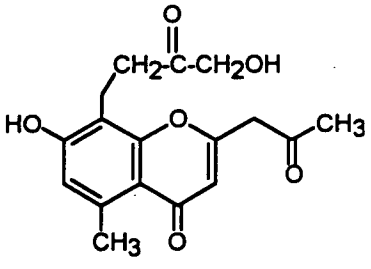
C1	Aloesin Holdsworth, D.K. (1971) Source: *Aloe capensis*		 λUV max 215, 234, 265, 297
C2	Aloesone Holdsworth, D.K. (1972) Source: *Aloe*		λUV MeOH max 243, 252, 296
C3	Aloeresin A Makino, K. *et al.* (1974) Gramatica, P. *et al.* (1982) Source: *Aloe spp.*		 λUV max 210, 225sh, 248sh, 300
C4	2-*O*-Feruloylaloesin Makino, K. *et al.* (1974) Source: *Aloe arborescens*		λUV MeOH max 243, 252, 296
C5	Aloeresin C Speranza, G. *et al.* (1985) Source: Cape aloe		 λUV max 210, 224, 248sh, 300

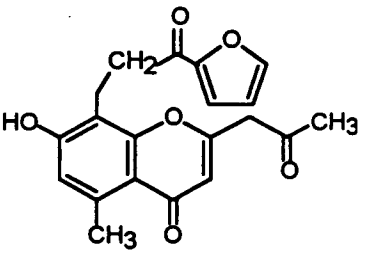
C6	Aloeresin D Speranza, G. *et al.* (1986) Source: Kenya aloe		 λUV_{max} 210, 225, 248sh, 298
C7	2'-p-*O*-Methylcoumaroyl-aloesin Mebe, P.P. *et al.* (1987) Source: *Aloe excelsa*		λUV_{max}^{EtOH} 226, 251sh, 298
C8	Iso-aloeresin A Speranza, G. *et al.* (1988) Source: Cape aloe		λUV_{max}^{MeOH} 213, 228, 242sh, 252, 300
C9	Rabaichromone Conner, J.M. *et al.* (1989) Source: *Aloe rabaiensis*		λUV_{max}^{MeOH} 234, 242, 296, 318
C10	2-(carboxyethenyl)-5,7-di-hydroxychromone Conner, J.M. *et al.* (1990) Source: *Aloe cremnophila*		λUV_{max}^{MeOH} 244, 271, 323

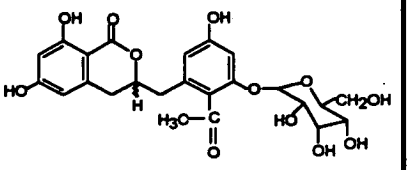
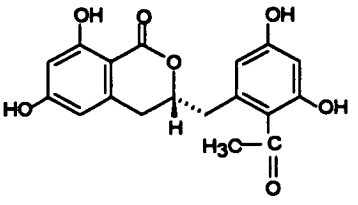
C11	2-'O-Tigloylaloesin Conner, J.M. *et al.* (1990) Source: *Aloe spp.*		λUV_{max}^{MeOH} 244, 252, 294
C12	Furoaloesone Speranza, G. *et al.* (1994) Source: Cape aloe		λUV_{max}^{MeOH} 215, 222, 240, 256sh, 308
C13	7-hydroxy-2,5-dimethyl-chromone Speranza, G. *et al.* (1994) Source: Cape aloe		λUV_{max}^{MeOH} 243, 252, 296
C14	Aloeresin E Van Heerden, F.R. *et al.* (1996) Source: *Aloe peglerae*		 λUV_{max} 215, 249, 281
C15	Aloeresin F Van Heerden, F.R. *et al.* (1996) Source: *Aloe peglerae*		 λUV_{max} 212, 249, 281

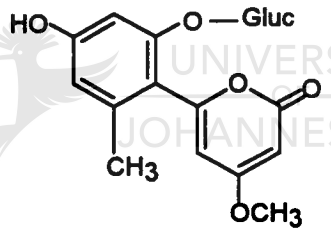
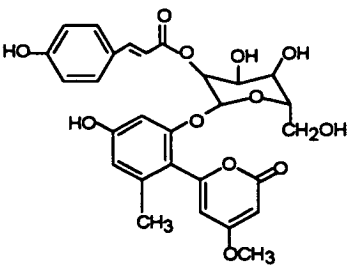
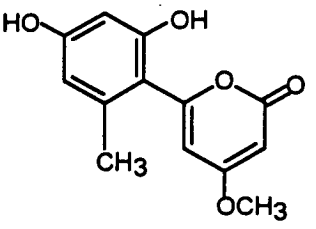
C16	8-*C*-glucosyl-7-*O*-methyl-(*S*)-aloesol Okamura, N*et al.* (1996) Source: *Aloe vera*		λUV$^{MeOH}_{max}$214, 226, 243, 252
C17	Isoaloeresin D Okamura, N. *et al.* (1996) Source: *Aloe vera*		λUV$^{MeOH}_{max}$213, 228, 242sh, 252, 300
C18	"Aloeresin E" (see chapter 11) Okamura, N. *et al.* (1996) Source: *Aloe vera*		λUV$^{MeOH}_{max}$205sh, 217, 232, 244, 252, 28
C19	Neoaloesin A Park, M.K. *et al.* (1996) Source: *Aloe barbadensis*		λUV$^{MeOH}_{max}$214, 245, 253, 296
C20	8-*C*-glucosyl-(*S*)-aloesol Okamura, N. *et al.* (1997) Source: *Aloe barbadensis*		λUV$^{MeOH}_{max}$215, 224, 244, 252, 293

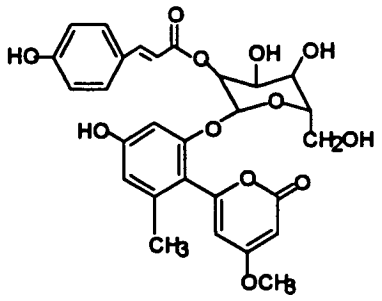
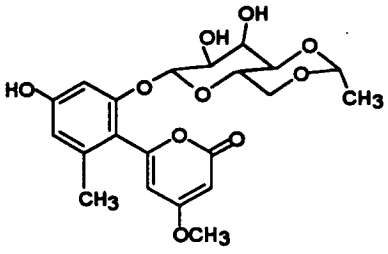
C21	8-*C*-glucosyl-7-*O*-methyl-aloediol Okamura, N. *et al.* (1997) Source: *Aloe barbadensis*		λUV_{max}^{MeOH} 214, 227, 244, 252, 294
C22	isorabaichromone Okamura, N. *et al.* (1997) Source: *Aloe barbadensis*		λUV_{max}^{MeOH} 220, 244, 251, 296, 330
C23	(E)-2-acetonyl-8-(2'-6'-di-*O*,*O*-coumaroyl-beta-D-gluco-pyranosyl)-7-methoxy-5-methyl chromone Holzapfel, C.W. *et al.* (1997) Source: *Aloe speciosa*		 λUV_{max} 210, 225, 248sh, 305
C24	(E)-2-acetonyl-8-(2'-O-feruloyl)-beta-D-glucopyranosyl)-7-methoxy-5-methyl chromone Holzapfel, C.W. *et al.* (1997) Source: *Aloe africana*		λUV_{max}^{MeOH} 217, 238sh, 298, 326sh
C25	(E)-2-acetonyl-8-(2'-*O*-caffeoyl-beta-D-gluco-pyranosyl)-7-methoxy-5-methyl chromone Holzapfel, C.W. *et al.* (1997) Source: *Aloe broomii*		 λUV_{max} 212, 244, 297, 329

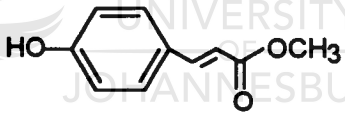
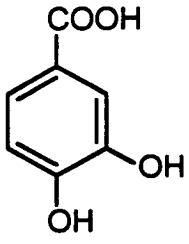
C26	(E)-2-acetonyl-8-(2'-*O*, cinnamoyl-beta-D-gluco-pyranosyl-7-methoxy-5-methy chromone Holzapfel, C.W. *et al.* (1997) Source: *Aloe broomii*		 λUV$_{max}$ 211, 249, 283
C27	7-*O*-methylaloesin In press, Dagne, E. *et al.* Source: *Aloe rupestris*		 λUV$^{MeOH}_{max}$ 243, 252, 296
C28	3'6'-di-coumaroylaloesin Van Heerden F.R. *et al.* (1997) Source: *Aloe lutescens*		 λUV$_{max}$ 210, 223, 252sh, 300
C29	3'-O-coumaroylaloesin Van Heerden, F.R. *et al.* (1997) Source: *Aloe lutescens*		 λUV$_{max}$ 213, 223, 248, 300
C30	2-acetonyl-7-hydroxy-8-(3-hydroxyacetonyl)-5-methy chromone Speranza, G. *et al.* (1997) Source: Cape aloe		

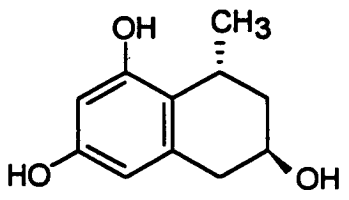
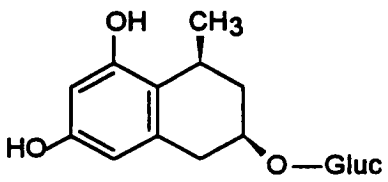
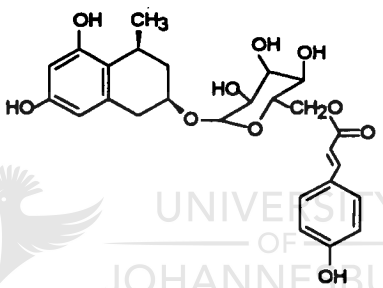
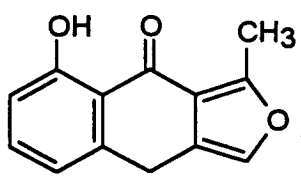
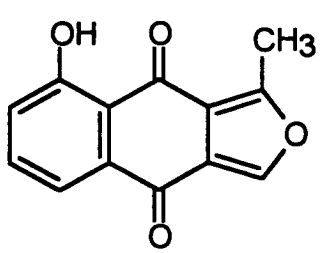
C31	2-acetonyl-8-(2-feroylmethyl)-7-hydroxy-5-methychromone Speranza, G. *et al.* (1997) Source: Cape aloe	

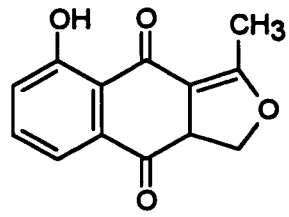
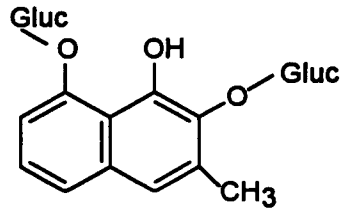
Co1	3,4-dihydro-6-8-dihydroxy-3-(2'-acetyl-3'-beta-D-gluco-pyranosyl-5'-hydroxyphenyl) methyl-2 (1H)-benzopyran-1-one Veitch, N.C. *et al.* (1994) Source: *Aloe hildebrandtii*		 UV^{MeOH}_{max} 244, 271, 323
Co2	Feralolide Speranza, G. *et al.* (1993) Source: Cape aloe		UV^{MeOH}_{max} 244, 271, 323

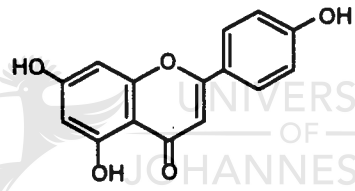
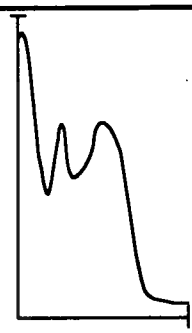
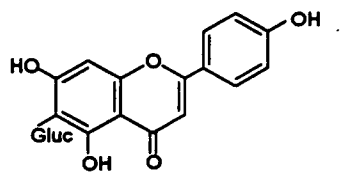
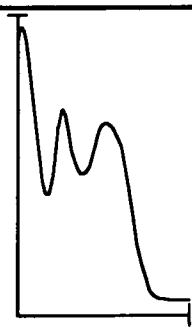
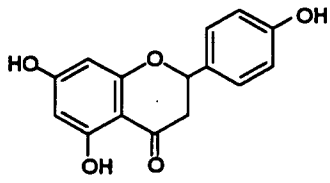
P1	Aloenin Makino, K. *et al.* (1973) Suga, T. *et al.* (1974) Hirata, T. *et al.* (1976) Hirata, T. *et al.* (1978) Conner, J.M. *et al.* (1987) Source: *Aloe cremnophila*		 UV^{MeOH}_{max} 244, 271, 323
P2	Aloenin B Speranza, G. *et al.* (1986) Source: Kenya aloe		UV^{MeOH}_{max} 244, 271, 323
P3	Aloenin aglycone Conner, J.M. *et al.* (1987) Source: *Aloe nyeriensis*		UV^{MeOH}_{max} 244, 271, 323

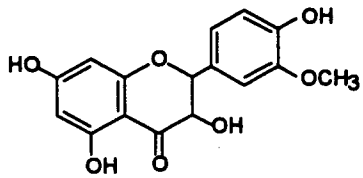
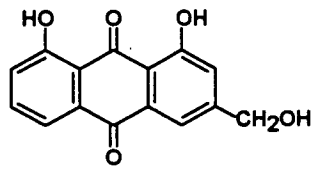
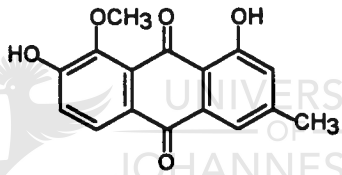
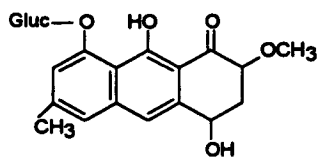
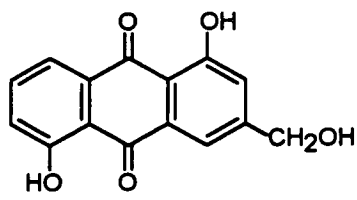
P4	Aloenin-2"-*O*-p-coumaroyl ester Conner, J.M. *et al.* (1987) Source: *Aloe nyeriensis*		UV_{max}^{MeOH} 244, 271, 323
P5	Aloenin acetal Woo, W.S. *et al.* (1987) Source: *Aloe arborescens*		UV_{max}^{MeOH} 244, 271, 323

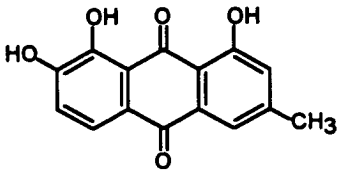
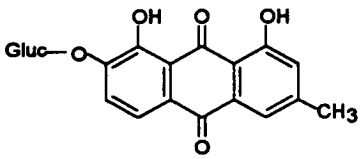
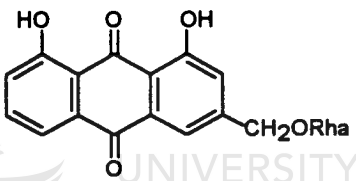
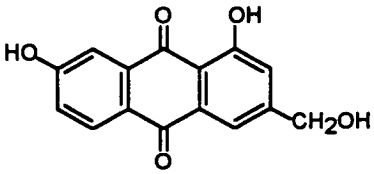
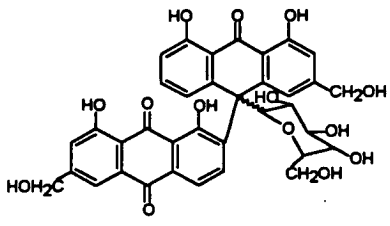
B1	Methyl p-coumarate Graf, E. *et al.* (1982) Source: Cape aloe		UV_{max}^{MeOH} 244, 271, 323
B2	Protocatechuic acid Dagne, E. *et al.* (1991) Source: *Aloe berhana*		UV_{max}^{MeOH} 244, 271, 323

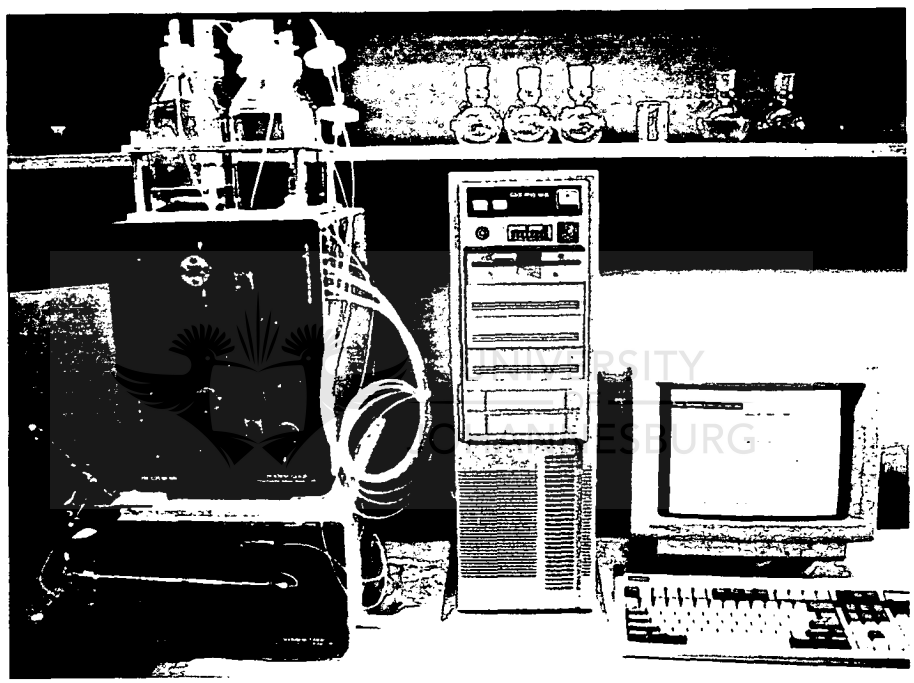
N1	Feroxidin Speranza. *G. et al.* (1990) Source: Cape aloe		UV_{max}^{MeOH} 244, 271, 323
N2	Feroxin A Speranza, G. *et al.* (1992) Source: Cape aloe		UV_{max}^{MeOH} 244, 271, 323
N3	Feroxin B Speranza, G. *et al.* (1992) Source: Cape aloe		UV_{max}^{MeOH} 244, 271, 323
N4	5-hydroxy-3-methylnaphto [2,3-c]furan-4(9*H*)-one Speranza, G. *et al.* (1994) Source: Cape aloe		UV_{max}^{MeOH} 244, 271, 323
N5	5-hydroxy-3-methylnaphto [2,3-c] furan-4,9-dione Speranza, G. *et al.* (1994) Source: Cape aloe		UV_{max}^{MeOH} 244, 271, 323

N6	5-hydroxy-3-methylnaphto [2,3-c] furan-4,9-dione Speranza, G. *et al.* (1994) Source: Cape aloe		UV_{max}^{MeOH} 244, 271, 323
N7	Plicataloside Wessels, P.L. *et al.* (1996) Source: *Aloe plicatilis*		 UV_{max}^{MeOH} 244, 271, 323

F1	Apigenin Williams, C.A. (1975) Viljoen, A.M. *et al.* (1997) Source: *Aloe spp.* (*A. suzannae*)		 UV_{max}^{MeOH} 244, 271, 323
F2	Isovitexin Viljoen, A.M. *et al.* (1997) Source: *A. verecunda*		 UV_{max}^{MeOH} 244, 271, 323
F3	Naringenin Viljoen, A.M. *et al.* (1997) Source: *Aloe lineata*		 UV_{max}^{MeOH} 244, 271, 323

F4	Dihydroisorhamnetin Viljoen, A.M. *et al.* (1997) Source: *Aloe lineata*		 UV_{max}^{MeOH} 244, 271, 323
Aq1	Aloe-emodin Conner, J.M. *et al.* (1990) Source: *Aloe spp.*		UV_{max}^{MeOH} 244, 271, 323
Aq2	Nataloe-emodin-8-methyl ether Thomson, R.H. (1971) Source: *Aloe speciosa*		UV_{max}^{MeOH} 244, 271, 323
Aq3	Aloesaponol IV-8-*O*-glc Yagi, A, *et al.* (1983) Source: *A. saponaria*		UV_{max}^{MeOH} 244, 271, 323
Aq4	1,5-Dihydroxy-3-hydroxymethyl-anthraquinone Mebe, P.P. (1987) Source: *Aloe excelsa*		UV_{max}^{MeOH} 244, 271, 323

Aq5	Nataloe-emodin Conner, J.M. *et al.* (1987) Source: *Aloe nyeriensis*		UV_{max}^{MeOH} 244, 271, 323
Aq6	Nataloe-emodin-2-*O*-glucoside Conner, J.M. *et al.* (1987) Source: *Aloe nyeriensis*		UV_{max}^{MeOH} 244, 271, 323
Aq7	Aloe-emodin-11-*O*-rhamnoside Conner, J.M. *et al.* (1989) Source: *Aloe rabaiensis*		UV_{max}^{MeOH} 244, 271, 323
Aq8	7-hydroxyaloe-emodin Sigler, A. *et al.* (1994) Source: *Aloe succotrina*		UV_{max}^{MeOH} 244, 271, 323
Bq9	Elgonica dimer A/B Conner, J.M. *et al.* (1990) Source: *Aloe elgonica*		UV_{max}^{MeOH} 244, 271, 323



Chapter 3

Materials & Methods

CHAPTER 3

MATERIALS & METHODS

Sampling strategy

To ensure accuracy and thoroughness of study it was imperative to obtain leaf samples (exudate or leaf material) from as many species of *Aloe* as possible. Due to the expansive distribution of the genus and the large number of species, international collaboration was critical to obtain sufficient and representative material. This study has mostly been concerned with the leaf exudate chemistry of *Aloe*. Leaf exudate from species were collected *in situ* and in garden collections or received from various collaborators and succulent hobbyists as tabulated in Table 3.1.

Table 3.1: Origin of exudate samples.

Institution or Person	Comment
The National Botanical Institute (NBI, Pretoria)	An excellent collection of most South African species, tropical aloes and Malagasy endemics.
The National Botanical Gardens (NBG, Kirstenbosch)	Mostly South African species collected by Ernst van Jaarsveld.
The Johannesburg Botanical Garden (JBG)	Rare species endemic to Namibia.
Royal Botanical Gardens, Kew, England, (Kew, RBG)	Large collection of aloes mostly distributed in tropical east Africa.
Bot. Staats. München (BSM)	Various species from East Africa.
Prof L.E. Newton Department of Botany, Kenyatta University, Nairobi.	Impressive personal collection of east African aloes including a large number of type specimens.
Mr J. Lavranos Loulé Portugal	Veteran aloe specialist who supplied various samples of aloes endemic to the Arabian Peninsula and Somalia including type material.
Mr P. Favell California USA	Extensive collection of aloes.
Mr Sebsebe Demissew Department of Botany Addis Ababa University, Ethiopia	The University has established a garden containing a large number of Ethiopian aloes studied in a photochemical project.
Mr Anthon Ellert Zimbabwe	Succulent hobbyist. Supplied exudate samples of many Zimbabwean species.

The HPLC equipment with which all samples were analysed (Photo: Ben-Erik van Wyk).

Institution or Person	Comment
Mr D. Hardy Previously from the NBI, Pretoria	Succulent hobbyist with an impressive collection of Malagasy endemics.
Mr C. Craib Johannesburg, South Africa	Boasts an impressive collection of the grass-like aloes.
Mr B. Kemble USA	Succulent hobbyist. Supplied a number of species not in the collection of P. Favell.
Prof G.F. Smith NBI, Pretoria	Collected a large number of exudate samples *in situ*.
Mr E. van Jaarsveld NBG, Kirstenbosch	Succulent specialist who supplied type material of many highly localised species.
Prof M.C.B. van Oudtshoorn South African Druggists	Collected exudate samples of *A. marlothii* *in situ*.

The extensive list of collaborators and interested persons made it possible to survey almost the entire genus. The total number of known species of *Aloe* is close to 400 of which 340 species were studied. It should here be emphasised that species pertaining to *Aloe* series *Saponariae*, a large group of *ca.* 34 species were intentionally excluded as they did not contain anthrones and chromones and no attempt was made to obtain samples of these species. Figure 3.1 shows the number of species studied in each of the taxonomic groups.

Many of the species not included in this study either have an extremely localised habitat and / or do not perform well when transplanted from nature. A complete list of all species, voucher details and the number of samples for each species which have been analysed is included in Table 3.3 at the end of this Chapter.

Analysis of leaf exudate and leaf extracts

The tip of the succulent leaf was removed with a blade and the exudate allowed to accumulate on the excised leaf tip. The exudate was transferred to a strip of filter paper (Whatman No. 1) and left to dry. In the laboratory the filter paper containing the exudate sample was placed in a vial and submerged in 1 ml of methanol. The exudate samples were investigated initially on TLC but later the analysis was restricted to HPLC. The dissolved samples were passed through C_{18} cartridges to remove substances of high retention time. These purified samples were dissolved in methanol-water (1:1) and injected into the HPLC system. Operating conditions were as follows: A C_{18} Phenomenex IB-Sil column was used (5μm particle size,

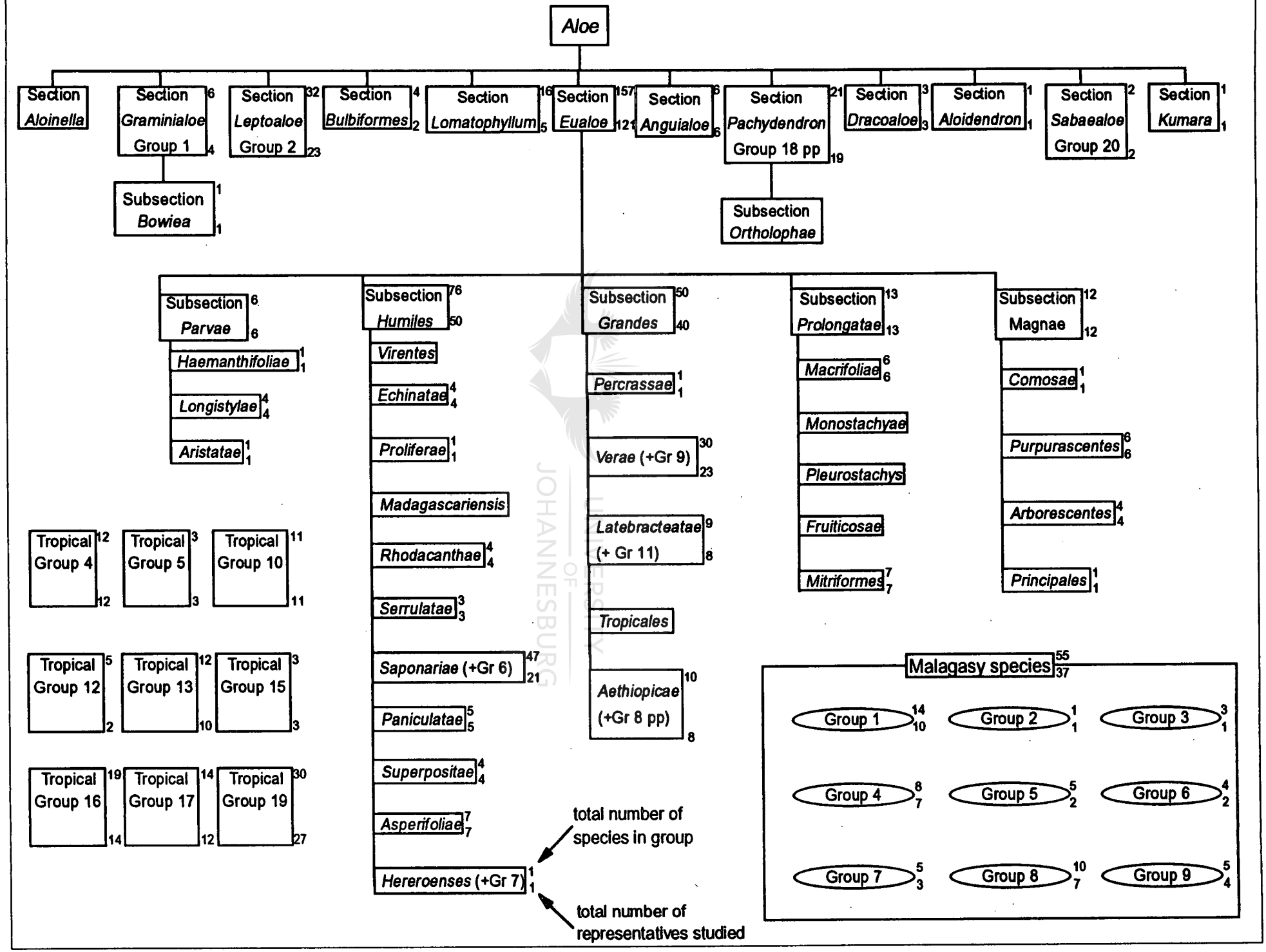


Figure 3.1: Taxonomic representation of species studied.

250 mm X 4.6 mm internal diameter; flow rate 1 ml min^{-1}; 20 μl sample loop). The solvent system comprised a 30 % to 60 % linear gradient of methanol in water over 25 min, 3 min isocratic, 100% in 2 min, 4 min isocratic. (Figure 3.2) Detection was by diode array detector, using two channels (A set at 275 ± 70 nm; B set at 365 ± 40 nm). The System Gold software package (Beckman) was used to evaluate the chromatograms and UV spectra. TLC was carried out on silica gel (Merck) plates using ethylacetate-methanol-water (100 : 16.5 : 13.5) as eluent. Compounds were identified by comparison (the R_f-values, visibility/colour under UV 254 and 366 nm, retention times, UV/VIS spectra) with reference samples. A large number of authentic samples of chromones and anthrones were made available by various collaborators (Table 3.3) or were isolated during this study. Some samples (mostly the flavanone-containing species) were subjected to acid hydrolysis (4N HCl for 60 min at 95 °C). The HPLC method described above using the gradient system as shown in Figure 3.2 was far from satisfactory for some species. This method, however, proved to give the best separation of the compounds under investigation and provided the best results for a comparative chromatographic study. The method could be adjusted to study species such as *A. microdonta* and *A. microstigma* to achieve better separation of the late eluting compounds. Deteriorating column conditions also resulted in the poor separation of various compounds e.g. microdontins A and B. Frequent replacement of the guard column resulted in a shift in retention times and were compared to previous analyses by co-injection of compounds and proportional adjustment of the retention times and comparison of the UV spectra.

All compounds have been identified by comparison of R_t and UV absorbance spectra. Although this method of identification is not infallible it does provide a rapid and rigorous comparison of the composition of leaf exudate compound. For example 3'-*O*-coumaroylaloesin and aloeresin A have identical retention times, R_f-values and display the same UV absorbance spectra. Under the analysing parameters it has been impossible so distinguish between the compound where the ester group is attached to the 3' or 2' position of the sugar moiety. For this reason taxonomic conclusions and hypothesis have mostly been founded on the entire chromatographic profile for a species in which the class of compound and the co-occurrence of exudate compounds have been considered. Retention times and UV absorbance spectra were compared to standards where possible. The standards used in this study and their origin are shown tabulated in Table 3.2.

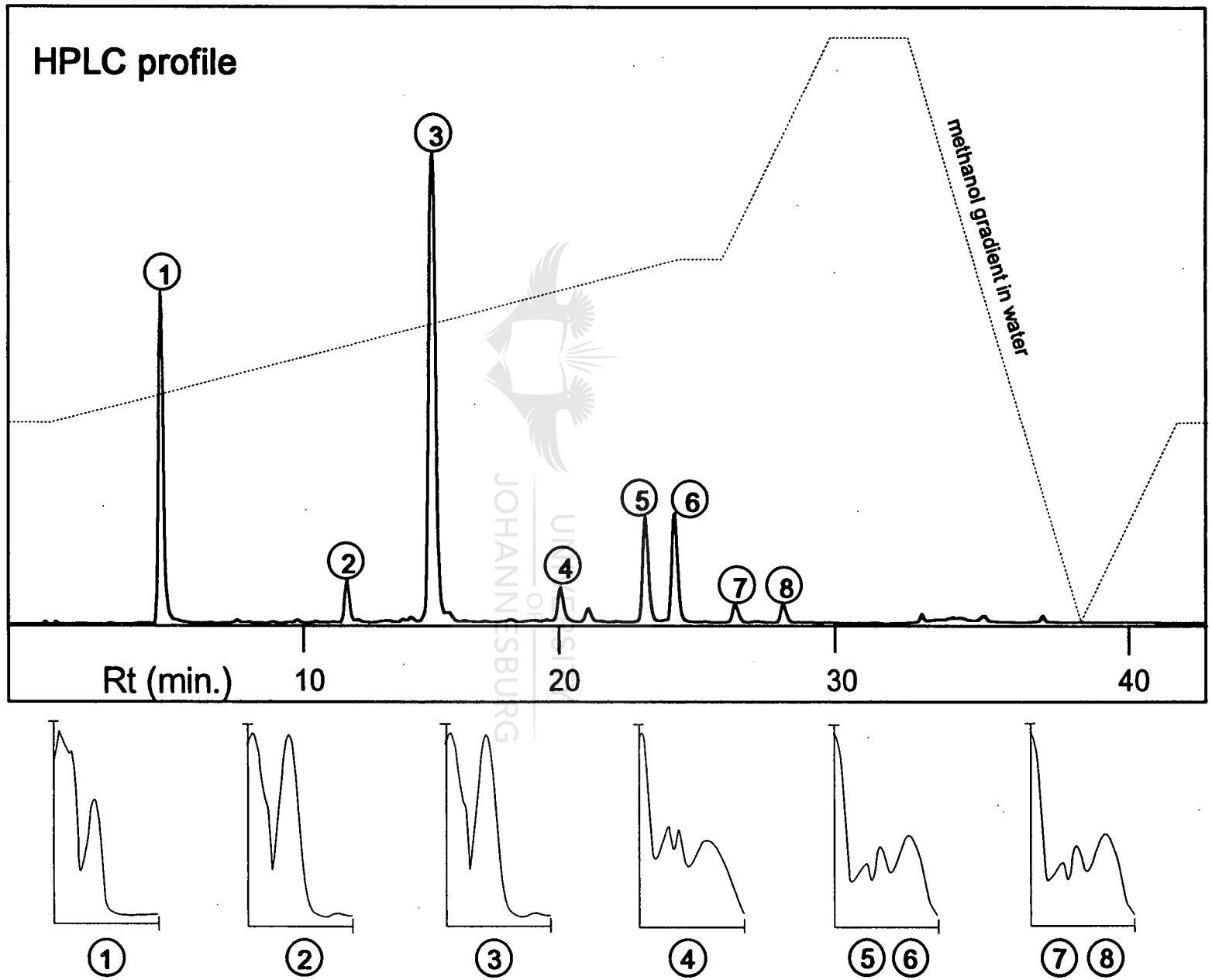


Figure 3.2: A typical HPLC separation of leaf exudate compounds. The UV spectum for each of the compounds is also illustrated.

Table 3.2. Reference compounds used in the study. The species from which the reference compound was isolated and the supplier of the sample is also included.

Compound	Comment / Source
10-hydroxyaloin A	Isolated from *A. barbadensis* (ex Hill Park)
10-hydroxyaloin B	Isolated from *A. claviflora* (ex Dagne)
10-hydroxyaloin-6'-*O*-mono-acetate B	Isolated from *A. claviflora* (ex Dagne)
3'-*O*-coumaroylaloesin	Isolated from *A. lutescens* (Viljoen)
3'6'-di-coumaroylaloesin	Isolated from *A. lutescens* (Viljoen)
5-hydroxyaloin B	Isolated from *A. broomii* (ex Holzapfel)
6'-*O*-coumaroylaloesin	Isolated from *A. castanea* (Viljoen)
7-hydroxyaloin	Isolated from *A. pulcherrima* (ex Dagne)
7-*O*-methylaloesin	Isolated from *A. rupestris* (ex Dagne)
7-*O*-methylisoaloesinol	Isolated from *A. barbadensis* (ex Hill Park)
8-*O*-methyl-7-hydroxyaloin B	Isolated from *A. schelpei* (Viljoen)
Aloeresin C	Isolated from Cape aloes (ex Speranza)
Aloenin	Isolated from *A. debrana* (ex Dagne)
Aloeresin E (Okamura)	Isolated from *A. barbadensis* (ex Hill Park)
Aloeresin E (Van Heerden)	Isolated from *A. peglerae* (Viljoen)
Aloeresin F	Isolated from *A. peglerae* (Viljoen)
Aloeresin A	Isolated from Cape aloes (ex Speranza)
Aloeresin D	Isolated from Cape aloes (ex Speranza)
Aloesin	Isolated from Cape aloes (ex Speranza)
Aloin A and B	Isolated from *A. megalacantha* (ex Dagne)
Aloinoside A and B	Isolated from *A. megalacantha* (ex Dagne)
Apigenin	Isolated from *A. suzannae* (Viljoen)
Broomii chromone 1	Isolated from *A. broomii* (ex Holzapfel)
Broomii chromone 2	Isolated from *A. broomii* (ex Holzapfel)
Deacetyllittoraloin	Isolated from *A. claviflora* (ex Dagne)
dihydroisocoumaringlucoside	*Aloe hildebrandtii* used as reference
dihydroisorhamnetin	Isolated from *A. pretoriensis* (Viljoen)

Compound	Comment / Source
Homonataloin A and B	Isolated from *A. speciosa* (ex Holzapfel)
Homonataloside B	Isolated from *A. lutescens* (Viljoen)
Isoaloeresin D	Isolated from *A. barbadensis* (ex Hill Park)
Isovitexin	Isolated from *A. verecunda* (Viljoen)
Littoraloin	Isolated from *A. littoralis* (ex Dagne)
Microdontin A and B	Isolated from *A. schelpei* (Viljoen)
Microstigmin	Isolated from *A. microstigma* (ex Dagne)
Naringenin	Isolated from *A. lineata* (Viljoen)
Nataloin A and B	Isolated from *A. pulcherrima* (ex Dagne)
Neoaloesin A	Isolated from *A. barbadensis* (ex Hill Park)
Plicataloside	Isolated from *A. plicatilis* (ex Holzapfel)
Speciosa chromone	Isolated from *A. speciosa* (ex Holzapfel)

Most reference samples were obtained from authors who have reported new structures from *Aloe*. For the purpose of this study, 11 compounds of chemotaxonomic value were isolated. In most cases the compounds were isolated by the author and the structural elucidation of the compounds using various spectroscopic methods were completed by Prof F.R. van Heerden from the Department of Chemistry and Biochemistry at the same university.

Isolation of aloeresins E and F

Fresh leaves of *Aloe peglerae* were collected at a locality in the Magaliesberg, South Africa. The leaves (771 g) were soaked in methanol for 24 hours at room temperature. The exudate extract was filtered and evaporated to yield a brown residue (12 g). A portion of this extract (0.95 g) was subjected to PHPLC to afford aloeresin E* (11 mg) and aloeresin F (5 mg). Structural elucidation of the compounds was done by Prof F.R van Heerden at the Department of Chemistry, Rand Afrikaans University. For full details see Van Heerden *at al.* (1996).

*Okamura *et al.* (1996) published a new compound from *A. barbadensis* and also named it Aloeresin E. Aloeresin E as described by Van Heerden *et al.* (1996) was published before that of Okamura *et al.* hence its validity.

Isolation of homonataloside B, 3'6'-di-coumaroylaloesin and 3'-O-coumaroylaloesin.

The leaves of *A. lutescens* were extracted as described above. The compounds were isolated using PTLC to yield 22 mg of homonataloside B, 14 mg of 3'6'-di-coumaroylaloesin and 16 mg of 3'-O-coumaroylaloesin (Van Heerden *et al.* 1997)

Isolation of 8-*O*-methyl-7-hydroxyaloin B

Leaf material of *Aloe schelpei* was collected at the NBI institute Pretoria. The leaves were extracted as described above. PHPLC was used to isolate 8-*O*-methyl-7-hydroxyaloin. Results obtained with NMR suggested the isolated compound to be a mixture of 8-*O*-methyl-7-hydroxyaloin A and B isomers. Structural elucidation was done by Prof F.R. van Heerden, Department of Chemistry, RAU and the NMR data was congruent with that reported by Rauwald (1990).

Isolation of dihydroisorhamnetin

Leaves of *A. pretoriensis* were collected at Soutpan near Pretoria, South Africa. The leaves were extracted as described above. The exudate was subjected to acid hydrolysis (4N HCl) at 100°C for 60 min. and the dihydroflavonol was isolated using PHPLC. The structure was resolved by Prof F.R. van Heerden, Department of Chemistry, Rand Afrikaans University. For full details see Viljoen *et al.* (1998).

Isolation of naringenin

Leaves of *A. lineata* were collected near Vaalkranz, South Africa. The leaves were extracted as described above. Naringenin was isolated using PTLC, methanol:water (9.5 : 0.5). NMR data confirmed the identity when matched to that of a commercial sample. For full details see Viljoen *et al.* (1998).

Isolation of Isovitexin

Aloe verecunda leaves (600 g) were collected at Melville Koppies and extracted as described for aloeresins E and F. Both PTLC and PHPLC was used to isolate the flavone which is present as the main compound in the leaf extract. The structure was resolved by Prof F.R. van Heerden, Department of Chemistry, Rand Afrikaans University. For full details see Viljoen *et al.* (1998).

Isolation of compounds from *A. elegans*

Leaves of *Aloe elegans* (506 g) were extracted as described above to yield an exudate residue of 2.2 g . Five compounds were isolated from this species. The first two compounds were confirmed to be aloinoside A and B. More material was required of the three remaining compounds to determine the structure. At this time microdontin A and B were sent from Prof E. Dagne, Addis Ababa. Compound 3 and 4 isolated from *Aloe elegans* corresponded to the R_t and UV spectra of microdontin A and B.

Isolation of 6'-*O*-coumaroylaloesin from *A. castanea*

The widespread *Aloe castanea* was collected at the 'Three Rondawel view site' in Mpumalanga, South Africa. The leaves (1.1 kg) were left to exude (24 hr at room temp.). After filtration and evaporation a yellow residue (15 g) was obtained. Analytical HPLC analysis confirmed the presence of aloesin, an unidentified chromone and aloin A & B. Aloesin, aloin A and B were confirmed by HPLC comparison with authentic standards. The unidentified chromone, a reliable chemotaxonomic marker for the section *Anguialoe*, was isolated. A portion of the exudate (5.8 g) was subjected to flash column chromatography using solvent system $ChCl_3$:MeOH (8:2) to yield 236 mg pure 6'-*O*-coumaroylaloesin. For details see Van Heerden *et al.* (in press).

The intention of the study was not to isolate compounds from *Aloe* but rather to do a rigorous comparison and interpretation of chromatographic data. This comprehensive screening indicated chemotaxonomic markers which were isolated (as described above) while some compounds were isolated in collaboration with Dr E. Dagne from the Department of Chemistry, Addis Ababa, Ethiopia.

The chemotaxonomic markers of *Aloe* series *Asperifoliae* were identified during the initial screening. Bulk leaf exudate samples of *Aloe littoralis* was collected near Vivo and also from *A. claviflora* near Strydenburg. From *A. littoralis* 10-hydroxyaloin B, littoraloin and deacetyllittoraloin was isolated (Dagne *et al.* 1996). A fourth related compound, 10-Hydroxyaloin-6'-O-monoacetate B was isolated from *A. claviflora* (Dagne *et al.* 1997). The chemotaxonomic value of these four compounds are summarised in Chapter 11.

The pilot study also indicated a chemotaxonomic marker for *Aloe* series *Purpurascentes* and related species. For the isolation of this compound bulk leaf exudate material was collected of *Aloe microstigma* near Robertson in South Africa. The isolation and structural elucidation

of this compound was reported by Dagne *et al.* 1997 and the chemotaxonomic value is discussed in Chapter 8.

Hennig 86 (Farris, 1988) and Tree Gardiner (Ramos, 1997) were used for the cladistic analyses. Phenetic analyses were done with NTSYSpc version 2.00 (Rohlf, 1997).

Table 3.3: Voucher details of all species examined. Column 3 represents the number of samples analysed for the particular species and the + sign in column 4 indicates the inclusion of an HPLC profile in Appendix 2.

Species	Voucher / Locality Details	3	4
A. aageodonta	L. E. Newton 3643	1	+
A. abyssicola	NBI 15813	1	+
A. aculeata	NBG 786/69, *ex hort* WBG	2	+
A. acutissima var. *acutissima*	Lavranos *et al.*30009	1	+
A. adigratana	NBI 31507, Sebsebe 394	2	
A. africana	Port Elizabeth, Tipper's Creek, Fort Brown, Ann's Villa	4	+
A. albovestita	RBG, Kew 89678	1	
A. aldabrensis	NBI, Wickens 3519	1	+
A. alooides	The Bonnet	1	+
A. ambigens	NBI 31335	1	
A. amicorum	L. E. Newton 3217	1	+
A. amudatensis	A. Ellert 16	1	+
A. andongensis	*ex hort* NBI	1	
A. angelica	Waterpoort	1	+
A. antandroi	*ex hort* D. Hardy, NBI 14685	2	+
A. arborescens	18 localities	18	+
A. archeri	L. E. Newton 3118	1	+
A. arenicola	*ex hort* JBG, NBI 1283/92	2	+
A. argenticauda	*ex hort* JBG	2	+
A. aristata	*ex hort* NBI	1	
A. asperifolia	Van Jaarsveld 2850, *ex hort* JBG, NBI 432/72	3	+
A. babatiensis	RBG, Kew 1974-4463	1	+
A. bakeri	NBI 31548	1	+
A. ballii	A. Ellert 529	1	
A. barberae	*ex hort* NBI, *ex hort* NBG	2	+
A. bargalensis	NBI 16949	1	+
A. bella	NBI 31546	1	+
A. bellatula	NBI 16648	1	+
A. betsileensis	Lavranos 30045	1	
A. buettneri	*ex hort* NBI, RBG, Kew 19826029	2	
A. boiteaui	*ex hort* B. Kemble, *ex hort* P. Favell	2	
A. boscawenii	*ex hort* P. Favell	1	+
A. bowiea	*ex hort* NBI	1	
A. boylei	*ex hort* C. Craib, NBI 31524	2	+
A. brachystachys	NBI 17388	1	+
A. brandhamii	S. Carter *et al.*2600	1	+
A. branddraaiensis	*ex hort* JBG, exhort NBG	2	
A. brevifolia	*ex hort* JBG	1	+

Species	Voucher / Locality Details	3	4
A. breviscapa	NBI 17034	1	+
A. broomii	Springfontein, Middelburg, Bethulie	3	+
A. brunneostriata	*ex hort* NBI	1	+
A. buchlohii	*ex hort* D. Hardy, NBI 14645	2	+
A. buhrii	*ex hort* NBG, *ex hort* JBG	2	
A. bukobana	RBG, Kew 1990-1816	1	+
A. bulbillifera	*ex hort* D. Hardy	1	+
A. bussei	*ex hort* P. Favell, RBG, Kew 1990-1816	2	+
A. calidophila	RBG, Kew 1974-4199	1	+
A. cameronii	NBI 15231, A. Ellert 79	2	+
A. camperi	Sebsebe 208, *ex hort* NBI	2	+
A. canarina	RBG, Kew 1977-3888	1	+
A. capitata var. gneissicola	NBI 16218	1	+
A. castanea	Three Rondawels, Elandslaagte	2	+
A. castellorum	RBG, Kew 1981-2893	1	
A. catengiana	*ex hort* P. Favell, RBG, Kew 1960-70602	2	+
A. chabaudii	A. Ellert 32, Steelpoort, Zimbabwe	3	+
A. cheranganiensis	*ex hort* P. Favell, *ex hort* B. Kemble	2	+
A. chlorantha	Lavranos 10024	1	+
A. chortolirioides var. *woolliana*	*ex hort* C. Craib	1	+
A. chortolirioides	*ex hort* C. Craib, NBI 29453	2	+
A. christianii	A. Ellert 591	1	+
A. chrysostachys	L. E. Newton 4040 & 4246	2	+
A. ciliaris	*ex hort* NBG, NBI 10674	2	+
A. citrina	*ex hort* P. Favell	1	+
A. classenii	L. E. Newton 3910	1	+
A. claviflora	Strydenburg, Graaff-Reinet, Beaufort West, Namibia	4	+
A. collenetteae	Type plant	1	
A. commixta	*ex hort* NBG, NBI 29455	2	+
A. comosa	Pakhuis Pass	1	+
A. compressa	*ex hort* D. Hardy	1	
A. comptonii	NBI 29356, Perdepoort	2	+
A. confusa	*ex hort* Uitenhage, RBG, Kew 1977-5436	2	+
A. congdonii	Image Mt.	1	+
A. conifera	*ex hort* D. Hardy, Lavranos 29981	2	+
A. cooperi	NBI 4202	1	
A. corallina	NBI 20079	1	+
A. cremnophila	RBG, Kew 1958-29517	1	+
A. cryptopoda	*ex hort* NBI, A. Ellert 8	2	+
A. dabenorisana	Dabenorisberg	1	+
A. dawei	RBG, Kew 1951-35701, BSM	2	+
A. debrana	Sebsebe 206 & 288	2	+
A. decurva	*ex hort* P. Favell	1	+
A. deltoideodonta	*ex hort* Hardy, NBI 15003	2	

Species	Voucher / Locality Details	3	4
A. descongsii	*ex hort* NBI	1	+
A. deserti	L. E. Newton 3608, RBG, Kew 16970	2	+
A. dewetii	*ex hort* NBI	1	
A. dewinteri	*ex hort* NBG, Warmbad	2	+
A. dhufarensis	RBG, Kew 409-77	1	+
A. dichotoma	*ex hort* NBG, NBI 293322	2	+
A. dinteri	NBI 28177	1	
A. diolii	L. E. Newton 3508	1	+
A. distans	Saldanha	1	+
A. divaricata	RBG, Kew 1988 2467, NBI 30617	2	+
A. dolomitica	Wolkberg	1	+
A. dominella	*ex hort* C. Craib	1	+
A. dorotheae	NBI 17305, RBG, Kew 295-58-29212	2	+
A. duckeri	*ex hort* L. E. Newton	1	+
A. dyeri	NBI 21990, *ex hort* D. Hardy	2	
A. ecklonis	Middelburg, NBI 29453	2	+
A. elata	S. Carter & L.E Newton 3946	1	
A. elegans	*ex hort* NBI	1	+
A. elgonica	*ex hort* JBG	1	+
A. ellenbeckii	L. E. Newton 3231	1	
A. eminens	*ex hort* NBI	1	+
A. enotata	*ex hort* NBI	1	
A. erensii	RBG, Kew 29558	1	+
A. erinacea	NBI 13426, NBI 24391, NBG 168/60	3	+
A. erythrophylla	ex A. Razafindratsira	1	
A. esculenta	NBI 27823	1	+
A. excelsa	NBI 27286	1	+
A. falcata	Van Rhynsdorp	1	+
A. ferox	22 localities (see Chapter 16)	66	+
A. fibrosa	*ex hort* P. Favell	1	+
A. fievetii	*ex hort* NBI	1	
A. fimbrialis	L. E. Newton 5605	1	
A. fleurentiniorum	*ex hort* D. Hardy, RBG, Kew 1977-3317	2	+
A. flexilifolia	*ex hort* P. Favell, RBG, Kew 258-90-0811	2	+
A. forbesii	*ex hort* NBI	1	+
A. fosteri	*ex hort* D. Hardy, A. Ellert 30, NBI 27137	3	
A. fouriei	NBI 27652	1	+
A. fragilis	Lavranos 28737, *ex hort* Hardy	2	+
A. framesii	NBI 29271	1	+
A. francombei	L. E. Newton 4130	1	+
A. gariepensis	Lavranos 29597, NBI 29275	2	+
A. gerstneri	Bababango, NBG 11 96/83	2	+
A. gilbertii	RBG, Kew 1990-1301, Sebsebe 226	2	+
A. gillettii	Gillett & Wilson, RBG, Kew 1981-3490	2	

Species	Voucher / Locality Details	3	4
A. glauca	*ex hort* WBG, Bonnievale, NBI JV 16716	3	+
A. globuligemma	A. Ellert 606, A. De Castro 147, Brandfort, Dendron	4	+
A. gossweileri	*ex hort* RBG, Kew	1	+
A. gracilicaulis	NBI 13500	1	
A. gracilis	*ex hort* NBG	1	+
A. gracilis var. *decumbens*	*ex hort* NBG	1	+
A. grandidentata	NBI 23900	1	
A. greatheadii var. *davyana*	ex hort NBI, Springfontein	2	
A. grisea	RBG, Kew 19-8-83	1	
A. guillaumetii	Lavranos 28738	1	+
A. haemanthifolia	Bainskloof	1	
A. hardyi	*ex hort* Hardy, ex hort Van Jaarsveld	2	+
A. harlana	*ex hort* BSM	1	+
A. haworthioides	*ex hort* NBI	1	
A. helenae	*ex hort* D. Hardy	1	+
A. heliderana	NBI 31545	1	
A. hemmingii	NBI 11170, RBG, Kew 08481-01059	2	+
A. hereroensis	NBI 28966, *ex hort* JBG	2	+
A. hildebrandtii	RBG, Kew 144-73-01211, & 1981-886	2	+
A. hlangapies	*ex hort* C. Craib	1	+
A. howmanii	RBG, Kew 2708	1	
A. humilis	NBI 27971	1	+
A. ibityensis	NBI 14743	1	
A. imalotensis	*ex hort* D. Hardy	1	
A. inamara	*ex hort* Hardy	1	
A. inconspicua	*ex hort* C. Craib	1	+
A. inermis	Lavranos 4338, NBI 10254	2	+
A. integra	*ex hort* C. Craib	1	+
A. inyangensis	*ex hort* NBI, A. Ellert 171	2	
A. isaloensis	*ex hort* NBI	1	+
A. jacksonii	L. E. Newton 3956, *ex hort* D. Hardy, NBI 5570	3	+
A. jucunda	L. E. Newton 4082, NBI 544	2	+
A. juvenna	*ex hort* NBI	1	
A. kedongensis	NBI 11210	1	+
A. keithii	NBI 22498	1	
A. khamiesensis	Skuinshoogte, *ex hort* JBG	2	+
A. kilifiensis	L. E. Newton 3631	1	
A. kniphofioides	*ex hort* C. Craib	1	+
A. krapohliana	Lavranos 29442	1	+
A. kraussii	*ex hort* C. Craib, NBI 29453	2	+
A. kulalensis	L. E. Newton 3219	1	+
A. labworana	NBI 17305, RBG, Kew 295-58-29212	2	+
A. lateritia var. *lateritia*	NBI 20829, ex Kenya	2	
A. leachii	RBG, Kew 1990-1820	1	+

Species	Voucher / Locality Details	3	4
A. lensayuensis	L. E. Newton 5571, RBG, Kew 242 63 24204	2	+
A. leptosiphon	RBG, Kew 1990-1812	1	+
A. linearifolia	*ex hort* C. Craib	1	+
A. lineata	Uitenhage, Tipper's Creek, Vaalkranz	3	+
A. littoralis	PRE (Etosha & Windhoek), Vivo	3	+
A. lomatophylloides	*ex hort* NBI	1	+
A. longistyla	Calitzdorp	1	+
A. lateritia var. graminicola	Nanyki (ex Kenya)	9	
A. luntii	NBI 31417	1	
A. lutescens	JBG 85-5332, *ex hort* NBG, Kingskloof	3	+
A. macrocarpa	Sebsebe 317	1	
A. macroclada	Lavranos *et al.*30049	1	+
A. macrosiphon	*ex hort* P. Favell, L. E. Newton 4250, NBI 11157	3	+
A. maculata	A. Ellert 170	1	
A. madecassa	*ex hort* D. Hardy	1	
A. marlothii	28 localities (see Chapter 16)	1400	+
A. massawana	L. E. Newton 4435, RBG, Kew 2287412104	2	+
A. mawii	L. E. Newton 3836, NBI 315051	2	+
A. mayottensis	RBG, Kew 1976-451	1	+
A. mcloughlinii	RBG, Kew 595-59-59512 & 485-84-04966	2	+
A. medishiana	NBI 13488	1	
A. megalacantha	Sebsebe 325, RBG, Kew 144-93-01240	2	+
A. melanacantha	JBG 83-5-440	1	+
A. menachensis	RBG, Kew 439-7504-505	1	+
A. mendesil	NBI 11992	1	+
A. metallica	NBI 11764		
A. meyeri	Roesyntjieberg	1	+
A. microdonta	*ex hort* P. Favell, RBG, Kew 1966-12803, NBI 13501	3	+
A. microstigma	Robertson, Lavranos 29578, Jansenville, Cradock	4	+
A. millottii	Hardy 2829, NBI 14657	2	+
A. minima	*ex hort* C. Craib, NBI 31461, Coralina	3	+
A. mitriformis	Du Toitskloof, Kogman'skloof, Slanghoek, NBI 28570, Gifberg	5	+
A. modesta	*ex hort* NBI	1	+
A. molederana	NBI 11194	1	+
A. monotropa	Lavranos 29575, *ex hort* NBG	2	
A. monticola	*ex hort* P. Favell	1	+
A. morijensis	L. E. Newton 3661	1	+
A. multicolor	L. E. Newton 4133	1	+
A. munchii	A. De Castro 144	1	+
A. murina	L. E. Newton 2497	1	+
A. musapana	A. Ellert 551	1	
A. mutabilis	A. Ellert 25, *ex hort* NBI, Chuniespoort	3	+
A. mzimbana	RBG, Kew 364 85038/2	1	+
A. namibensis	NBI 28193	1	+

Species	Voucher / Locality Details	3	4
A. ngongensis	L. E. Newton 3531	1	+
A. niebuhriana	RBG, Kew 1975-4506, NBI 10221	2	+
A. nubigena	God's Window	1	+
A . nyeriensis	Gil-Gil & Rhumeruti (Kenya)	6	+
A. occidentale	ex hort NBI	1	+
A. officinalis	RBG, Kew 206-84-01590	1	+
A. orientalis	NBI 19481	1	+
A. ortholopha	A. Ellert 45, BSM	2	+
A. otallensis	RBG, Kew 194-09-012941	1	+
A. pachygaster	*ex hort* JBG, NBI 1120/70	2	+
A. palmiformis	RBG, Kew 224-94-020-95	1	+
A. parallelifolia	*ex hort* BSM	1	
A. parvibracteata	NBI 29663	1	
A. parvidens	L. E. Newton 4384, RBG, Kew 1985-4219	2	+
A. parvula	*ex hort* NBI	1	
A. pearsonii	Helskloof, NBI 29382	2	+
A. peckii	RBG, Kew 084-81-011-40, *ex hort* JBG, *ex hort* D. Hardy	3	+
A. peglerae	Kingskloof, Scheerpoort	2	+
A. pendens	NBI 19398, RBG, Kew 060-77-00400	1	
A. penduliflora	L. E. Newton 3543, RBG, Kew 349-63-34907	2	+
A. percrassa	Sebsebe 4616, RBG, Kew 368-70-03585, *ex hort* JBG, Sebsebe 206	4	+
A. perryi	NBI 113600	1	
A. petricola	NBI 26458	1	+
A. pictifolia	NBI 2339, *ex hort* D. Hardy, *ex hort* JBG	3	+
A. pillansii	ex hort NBG (Worcester)	1	
A. pirottae	RBG, Kew 391-85-04-164	1	
A. plicatilis	NBG 19503	1	+
A. pluridens	Tipper's Creek	1	
A. polyphylla	Likalaneng, Molomo	2	+
A. pratensis	*ex hort* JBG	1	+
A. pretoriensis	Soutpan, NBI 2483, *ex hort* NBI	3	+
A. prinslooi	*ex hort* D. Hardy	1	
A. pubescens	Sebsebe 316, RBG, Kew 439-75-04512	2	+
A. pulcherrima	Sebsebe 171	1	+
A. purpurea	NBI 31155	1	+
A. pustuligemma	L. E. Newton 3739	1	+
A. rabaiensis	RBG, Kew 1975-903	1	+
A. ramosissima	NBI 29276, *ex hort* NBG 1121/70	2	+
A. rauhii	NBI 16243	1	
A. reitzii	NBG 503/61	1	+
A. retrospiciens	RBG, Kew 630 54 63008	1	+
A. reynoldsii	*ex hort* Hardy	1	
A. rhodesiana	A. Ellert 534	1	
A. rigens	RBG, Kew 1973-1245, Reynolds 7618	2	+

Species	Voucher / Locality Details	3	4
A. rivae	Sebsebe 321	1	+
A. rivierei	*ex hort* NBI	1	
A. rubroviolacea	NBI 15816, RBG, Kew 1977-1247, *ex hort* D. Hardy	3	+
A. rugosifolia	Sebsebe 22	1	+
A. rupestris	*ex hort* NBG, NBI 8284, Muden, NeBG	3	+
A. rupicola	*ex hort* NBI	1	
A. ruspoliana	NBI 20554, *ex hort* L. E. Newton	2	
A. sabaea	*ex hort* JBG, ex hort BSM	2	
A. saundersiae	*ex hort* C. Craib	1	+
A. scabrifolia	L. E. Newton 3272	1	+
A. schelpei	*ex hort* NBI, RBG, Kew 427-64-42705	2	+
A. schweinfurthii	*ex hort* NBI	1	+
A. scobinifolia	*ex hort* BSM, RBG, Kew 084-81-01110	2	+
A. scorpioides	RBG, Kew 224-74-0209-0, *ex hort* NBI	2	+
A. secundiflora var. secund	L. E. Newton 4016, Sebsebe 219	2	+
A. schomeri	ex Tzimbazaza	1	
A. sinana	Sebsebe 4659	1	+
A. sinkatana	*ex hort* BSM	1	+
A. sladeniana	NBI 29045	1	
A. somaliensis	RBG, Kew 084-81-01055, NBI 11169	2	+
A. soutpansbergensis	*ex hort* C. Craib, *ex hort* D. Hardy	2	+
A. speciosa	Fort Brown	1	+
A. spicata	Bourke's Luck, NBI 24959	2	+
A. splendens	NBI 10214	1	+
A. squarrosa	*ex hort* NBI & NBI 24749	2	+
A. steudneri	RBG, Kew 1987-4090, *ex hort* BSM	2	+
A. striata ssp. *karasbergensis*	NBI 24383	1	
A. striata ssp. *komaggasensis*	ex hort NBG	1	
A. striata spp. *striata*	Koega Kop, Kleinpoort	2	
A. striatula	*ex hort* NBG, *ex hort* JBG	2	+
A. succotrina	Hermanus, Table Mountain	2	+
A. suffulta	Mahatini Flats, *ex hort* JBG	2	+
A. suprafoliata	Louwsburg	1	+
A. suzannae	NBI 16988	1	+
A. swynnertonii	A. Ellert 304	1	
A. tauri	A. Ellert 547	1	+
A. tenuior	*ex hort* NBI (3 localities)	3	+
A. tewoldei	Asbe Teferri	1	+
A. thompsoniae	NBI 29456	1	+
A. thorncroftii	NBI 28436	1	+
A. thraskii	Illovo River, Zinkwasi, Umkomaas, Port Elizabeth	4	+
A. tomentosa	RBG, Kew 305-70-02870, NBI 21758	2	+
A. tororoana	*ex hort* P. Favell	1	+
A. trachyticola	*ex hort* P. Favell	1	

Species	Voucher / Locality Details	3	4
A. trichosantha	Sebsebe 4658, NBI 11217	1	+
A. tugenensis	L. E. Newton 3514	1	+
A. turkanensis	RBG, Kew 1977-3733	1	+
A. tweediae	RBG, Kew 1970-1752	1	+
A. ukambensis	NBI 20505	1	+
A. umfoloziensis	NBI 22712	1	
A. vacillans	RBG, Kew 06077-00398 & 1977-3664, ex hort P. Favell	3	+
A. vanbalenii	*ex hort* D. Hardy, *ex hort* The Wilds	2	+
A. vaombe	*ex hort* D. Hardy, *ex hort* NBI	2	+
A. vaotsanda	*ex hort* D. Hardy	1	+
A. variegata	NBI 29309	1	
A. vera	RBG, Kew 1969 12338, BGM	2	+
A. verecunda	Melville Koppies	1	+
A. versicolor	*ex hort* P. Favell	1	
A. veseyi	*ex hort* D. Hardy	1	+
A. viguieri	*ex hort* D. Hardy, NBI 14542	1	
A. viridiflora	NBI 28700, *ex hort* JBG	2	+
A. vituensis	*ex hort* P. Favell	1	
A. volkensii ssp. *volkensii*	L. E. Newton 3770	1	+
A. vossii	*ex hort* C. Craib	1	+
A. vryheidensis	Vryheid	1	+
A. wollastonii	L. E. Newton 4092	1	
A. whitcombei	*ex hort* Lavranos	1	
A. wickensii	*ex hort* NeBG, JBG 85-5-336	2	+
A. wilsonii	L. E. Newton 3509	1	+
A. wrefordii	RBG, Kew 1977-4192	1	+
A. yavellana	*ex hort* L. E. Newton, *ex hort* RBG (Kew)	2	+
A. yemenica	*ex hort* NBI	1	
A. zebrina	NBI 31404, A. Ellert 18	2	

Chapter 4

The data matrix, data analysis and interpretation

CHAPTER 4

THE DATA MATRIX, ANALYSIS AND INTERPRETATION

Although the chemical groups are obvious from a data matrix and by basic comparison of the HPLC profiles, cluster analyses which is tailor made for chemometric analysis has been used to allow for an easy visual assessment through the construction of a dendrogram. The data matrix (Table 4.1) includes all species (240 species) which contained phenolic compounds in the leaves. Twenty nine chemical variables (leaf compounds) were used in the analysis to construct the dendrogram shown in Figure 4.1. Figure 4.2 is a 'compressed version' of the dendrogram illustrated in Figure 4.1 but clusters have been colour-coded.
The arbitrary cut (indicated by the broken line on the left of Figure 4.1) shows four main groupings or clusters:

A) Species containing anthrones (aloin and homonataloin) and chromones (cinnamoyl and coumaroyl chromones). This is the characteristic pattern for *Aloe* and these two classes of compounds are generally associated with the genus.

B) Flavonoid-producing species. This group includes both the flavone and flavanone accumulating species.

C) The 20 species which produce plicataloside as the major (and mostly the only) exudate compound.

D) An assemblage of chemically anomalous species which do not fall into any of the clusters A - C. These species, collectively represented by D, have a chemical profile not matched by any other species included in this study. (A large number of species showed the complete absence of the phenolics, these species would also be included as a sub-cluster in group F. This large number of species devoid of phenolic compounds have been omitted in the analysis).

These clusters clearly show distinct chemical discontinuities with neighbouring clusters. Of the 340 species analysed, most contained chromones and anthrones. All these species showing the general pattern in *Aloe* are united in a 'mega-cluster' denoted by the AA node. This group contains all the species which produce one (or a combination) of the following anthrones; aloin, aloinoside, microdontin, homonataloin, homonataloside, 5-hydroxyaloin A, 10-hydroxyaloin,

Aloe dichotoma (Photo: Ben-Erik van Wyk).

nataloin, 7-hydroxyaloin and microstigmin.

The major cluster AA cluster immediately divides into three groups; AA, AH and AO. This division corresponds to the major anthrones produced i.e AA (aloin), AH (homonataloin) and a smaller group AO representing species which accumulate 8-*O*-methyl-7-hydroxyaloin in the absence of aloin and homonataloin. The AA-group separates into four distinct clusters;

AA1 - represents all species accumulating aloin or derivatives thereof.

AA2 - unites all species producing 10-hydroxyaloin in the absence or presence of aloin.

AA3 - an assemblage of species containing derivatives of aloin and / or aloin.

AA4 - represents two outlier species producing unique anthrone derivatives.

The AA1 cluster is the largest cluster in the analysis with four prominent sub-groups. The most apical cluster (orange) denoted by ❶ groups all the aloin / aloinoside / microdontin producing species. This is the largest of the chemical groups that have been identified in this chemotaxonomic survey and the taxonomic value of this combination of anthrones are discussed in Chapter 5. These six compounds (three isomer pairs) are strongly correlated and may occur in the absence or presence of the chromones characteristic of *Aloe*. The top cluster represents 13 species producing aloin and aloinoside and chromones (usually 7-O-methylaloesin and aloeresin D). The larger cluster contains all species in which aloin, aloinoside and microdontins have been detected in high concentrations.

Cluster ❷ represents a number of species producing aloin with a range of chromones, usually a combination characteristic for a single species. These species do not fit comfortably into any of the 'neat chemical groups' and are broadly discussed in Chapters 14 and 15.

The next cluster (purple) designated by ❸ unites all species producing 8-*O*-methyl-7-hydroxyaloin. Studying the occurrence of other anthrones with 8-*O*-methyl-7-hydroxyaloin leads to speculation that the presence of 8-*O*-methyl-7-hydroxyaloin is not homologous in all species. Three species (*A. mutabilis*, *A. retrospiciens* and *A. pubescens*) which contain both aloin and homonataloin, a rare occurrence in *Aloe*, is also included in this group. The distribution of this compound together with biogeographical and taxonomic implications are discussed in Chapter 6.

The last cluster (mustard) in the AA1-group is denoted by ❹ and is characterised by species accumulating the unique phenyl-pyrone aloenin with the co-occurrence of aloin. One single species, *A. kedongensis*, produces nataloin and not aloin. It is suggested that this is a natural group of tropical origin of which the chemotaxonomic results are presented in Chapter 7.

The smaller group AA2 (pink) represents the species containing 10-hydroxyaloin B and various derivatives thereof. This group of species all pertain to *Aloe* section *Asperifoliae* and demonstrates a degree of congruence between exudate chemistry and the present infrageneric classification (Reynolds 1950). *Aloe scorpioides* shows a superficial association with this group as the unusual combination of compounds places it close to this group. Only one other species has 10-hydroxyaloin in the leaf exudate in co-occurrence with aloenin, *A. gossweileri.* This species is suspected to be of hybrid origin. The chemotaxonomic value of 10-hydroxyaloin B is discussed in Chapter 8.

The last significant group in the AA megacluster is denoted by AA3 and consists of three smaller clusters. The first group (1) unites all species included in section *Anguialoe* (orange). This group is characterised by a diagnostic chemical profile and is another example where the chemistry is in full agreement with the present infrageneric grouping presented by Reynolds (1950). The third cluster (3) does not contain aloin but various derivatives thereof with microstigmin being the chemotaxonomic marker for this group (green). Chapter 9 discusses the possible relationship between the *Anguialoe* group with species in cluster 3 while *A. broomii* is suggested to be a transitional species between these two group. The second cluster wedges in between 1 and 3 is somewhat 'noisy'. These species are quite different from those contained in group 1 and 3. The presence of aloin usually co-occurring with unique compounds for each of these species has superficially associated them with this group.

The second sub-cluster in the cluster denoted by AH is all the homonataloin-producing species. Within this group four significant clusters are defined:

❶ Represents all species containing the only known diglucoside anthrone in *Aloe*, homonataloside B (blue). This compound is always associated with homonataloin and its taxonomic distribution in *Aloe* has been elaborated in Chapter 10.

❷ Unites all species accumulating homonataloin with various chromones, mostly of the cinnamoyl type. These species are not convincingly associated with any group and have been discussed in Chapter 14.

❸This grouping could be subdivided into smaller clusters of which 3.1 (red) is the most significant. This group accumulates two cinnamoyl chromones aloeresin E and F usually in the presence of homonataloin. The chemotaxonomy and phylogenetic relationships of this group are discussed in Chapter 11. The smaller cluster, 3.2 is a grouping of homonataloin producing species in co-occurrence with other cinnamoyl chromones (see Chapter 14).

❹This somewhat 'untidy' group combines all species that may have homonataloin while most could have coumaroyl and / or cinnamoyl chromones present in the leaf exudate. Most species in this group could best be described as being 'chemical misfits' in *Aloe*.

The last cluster in the A assemblage is indicated by AO. This cluster, consisting of three species which all produce 8-O-methyl-7-hydroxyaloin, may produce homonataloin or unidentified anthrones which do not associate them with either the aloin or homonataloin megacluster. These three Malagasy species are discussed in Chapter 6 alongside the other species shown in cluster AA1 (3).

The arbitrary line next cuts through cluster B which separates into two groups B1 and B2. The B cluster represents the flavonoid producing species of *Aloe*. The B1 grouping consists of two sub-clusters 1 and 2. Cluster 1 (yellow) groups all species which produce flavones in the presence of aloin. Species belonging to *Aloe* section *Lomatophyllum* and series *Macrifoliae* are included in this group. Cluster 2 represents all species containing flavones only with chromones and anthrones being absent. This group corresponds with Reynolds' section *Leptoaloe* and *Graminialoe* and some species of series *Macrifoliae*. The distribution of flavones are discussed in Chapter 12. The B2 cluster (apricot) represents the 11 flavanone producing aloes. These species which exudes large quantities of flavanones are found in southern Africa and Madagascar. The chemotaxonomic significance of these flavanone-producing species are discussed in Chapter 12. The flavones and flavanones were found to be mutually exclusive, except in the case of *A. suzannae* where these compounds co-occur, hence the intermediate placement of this species in the phenetic analysis.

The next major cluster is denoted by C (green) and consists of all the plicataloside producing species. This compound usually occurs as the only phenolic in the exudate with the anthrones and chromones being absent. Some species do however produce additional compounds not detected in other species or trace amounts aloin, hence the cluster is not totally homogenous. The basal part of the dendrogram represents all the 'chemically anomalous' species which show exudate compositions not found in any other species in this survey.

It has to be emphasised that the value of this analysis is not to establish how individual species are related to one another but to show the major chemical groups detected in this study. To summarise, the following groups have been defined in this study (from top to bottom on the dendrogram):

Table 4.2: Summary of major chemical groups identified in this study. Cluster numbers and colours refer to the dendrogram in Figures 4.1. and 4.2.

Exudate compounds defining the group	Colour	Cluster	Chapter
Aloin / aloinoside / microdontin	orange	AA1 - 1	5
8-*O*-methyl-7-hydroxyaloin	purple	AA1 - 3	6
Aloenin	mustard	AA1 - 4	7
10-hydroxyaloin and derivatives	pink	AA2	9
6'-*O*-coumaroylaloesin	orange	AAB - 1	8
Microstigmin	green	AAB - 3	8
Homonataloin & homonataloside	blue	AH - 1	10
Aloeresins E and F	red	AH - 3(3.1)	11
Flavones	yellow	B1	12
Flavanones	apricot	B2	12
Plicataloside	green	C	13

	aloesin	7-O-methylaloesin	aloenin	homonataloside B	10-hydroxyaloin B	8-O-Methyl-7-OH-aloin	dihydroisocoumaring.	3'-O-coumaroylaloesin	aloeresin A	plicataloside	7-hydroxyaloin	microstigmin	aloeresin E	flavones	5-hydroxyaloin A	anguialoechromone	10-OH-aloin-monoacetate	aloeresin D	aloeresin F	aloin A & B	6'-O-coumaroylaloesin	homonataloin A & B	"aloin co-elute"	deacetyllittoraloin	aloinoside A & B	nataloin A & B	littoraloin	microdontin	flavanones
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29
A. aageodonta	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	1	0	0	0	0	1	0	0	0	0
A. abyssicola	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0
A. aculeata	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0
A. acutissima	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. africana	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	1	0	0	0	0
A. aldabrensis	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0
A. alooides	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	1	1	0	0	0	0	0	0	0	0
A. amicorum	0	0	0	1	0	0	0	0	1	0	0	0	0	0	0	0	0	1	0	0	0	1	0	0	0	0	0	0	0
A. amudatensis	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. angelica	1	0	0	0	0	0	0	0	1	0	0	0	1	0	0	0	0	0	1	0	0	1	0	0	0	0	0	0	0
A. antandroi	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. arborescens	1	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	1	0	0	0	0	0	0	0	0	0
A. archeri	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. arenicola	1	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	1	0	0	1	0	0	0	0	0	0	0
A. argenticauda	0	1	0	0	1	0	0	0	0	0	0	0	0	0	0	0	1	0	0	1	0	0	0	1	0	0	1	0	0
A. asperifolia	0	1	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	1	0	0	0	0	0
A. babatiensis	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. bakeri	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1
A. barberae	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. bargalensis	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	1	0	0	0	0	0	0	0
A. bella	0	1	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	1	0	1	0	0	0	0	0	0	0	0	0
A. bellatula	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1
A. boscawenii	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	1	0	0	1	0
A. boylei	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. brachystachys	1	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0
A. brandhamii	1	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	1	0	0	0	0	0	0	0	0	0
A. brevifolia	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. breviscapa	1	1	0	1	0	0	0	0	1	0	0	0	0	0	0	0	0	1	0	0	0	1	0	0	0	0	0	0	0

	aloesin	7-O-methylaloesin	aloenin	homonataloside B	10-hydroxyaloin B	8-O-Methyl-7-OH-aloin	dihydroisocoumaring.	3'-O-coumaroylaloesin	aloeresin A	plicataloside	7-hydroxyaloin	microstigmin	aloeresin E	flavones	5-hydroxyaloin A	anguialoechromone	10-OH-aloin-monoacetate	aloeresin D	aloeresin F	aloin A & B	6'-O-coumaroylaloesin	homonataloin A & B	"aloin co-elute"	deacetyllittoraloin	aloinoside A & B	nataloin A & B	littoraloin	microdontin	flavanones
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29
A. broomii	1	0	0	0	0	0	0	0	0	0	0	1	0	0	1	0	0	0	0	1	0	0	0	0	0	0	0	0	0
A. brunneostriata	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	1	0	0	1	0
A. buchlohii	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	1	0
A. bukobana	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0
A. bulbillifera	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. bussei	1	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0
A. calidophila	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	1	0	0	1	0
A. cameronii	1	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	1	0	1	0	0	0	0	1	0	0	0	0
A. camperi	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	1	0	0	1	0
A. canarina	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	1	0	0	0	0	1	0	0	1	0
A. capitata	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0
A. castanea	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	1	1	0	0	1	0	0	0	0	0
A. catengiana	1	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0
A. chabaudii	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. cheranganiensis	1	1	1	0	0	0	0	0	1	0	0	0	0	0	0	0	0	1	0	1	0	0	1	0	0	0	0	0	0
A. chlorantha	1	1	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	1	0	0	0	0	0	0	0	0	0
A. chortolirioidesc	1	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0
A. chortolirioidesw	1	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0
A. christianii	1	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0
A. chrysostachys	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	1	0	0	0	0	1	0	0	0	0
A. ciliaris	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. citrina	1	1	0	1	0	0	0	0	1	0	0	0	0	0	0	0	0	1	0	0	0	1	0	0	0	0	0	0	0
A. classenii	1	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	1	0	0	1	0	0	0	0	0	0
A. claviflora	0	1	0	0	1	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	1	0	0	1	0	0
A. commixta	1	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0
A. comosa	1	1	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	1	0	0	0	1	0	0	0	0	0	0	0
A. comptonii	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	1	0	0	0	0	0	0	0
A. confusa	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0

	aloesin	7-O-methylaloesin	aloenin	homonataloside B	10-hydroxyaloin B	8-O-Methyl-7-OH-aloin	dihydroisocoumaring.	3'-O-coumaroylaloesin	aloeresin A	plicataloside	7-hydroxyaloin	microstigmin	aloeresin E	flavones	5-hydroxyaloin A	anguialoechromone	10-OH-aloin-monoacetate	aloeresin D	aloeresin F	aloin A & B	6'-O-coumaroylaloesin	homonataloin A & B	"aloin co-elute"	deacetylilittoraloin	alоinoside A & B	natalоin A & B	littoraloin	microdontin	flavanones
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29
A. congdonii	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0
A. conifera	1	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0
A. corallina	1	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0
A. cremnophila	1	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0
A. cryptopoda	1	0	0	1	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0
A. dabenorisana	1	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	1	0	0	1	0	0	0	0	0	0	0
A. dawei	1	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	1	0	0	0	0	0	0
A. debrana	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0
A. decurva	1	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	1	0	1	0	0	0	0	0	0	0	0	0
A. descongsii	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. deserti	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. dewinteri	0	1	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0
A. dhufarensis	1	0	0	1	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0
A. dichotoma	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. diolii	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	.1	0	0	0	0	1	0	0	1	0
A. distans	1	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	1	0	0	1	0	0	0	0	0	0	0
A. divaricata	0	1	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0
A. dolomitica	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	1	1	0	0	0	0	0	0	0	0
A. dominella	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. dorotheae	1	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	1	0	0	0	0	0	0
A. duckeri	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. ecklonis	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. elegans	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	1	0	0	0	1	0
A. eminens	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0
A. erensii	0	1	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	1	0	0	0	0	0	0	0
A. erinacea	1	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	1	0	0	0	0	0	0	1	0	0	0
A. esculenta	0	1	0	0	1	0	0	0	0	0	0	0	0	0	0	0	1	0	0	1	0	0	0	1	0	0	0	0	0
A. excelsa	1	1	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	1	0	1	0	0	0	0	0	0	0	0	0

	aloesin	7-O-methylaloesin	aloenin	homonataloside B	10-hydroxyaloin B	8-O-Methyl-7-OH-aloin	dihydroisocoumaring.	3'-O-coumaroylaloesin	aloeresin A	plicataloside	7-hydroxyaloin	microstigmin	aloeresin E	flavones	5-hydroxyaloin A	anguialoechromone	10-OH-aloin-monoacetate	aloeresin D	aloeresin F	aloin A & B	6'-O-coumaroylaloesin	homonataloin A & B	"aloin co-elute"	deacetyllittoraloin	aloinoside A & B	nataloin A & B	littoraloin	microdontin	flavanones
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29
A. falcata	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	1	0	0	1	0	0
A. ferox	1	0	0	0	0	0	0	0	1	0	0	0	0	0	1	0	0	0	0	1	0	0	0	0	1	0	0	0	0
A. fibrosa	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. fleurentiniorum	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	1	0	0	1	0
A. flexilifolia	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	1	0	0	0	0	1	0	0	0	0
A. forbesii	1	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0
A. fouriei	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. fragilis	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. framesii	1	1	0	0	0	0	0	0	0	0	0	1	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. francombei	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. gariepensis	1	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0
A. gerstneri	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0
A. gilberti	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	1	0	0	1	0
A. glauca	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1
A. globuligemma	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0
A. gosweileri	1	0	1	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0
A. gracilis	1	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0
A. gracilis var. decum	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. guillaumetii	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	1	0	0	0	0
A. hardyi	1	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0
A. harlana	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	1	0	0	1	0
A. helenae	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	1
A. hemmingii	1	0	0	0	0	1	1	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	1	0	0	0	0
A. hereroensis	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0
A. hildebrandtii	1	1	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0
A. hlangapies	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. humilis	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1
A. inconspicua	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

	aloesin	7-O-methylaloesin	aloenin	homonataloside B	10-hydroxyaloin B	8-O-Methyl-7-OH-aloin	dihydroisocoumarin.	3'-O-coumaroylaloesin	aloeresin A	plicataloside	7-hydroxyaloin	microstigmin	aloeresin E	flavones	5-hydroxyaloin A	anguialoechromone	10-OH-aloin-monoacetate	aloeresin D	aloeresin F	aloin A & B	6'-O-coumaroylaloesin	homonataloin A & B	"aloin co-elute"	deacetylLittoraloin	aloinoside A & B	nataloin A & B	littoraloin	microdontin	flavanones
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29
A. inermis	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. integra	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. isaloensis	1	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0
A. jacksonii	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. jucunda	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0
A. kedongensis	1	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0
A. khamiesensis	1	0	0	0	0	0	0	0	0	0	0	1	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. kniphofioides	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. krapohliana	1	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0
A. kraussii	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. kulalensis	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	1	0	0	0	0	0	0	0	0	0
A. labworana	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0
A. leachii	1	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	1	0	0	0	0	0	0	0	0	0
A. lensayuensis	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	1	0	0	0	0	0
A. leptosiphon	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	1	0	0	0	0	0	0
A. linearifolia	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. lineata	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1
A. littoralis	1	1	0	0	1	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	1	0	0	1	0	0
A. lomatophylloides	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0
A. longistyla	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. lutescens	1	0	0	1	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0
A. macroclada	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0
A. macrosiphon	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0
A. marlothiia	1	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	1	0	1	0	0	0	0	0	0	0	0	0
A. marlothiih	1	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	1	0	0	0	1	0	0	0	0	0	0	0
A. massawana	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	1	0	0	0	0	0	0	0	0	0
A. mawii	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0
A. mayottensis	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0

	aloesin	7-O-methylaloesin	aloenin	homonataloside B	10-hydroxyaloin B	8-O-Methyl-7-OH-aloin	dihydroisocoumarin.	3'-O-coumaroylaloesin	aloeresin A	plicataloside	7-hydroxyaloin	microstigmin	aloeresin E	flavones	5-hydroxyaloin A	anguialoechromone	10-OH-aloin-monoacetate	aloeresin D	aloeresin F	aloin A & B	6'-O-coumaroylaloesin	homonataloin A & B	"aloin co-elute"	deacetylittoraloin	aloinoside A & B	nataloin A & B	littoraloin	microdontin	flavanones
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29
A. mcloughlinii	1	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	1	0	1	0	0	0	0	1	0	0	0	0
A. megalacantha	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	1	0	0	1	0
A. melanacantha	1	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. menachensis	1	1	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	1	0	1	0	0	0	0	0	0	0	0	0
A. mendesii	1	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	1	0	0	0	0	0	0	0
A. meyeri	1	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	1	0	0	1	0	0	0	0	0	0	0
A. microdonta	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	1	0	0	1	0
A. microstigma	1	1	0	0	0	0	0	0	0	0	0	1	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. millottii	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. minima	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. mitriformis	1	0	0	0	0	0	0	0	1	0	0	0	1	0	0	0	0	0	1	0	0	1	0	0	0	0	0	0	0
A. modesta	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. molederana	1	1	0	1	0	0	1	0	0	0	0	0	0	0	0	0	0	1	0	1	0	0	0	0	0	0	0	0	0
A. monticola	1	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0
A. morijensis	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. multicolor	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. munchii	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0
A. murina	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. mutabilis	1	0	0	0	0	1	0	0	1	0	0	0	0	0	0	0	0	0	0	1	0	1	0	0	0	0	0	0	0
A. mzimbana	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0
A. namibensis	0	1	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0
A. ngongensis	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	1	0	0	0	0	1	0	0	1	0
A. niebuhriana	0	1	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	1	0	1	0	0	0	0	0	0	0	0	0
A. nubigena	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. nyeriensis	1	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	1	0	0	0	0	0	0	0	0	0
A. occidentalis	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0
A. officinalis	1	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	1	0	1	0	0	0	0	0	0	0	0	0
A. orientalis	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0

	aloesin	7-O-methylaloesin	aloenin	homonataloside B	10-hydroxyaloin B	8-O-Methyl-7-OH-aloin	dihydroisocoumarin.	3'-O-coumaroylaloesin	aloeresin A	plicataloside	7-hydroxyaloin	microstigmin	aloeresin E	flavones	5-hydroxyaloin A	anguialoechromone	10-OH-aloin-monoacetate	aloeresin D	aloeresin F	aloin A & B	6'-O-coumaroylaloesin	homonataloin A & B	"aloin co-elute"	deacetylilitoraloin	aloinoside A & B	nataloin A & B	litoraloin	microdontin	flavanones
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29
A. ortholopha	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. otallensis	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. pachygaster	0	1	0	0	1	0	0	0	0	0	0	0	0	0	0	0	1	0	0	1	0	0	0	0	0	0	1	0	0
A. palmiformis	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. parvidens	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. pearsonii	1	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	1	0	0	1	0	0	0	0	0	0	0
A. peckii	1	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	1	0	1	0	0	0	0	1	0	0	0	0
A. peglerae	1	1	0	0	0	0	0	0	1	0	0	0	1	0	0	0	0	0	1	0	0	1	0	0	0	0	0	0	0
A. penduliflora	0	1	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	1	0	0	0	0
A. percrassa	1	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0
A. petricola	1	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0
A. pictifolia	1	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. pillansii	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. plicatilis	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. polyphylla	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. pratensis	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1
A. pretoriensis	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1
A. pubescens	1	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	1	0	1	0	1	0	0	0	0	0	0	0
A. pulcherrima	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0
A. purpurea	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0
A. pustuligemma	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. rabaiensis	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	1	0	0	0	0	1	0	0	0	0
A. ramosissima	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. reitzii	1	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0
A. retrospiciens	0	1	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	1	0	1	0	1	0	0	0	0	0	0	0
A. rigens	1	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	1	0	0	0	1	0	0	0	0	0	0	0
A. rivae	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	1	0	0	1	0
A. rubroviolacea	1	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

	aloesin	7-O-methylaloesin	aloenin	homonataloside B	10-hydroxyaloin B	8-O-Methyl-7-OH-aloin	dihydroisocoumaring.	3'-O-coumaroylaloesin	aloeresin A	plicataloside	7-hydroxyaloin	microstigmin	aloeresin E	flavones	5-hydroxyaloin A	anguialoechromone	10-OH-aloin-monoacetate	aloeresin D	aloeresin F	aloin A & B	6'-O-coumaroylaloesin	homonataloin A & B	"aloin co-elute"	deacetyllittoraloin	aloinoside A & B	nataloin A & B	littoraloin	microdontin	flavanones
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29
A. rugosifolia	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. rupestris	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. saundersiae	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. scabrifolia	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	1	0	0	1	0
A. schelpei	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	1	0
A. schweinfurthii	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. scobinifolia	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	1	0	0	1	0
A. scorpioides	1	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0
A. secundiflora	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	1	0	0	0	0	0	0	0	0	0
A. sinana	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0
A. sinkatana	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	1	0	0	0	0
A. somaliensis	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	1	0	0	1	0
A. soutpansbergensis	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. speciosa	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0
A. spicata	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	1	1	0	0	0	0	0	0	0	0
A. splendens	1	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	1	0	0	0	1	0	0	0	0	0	0	0
A. squarrosa	1	1	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0
A. steudneri	0	0	0	0	0	1	1	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	1	0
A. striatula	1	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0
A. succotrina	1	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. suffulta	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0
A. suprafoliata	1	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0
A. suzannae	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1
A. tauri	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	1	1	0	0	0	0	0	0	0	0
A. tenuior	1	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. tewoldei	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	1	0	0	1	0
A. thompsoniae	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. thorncroftii	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1

	aloesin	7-O-methylaloesin	aloenin	homonataloside B	10-hydroxyaloin B	8-O-Methyl-7-OH-aloin	dihydroisocoumaring.	3'-O-coumaroylaloesin	aloeresin A	plicataloside	7-hydroxyaloin	microstigmin	aloeresin E	flavones	5-hydroxyaloin A	anguialoechromone	10-OH-aloin-monoacetate	aloeresin D	aloeresin F	aloin A & B	6'-O-coumaroylaloesin	homonataloin A & B	"aloin co-elute"	deacetyllittoraloin	aloinoside A & B	nataloin A & B	littoraloin	microdontin	flavanones
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29
A. thraskii	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0
A. tomentosa1	1	1	0	1	0	0	1	0	0	0	0	0	0	0	0	0	0	1	0	0	0	1	0	0	0	0	0	0	0
A. tomentosa2	1	1	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	1	0	1	0	0	0	0	0		0	0	0
A. tororoana	1	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	1	0	0	0	0	0	0
A. trichosantha	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0
A. tugenensis	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. turkanensis	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0
A. tweediae	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	1	0	1	0	0	0	0	1	0	0	0	0
A. ukambensis	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. vacillans	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. vanbalenii	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0
A. vaombe	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. vaotsanda	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	1
A. vera	1	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	1	0	1	0	0	0	0	0	0	0	0	0
A. verecunda	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. veseyi	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0
A. viridiflora	1	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0
A. volkensii	1	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0
A. vossii	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. vryheidensis	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	1	1	0	0	0	0	0	0	0	0
A. wickensii	1	0	0	1	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0
A. wilsonii	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	1	0	0	0	0	0	0	0
A. wrefordii	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. yavellana	1	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	1	0	0	1	0	0	0	0	0	0	0

Table 4.1 Data matrix showing the presence and absence for 29 exudate compounds in 240 species of Aloe.
Species devoid of anthrones and chromones have not been included in the analysis.

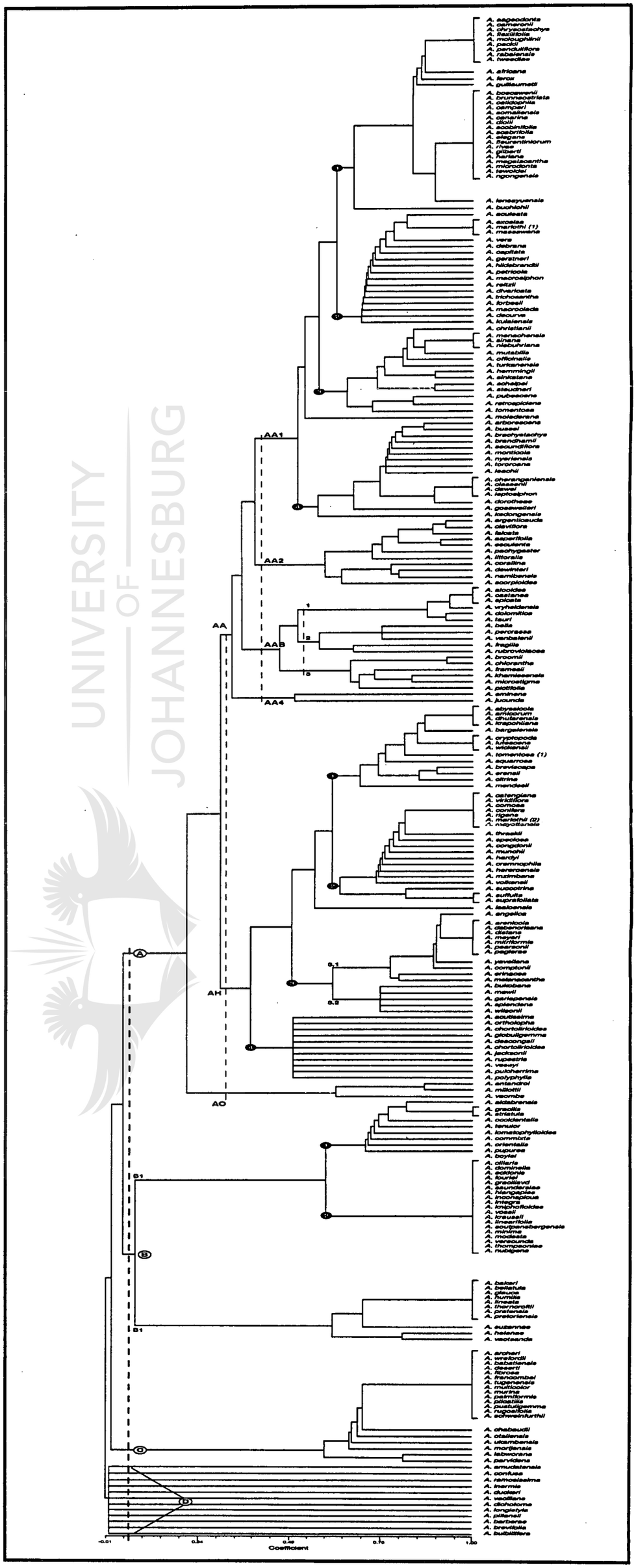


Figure 4.1: Dendrogram constructed from chemical data presented in Table 4.1.

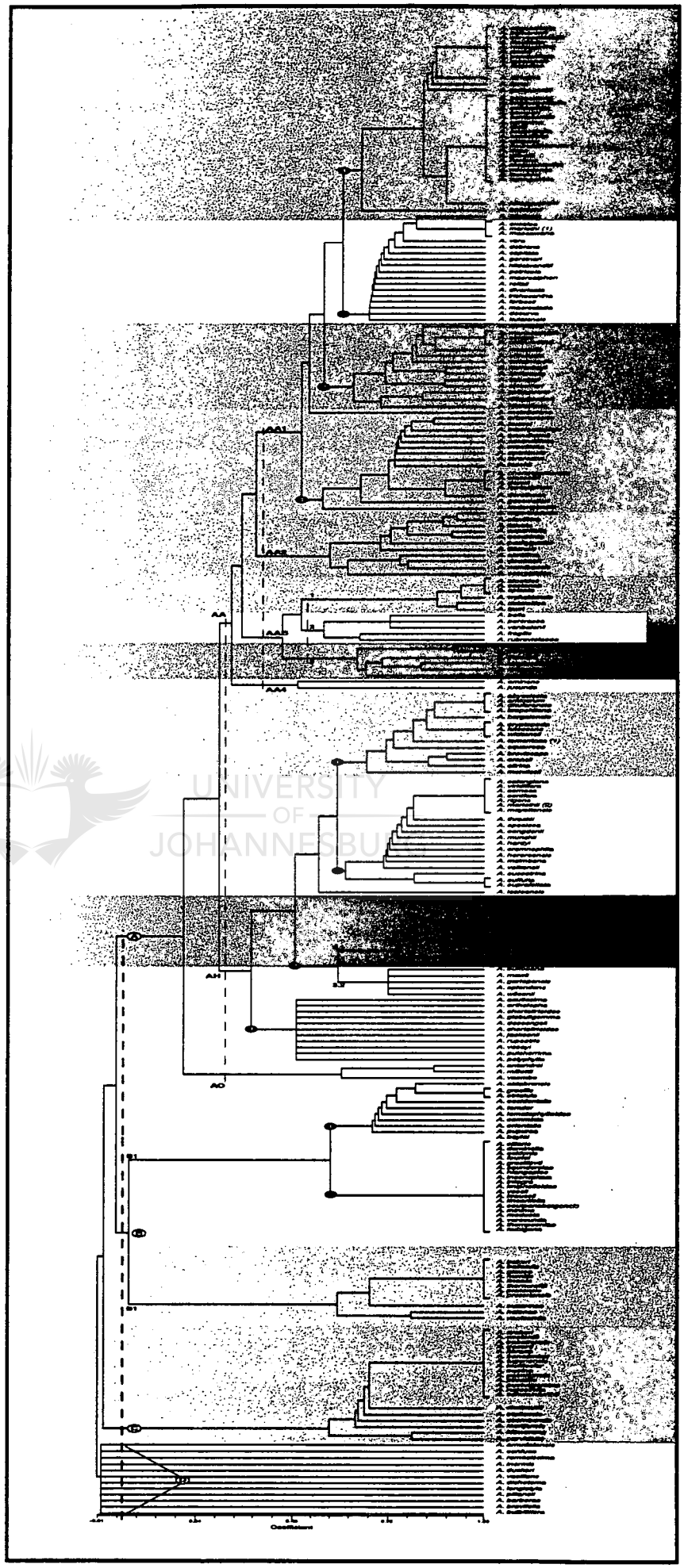


Figure 4.2: "Compressed dendrogram" (see Figure 4.1).

Chapter 5

The occurrence and taxonomic distribution of the anthrones aloin, aloinoside and microdontin

CHAPTER 5

THE OCCURRENCE AND TAXONOMIC DISTRIBUTION OF THE ANTHRONES ALOIN, ALOINOSIDE & MICRODONTIN

This chemotaxonomic survey of 380 species indicated the presence of the anthrones aloin A and B together with the aloinoside isomers and microdontin A and B in 36 species (10%) of *Aloe* (Table 5.1). This is the largest of the chemical groups which has been defined in this study and the combination of these exudate compounds suggest a degree of chemotaxonomic coherence between the taxa. This group is characterised by a combination of exudate compounds and not merely a single phytochemical marker reinforcing its chemotaxonomic significance. The representatives of this group occupy disparate taxonomic positions in the largely artificial hierarchy of the present classification system. Although many of the species have previously been suggested to be related (based on macromorphology only) a large number of species have not been associated with one another. As expected, this group is further characterised by immense morphological variation, almost representative of the entire range of variation for a single character encountered in the genus as a whole.

This group is firstly introduced by referring the present taxonomic position of the species. The morphological variation is briefly mentioned followed by a comparison of the chemical profiles and leaf exudate compositions. This chapter concludes with the geographical distribution of the species and thoughts on relationships between the taxa.

Table 5.1 Species producing aloin / aloinoside / microdontin with the corresponding voucher and distribution details. The chromatogram and specific distribution each of the species is shown in Appendix 2.

Species	Voucher	Distribution
A. aageodonta	LEN 3543 (type material)	Kenya
A. africana	Aloes, Fort Brown, Ann's Villa	South Africa
A. boscawenii	ex hort P. Favell	N Tanzania
A. brunneostriata	ex hort NBI	N Somalia
A. buchlohii	ex hort D. Hardy & NBI 14645	Madagascar
A. calidophila	RBG, Kew 1974-4199	Kenya & Ethiopia
A. cameronii	NBI 15231 & WE 79	Malawi, Zimbabwe Zambia & Mozambique
A. camperi	EDS 208, ex hort NBI	Ethiopia
A. canarina	RBG, Kew 1977-3888	Uganda & Sudan
A. chrysostachys	LEN 4040 (type locality)	Kenya

Aloe microdonta, the species from which microdontin was first isolated (Photo: Reynolds, 1966).

Species	Voucher	Distribution
A. diolii	LEN 2508 (type material)	S Sudan
A. elegans	ex hort NBI	Ethiopia
A. ferox	24 localities	South Africa
A. fleurentiniorum	RBG, Kew 1977-3317	Yemen
A. flexilifolia	RBG, Kew 258-90-01811	N Tanzania
A. gilberti	RBG, Kew 1990-1301 & EDS 226	Ethiopia
A. guillaumetii	Lavranos 28738	N Madagascar
A. harlana	ex hort BSM	Ethiopia
A. hemmingii	NBI 11170 & RBG, Kew 0848-01059	Somalia
A. lensayuensis	RBG, Kew 242-63 24204 & LEN 5571	Kenya
A. mcloughlinii	RBG, Kew 5955959502 & 4858404966	Ethiopia
A. megalacantha	EDS 325 & RBG, Kew 144-93-01240	Ethiopia & Somalia
A. microdonta	RBG, Kew 1966-12803, NBI 13501	Kenya & Somalia
A. ngongensis	LEN 3531	Kenya & Tanzania
A. peckii	RBG, Kew 084-81011-40	N Somalia
A. penduliflora	RBG, Kew 34963-34907 & LEN 3543	S Kenya
A. rabaiensis	RBG, Kew 1975-903	Kenya & Tanzania
A. rivae	EDS 321	Kenya & Ethiopia
A. scabrifolia	LEN 3272	Kenya
A. schelpei	RBG, Kew 427-64-42705	Ethiopia
A. scobinifolia	RBG, Kew 084-81-01110 & ex BSM	N Somalia
A. sinkatana	ex hort BSM	N Sudan
A. somaliensis	RBG, Kew 084-81-01055 & NBI 11169	N Somalia
A. steudneri	RBG, Kew 1987-4090 & ex BSM	N Ethiopia
A. tewoldei	ex EDS (type locality)	S Ethiopia
A. tweediae	RBG, Kew 1970-1752	Sudan, Kenya & Uganda

Relationships within the aloin / aloinoside / microdontin group as represented in Figure 5.1

Previous suggested affinities between species included in this group are shown in Figure 5.1 The classification of Reynolds (1950 & 1966) has been used. Post-Reynolds species have been transferred to the group containing the species to which the author suggested the new species to be related. Aloin / aloinoside / microdontin containing species appear first in each block (or group) and is designated by a solid block bullet. The remaining species in each group

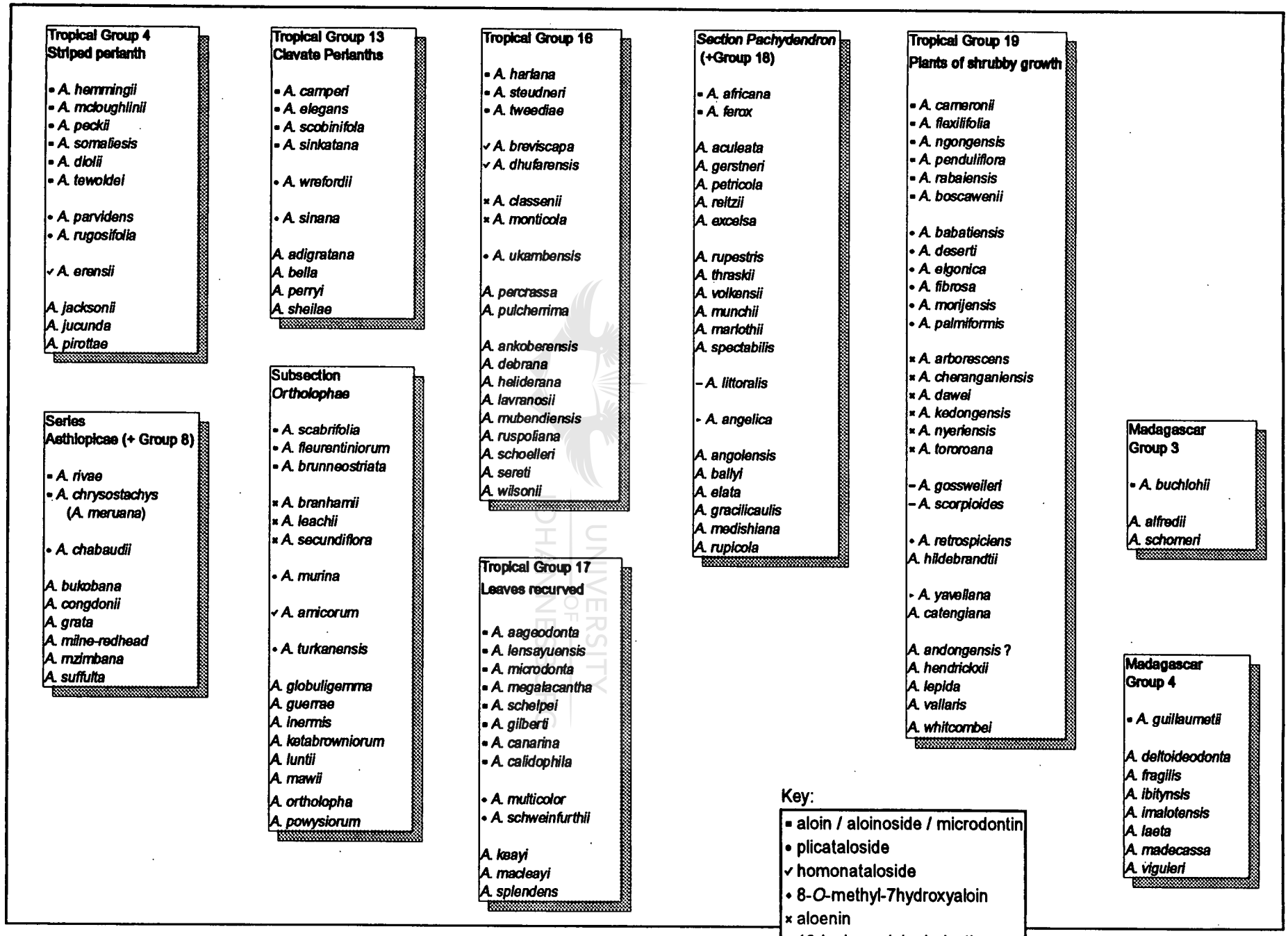


Figure 5.1: Taxonomic position of species containing aloin / aloinoside / microdontin.

have been arranged according to the chemotaxonomic character with each bullet denoting a chemical group created in this survey (see the key in Figure 5.1). The species at the bottom of each block (no bullet) refer to those species where the chemotaxonomic affinity of the species is uncertain or where no leaf exudate could be obtained of a particular species.

Reynolds created Group 4 to delineate all species which have striped flowers. The plants in this group are also characterised by fairly small rosettes. The first four species were included by Reynolds (1966) in this group while *A. diolii* and *tewoldei* were added later. The former species was described by Newton (1995) from the southern parts of Sudan and being guided by gross morphology Newton suggests his new species to be related to *A. jacksonii*. *Aloe tewoldei* was described by Gilbert and Demissew (1997) with suggestions that this Ethiopian species too is related to *Aloe jacksonii*. *Aloe jacksonii* produces a unique combination of leaf exudate compounds not found in any other species included in this study (see Appendix 1). The characteristic chemical identity of *A. jacksonii* is also emphasised through the work of Conner (1988) who isolated a series of interesting compounds from this species. It is worthy to note that based on the obscurely striped flowers, *A. jacksonii* is placed in Group 4 (Reynolds, 1966). Gilbert and Demissew (1996) suggest that *A. jacksonii* should rather be placed in Group 10 (Reynolds 1966) with the other pendent / semi-pendent species together with *A. tewoldei*. It is further interesting to note that the two authors emphasise the morphological anomaly of *A. jacksonii*, an observation which is emphasised on the chemical level. Figure 5.1 shows two species in this group to contain plicataloside (see Chapter 13) while *A. erensii* is a homonataloside-producing species discussed in Chapter 10. It is evident that Reynolds placed emphasis on perianth characters as this character is used extensively in his infrageneric groupings. Reynolds (1966) created a group consisting of 10 species containing aloes which have clavate perianths (Group 13). In some instances (e.g. *A. camperi*) the perianth is distinctly clavate while in others a measure of imagination is required to visualise the inflated perianth. Four of the 10 species which are placed in this group produce the same exudate profile placing them in this chemical group. *A. perryi* and *A. adigratana* were found to be devoid of the chromones and anthrones typical of *Aloe* and no HPLC profile has been recorded for these two species. *Aloe sinana* contains aloin together with 8-O-methyl-7-hydroxyaloin while *A. wrefordii* is a plicataloside-accumulating species.

Aloe chrysostachys is suggested by Lavranos and Newton (1976) to be related to *A. rivae* in Group 8 (series *Aethiopicae*). A species later decried by Lavranos (1980) as *A. meruana* was

reduced to synonymy under *A. chrysostachys* (Newton 1996), both taxa produced identical exudate profiles. *Aloe chabaudii* accumulates plicataloside while the affinities of the remaining species in Group 8 remain obscure.

Aloe scabrifolia has mature flowers secund, hence its placement by Newton & Lavranos (1990) in Group 14 (Subsection *Orthlophae*), alongside *A. turkanensis*. The latter species however together with other species producing their flowers in a secund orientation fit into chemical group 2 (Chapter 6). Reynolds (1996) reported a comprehensive chromatographic comparison between *A. scabrifolia* and *A. turkanensis*. These results showed the two species to be different in leaf exudate composition dismissing previous suggested taxonomic affinities. The results presented here are in full agreement with those reported by Reynolds (1996). *Aloe fleurintinorum* is mentioned by Lavranos & Newton (1977) to be taxonomically related to *A. inermis*, an affinity suggested by the shape of the perianth and the entire leaf margin. As mentioned in the case of *A. jacksonii* above, *A. inermis* produces a characteristic leaf exudate profile comprising a series of unidentified compounds not correlating to any other species chemically. In discussing *Aloe inermis,* Lavranos (1992) describes *Aloe brunneostriata* as a new species emphasising the taxonomic affinity between the former and the latter species. *Aloe brunneostriata* is also included in this chemical grouping and the character i.e. entire leaf margin which inspired Lavranos and Newton (1977) to suggest an affinity between this species and *A. luntii* is also prominent in *A. brunneostriata*. The leaf exudate of *A. luntii* and *A. inermis* did not contain any chromones and anthrone C-glycosides. The subsection *Orthlophae* is a morphological and chemical heterogenous collection of species. Five of the prominent chemical grouping identified in this study is represented in this single group. Three species contain the phenyl-pyrone aloenin and are discussed in Chapter 7, one produces plicataloside (Chapter 13), *A. amicorum* accumulated homonataloside B while *A. turkanensis* is included in Chapter 6 with the 8-*O*-methyl-7-hydroxyaloin-producing species. Newton (1993) suggested that the secund flowers, the defining character for Subsection *Orthlophae* probably evolved independently in several groups and that uniting all aloes with secund flowers in a single group is largely artificial.

Group 17 (Reynolds 1996) represents 13 species of which eight fall within this chemical group. This group is defined by the leaves of the plants which are deeply canaliculate and recurved, a character which is also prominent in other species included in this chemical group 1 (e.g. *A. camperi*, *A. calidophila* and *A. africana*). Since the time of Reynolds four species have been described and associated with this group. *Aloe canarina* (Carter 1994) and *A. lensayuensis*

(Lavranos & Newton 1976) have been suggested by the respective authors to be allied to *A. microdonta* while Newton (1993) suggested *A. aageodonta* to show a taxonomic affinity to *A. lensayuensis*. In their species description of *A. gilberti*, Demissew and Brandham (1992) draws a taxonomic correlation between this species with *A. megalacantha* and *A. calidophila*, both the latter species are also represented in this chemical group 1.

The only two species in this chemical group to have a distribution in South Africa are two members of *Aloe* section *Pachydendron*; *A. ferox* and *A. africana*. The relationship of these two species within this group are discussed elsewhere in this Chapter.

Six species in Group 19 produce the characteristic range of anthrones and fall within Reynolds' concept of 'plants with shrubby growth'. These species are characterised by long prolongate stems. This is a very large and complex group with each species displaying degrees of variation throughout the geographical distribution. This is another large group created by Reynolds containing species which are chemically divergent. Six species are plicataloside-producers (Chapter 13) while a another six species produce aloenin (see Chapter 6).

The only two Malagasy endemics included in this chemical group is *A. guillaumettii* and *A. buchlohii*. In his species description of *A. guillaumettii*, Cremers (1976) suggests an affinity between this species and *A. deltoideodonta* and *A. viguieri*. This similarity is dismissed by Lavranos (1994) as a 'matter of convergence'. In a separate article by Glen *et al.* (1992), the authors (of which J. Lavranos unknowingly was one and later distanced him from the content of the article) suggests a taxonomic affinity between *A. guillaumetii* and five other Malagasy endemics of which *A. buchlohii* was one. The latter species is the other Malagasy-aloe to fall within this chemical category. Lavranos (1994) describes a new species, *A. fragilis* from the NE coast of Madagascar with suggestions that this new species could be related to *A. guillaumetii*. The exudate sample of *A. fragilis* produced an exudate profile unmatched by any other species of *Aloe*, which is characteristic of the Malagasy aloes.

Morphological Characters:

The discussion above is a summary of the suggested relationships as extracted from literature references. Following is an analytical account of each of the morphological characters as summarised in Table 5.1. The species which have been chemically delineated above show extreme morphological variation. It would suffice to show this degree of variation by referring to a selection of the morphological characters listed in Table 5.2.

Habit characters (caulescence, branching and orientation):

Based on habit characters the species could be divided into two main groups; those which are caulescent (distinctly or shortly so) and those which are acaulescent. The caulescent species are erect and branching (not suckering) to form dense groups (*A. aageodonta*, *A. cameronii*, *A. flexilifolia*, *A. gilberti*, *A. megalacantha*, *A. microdonta* and *A. penduliflora*.). The two South African species; *A. africana* and *A. ferox* are the only two species in this group which are distinctly caulescent, erect, and occur as single plants. Six species in this group are caulescent but with a procumbent stem (*A. boscawenii*, *A. calidophila*, *A. camperi*, *A. lensayuensis*, *A. ngongensis* and *A. scabrifolia*). *Also schelpei* is not as distinctly caulescent as the species listed above but also produces a short procumbent stem and grows in dense groups. *Aloe brunneostriata* and *A. canarina* are two suckering species which are shortly caulescent. (the general pattern in *Aloe* is that suckering species are usually acaulescent). *Aloe rivae* and *A. tewoldei* are also shortly caulescent but *A. rivae* is extremely variable in habit characters as individuals are either tightly clustered in groups solitary with a procumbent or erect stem. *Aloe tewoldei* is the only species in this group which is pendent. Newton (1991) considers the epithet of *A. penduliflora* to be a misnomer as this species is not pendent in habit.

Most of the acaulescent species are usually solitary and not grouped. Species in this category are *A. buchlohii*, *A. fleurentiniorum*, *A. somaliensis*, *A. scobinifolia*, *A. sinkatana*, *A. harlana*, *A. peckii* and *A. hemmingii*. *Aloe chrysostachys* rarely produce a stem and could be grouped or occur as single individuals.

Species in this group are either acaulescent, shortly caulescent, or distinctly caulescent. In the case of the latter category the stem could have an erect orientation as in *A. ferox* and *A. africana*. In most species the stem is slender and erect only if supported, but in most instances the stem becomes procumbent.

Leaf characters (leaf architecture, texture, thorns and maculation):

Most species in this group have leaves which are spreading to recurved. The leaf curvature could only be the apices while in most cases almost half the leaf length is recurved. Five species produce leaves which are spreading to recurved, smooth in texture, pungent thorns on the leaf margin and spotted. These species are *A. buchlohii*, *A. mcloughlinii*, *A. tweediae*, *A. sinkatana*, *A. somaliensis*. *A. hemmingii* and *A. peckii*. The last three species are very similar in leaf characters when compared to the species mentioned above with the differences

that they are distinctly maculate. Species sharing the same characters as those for the five species above, with the exception that the leaves are completely immaculate and unspotted include *A. cameronii*, *A. canarina*, *A. schelpei*, *A. ferox*, *A. rabaiensis*, *A. gilberti*, *A. harlana*, *A. ngongensis* and *A. meruana*. Three species bear their leaves in an incurved way (*A. chrysostachys*, and *A. steudneri*). In the case of *A. africana*, *A. camperi* and *A. megalacantha* the leaves are strongly recurved, smooth, immaculate and bear pungent thorns. *Aloe brunneostriata* deviates from the broader pattern as the leaves are distinctly striate and have small cartilaginous thorns. *Aloe fleurentiniorum* and *A. scobinifolia* also have an entire leaf margin. In all the species the leaves are smooth, but in the case of *A. scobinifolia*, *A. lensayuensis*, *A. scabrifolia* and *A. fleurintinorum* the leaves are distinctly asperous.

Inflorescence and flower characters (inflorescence structure, perianth shape, perianth markings, flower orientation):

Based on the characters in parenthesis above the species could be placed into six categories:

1. Species in which the inflorescence is a branched panicle and the flowers are cylindrical-trigonous in shape with no markings on the perianth and the flowers are secund. Eight species are included in this group: *A. aageodonta*, *A. brunneostriata*, *A. canarina*, *A. chrysostachys*, *A. lensayuensis*, *A. meruana*, *A. scabrifolia* and *A. microdonta*.

2. Species in which the inflorescence is 1 - 3 branched, the flowers are cylindrical-trigonous without markings and arranged symmetrical around the floral axis. Species sorting under this group is *A. boscawenii*, *A. flexilifolia*, *A. tweediae*, *A. harlana*, *A. megalacantha*, *A. rivae*, *A. penduliflora*, *A. rabaiensis*, *A. ngongensis*. Most of the species listed are placed by Reynolds in his group 19.

3. Species in which the inflorescence is a branched panicle, the flowers are clavate with no markings and arranged symmetrical around the floral axis. Eight species fit the description of this group: *A. calidophila*, *A. scobinifolia*, *A. camperi*, *A. sinkatana*, *A. gilberti*, *A. fleurentiniorum*, *A. ferox* and *A. elegans*. Most of these species are placed in Group 13 (Reynolds, 1966).

4. Species in which the perianth is striped or spotted: Four species are included in this category and corresponds to Group 4 (Reynolds, 1966). This group comprises *A.*

Table 5.2. Morphological characters (habit, leaf, inflorescence and flower characters) for species included in the aloin / aloinoside / microdontin chemical group.

species	caulescence	branching	stem orientation	leaf orientation	texture	thorns (mm)	maculation
A. aageodonta	caulescent	from base, grouped	erect / decumbent	erect - spreading	smooth	pungent, 3 - 4	indistinctly spotted
A. africana	distinctly caulescent	solitary	erect	recurved	smooth	pungent	immaculate
A. boscawenii	caulescent	from base, grouped	sprawling	spreading	smooth	cartilaginous, 2 - 3	immaculate
A. brunneostriata	shortly caulescent	suckering, grouped	erect	spreading / recurved	smooth	cartilaginous, blunt	striate
A. buchlohii	acaulescent	solitary or grouped	-	erect / spreading	smooth	pungent, 3	indistinctly spotted
A. calidophila	caulescent	grouped	procumbent	recurved	smooth	cartilaginous, 4 - 5	immaculate
A. cameronii	caulescent	grouped	erect	erect / spreading	smooth	pungent, 2 - 3	immaculate
A. camperi	caulescent	grouped	erect / decumbent	recurved	smooth	pungent, 2 - 3	mostly immaculate
A. canarina	shortly caulescent	groups / suckering	decumbent	spreading / recurved	smooth	pungent, 2 - 3	immaculate
A. chrysostachys	mostly acaulescent	groups / suckering	-	erect / incurved	smooth	pungent, 4	immaculate
A. diolii	shortly caulescent	groups	sprawling	recurved	slightly rough	small, 1	indistinctly spotted
A. elegans	mostly acaulescent	solitary	decumbent	erect	smooth	pungent, 3 - 4	immaculate
A. ferox	distinctly caulescent	solitary	erect	erect / spreading	smooth	pungent, 6	immaculate
A. fleurentiniorum	acaulescent	solitary	-	spreading	rugulose / tuberculate	entire or 1 - 1.5	immaculate
A. flexilifolia	caulescent	grouped	erect / sprawling	spreading / recurved	smooth	small, 1 - 2	immaculate
A. gilberti	mostly caulescent	grouped	erect	spreading / apices recurved	smooth	pungent, 3 - 5	immaculate
A. guillaumetii	?	?	?	erect	?	?	spotted
A. harlana	mostly acaulescent	mostly solitary	-	spreading / recurved	smooth	pungent, 3 - 4	immaculate
A. hemmingii	mostly acaulescent	solitary or grouped	-	spreading / recurved	smooth	pungent, 2	maculate

Species	caulescence	branching	stem orientation	leaf orientation	texture	thorns	maculation
A. lensayuensis	caulescent	grouped	procumbent	spreading	rough	cartilaginous, 3 - 5	spotted
A. mcloughlinii	usually acaulescent	grouped	-	spreading / apices recurved	smooth	sub-pungent, 3 - 5	spotted
A. megalacantha	caulescent	grouped	erect	recurved	smooth	blunt, 5 - 6	immaculate
A. microdonta	caulescent	grouped	procumbent	recurved	smooth	small, 1	rarely spotted
A. ngongensis	caulescent	grouped	procumbent	spreading / recurved	smooth	pungent, 3 - 4	immaculate
A. peckii	acaulescent	solitary or grouped	-	erect / spreading	smooth	pungent, 3 - 4	maculate
A. penduliflora	caulescent	grouped	erect / spreading	erect / incurved	smooth	2	immaculate
A. rabaiensis	caulescent	grouped	erect / spreading	sub-erect / recurved	smooth	2 - 3	immaculate
A. rivae	shortly caulescent	solitary / grouped	erect / procumbent	spreading	smooth	cartilaginous, 4	immaculate
A. scabrifolia	caulescent	grouped	decumbent	spreading	rough	2	spotted
A. schelpei	shortly caulescent	grouped	decumbent	spreading / recurved	smooth	pungent, 2 - 3	rarely spotted
A. scobinifolia	acaulescent	solitary / groups	-	erect	rough	entire	immaculate
A. sinkatana	acaulescent	solitary / grouped	-	erect / spreading	smooth	sub-pungent, 2 - 3	spotted / maculate
A. somaliensis	acaulescent	solitary / grouped	-	spreading / recurved	smooth	pungent, 2 - 3	spotted
A. steudneri	shortly caulescent	?	?	spreading / incurved	smooth	2	immaculate
A. tewoldei	shortly caulescent	?	pendent	pendent	smooth	small, 0.5	obscurely spotted
A. tweediae	acaulescent	solitary / groups	-	spreading / recurved	smooth	pungent, 4	spotted

Table 5.2 continued /...

Table 5.2 cont. (Inflorescence and flower characters).

Species	inflorescence orientation	inflorescence branching	raceme shape	bract size mm	pedicel size mm	perianth shape	flower orientation
A. aageodonta	erect	6 - 10 branched	conical	4 - 6 X 2 - 3	10 - 13	cylindrical-trigonous	secund / nutant
A. africana	erect	2 - 3 branched	conical	11 X 7 - 8	5 - 6	curved-cylindrical	symmetrical / erect
A. boscawenii	erect	± 7 branched	cylindrical	7 X 3	18	cylindrical	symmetrical / erect
A. brunneostriata	erect / sub-oblique	6 - 7 branched	laxly cylindrical	5 - 6 X 5 - 6	5 - 6	cylindrical trigonous	sub-secund
A. buchlohii	erect	single	sub-capitate	7 x 2.5	15 X 20	cylindrical trigonous	symmetrical / erect
A. calidophila	erect - suberect	branched	cylindrical	3 - 4 X 2	10	cylindrical / clavate	symmetrical / erect
A. cameronii	erect	2 - 3 branched	cylindrical	2 X 3	3 - 5	cylindric / curved / clavate	erect / nutant
A. camperi	erect	branched	conical	2 X 2	12 - 18	cylindrical / clavate	sub-pendulous
A. canarina	erect	branched	cylindrical	2 - 3 X 2 - 5	6 - 7	cylindrical-trigonous	symmetrical / ± secund
A. chrysostachys	erect	5 - 10 branched	laxly cylindrical	5 - 7 X 3	10 - 12	cylindrical-trigonous	symmetrical / ± secund
A. diolii	erect	2 - 6 branched	cylindrical	5 X 4	?	cylindrical-trigonous	symmetrical
A. elegans	erect	branched	conical / sub-capitate	8 X 2 - 3	15	cylindrical / ± clavate	symmetrical / erect
A. ferox	erect	branched	cylindrical	8 - 10 X 3 - 5	4 - 5	clavate / cylindrical	erect
A. fleurentiniorum	erect	branched	laxly cylindrical	6 - 8	11	cylindrical	nutant
A. flexilifolia	sub-oblique	± 8 branches	cylindrical	8 - 12 X 13	12 - 18	cylindrical	erect / nutant
A. gilberti	erect	branched	laxly cylindrical	4 - 6 X 2 - 3	9 -10	cylindrical / sub-clavate	erect / nutant
A. guillaumetii	erect	single	laxly	4 X 2	15 - 20	?	?
A. harlana	erect	branched	cylindric-acuminate	10 X 5 - 7	15	cylindrical-trigonous	sub-pendulous
A. hemmingii	erect	simple	laxly cylindrical	8 X 3	6 - 8	const.-cylindrical-spotted	nutant
A. lensayuensis	erect	branched	laxly cylindrical	1 - 3 X 1.5	5 - 8	cylindrical trigonous	± secund

Species	inflorescence orientation	inflorescence branching	raceme shape	bract size	pedicel size	perianth shape	flower orientation
A. mcloughlinii	erect	branched	cylindrical	5 X 2	10	cylindrical / stripped	sub-pendulous
A. megalacantha	erect	branched	cylindrical	5 X 2 - 3	10 - 15	cylindrical trigonous	nutant
A. microdonta	erect, raceme oblique	branched	laxly cylindrical	2 - 4 x 2	5 - 6	cylindrical-trigonous	± secund
A. ngongensis	erect	6 - 8 branched	sub-capitate	7 - 10 x 3	10 - 12	cylindrical-trigonous	symmetrical
A. peckii	erect	branched	cylindrical	10 - 12 x 4	10	cylindrical stripped	lax, pendulous
A. penduliflora	erect	2 - 5 branched	sub-capitate	10 x 3	15 - 22	cylindrical-trigonous	symmetrical
A. rabaiensis	erect	5 - 9 branched	sub-capitate	10 - 12 x 3	10 - 15	cylindric-trigonous	laxly symmetrical
A. rivae	erect	branched	laxly cylindrical	2 - 4 x 2 - 3	12	cylindric-trigonous	spreading / nutant
A. scabrifolia	erect	branched	laxly cylindrical	3 x 2 - 3	5	cylindrical-trigonous	secund
A. schelpei	erect	simple	cylindrical	5 x 3	13 - 15	cylindrical-trigonous	sub-pendulous / nutant
A. scobinifolia	erect	branched	corymbose-capitate	8 x 2	15 - 18	cylindric-clavate	pendulous / nutant
A. sinkatana	erect	branched	sub-capitate	3 - 4 x 2	16 - 20	cylindrical-clavate	sub-pendulous / nutant
A. somaliensis	oblique / sub-erect	branched	cylindric	8 x 4	8	cylindric / stripped /	sub-secund / nutant
A. steudneri	erect	simple or branched	cylindrical	15 - 20	15 - 20	cylindrical-trigonous	sub-pendulous
A. tewoldei	?	simple	cylindric	4 x 2	12	cylindrical-trigonous	?
A. tweediae	erect	branched	cylindric	2 x 2	7	cylindrical-trigonous	sub-pendulous

mcloughlinii, *A. peckii*, *A. somaliensis* and *A. hemmingii*.

5. Species in which the inflorescence is simple, the flowers are cylindrical-trigonous, immaculate and symmetrically arranged around the floral axis. *Aloe buchlohii*, *A. schelpei*, *A. tewoldei* and *A. steudneri* are members of this group.

6. The last group consists of only two species; *A. africana* and *A. cameronii*. These two species bear an inflorescence which is 1 - 3 branched, the flowers are strongly curved and positioned symmetrically around the axis.

The leaf exudate chemistry:

Microdontin was isolated by Farah *et al.* (1996) from *A. microdonta*, a species used in Somali traditional medicine to treat jaundice and skin diseases. Groom & Reynolds (1987) indicated the presence of aloin in this species but no mention was made on the chemotaxonomic potential of this anthrone in co-occurrence with aloinoside and microdontin. References to literature indicate that the compounds under discussion have been isolated from the following species by Dagne (1996): *A. camperi*, *A. elegans*, *A. gilberti*, *A. megalacantha*, *A. rivae*, and *A. secundiflora*. In this study these compounds have been identified in the first five species. Reynolds (1996) compared the chemistry of *A. scabrifolia* and *A. turkanensis*. He mentions a series of compounds (R_t 29.1 - 36.5) as unidentified compounds. The first two in this range are most probably microdontin B and A as these compounds were positively identified in our study with authentic standards obtained from Dagne.

Considering the extreme morphological variation summarised above it becomes evident that *Aloe* presents a range of variable and perplexing morphological characters. None of the morphological characters seem to correlated and mostly represents a mosaic pattern of variation. This group best illustrates the desperate desire to explore additional characters as possible taxonomic markers at the infrageneric level.

Inspection of a typical HPLC chromatogram of a representative of this group (Figure 5.2) shows a distinct pattern. Most of the chemical groups that have been defined in this study is based on a single compound (e.g. plicataloside) or a specific class of compound (e.g. flavanones). Here, the chemical group is defined by the presence of a combination of compounds i.e. usually six compounds (chemical characters). This characteristic pattern is shown in Figure 5.2. Aloin B (1) and aloin A (2) are always present. It is interesting to note than

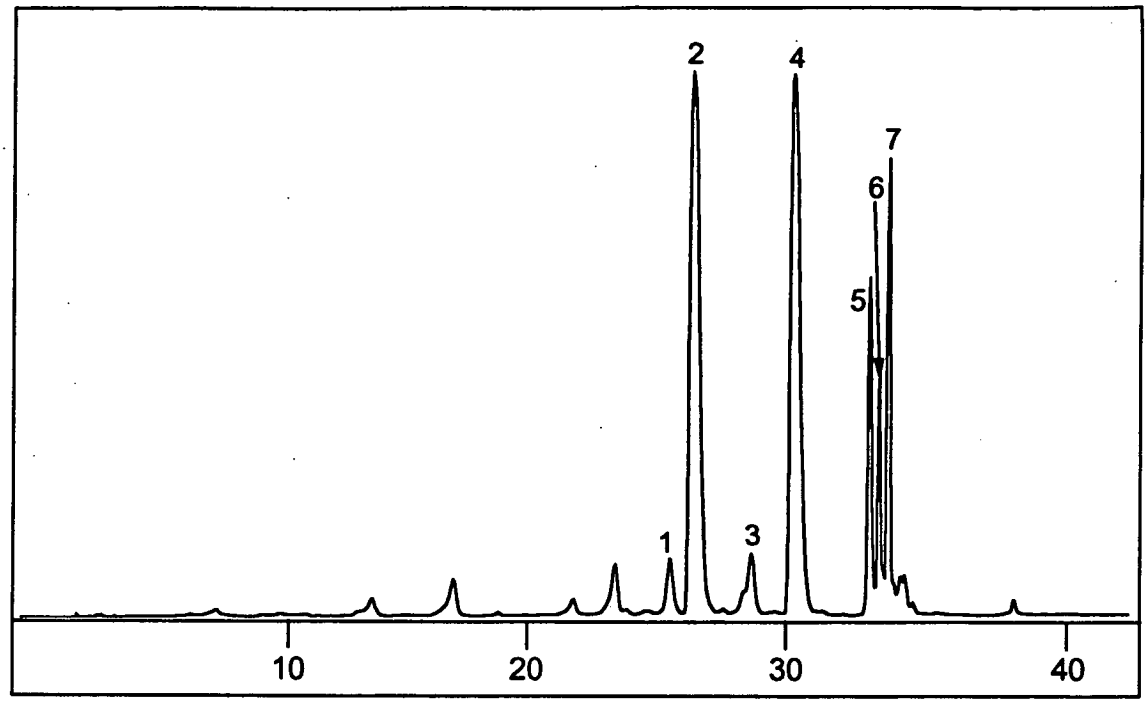


Figure 5.2 A typical HPLC chromatogram of a species containing aloin B (1) aloin A (2), aloinoside B (3), aloinoside A (4), microdontin B (5), microdontin A (6) & unidentified anthrone (7). Note the quantitative imbalance between the anthrone isomers and the absence of chromones. Structures and UV spectra of compounds are illustrated below.

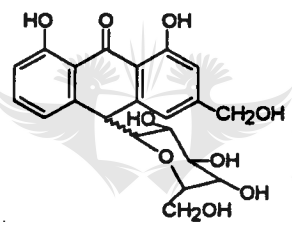
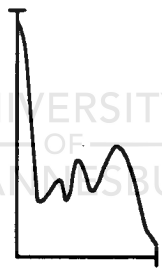
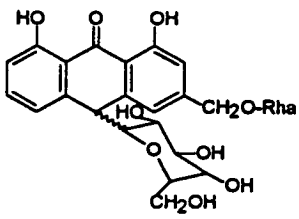
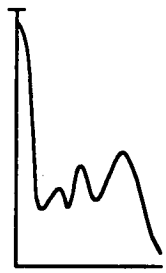
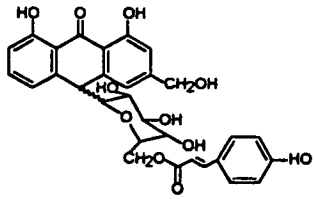
	structure	UV spectrum
aloin A / B (1 & 2)		
aloinoside A / B (3 & 4)		
microdontin A / B (5 & 6)		

Table 5.3: Presence of the major leaf exudate compounds in the aloin aloinoside / microdontin group.

	1	2	3	4	5	6	7	8	9	10	11	12	13
	aloesin	7-O-methylaloesin	aloeresin A	dihydroisocoumaringlucoside	8-O-methyl-7-hydroxylaoin	aloeresin D	aloin B	aloin A	aloinoside B	aloinoside A	microdontin B	microdontin A	unidentified anthrone
Rt (min)	5.4	8.2	14.7	15.7	16.7	20	23.6	24	28.9	30.9	32.3	32.9	33.8
A. aageodonta		■				■	■	■	■	■	■	■	
A. africana	■						■	■	■	■			
A. boscawenii							■	■	■	■	■	■	■
A. brunneostriata				■			■	■	■	■	■	■	
A. buchlohii							■	■			■	■	
A. calidophila				■			■	■	■	■	■	■	
A. cameronii	■		■			■	■	■	■	■			
A. camperi				■			■	■	■	■	■	■	■
A. canarina	■					■	■	■	■	■	■	■	■
A. chrysostachys		■				■	■	■	■	■			
A. diolii							■	■	■	■	■	■	
A. elegans				■			■	■	■	■	■	■	■
A. ferox	■		■				■	■	■	■			
A. fleurentiniorum				■			■	■	■	■	■	■	■
A. flexilifolia	■	■				■	■	■	■	■			
A. gilberti	■	■					■	■	■	■	■	■	
A. guillaumetii		■					■	■	■	■			
A. harlana							■	■	■	■	■	■	■
A. hemmingii	■				■		■	■	■	■			
A. lensayuensis							■	■	■	■	■	■	■
A. mcloughlinii	■			■		■	■	■	■	■			
A. megalacantha				■			■	■	■	■	■	■	■
A. microdonta							■	■	■	■	■	■	■
A. ngongensis						■	■	■	■	■	■	■	■
A. peckii	■			■		■	■	■	■	■			
A. penduliflora		■		■			■	■	■	■			
A. rabaiensis						■	■	■	■	■			
A. rivae				■			■	■	■	■	■	■	■
A. scabrifolia				■			■	■	■	■	■	■	■
A. schelpei					■		■	■			■	■	
A.scobinifolia				■			■	■	■	■	■	■	■
A. sinkatana					■		■	■	■	■			
A. somaliensis				■			■	■	■	■	■	■	■
A. steudneri				■	■		■	■			■	■	
A. tewoldei				■			■	■	■	■	■	■	
A. tweediae				■		■	■	■	■	■			

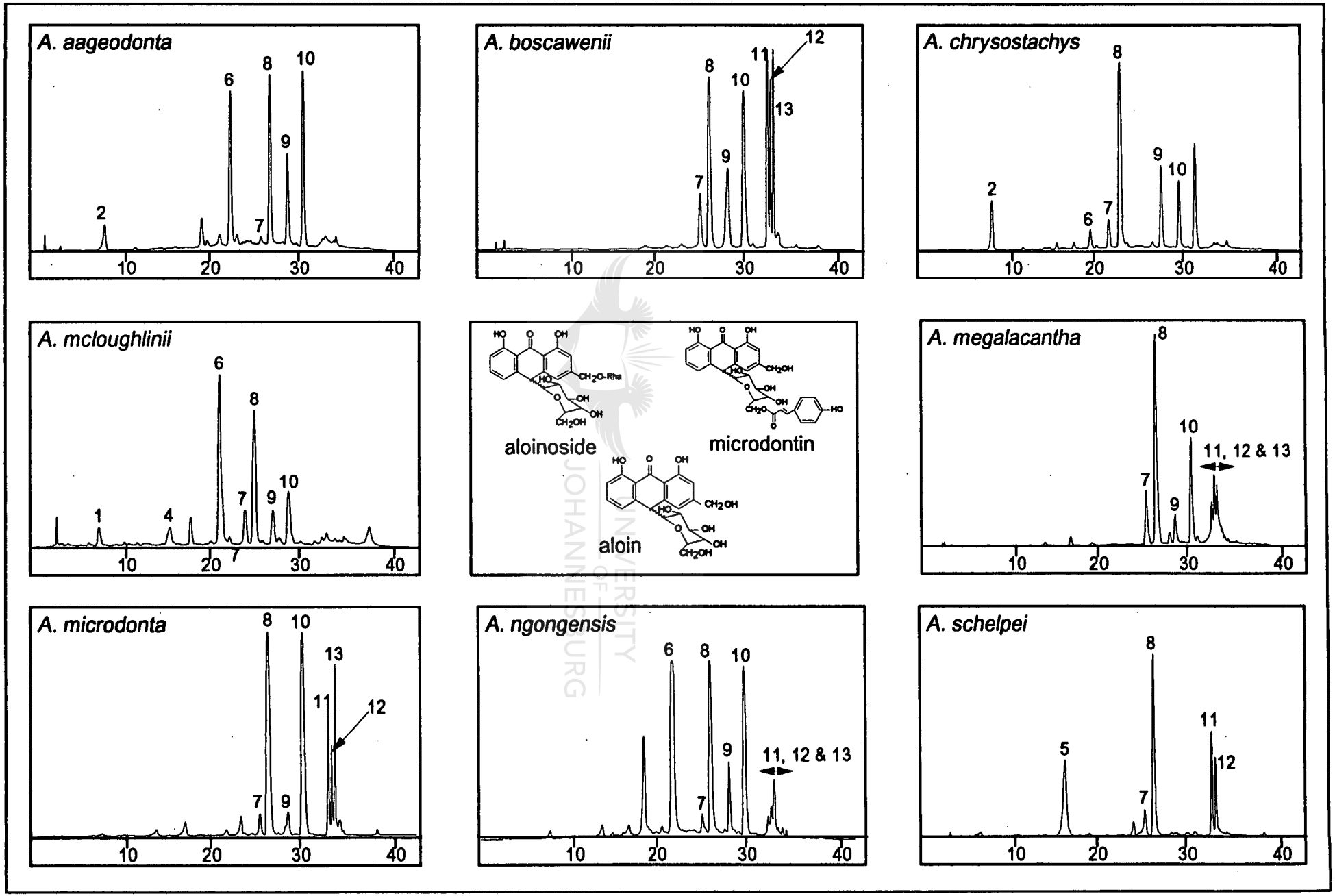


Figure 5.3: HPLC chromatograms of eight species containing aloin / aloinoside / microdontin. Numbers of peaks correspond to compounds in Table 5.3. The chemical structure of aloin, aloinoside and microdontin is shown in the centre block.

in the case of this group the two aloin isomers are usually in a quantitative imbalance i.e. less aloin B than aloin A is produced. The second set of isomers which are present are aloinoside B and A. These two isomers are also quantitatively unequal. Only three species did not produce the aloinosides in the presence of aloin A and B;. *A. buchlohii*, *A. schelpei* and *A. steudneri*. In the case of *A. ferox* only a isolated chemotype produces the aloinosides. This result emphasises the importance of geographical variation studies as it was only this single chemotype that initiated the idea that *A. ferox* could be included in this chemical group. It could be speculated that this is a relictual chemical compound which was much wider distributed throughout the expansive distributional geographic range of *A. ferox* and has only been retained in this single isolated population. The third set of anthrones characteristic of this group are microdontin B (5) and microdontin A (6). In most species these compounds were present as clearly defined peaks on the chromatogram while in others a 'noisily base-line' in the retention region of the microdontins suggested their presence. Evaluation of the UV spectra in this region could usually confirm the presence. The author believes that the microdontin compounds could be unstable as a microdontin containing sample has been re-analysed after a storage period of two years. The observation was made that the aloin and aloinoside isomers remain unchanged while the microdontin yield diminishes drastically. It is further interesting to note that although only microdontin A and B have been isolated as natural products a third compound is usually associated with the two isomers. The third unidentified compound (peak 7 in Figure 5.2) displays the same UV absorbance spectrum as for the microdontin isomers. Table 5.3 shows the total leaf exudate compositions for all the species while Figure 5.3 displays a selection of chromatograms of species in this chemical group. It is of interest that the chromones (a group of compounds generally detected in *Aloe*) are absent in a large number of species while others usually produce the chromones aloesin, aloeresin A and aloeresin D. Four species show the presence of 8-*O*-methyl-7-hydroxyaloin and are also discussed in Chapter 6.

Hypothesis on relationships:

Not a single or a combination of morphological character(s) unifies all of these species into a monophyletic group. It would also be premature to suggest that the leaf exudate chemistry (also in combination with the morphology) is a reliable apomorpy to draw all species into a natural group. There is no consistancy in leaf exudate composition and the group displays large variation in total leaf exudate composition. Some species produce only anthrones, some produce anthrones with chromones, others produce anthrones in co-occurrence with other

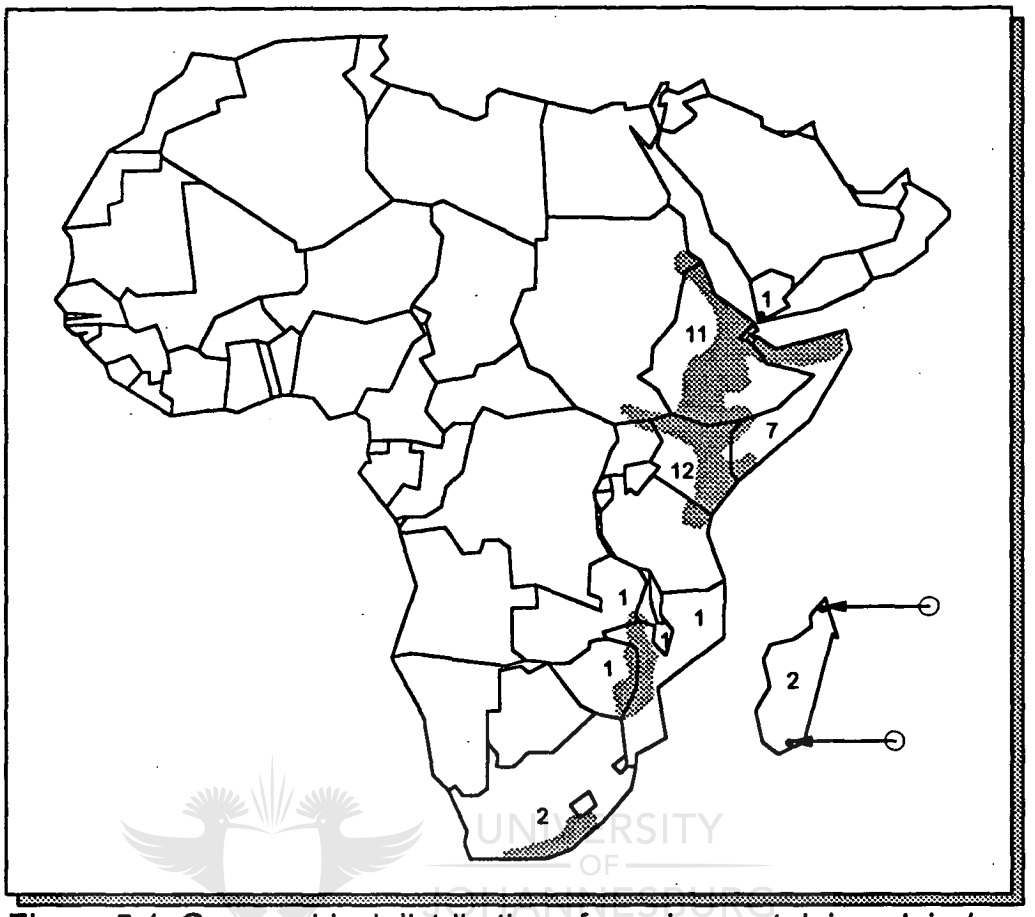


Figure 5.4: Geographical distribution of species containing aloin / aloinoside / microdontin as major anthrones. The number in each country represents the total number of species with the characteristic chemical profile.

chromones, in some species aloinoside is not present while in other species microdontin could not be positively identified.

The highest number of species (95%) in this group have a distribution in north-east Africa (Figure 5.4). One is expected to believe that this specie-complex would have its origin in this area from where the speciation took place in a southerly direction. The only species to occur on the Arabian Peninsula is *Aloe fleurentiniorum*. It could be possible that the species from N Somalia, *A. brunneostriata* (also containing aloinoside) could provide a 'link' between this single species in S Yemen with its chemical counterparts on the African continent. This could have taken place during the time when the Gondwana-reconstruction shows the Arabian Peninsula still attached to Africa. This separation of these two land masses is considered to be a very recent event in geological time (*ca.* 10 Ma). If *Aloe* should have evolved more recently the geographical area separating these two areas on a macro-geological scale is relatively small and does not provide an 'obstacle' for the dispersal of genetic material from possible relatives on the African continent. The same argument is relevant for the two species from Madagascar; *A. buchlohii* and *A. guillaumetii* are found in the north and south of Madagascar respectively. Research has confirmed that Madagascar was firmly wedged in adjacent to Kenya and Tanzania on the African continent. If one should consider that species of this group 'migrated' to what is now known as Madagascar prior to the 'Gondwana-break-up' then this event had to take place *ca.* 260 Ma years ago. It is estimated that Angiosperms only evolved *ca.* 150 Ma years ago. Although the initial separation of the two land masses occurred 260 Ma years ago, the drift of Madagascar to its present position is expected to have been a very slow process and considering the distance between the two contents today then it could also be reasoned that genetic material from possible related species on the African continent could be freely dispersed over this 'relatively short' distance.

These results are in-line with many examples where species on the African continent show a characteristic chemical profile which is shared by one or two Malagasy endemics. This correlation has been found between Madagascar and east Africa and also between Madagascar and southern Africa. In contrast to the arguments above, convergent evolution could not be ruled out as possible explanation for the chemically similarity between these geographical distant species.

With references to the present day distribution of the species shown in Figure 5.4 a possible route of migration to the present distributional patterns could be explained as follows: Although the level of morphological variation in this group is so vast, salient morphological features which are rare in *Aloe* could possible provide some answers on relationships.

Considering the curved perianth characteristic of *A. cameronii* and *A. africana* which is a feature not very widespread in the genus then it is taxonomically noteworthy that the very widespread and variable *A. cameronii* which has an extensive distribution in Malawi, Zimbabwe, Zambia and Mozambique could be considered a taxonomic intermediate between the southern and northern taxa in this group. This resemblance forces one to consider other species with a similar character i.e. *A. reitzii*. Close scrutiny of the chromatograms (Appendix 1) shows that two late eluting anthrones are present. The quantities are extremely low and the UV spectrum could not confirm wether these are the aloinosides. The same profile has been recorded for *A. aculeata*, *A. petricola* and *A. gerstneri*. It is here postulated that this group is of tropical origin from where speciation took place through the variable and widespread *A. cameronii* to *A. ferox* and *A. africana* in the far south. *Aloe reitzii* (and its three close relatives) have a very distant connection with this group which is indicated by the very low quantities of what seems to be aloinosides which is not found (even in trace amounts) in any other species of *Aloe* in South Africa. To suggest possible trends amongst the aloes of tropical east Africa would verge on mere guesswork at this stage. The reticulate distribution of chemical and morphological characters in this group indicate the influence of hybridization events. It is demonstrated in Chapter 6 that hybrids could obscure the pattern where species are obviously related as various chemical profiles can result from an intermediate species. The value of the distribution of these compounds lie in the remarkable similarity in leaf exudate composition for these 36 species indicating a measure of taxonomic coherence, how distant is may be, between a large group of species not previously associated with one another.

Figure 5.5: Representatives in the aloin / aloinoside / microdontin chemical group. ⇨

Photo: Newton 1993

Aloe aageodonta

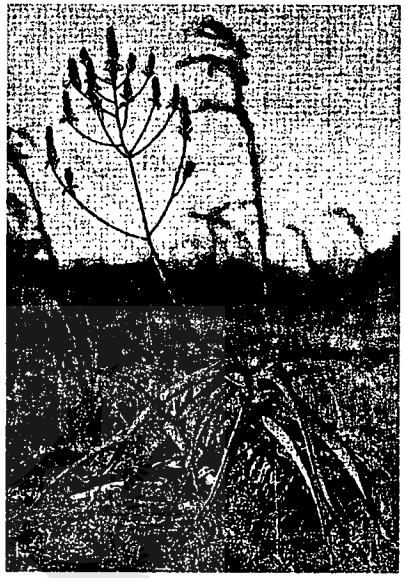


Photo: Reynolds 1966

Aloe calidophila

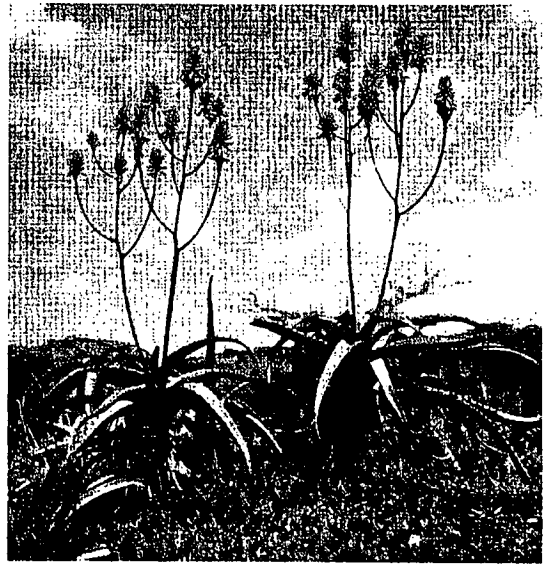


Photo: Reynolds 1966

Aloe camperi

Photo: Newton 1996

Aloe chrysostachys

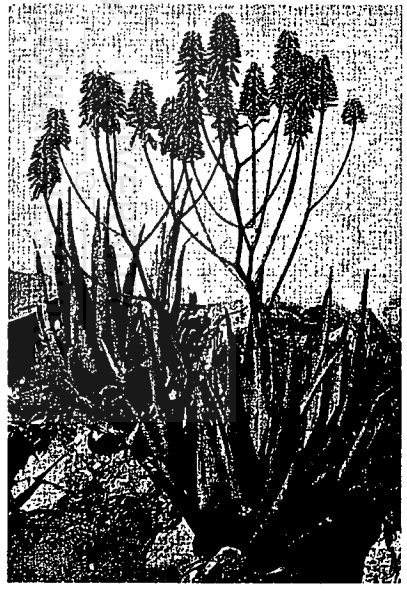


Photo: Reynolds 1966

Aloe elegans

Photo: Reynolds 1966

Aloe megalacantha

Photo: Reynolds 1966

Aloe flexilifolia

Photo: Reynolds 1966

Aloe scobinifolia

Photo: Reynolds 1966

Aloe africana

Photo: Reynolds 1966

Aloe sinkatana

Photo: Reynolds 1966

Aloe somaliensis

Chapter 6

8-*O*-methyl-7-hydroxyaloin - chemical evidence of hybridization in *Aloe*

CHAPTER 6

THE TAXONOMIC DISTRIBUTION OF 8-*O*-METHYL-7-HYDROXYALOIN

CHEMICAL EVIDENCE OF HYBRIDIZATION IN *ALOE*

The anthrone 8-*O*-methyl-7-hydroxyaloin has been an important and interesting chemotaxonomic focal point throughout this study. This compound has been instrumental in understanding the value and restriction of chemical compounds in chemotaxonomy and has also shed light on speciation processes in *Aloe*. This chapter will follow the same course of reasoning as has developed since it was isolated from *Aloe schelpei*. Initially it was thought that this compound could be a possible chemotaxonomic marker for a number of species and that it suggests likely trends in evolution between the aloes of Madagascar and Africa. Later evidence indicated that the presence of this compound could also be interpreted as a non-homologous similarity between various species as it could form along two different biochemical pathways. Most intriguing of all was the discovery that this compound forms readily when two chemically divergent species of *Aloe* are hybridized. Mention will also be made of the leaf exudate composition of various hybrids analysed during this study and will conclude with a summary on the role of hybridization in *Aloe* and as a mechanism of speciation in general.

Table 6.1. Taxa, voucher details and distribution of the 18 species containing 8-*O*-methyl-7-hydroxyaloin.

Species	Voucher	Distribution
A. antandroi	NBI 14685 & NBI 14685	S Madagascar
A. christianii	WE 591	Zambia, Zimbabwe & Mozambique
A. hemmingii	RBG, Kew 08481-01059 & NBI 11170	Somalia
A. isaloensis	ex hort NBI	Madagascar
A. menachensis	RBG, Kew 439-7504-505	Yemen
A. millottii	Hardy 2829 & NBI 14657	S Madagascar
A. mutabilis	WE 25, Chuniespoort, Blouberg	South Africa
A. niebuhriana	RBG, Kew 1975-4506 & NBI 10221	South Yemen
A. officinalis	RBG, Kew 206-84-01590	Yemen
A. pubescens	EDS 316 & RBG, Kew 439-75-04512	Ethiopia
A. retrospiciens	RBG, Kew 630-54-63008	Somalia
A. schelpei	RBG, Kew 427-64-42705, ex hort NBI	Ethiopia
A. sinana	EDS 4659	Ethiopia
A. sinkatana	ex hort BSM	N Sudan
A. steudneri	RBG, Kew 1987-4090 & ex hort BSM	N Ethiopia
A. tomentosa	RBG, Kew 305-70-02870 & NBI 21758	Yemen & N Somalia
A. turkanensis	RBG, Kew 1977-3733	Uganda and Kenya
A. vaombe	ex hort D. Hardy & ex hort NBI	S Madagascar

Aloe ferox X *A. thraskii*, one of the numerous aloe garden hybrids (Photo: Andy de Wet / Leo Thamm).

Taxonomic arrangement of species containing 8-*O*-methyl-7-hydroxyaloin as represented in Figure 6.1.

The present comprehension of the taxonomic positions of the 8-O-methyl-7-hydroxyaloin-containing species is diagrammatically represented in Figure 6.1. Reynolds defines a very large group of species and places them in Group 9, *Verae* of the tropical aloes:

> Group 9: Plants acaulous rarely caulescent, solitary or in groups. Leaves densely rosulate, long attenuate, fleshy, glaucous, rarely spotted. Inflorescence short or tall, simple or few branched, branches erect, rarely many branched. Raceme mostly narrowly cylindric, sublax to subdense. Pedicels averaging 5 - 8 mm. Bracts reflexed, often twice as long as the pedicel. Perianth cylindric trigonous, averaging 25 - 30 mm long, mouth slightly upturned, red, orange or yellow, varying from glabrous to pubescent and tomentose-villose; outer segments connate to the middle and higher. (Reynolds, 1966).

Although five of the 18 species are placed by Reynolds in his Group 9 not too much should be read into this taxonomic agreement with the chemotaxonomy of these five species. Group 9 is morphologically extremely heterogenous and the description defining this artificial group could be applied to many species of *Aloe*. It is interesting to note that although Reynolds weighed perianth characters to be of great taxonomic importance, this group contains those species with a tomentose perianth, a rare occurrence in *Aloe*. (Reynolds defines Group 4 by "plants with a striped perianth", Group 6 is characterised by "a perianth with a pronounced basal swelling" and Group 8 is defined by "the perianth which is trigonously indented"). The geographical distribution of these five species in Group 9 are interesting in that all but one occurs in Yemen with *A. pubescens* distributed in Ethiopia and *A. tomentosa* found on both the African continent (Somalia) and on the Arabian Peninsula (Yemen). All of the species except for *A. officinalis* (which was not seen by Reynolds) are characterised by a tomentose perianth. It is well within the confines of taxonomic reason that the co-occurrence of a hairy perianth together with the anthrone glucoside 8-O-methyl-7-hydroxyaloin is indicative of a possible taxonomic relationship between the species. *Aloe hemmingii* with its striped perianth is the only species in Group 4 (striped perianth group) containing this compound. Most species with their striped perianths have been discussed in Chapter 5, while A. *hemmingii* together with *A. sinkatana* is the only species in this group to produce aloin and aloinosides together with 8-O-methyl-7-hydroxyaloin. This somewhat unusual combination of exudate anthrones indicates a possible exchange of genetic material between aloin / aloinoside / microdontin containing species with a 8-O-methyl-7-hydroxyaloin accumulating species. *Aloe turkanensis* with its oblique racemes and secund flowers is grouped within section *Ortholophae* uniting all taxa with secund flowers. It has been discussed in the foregoing chapter that this character

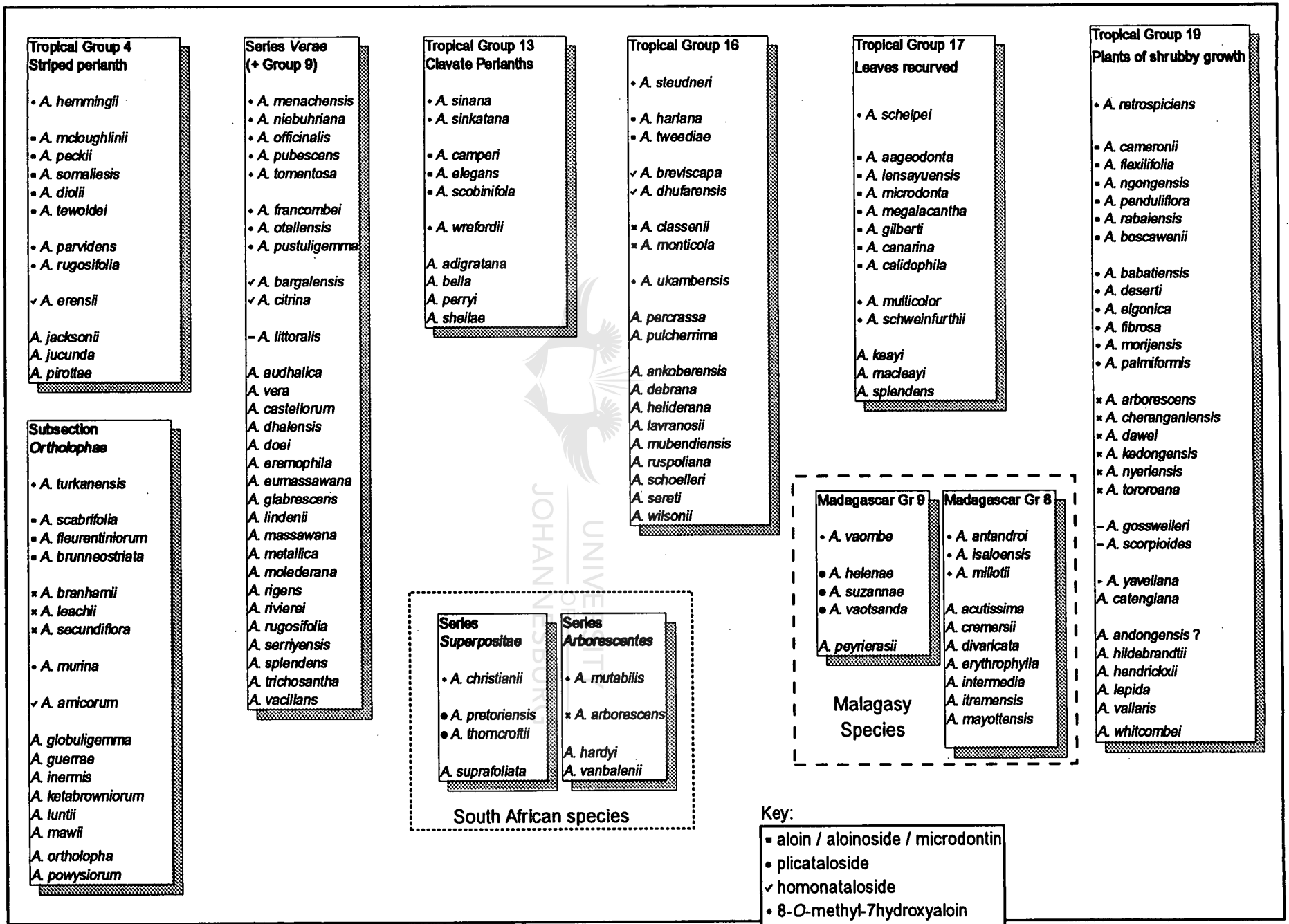


Figure 6.1: Taxonomic position of species containing 8-*O*-methyl-7-hydroxyaloin.

probably evolved more than once in the genus and does not represent a natural group. This is also reflected in the chemical composition of this group (*Orthlophae*) as it houses a 'chemical assortment' of species which are definitely not related. The strongly recurved leaves of *Aloe schelpei* places it in Group 17 of the tropical species. Most species in this group accumulate aloinoside / aloin / microdontin. *Aloe schelpei* too shows the presence of microdontin with the aloinoside being absent. This combination of leaf compounds once again hints on a possible hybridisation event, similar to the situation of *A. broomii* demonstrated in Chapter 8.

Three Malagasy endemics which are included in this group have this compound present in the leaf exudate. The only other species from Madagascar containing this compound is *Aloe vaombe* which is placed in Group 9 together with other distinctly caulescent species. Another distinctly caulescent species is *Aloe retrospiciens* included in Group 19. With reference to macromorphological features it is a distinctive species. *Aloe christianii* from southern Africa showed this compound to be present in trace amounts. It is the only species in series *Superpositae* containing this anthrone. Chapter 12 illustrates that the series *Superpositae* is an unnatural assemblage as it contains two species which produce flavanones via the flavonoid biochemical pathway. The other member of this group, *A. suprafoliata* produces the chromones and anthrones via the polyketide pathway which is the general pattern in *Aloe*. The only South African species containing 8-O-methyl-7-hydroxyaloin is *Aloe mutabilis* which is placed in series *Arborescentes*.

Morphological Characters (Table 6.2)

Habit characters (caulescence, branching and orientation):

Most species included in this chemical group are acaulescent or shortly caulescent. Two species; *A. retrospiciens* and *A. vaombe* are distinctly caulescent developing erect stems 2 - 3 m in length. *Aloe mutabilis* is the only species which is pendent usually hanging from vertical rock faces.

Leaf characters (leaf architecture, texture, thorns and maculation):

Most species bear their leaves in a spreading to recurved way. The leaf surface is smooth in all species and usually immaculate. In *Aloe hemmingi*, *A. turkanensis* and *A. sinkatana* the leaves are spotted while *A. christianii* and *A. mutabilis* show obscure lineation on the leaf surface.

The prominent leaf characteristic of this group is that most species have small, sub-pungent teeth and do not bear large, sharp pungent teeth usually associated with aloes. The three

Table 6.2 Summary of the salient morphological characters of the 8-*O*-methyl-7-hydroxyaloin-producing species of *Aloe*.

species	caulescence	branching	stem orientation	leaf orientation	texture	thorns (mm)	maculation
A. antandroi	caulescent	grouped	slender / erect	spreading to recurved	smooth	small / 0.5 - 1	slightly spotted
A. christianii	caulescent	solitary / grouped	erect / decumbent	erect / spreading	smooth	3 - 5	obscurely lineate
A. hemmingii	mostly acaulescent	solitary / grouped	-	spreading / recurved	smooth	pungent, 2	maculate
A. isaloensis	shortly caulescent	grouped	erect / procumbent	erect	smooth	sub-pungent, 1 - 1.5	immaculate
A. menachensis	?	grouped / solitary	erect / decumbent	incurved	smooth	blunt, 2	immaculate
A. millottii	shortly caulescent	grouped	decumbent	spreading / recurved	smooth	small, cartilaginous	immaculate
A. mutabilis	caulescent	grouped	pendent	spreading / recurved	smooth	2	obscurely lineate
A. niebuhriana	usually acaulescent	grouped / solitary	shortly procumbent	spreading	smooth	1.5 - 2	immaculate
A. officinalis	shortly caulescent	grouped / suckering	decumbent	erect spreading	smooth	thorns present	often spotted
A. pubescens	acaulescent	grouped	-	suberect / spreading	smooth	pungent, 2 - 3	immaculate
A. retrospiciens	distinctly caulescent	grouped	erect	spreading to recurved	smooth	small, 1	sparsely spotted
A. schelpei	shortly caulescent	grouped	decumbent	spreading	smooth	sub-pungent	rarely spotted
A. sinana	caulescent	grouped	erect	spreading / recurved	smooth	pungent, 3 - 4	sparsely spotted
A. sinkatana	acaulescent	solitary / grouped	erectly spreading	erectly spreading	smooth	sub-pungent, 2 - 3	spotted
A. steudneri	shortly caulescent	?	?	spreading to incurved	smooth	2	immaculate
A. tomentosa	shortly caulescent	grouped	decumbent	spreading / upcurved	smooth	blunt , 1	immaculate
A. turkanensis	shortly caulescent	grouped (suckering)	decumbent	erect / spreading	smooth	2	spotted
A. vaombe	distinctly caulescent	solitary	erect	spreading	smooth	sub-pungent, 5-6	immaculate

Table 6.2 cont./....

Table 6.2 cont.:

Species	inflorescence orientation	inflorescence branching	raceme shape	bract size	pedicel size	perianth shape	flower orientation
A. antandroi	erect	mostly simple	sub-capitate	4 x 3	8	cylindrical / constricted	pendulous
A. christianii	erect	branched	cylindrical	5 - 6 x 3	8 - 10	cylindrical-trigonous	cernuous/pendulous
A. hemmingii	erect	simple	laxly cylindrical	8 x 3	6 - 8	constricted / cylindrical / spotted	nutant
A. isaloensis	erect	simple / 3 - 5 br.	cylindrical	3 x 1 - 5	6 - 7	cylindrical / constricted	nutant
A. menachensis	erect	much branched	cylindrical	10 - 15	5 - 7	cylindric / shortly tomentose	pendulous
A. millottii	erect	simple	laxly cylindrical	7 x 4	6 - 8	cylindrical / constricted	pendulous
A. mutabilis	erect	mostly simple	cylindrical	13 x 5	20 - 25	cylindrical / clavate	pendulous
A. niebuhriana	erect	usually simple	cylindrical conical	8 x 3 - 4	4 - 6	cylindric / campanulate / toment.	spreading / nutant
A. officinalis	erect	branched	cylindrical	10	6 - 8	cylindrical-trigonous	pendulous
A. pubescens	erect	simple / 1-branched	cylindrical	20 x 6	15	cylindric / pubescent	sub-pendulous
A. retrospiciens	erect	branched	sub-capitate	5 x 2.5	5 - 6	cylindric / trigonous	secund
A. schelpei	erect	simple	cylindrical	5 x 3	13 - 15	cylindric / trigonous	sub-pendulous
A. sinana	erect	branched	sub-capitate	5 x 3	18 - 20	cylindric / clavate	nutant
A. sinkatana	erect	branched	sub-capitate	3 - 4 x 2	16 - 20	cylindric / clavate	sub-pendulous
A. steudneri	erect	simple / branched	cylindrical	15 - 20	15 - 20	cylindrical-trigonous	sub-pendulous
A. tomentosa	erect	branched	cylindrical	7 x 4	6 - 9	cylindric / tomentose	nutant
A. turkanensis	erect	branched	laxly cylindrical	5 - 7 x 3	8 - 10	cylindrical	pendulous
A. vaombe	erect	branched panicle	cylindrical	8 x 5	12	cylindrical / distinctly curved	sub-pendulous

Malagasy endemics (Group 8) have characteristically small teeth which are present on the rounded leaf apex.

Inflorescence and flower characters:

In all species the peduncle is erect with the inflorescence mostly simple although some species e.g. *A. vaombe* produces a much branched panicle. In most species the raceme is cylindrical, but a large number of species produce sub-capitate racemes. The bracts and pedicels of most species are relatively short with *A. mutabilis*, *A. pubescens* and *A. steudneri* having much larger bracts. The pedicels of *A. mutabilis*, *A. schelpei*, *A. sinana*, *A. sinkatana* and *A. steudneri* are also much longer than the average for the group. With reference to the perianth, this group shows immense variation. The species in Group 9 are characterised by a pubescent perianth surface. The three species in Group 8 from Madagascar show a slight constriction above the ovary which is prominent in *A. vaombe*. It is interesting to note that *A. hemmingi* which is placed in a group characterised by a striped perianth bears a floral resemblance to the three Malagasy species in Group 8. The flowers of *A. millottii* as depicted by Reynolds (1966 pp. 490) would easily fall within the category of 'perianths striped' as defined for Group 4. *Aloe sinana* and *A. sinkatana* are placed in Group 13 defined by the clavate perianth. The perianth of *A. mutabilis* could also be described as slightly clavate. In all species the flowers are pendent or nutant except for *A. turkanensis* where the flowers are secund on the oblique racemes.

Leaf exudate chemistry (Table 6.3)

Of all characters discussed above, the leaf exudate composition of this group of species could at its best be described as unique. The leaf exudate chemistry of all 18 species is summarised in Table 6.3 and a selection of representative HPLC profiles are shown in Figure 6.2. In his chemotaxonomic treatment of *Aloe*, Reynolds (1990) states that *A. mutabilis* is the only species of *Aloe* where the anthrones aloin and homonataloin co-occur. This study has shown two another species, *A. retrospiciens* and *A. pubescens* also displays this chemical anomaly. Two samples of *Aloe tomentosa* were analysed. In the one specimen aloin was accumulated as major anthrone and in the second homonataloin was accumulated as anthrones, both however produced 8-*O*-methyl-7-hydroxyaloin. (This 'dual accumulation' of the major anthrones has only been found in *Aloe marlothii*). The pattern of occurrence and co-occurrence of the major anthrones indicates that 8-*O*-methyl-7-hydroxyaloin could be formed out of aloin which requires methylation at the 8' position and hydroxylation at the 7' position (Figure 6.5). One

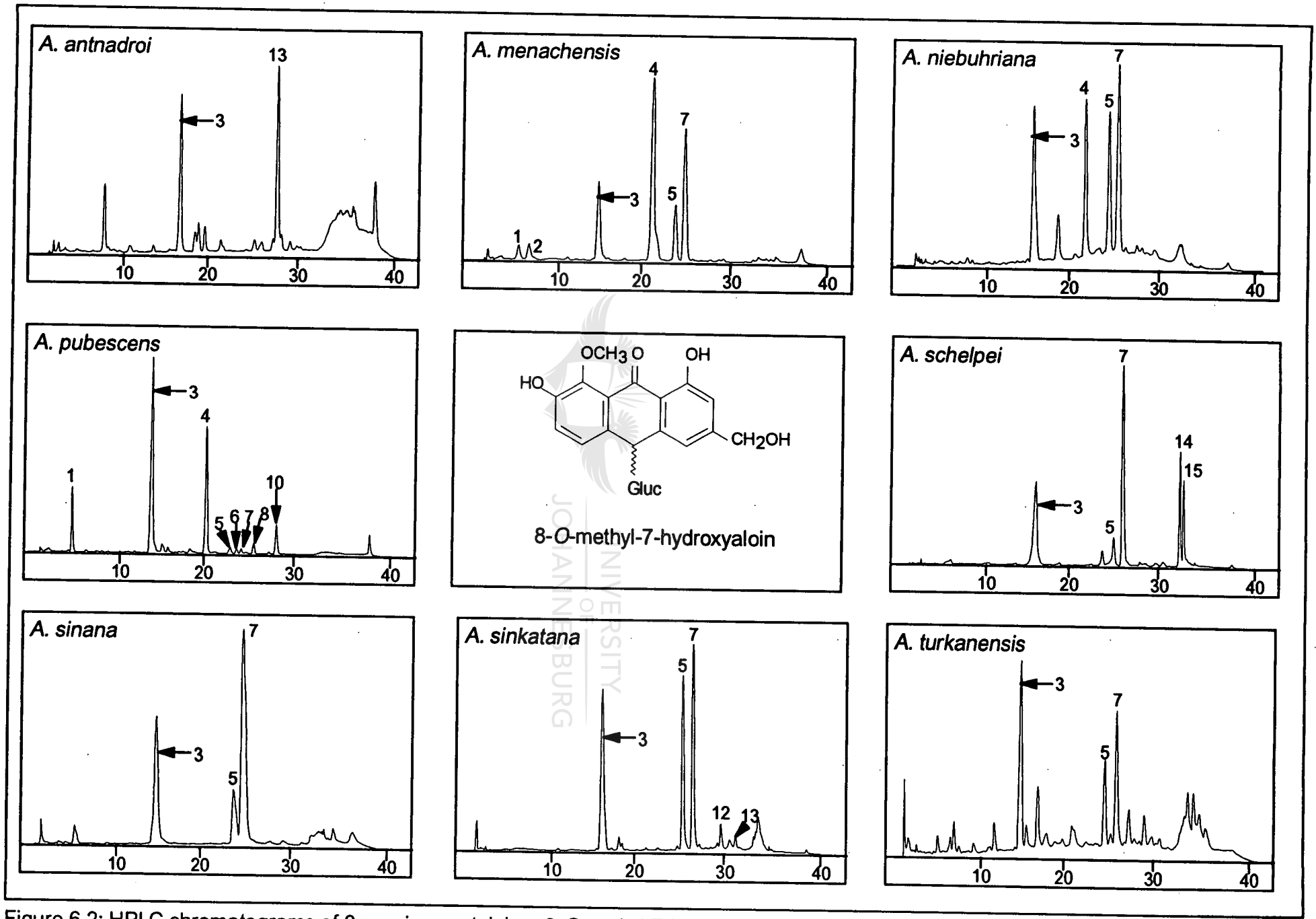


Figure 6.2: HPLC chromatograms of 8 species containing 8-*O*-methyl-7-hydroxyaloin. Numbers of peaks correspond to Table 6.3. The chemical structure of 8-*O*-methyl-7-hydroxyaloin is shown in the centre block.

Table 6.3: Presence of major compounds in the 8-O-methyl-7-hydroxyaloin group.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
	aloesin	7-O-methylaloesin	8-O-methyl-7-hydroxyaloin	aloeresin D	aloin B	homonataloin B	aloin A	homonataloin A	unidentified chromone	unidentified chromone	aloinoside B	aloinoside A	unidentified anthrone	microdontin B	microdontin A
Rt (min)	5.49	8.23	16.78	20.03	23.61	23.58	24.07	25.49	26.42	28.4	28.94	30.9	27.77	32.91	32.34
A. antandroi			■										■		
A. christianii	■		■		■		■								
A. hemmingii	■		■		■		■				■	■			
A. isaloensis	■		■			■		■							
A. menachensis	■	■	■	■	■		■								
A. millottii			■												
A. mutabilis	■		■		■	■	■	■	■						
A. niebuhriana		■	■	■	■		■								
A. officinalis	■		■	■	■		■								
A. pubescens	■		■	■	■	■	■	■		■					
A. retrospiciens	■		■	■	■	■	■	■		■					
A. schelpei			■		■		■							■	■
A. sinana			■		■		■								
A. sinkatana			■		■		■				■	■			
A. steudneri			■		■		■							■	■
A. tomentosa	■	■	■	■	■		■			■					
A. turkanensis			■		■		■								
A. vaombe			■												

homonataloin species also accumulated 8-O-methyl-7-hydroxyaloin which implies hydroxylation at the 3' position. It is impossible to know if the 8-O-methyl-7-hydroxyaloin in *A. mutabilis*, *A. pubescens* and *A. retrospiciens* is formed via aloin or homonataloin. Two species; *A. hemmingii* and *A. sinkatana* produce aloinoside while both *A. schelpei* and *A. steudneri* produce microdontin. This combination of exudate compounds are very unusual forcing one to speculate on hybridization events which could possibly be responsible for the co-occurrence of these compounds which are usually mutually exclusive. The two Malagasy endemics; *Aloe antandroi* and *A. millottii* accumulate 8-O-methyl-7-hydroxyaloin in the absence of aloin or homonataloin. Both these species have unidentified anthrones present in the leaf exudate, but mostly at low levels. It could be reasoned that the aloin / homonataloin isomers have been completely converted to 8-O-methyl-7-hydroxyaloin or that this compound could be derived from the unidentified compounds. The general chemical pattern observed in the Malagasy species is that they produce 'unique' chemical profiles which are unmatched by any other species of *Aloe* or that they are devoid of exudate compounds. Many species produce relatively little exudate. This opens another argument relating to a possible ecological explanation. It is generally believed that the pungent thorns and bitter tasting leaf exudate evolved for defence and antifeedant properties. Madagascar does not have many species of higher mammals and one could speculate that no selective pressure was 'induced' to develop mechanisms of protection against herbivores or that these morphological and chemical deterents have gone 'lost' over time.

Chemogeographical Patterns (Figure 6.3)

The categorised treatment of the genus in three sections: Aloes of Southern Africa (Reynolds 1950), Aloes of Tropical East Africa and The Aloes of Madagascar (Reynolds 1966) has resulted in 'taxonomic compartmentalisation'. Reynolds (1966) states: 'Compared with species found on the African mainland, any attempt to suggest trends of evolution would be mere guesswork.' The biogeographical analysis by Holland (1978) indicated that there is no comparison between the species of the African mainland and the Malagasy endemics. This conclusion is based on the absence of a communal species. This study has shown several chemical alliances between the species in each of the three "sub-regions" of the distribution. Only 8-O-methyl-7-hydroxyaloin and the occurrence of flavanones (Chapter 12) suggest possible biogeographical links between the Malagasy species and the aloeaceous counterparts on the African continent. Reynolds (1966) emphasises the great difficulty in suggesting trends

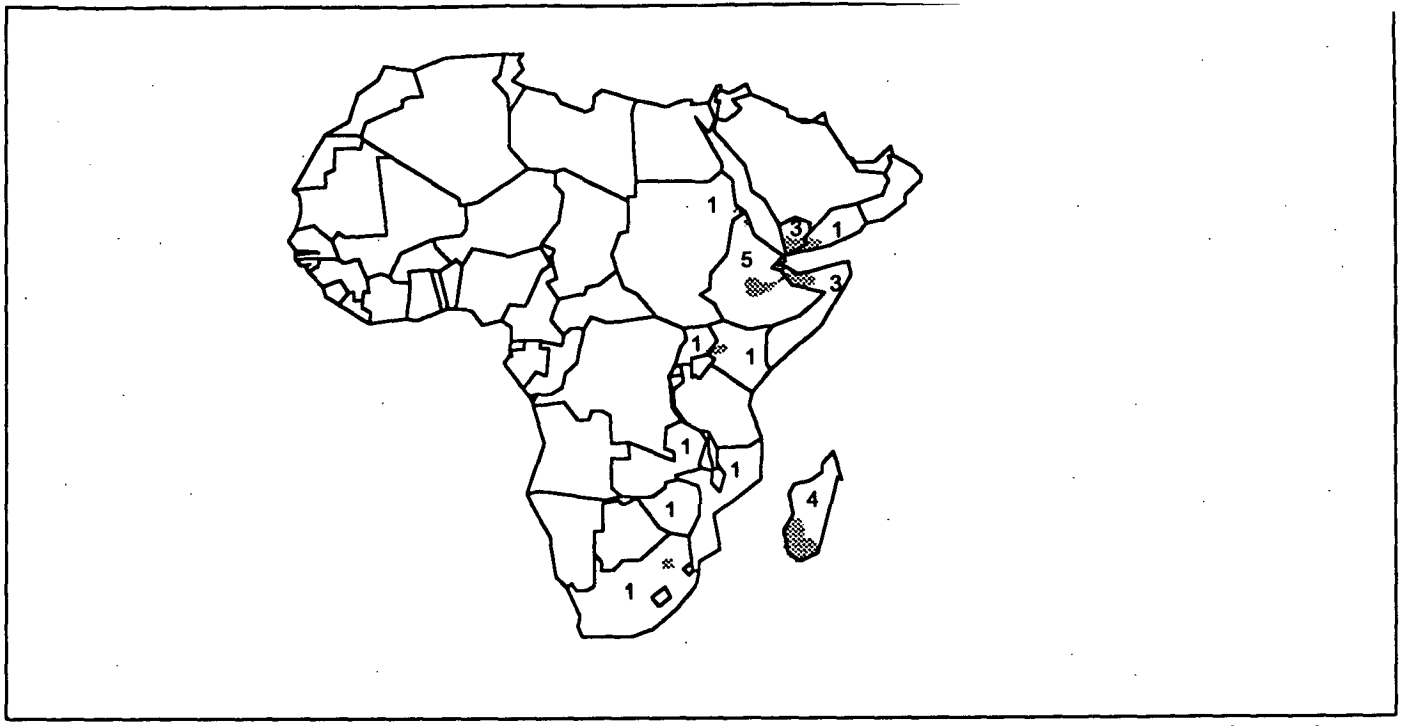


Figure 6.3: Geographical distribution of species containing 8-*O*-methyl-7-hydroxyaloin as major anthrone. The number in each country represents the total number of species with the characteristic chemical compound.

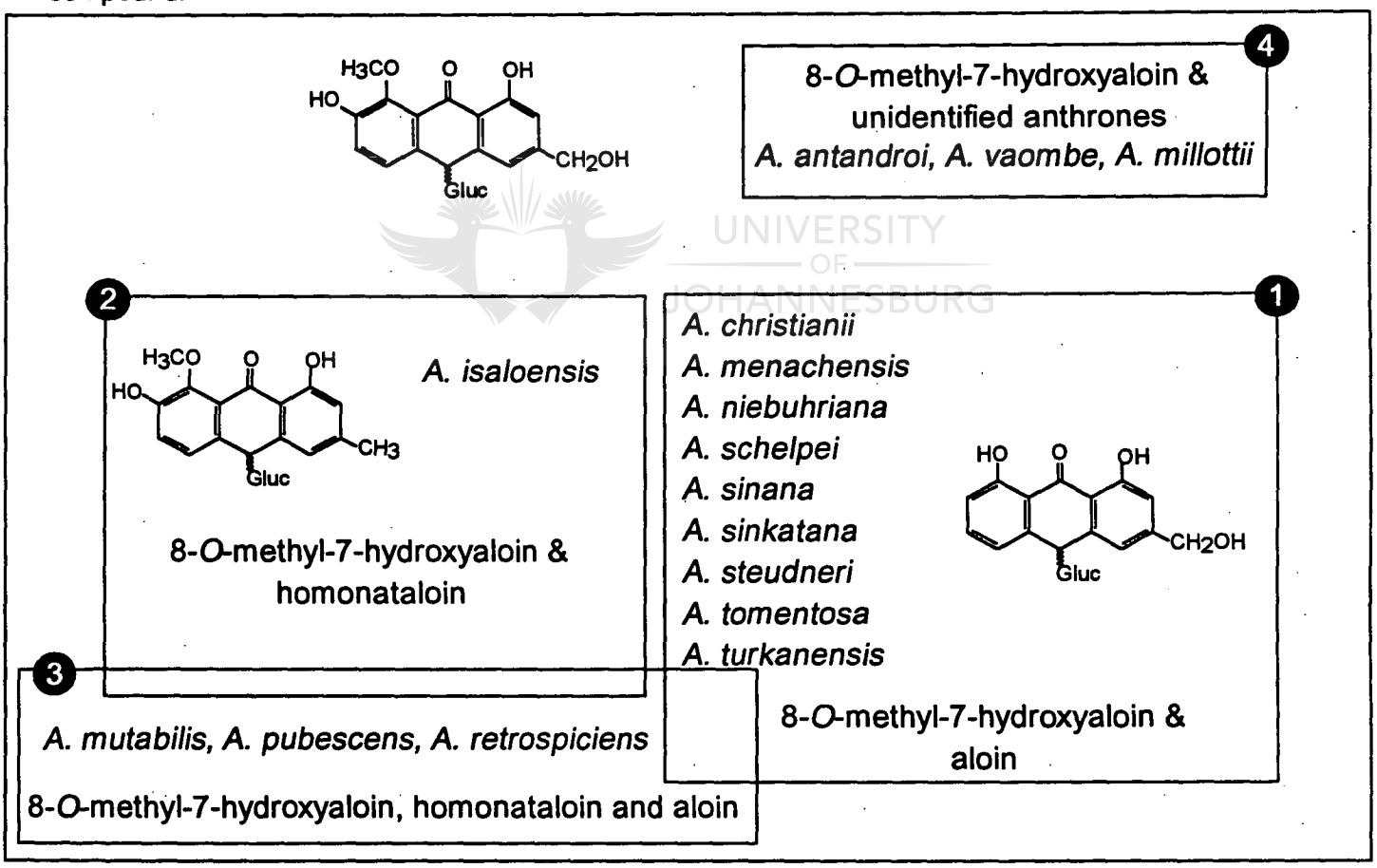


Figure 6.4: Diagrammatic summary of chemotypes in the 8-*O*-methyl-7-hydroxyaloin species complex.
1) in co-occurrence with aloin,
2) in co-occurence with homonataloin,
3) in co-occurrence with aloin and homontaloin,
4) in co-occurrence with unidentified anthrones.

of evolution in *Aloe*, especially to suggest relationships between the species on Madagascar with any other species. Morphologically they (the Malagasy species) are very distinct and it has proven virtually impossible to find a correlation in morphological patterns.

If one should consider that 18 species in this survey contain 8-*O*-methyl-7-hydroxyaloin of which four species are from Madagascar (Figure 6.3) then one is inclined to speculate that this data should not immediately be dismissed as convergence but that it could be chemotaxonomically meaningful. This chemical pattern suggests a possible relationship between the species on Madagascar with those in north east Africa while the distribution of flavanones (Chapter 12) implicates a possible taxonomic alliances between the aloes of Madagascar and the aloes of southern Africa.

The non-homology of 8-*O*-methyl-7-hydroxyaloin

The arguments presented above have assumed that 8-O-methyl-7-hydroxyaloin is homologous in all 18 species. However, considering the value of a single chemotaxonomic compound in isolation should be done with caution. Figure 6.4 summarises the various chemotypes present in the chemical complex. When 8-*O*-methyl-7-hydroxyaloin is evaluated in relation to the co-occurrence of other exudate compounds then an interesting hypothesis emerges. Figure 6.4 shows the following combinations:

1. 8-*O*-methyl-7-hydroxyaloin in co-occurrence with aloin (11 species)
2. 8-*O*-methyl-7-hydroxyaloin in co-occurrence with homonataloin (1 species)
3. 8-*O*-methyl-7-hydroxyaloin in co-occurrence with aloin and homonataloin (3 species)
4. 8-*O*-methyl-7-hydroxyaloin in co-occurrence with unidentified anthrones (4 species)

This interesting co-occurrence of exudate compounds has assisted in postulating a possible biochemical pathway leading to the formation of 8-*O*-methyl-7-hydroxyaloin as presented in Figure 6.5. Chrysaloin, although not isolated from *Aloe*, is known to occur in other anthrone accumulating plants such as *Rumex* and *Cassia* (Hata *et al.* 1978 & Masood *et al.* 1982). According to the biochemical scheme presented in Figure 6.5 it is possible for 8-*O*-methyl-7-hydroxyaloin to form via four possible routes as diagrammatically illustrated in Figure 6.6. In [a] 8-*O*-methyl-7-hydroxyaloin is formed via the 'aloin leg' of the pathway (e.g. *Aloe sinkatana*), only the compounds detected in the leaf exudate is presented by shaded circles meaning that the intermediated e.g. 7-hydroxyaloin in this case, is completely converted to 8-*O*-methyl-7-hydroxyaloin. The second possibility [b] illustrates the formation of 8-O-methyl-7-hydroxyaloin via the 'homonataloin leg' with nataloin presenting the intermediate compound (e.g. *A.*

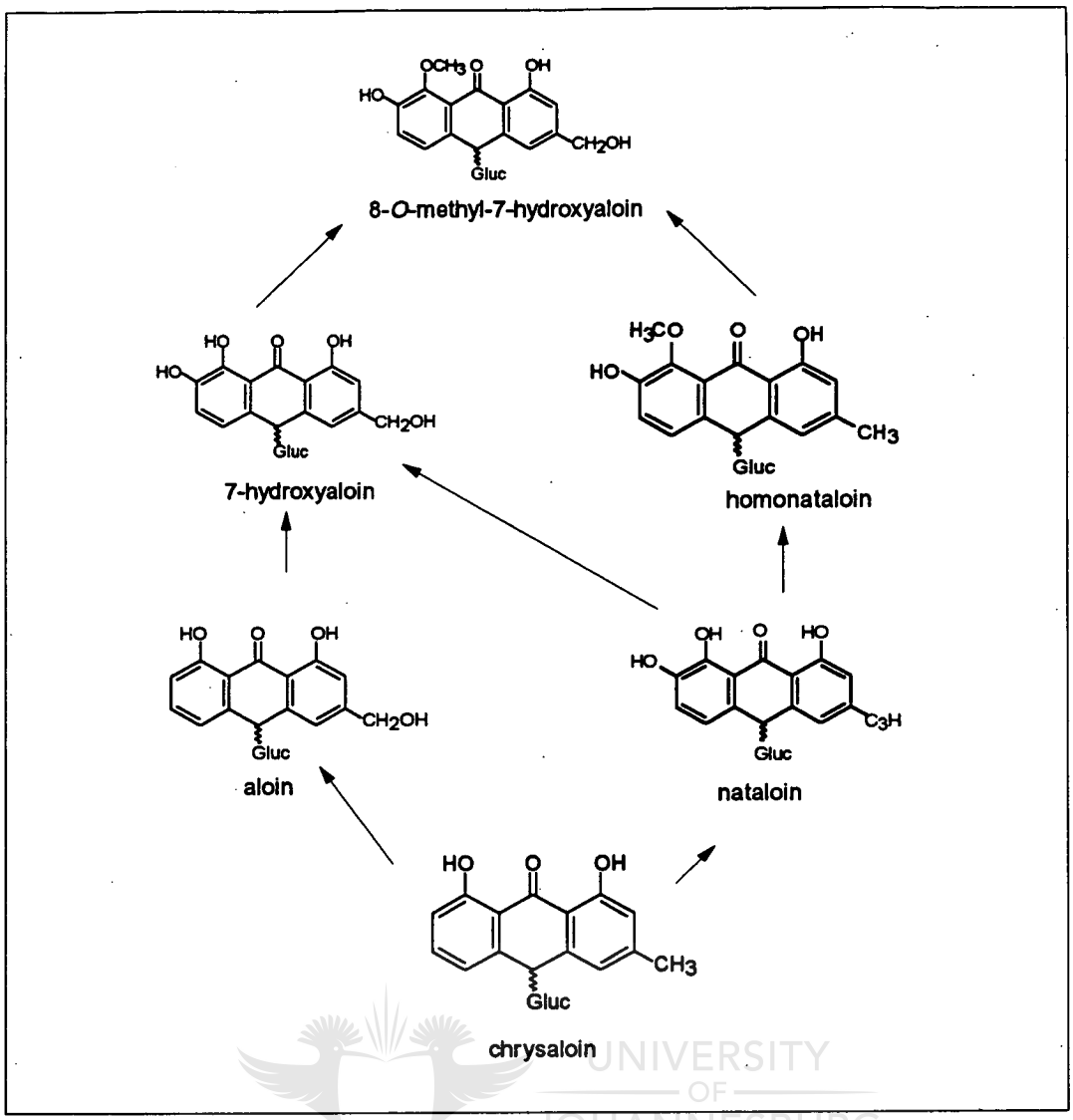


Figure 6.5. Proposed biochemical pathway for major anthrones in *Aloe*.

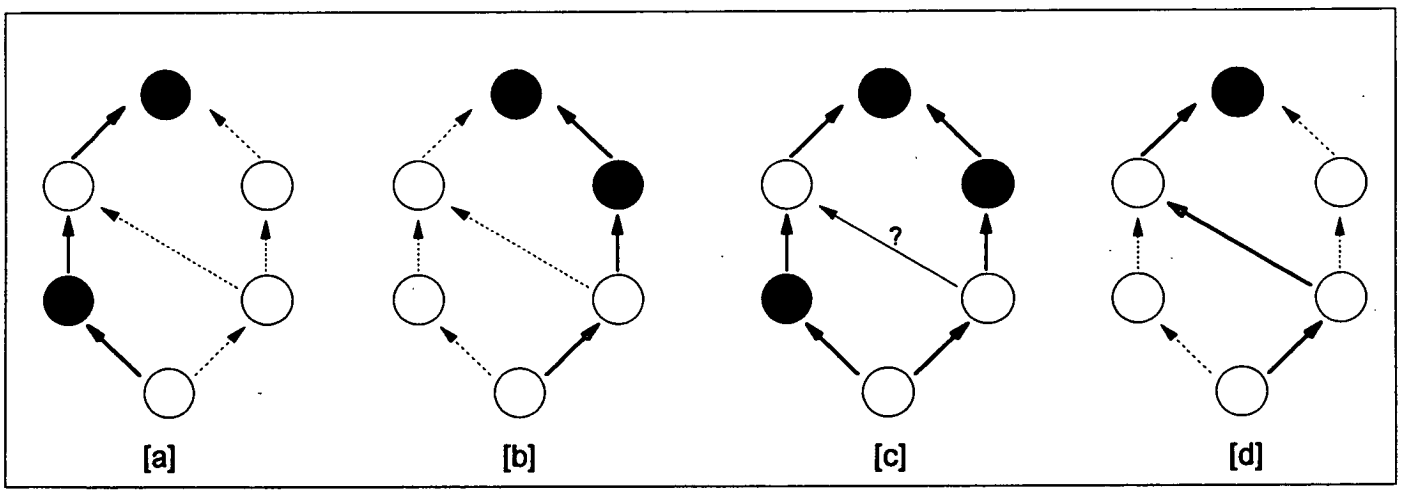


Figure 6.6. Diagrammatic representation of the biochemical pathways based on the model in Figure 6.5 illustrating various possibilities leading to the formation of 8-*O*-methyl-7-hydroxyaloin.

(See text for explanation)

isaloensis). In the third possibility [c] both 'legs' are activated implying the co-occurrence of both aloin and homonataloin with 8-O-methyl-7-hydroxyaloin (e.g. *Aloe pubescens*). The forth scenario [d] shows the formation of 8-O-methyl-7-hydroxyaloin via nataloin and 7-hydroxyaloin. Although possible, it would be difficult to prove that this pathway has been followed without confirmation of labourious carbon labelling experiments.

From a taxonomic perspective, the pathways presented in Figures 6.5 & 6.6 poses interesting problems. In the preceding examples the presence of 8-O-methyl-7-hydroxyaloin is not homologous as it could be formed via four possible pathways i.e the 8-O-methyl-7-hydroxyaloin in *A. isaloensis* is not homologous with the 8-O-methyl-7-hydroxyaloin in *Aloe sinkatana* and both of these are not homologous with the 8-O-methyl-7-hydroxyaloin in *Aloe pubescens* (Figure 6.4). A further elaboration is the possibility that it would be incorrect to assume that the 8-O-methyl-7-hydroxyaloin formed via pathway [a] in Figure 6.6 is homologous in all the aloin and 8-O-methyl-7-hydroxyaloin containing species shown in Figure 6.4. Would it not be possible for some species in this group to have followed the pathway shown in Figure 6.6 [c] and that the absence of homonataloin could be attributed to a secondary loss over time?

8-O-methyl-7-hydroxyaloin - a 'hybrid compound' in *Aloe*

The co-occurrence of the anthrones aloin and homonataloin is a rare exception as this chemical peculiarity has only been detected in four species in this study. These two compounds are found to be mutually exclusive which is further supported by the proposed biochemical pathway presented in Figure 6.5. Reynolds (1990) also concluded that the enzymes leading to the formation of aloin and homonataloin are not active (or present) in the same plant. It has also been suggested throughout this study that hybridization has probably been an important mechanism of evolution in *Aloe*. Considering the pathway presented in Figure 6.5 and the reality of possible hybridization events in *Aloe* as illustrated in Chapter 8 it seemed a feasible exercise to pursue the leaf exudate composition of synthetic hybrids of *Aloe*.

The HPLC profile in Figure 6.7a is a typical spectrum obtained for *Aloe arborescens*. This species is characterised by the presence of the phenyl pyrone aloenin and the anthrone isomers aloin A and B. The third profile (6.7c) is that of *Aloe suprafoliata*, a homonataloin accumulating species. The second profile (6.7b) shows the leaf exudate composition of the hybrid between the two species containing aloin (from *A. arborescens*), homonataloin (from *A. suprafoliata*) and a new compound not found in any of the two parents, 8-O-methyl-7-

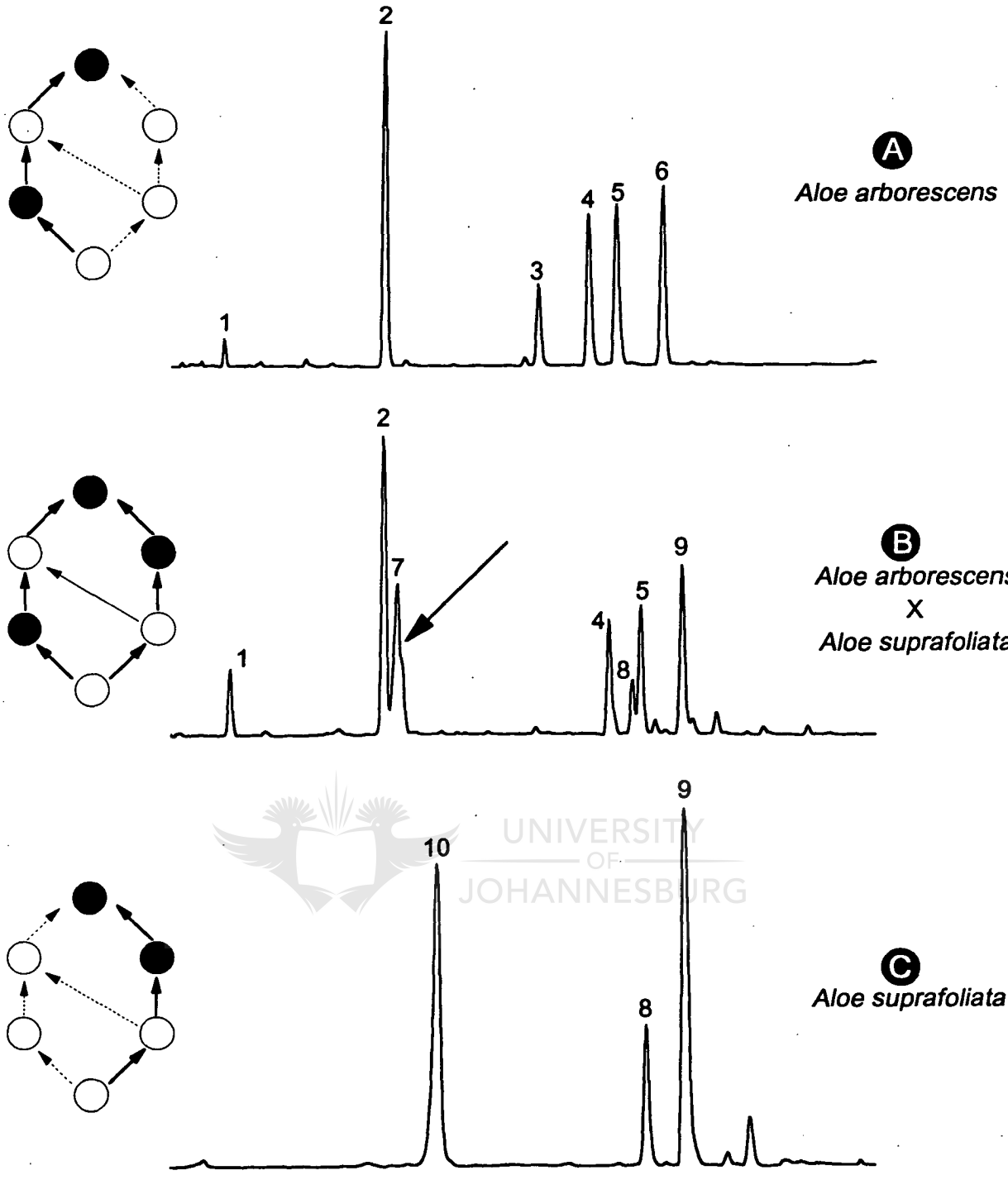


Figure 6.7: HPLC chromatograms of *A. arborescens* (A), *A. suprafoliata* (C) and their hybrid (B). The biochemical pathway for each taxon based on the model in Figure 6.5. is also illustrated. Peak numbers correspond to the compounds listed below:

1. aloesin
2. aloenin
3. aloeresin D
4. aloin B
5. aloin A
6. cinnamoyl chromone
7. 8-O-methyl-7-hydroxyaloin
8. homonataloin B
9. homonataloin A
10. aloeresin A

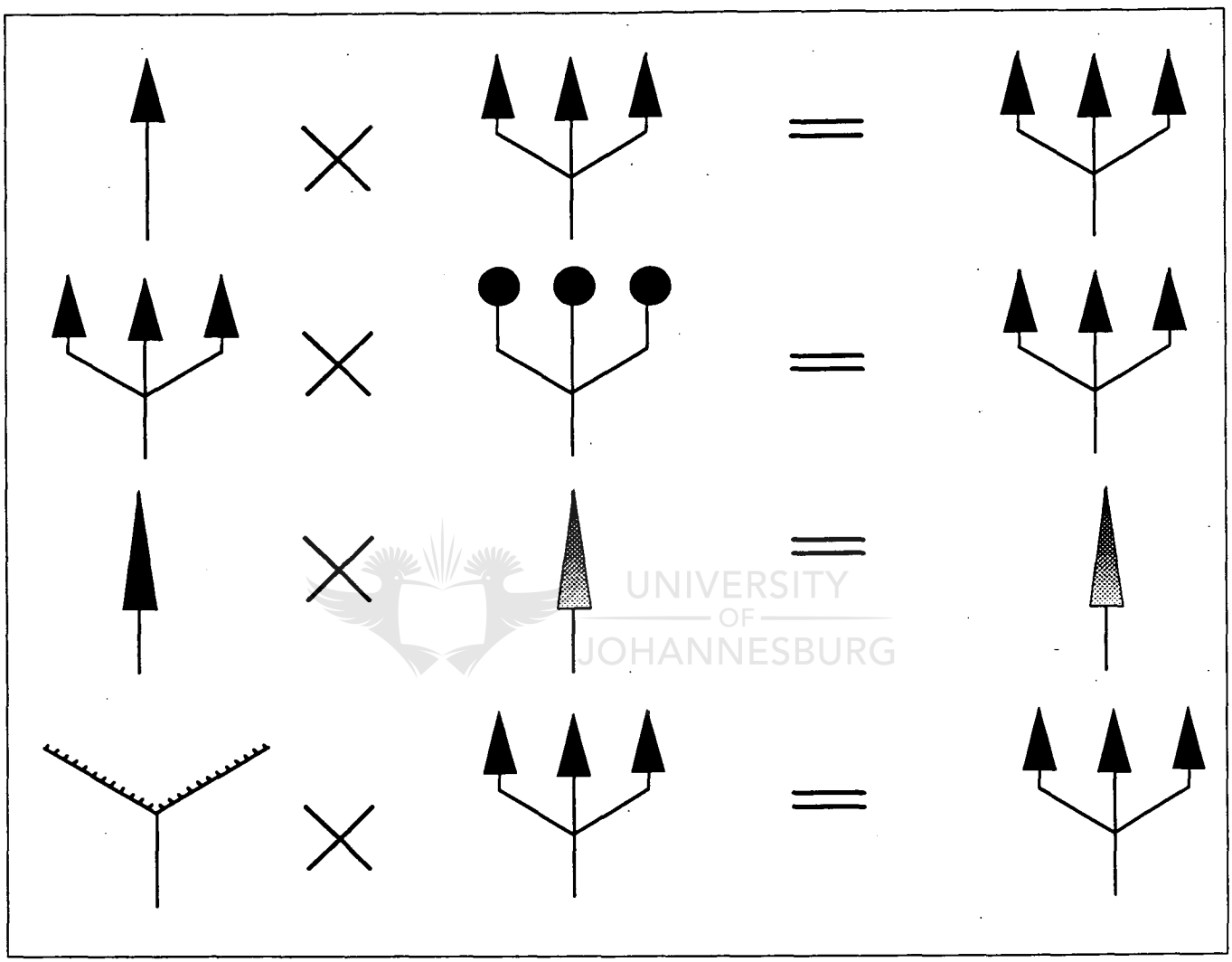


Figure 6.8. Dominant and recessive inflorescence characters as recorded by Reynolds (1950).

hydroxyaloin! The probable biochemical pathways for the three taxa are diagrammatically represented to the left of each chromatogram. The two pathways which were mutually exclusive in the parents combine in the hybrid to produce an amalgamation of the two anthrones (aloin and homonataloin) and in addition produced a new 'hybrid compound' 8-*O*-methyl-7-hydroxyaloin which is absent in the two parents. The exudate profile of this synthetic hybrid is identical to the profiles of *A. mutabilis*, *A. pubescens* (Figure 6.2) and *A. retrospiciens*. It is evident from this data that these three species could possibly be products of previous hybridizations events. One would have to investigate further what the result would be if introgression with one of the parents would take place. If such drastic chemical differences and recombination of exudate compounds appear in a simple F1 hybrid then successive crosses followed by introgression could form various chemical mosaics of which it would be difficult to determine the putative parents. It could also be speculated that the species containing 8-*O*-methyl-7-hydroxyaloin and aloin (Figure 6.4) are products of hybridization as illustrated in the *A. arborescens* and *A. suprafoliata* cross. Back-crossing of the hybrid with the aloin producing parent could lead to the decrease of homonataloin with aloin being accentuated in the hybrid. It would be presumptuous to assume that all 18 species in the 8-O-methyl-7-hydroxyaloin chemical complex originated through hybridization. It could be speculated that some 'species' have arisen through the hybridization event between aloin and homonataloin producing parents, followed by divergent speciation. The three species in Madagascar (*A. antandroi*, *A. millottii* and *A. isaloensis*) are very similar in macromorphological features and it is unlikely that all three taxa have arisen through independent hybridization events. In the case of these three species 8-*O*-methyl-7-hydroxyaloin is an unifying chemotaxonomic marker but it is questionable if these Malagasy endemics are related to *A. mutabilis* or *A. pubescens* as the 8-*O*-methyl-7-hydroxyaloin is a non-homologous similarity. In contrast, the three species in which aloin and homonataloin are in co-occurrence are probably the results of three separate hybridization events and these taxa are probably not related.

Continuing with *A. mutabilis*, one could speculate on putative parents of this natural hybrid. Reynolds (1950) realised the importance of hybridization in aloes and he devoted much time to the recording of hybrids and documenting dominant and recessive characters based on field observations. A summary of his observations are shown in Figure 6.8 which defies the notion that hybrids always display an intermediate state. This is also defied by the chemical data as new compounds arise after hybridization e.g 8-*O*-methyl-7-hydroxyaloin. Considering the case of *A. mutabilis* one could speculate that an aloin and a homonataloin producing species was

involved in hybridization as it is through such a cross that 8-*O*-methyl-7-hydroxyaloin can be formed, and it would explain the rare co-occurrence of aloin and homonataloin.

Reynolds places *A. mutabilis* in series *Arborescentes* due to the similarity with *Aloe arborescens*. Some authors consider *A. mutabilis* to be a geographical form of *Aloe arborescens* (Glen, 1987). Being guided by the present distribution patterns one would search for a homonataloin-producing species which is possibly sympatric with *A. mutabilis*. Not many species fit this criteria restricting the candidates to members of series *Latebracteatae*. Following the observations of Reynolds (Figure 6.8) one of the putative parents should have a bicoloured raceme as this character is dominant. The raceme in *A. mutabilis* is bicoloured and the raceme of *A. arborescens* is unicoloured. Being guided by present day taxa the only species which could be considered as a putative parent with *A. arborescens* to have given rise to *A. mutabilis* is A. *wickensii*. The possible inheritance of characters are summarised in Table 6.4.

Table 6.4: Possible inheritance of characters in *Aloe mutabilis*.

A. arborescens	*A. mutabilis*	*A. wickensii*
aloin⇨	aloin	
	homonataloin	⇦homonataloin
	8-*O*-methyl-7-hydroxyaloin	
unicoloured raceme	bicoloured raceme	⇦bicoloured raceme

A similar hypothesis could be presented for *A. pubescens* and *A. retrospiciens*. The occurrence of 8-*O*-methyl-7-hydroxyaloin has illustrated the importance of considering the biochemical pathways and that compounds should not be evaluated in isolation as the co-occurrence of compounds are important in chemotaxonomic treatments. This compound is clearly not homologous in all 18 species and it would be a daunting challenge, beyond the scope of this project, to prove homology or non-homology. Furthermore, the formation of 8-*O*-methyl-7-hydroxyaloin through hybridizing chemically divergent species demands a closer look at hybridization as a possible mechanism of speciation in *Aloe*.

Hybridization in *Aloe* - an introduction

The greatest veteran of *Aloe* taxonomy, G.W. Reynolds painstakingly recorded all natural hybrids he found during his numerous field expeditions. As he lived in South Africa his 1950 treatment of the aloes of Southern Africa contains a high number of natural aloe hybrids with

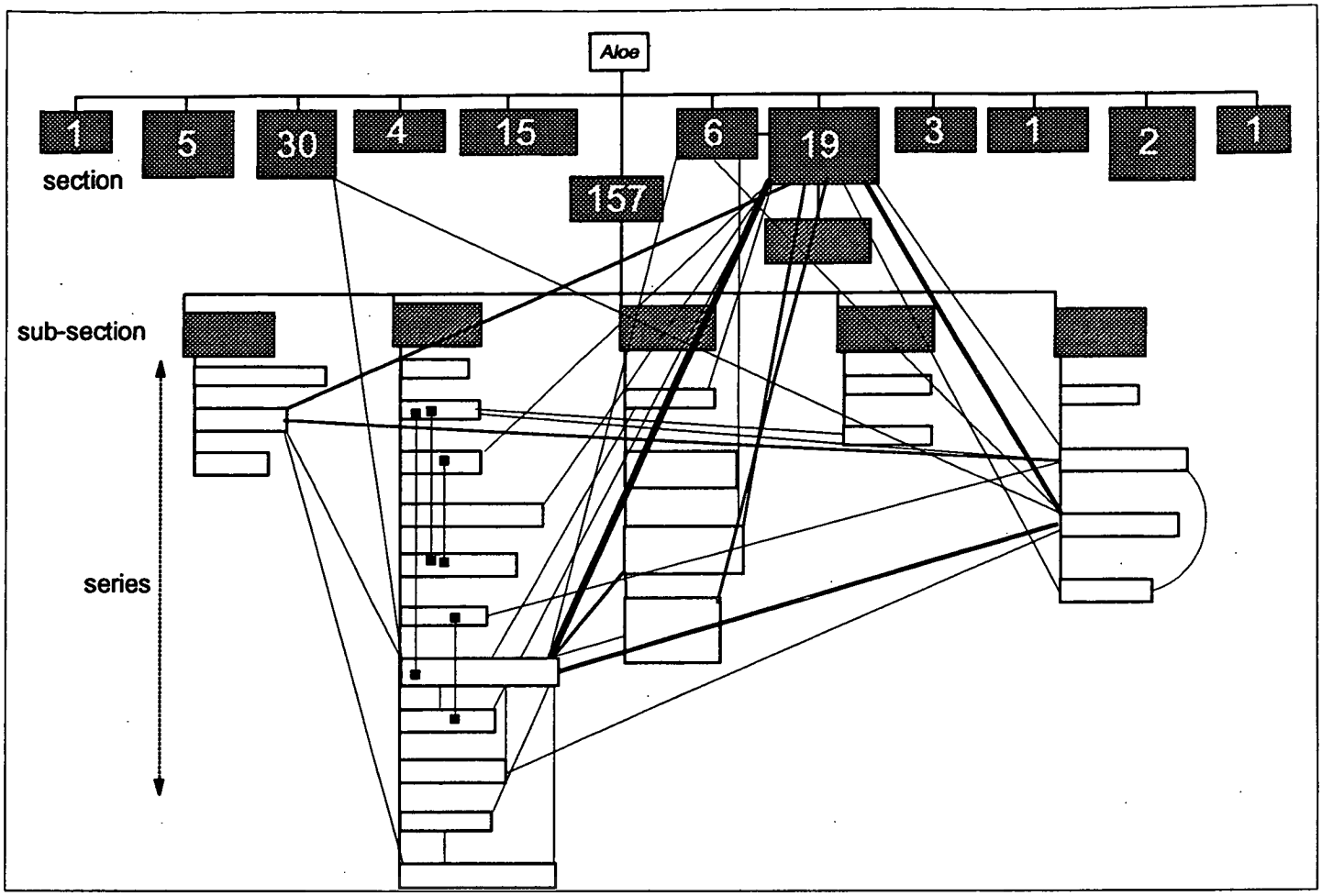


Figure 6.9: Natural hybrids between and within infrageneric groups superimposed over the present classification for *Aloe* (only for South African species).

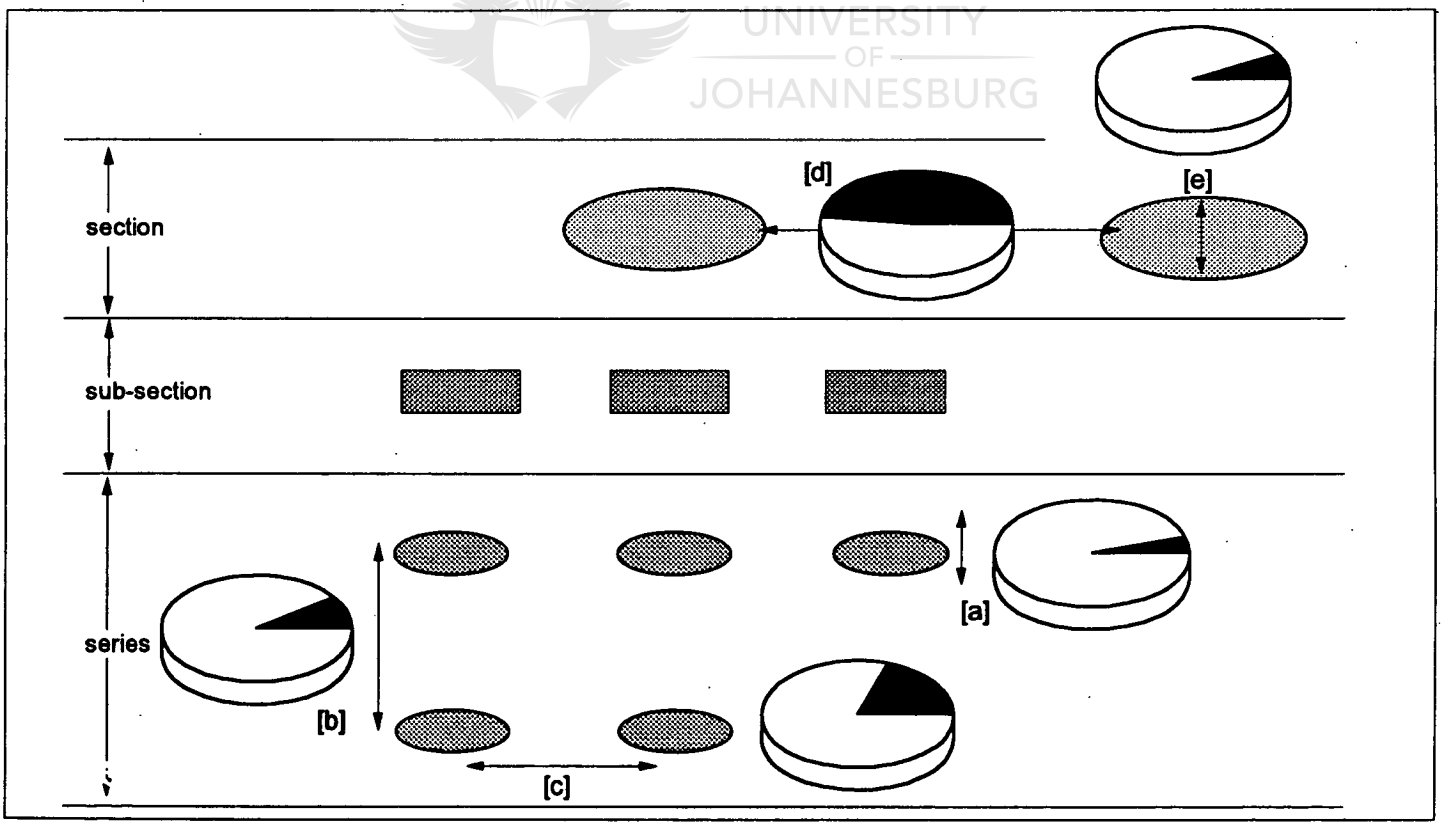


Figure 6.10: Diagrammatic representation of the frequency of hybridization between and within infrageneric groups (see text).

comments on the dominant and recessive expression of morphological traits.
He recorded *ca.* 150 natural hybrids in his two treatments (1950 & 1966). Figure 6.9 shows the crosses which have been recorded superimposed on the present classification of *Aloe*. The thatch-work pattern illustrated in Figure 6.9 shows the high crossibility between taxonomic extremes of the genus i.e. a grass-like aloe could easily hybridise with the caulescent *A. arborescens*. It is more likely that two very distant species will hybridize than species in the same infrageneric group. Figure 6.10 illustrates the number of hybrids between individuals in various taxonomic hierarchies. From this figure it is evident that there is little hybridization within an infrageneric group (series) of the same subsection [a], hybridization events are slightly higher between species in different series of the same subsection [b] but much higher between individuals in series belonging to different subsections [c]. The highest frequency of hybridization is detected between individuals in different sections [d] while hybridization is much lower within taxa of the same section [e]. This figure clearly illustrates the higher frequency of hybridization between taxa which are separated by a greater taxonomic distance. It is interesting to note that some classifications are based on crossibility experiments. Schilling and Heiser (1981) used this criteria to create sections within *Helianthus* where individuals between various sections are not able to hybridise. Figure 6.9 and 6.10 shows that any hybrid combination is possible and that there is a higher probability of individuals from different sections to hybridise.

CASE STUDIES

The examples mentioned earlier in this Chapter e.g *Aloe mutabilis* and *Aloe pubescens* are all hypothetical hybrids based on chemical evidence. Many authors have mentioned natural hybrids in *Aloe* (Reynolds 1950 & 1966, Newton 1976 & 1995, Bryns 1988, Giddy 1974) and it is especially the horticultural industry that have 'cashed in' on the ability of aloes to hybridize freely to produce some exquisite garden cultivars (Figure 6.11a & 6.11b). Some of the natural and artificial hybrids will be discussed below.

Aloe arborescens* and *A. ferox (Figure 6.11c, d & e)

Due to the wide and sympatric distribution of these two species natural hybrids between *A. ferox* and *A. arborescens* are very common. *Aloe ferox* occupies a taxonomic position in section *Pachydendron* while *A. arborescens* is placed in *Aloe* section *Eualoe* series *Arborescentes*.

In 1996 Van der Bank *et al.* used enzyme electrophoresis to show that *A. ferox* and *A. arborescens* hybridise freely to form an interspecific hybrid. The macromorphology and the leaf exudate chemistry for the parents and the inheritance of these characters in the hybrid are summarised in Table 6.5. Although *A. ferox* and *A. arborescens* are distinctive species placed in different infrageneric groups they share many salient morphological traits and the exudate composition is very similar. Figure 6.5 and 6.6 has shown, that from a chemical perspective, recombinations occur when two species producing different exudate anthrones hybridise. As can bee seen in HPLC profiles (Figure 6.12) both species contain aloin as the major anthrone and the hybrid simply contains an amalgamation of the two exudate profiles.

Table 6.5: Character expression and inheritance in *A. arborescens*, *A. ferox* and their hybrid.

A. arborescens	***A. arborescens* X *A. ferox***	***A. ferox***
caulescent⇨	caulescent	⇦caulescent
inflorescence simple	inflorescence a panicle	⇦inflorescence a panicle
soft thorns⇨	soft thorns	pungent thorns
leaves recurved⇨	leaves recurved	leaves erect
aloesin⇨	aloesin	⇦aloesin
aloin⇨	aloin	⇦aloin
aloeresin A⇨	aloeresin A	⇦aloeresin A
aloenin⇨	aloenin	

Aloe claviflora* and *A. ferox (Figure 6.11 f, g & h)

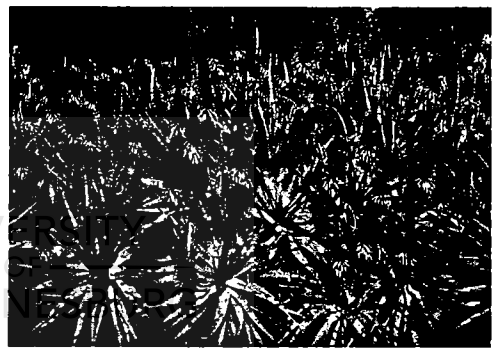
This second example is also taken from two species placed in different infrageneric groups. *Aloe ferox*, as mentioned above is placed in *Aloe* section *Pachydendron* while *A. claviflora* is housed in *Aloe* section *Eualoe* series *Asperifoliae*. Chapter 9 has elaborated extensively on the leaf exudate of the latter infrageneric group. The leaf exudate of this group is an further modification of the aloin pathway presented in Figure 6.5. The initial discovery of an isolated population in the Gamkapoort Nature Reserve in 1992 almost lead to the description of a new species as hybridization was not obvious. It was only later of the subsequent discovery of two populations near Kleinsleutelfontain and Aberdeen that it became clear that the Gamkapoort aloes are hybrids between *A. ferox* and *A. claviflora*. Using the RADP technique Barker *et al.* (1996) illustrated genetic evidence that the Gamkapoort aloe is a hybrid between *A. claviflora* and *A. ferox*. Table 6.6 illustrates the inheritance of characters in the hybrid and the exudate

a) garden hybrid

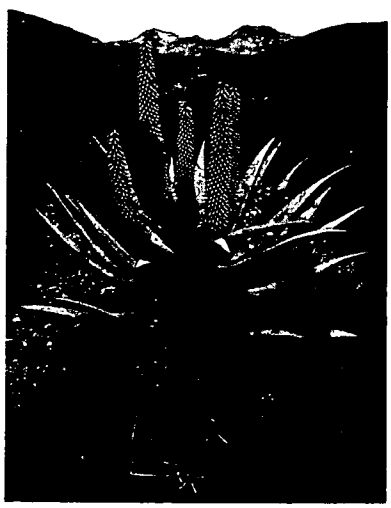
b) garden hybrid

c) *A. ferox*

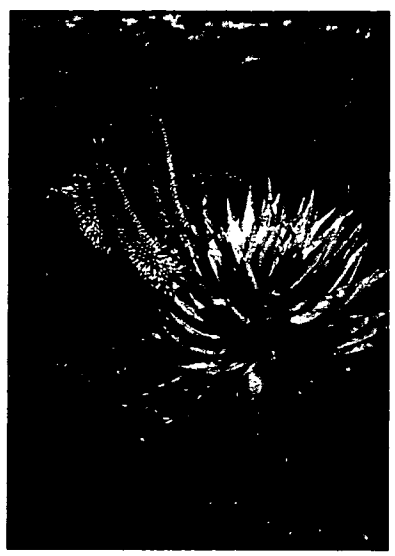
d) *A. ferox* X *A. arborescens*



e) *A. arborescens*



f) *A. ferox*



d) *A. ferox* X *A. claviflora*

h) *A. claviflora*

Figure 6.11. (see text)

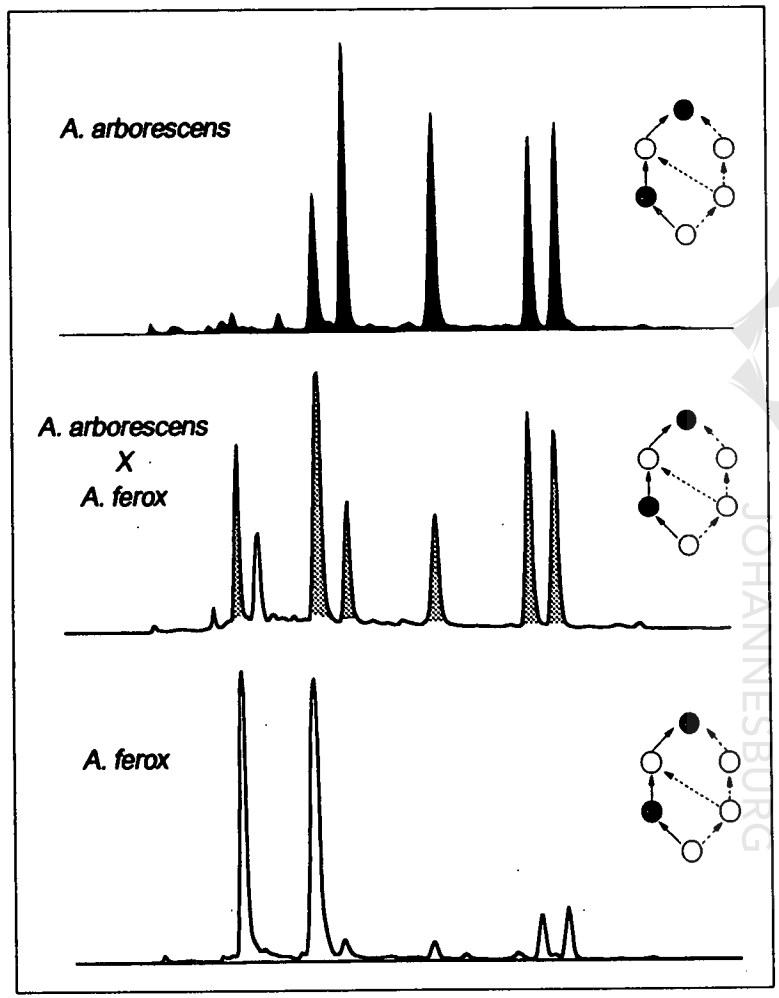


Figure 6.12: HPLC profiles of *A. arborescens*, *A. ferox* and their hybrid.
The biochemical pathway as presented in Figure 6.6 is also included.

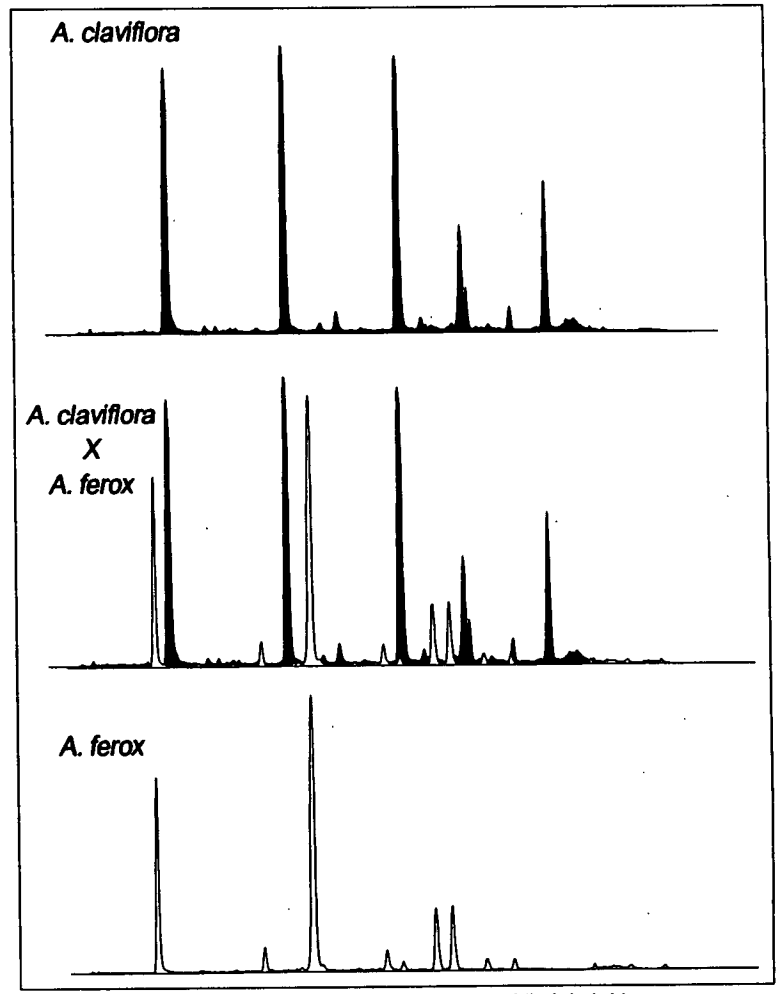


Figure 6.13: HPLC profiles of *A. claviflora*, *A. ferox* and their hybrid.

profiles are shown in Figure 6.13.

Table 6.6: Character expression and inheritance in *A. claviflora*, *A. ferox* and their hybrid.

A. claviflora	*A. claviflora* X *A. ferox*	*A. ferox*
acaulescent⇨	acaulescent	caulescent
inflorescence simple	inflorescence branched	⇦inflorescence branched
inflorescence oblique ⇨	inflorescence oblique	inflorescence erect
aloesin⇨	aloesin	⇦aloesin
	aloin	⇦aloin
	aloeresin A	⇦aloeresin A
10-hydroxyaloin⇨	10-hydroxyaloin	

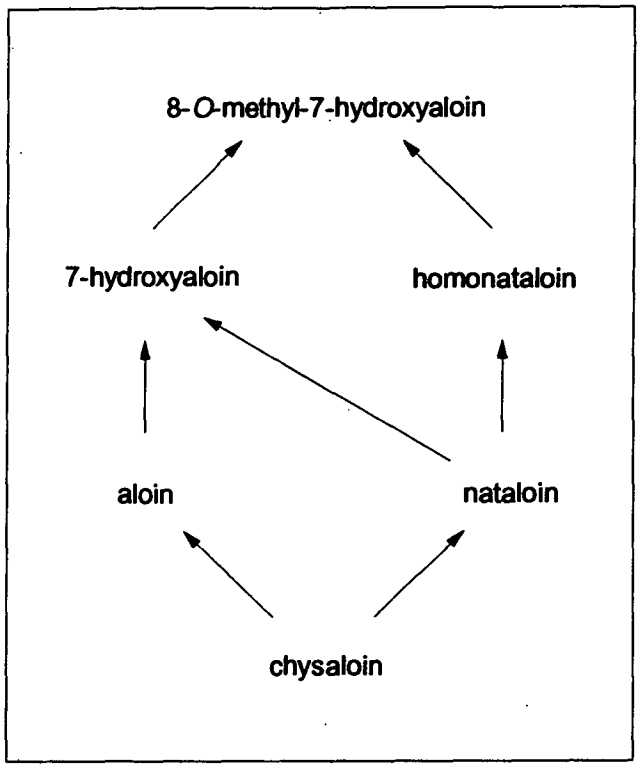
Although these two species have many features in common (morphologically and chemically) they do differ in a number of features which are selectively inherited by the hybrid. The leaf exudate of the two species, although very different, is only a mere modification of the aloin pathway in the case of *A. claviflora*.

These two examples show that when two aloin (or variations of aloin) producing species hybridise the leaf exudate of the resultant hybrid will be a blending of the two species. To recall the biochemical pathway presented in Figure 6.6 one can speculate that the enzymes responsible for the formation of 1) nataloin and 2) 7-hydroxyaloin will not be active as illustrated in Figure 6.14.

It has been demonstrated that interesting recombinations occur when an aloin-producing species hybridizes with a homonataloin-producing species (e.g. *A. suprafoliata* and *A. arborescens*). In the case of this example the pathway could be diagrammatically presented as in Figure 6.14. Nataloin will be completely transformed into homonataloin while 7-hydroxyaloin is completely converted into 8-O-methyl-7-hydroxyaloin, or alternatively, the pathway could be blocked after aloin with the 8-O-methyl-7-hydroxyaloin being formed through hydroxyaloin of homonataloin (Figure 6.14).

***Aloe ferox* and *Aloe speciosa*:**

The preceding paragraphs only represents part of the chemical complexity when crossing an aloin-accumulating species with an homonataloin-accumulating species. Another example is



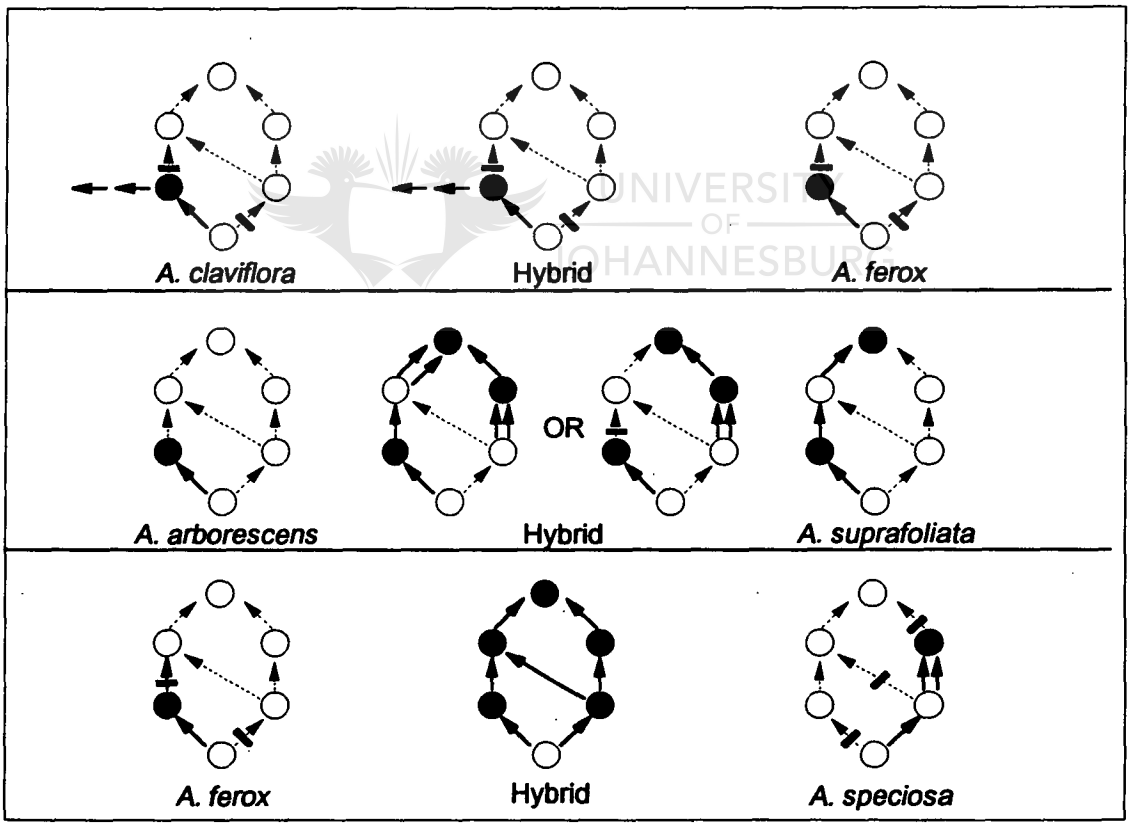


Figure 6.14: Diagrammatic representation of the biochemical pathways present in:
a) *A. claviflora*, *A. ferox* and their hybrid
b) *A. arborescens*, *A. suprafoliata* and their hybrid
c) *A. ferox*, *A. speciosa* and their hybrid

The graphic models are based on the pathway presented above.

taken from natural hybrids between *A. ferox* and *A. speciosa* near Grahamstown. Three natural hybrids were discovered and their leaf exudate was analysed. The leaf exudate for all three hybrid individuals were identical and displayed the chromatographic profile shown in Figure 6.15. The chemical composition in relation to the parents are tabulated in Table 6.7.
Table 6.7 and Figure 6.15 shows the hybrid to contain four new compounds not produced by the parents. This would imply that each step in the biochemical pathway is activated and all intermediate compounds are present in the hybrid (Figure 6.14). This example opens a plethora of arguments and implications: can 7-hydroxyaloin and nataloin also be considered 'hybrid compounds'? Can we assume that species containing nataloin and 7-hydroxyaloin are of hybrid origin as hypothesised in the case of 8-O-methyl-7-hydroxyaloin?

Table 6.7: Inheritance of chemical compounds in a natural hybrid between *A. ferox* and *A. speciosa*.

A. ferox	***A. ferox X A. speciosa***	***A. speciosa***
aloesin⇨	aloesin	
aloeresin A⇨	aloeresin A	
	8-*O*-methyl-7-hydroxyaloin	
	7-hydroxyaloin	
aloin A & B⇨	aloin A & B	
	homonataloin A & B	⇦homonataloin A & B
	nataloin A & B	

Chapter 12 has shown that the grass-like aloes all produce flavones and that they are devoid of anthrones - all for but one species, *A. chortolirioides* which contains nataloin. Is has to be considered that this chemical deviant in the grass-like aloe-group could be a results of an hybridization event. Chapter 11 has illustrated the chemotaxonomic value of the cinnamoyl chromones aloeresin E and F with all but one species containing homonataloin. *Aloe erinacea* accumulates aloeresin E and F together with nataloin A and B, a compound which is demonstrated above to form readily when an aloin and homonataloin species hybridise. It is here suggested that *A. erinacea* is of possible hybrid origin with one parent belonging to *Aloe* series *Mitriformis* (e.g. *A. pearsonii*) from which it will "inherit" the cinnamoyl chromones characteristic of the *Mitriformes* group and another species, perhaps a member of the *Asperifoliae* (e.g. *A. pachygaster*). Through hybridization of the aloin parent (e.g *A.*

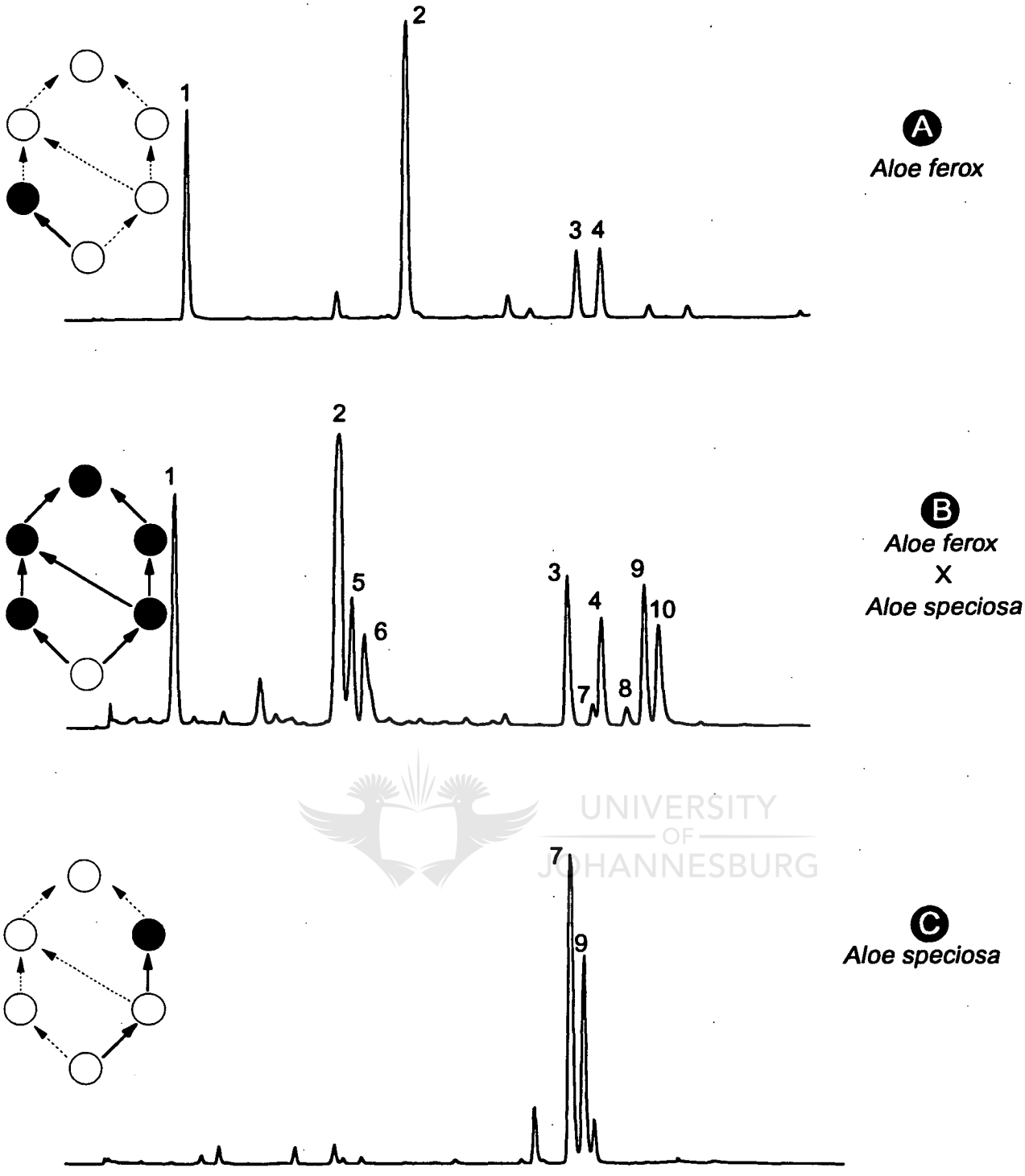


Figure 6.15: HPLC chromatograms of *A. ferox* (A), *A. speciosa* (C) and their hybrid (B). The biochemical pathway for each taxon based on the model in Figure 6.5. is also illustrated. Peak numbers correspond to the compounds listed below:

1. aloesin
2. aloeresin A
3. aloin B
4. aloin A
5. 8-*O*-methyl-7-hydroxyaloin
6. 7-hydroxyaloin
7. homonataloin B
8. nataloin B
9. homonataloin A
10. nataloin B

pachygaster) and the homonataloin parent (e.g. *A. pearsonii*) it would produce nataloin. The inheritance of chemical characters are illustrated in Table 6.8 below.

Table 6.8: A hypothesis of the inheritance of chemical compounds in *A. erinacea*.

Putative parent 1	*Aloe erinacea*	Putative parent 2
aloin		
		homonataloin
	nataloin	
	aloeresin E	⇦aloeresin E
	aloeresin F	⇦aloeresin F
A. pachygaster (?)		*A. pearsonii* (?)

In the same way as illustrated here for *A. erinacea* one could critically review all species containing these 'hybrid chemicals' (i.e. 8-*O*-methyl-7-hydroxyaloin, 7-hydroxyaloin and nataloin) and speculate on the possible hybrid origin of this species. It is important to emphasis that these results are not based on the single example of the *Aloe ferox* and *A. speciosa* cross but that numerous artificial hybrids between aloin and homonataloin producing species were examined. In *Aloe*, as demonstrated by Rieseberg (1995) it is a grave misconception that hybrids always represent the intermediate state. Hybrids represent a mosaic of parental, intermediate and extreme characters. This is clearly seen in chemotaxonomic data. For example consider the hybrid between *A. ferox* and *A. speciosa*. The hybrid contains aloin from *A. ferox*, homonataloin from *A. speciosa* and in additional produces a series of new compounds not found in any of the two parents; 7-hydroxyaloin, 8-*O*-methyl-7-hydroxyaloin and nataloin A & B.

The numerous hybrids mentioned in this Chapter, the numerous reference to hybridization in *Aloe* obtained in literature and the chemical basis for predicting possible hybridization events has a pronounced impact on the understanding of taxonomic relationships within *Aloe*.

According to Arnold (1997) a natural hybrid individual derives from crosses in nature between individuals from two populations, or groups of populations , which are distinguishable on the basis of one or more inheritable character. The importance of hybridization was noticed by Linnaeus who proposed a model for speciation through hybridization. Darwin (1859) also presented experimental data and observations indicating 'products' between divergent individuals. Lotsy (1916, 1931) explicitly stated that hybridization is the most important factor

in evolutionary change. It was especially the work of botanists such as Stebbins (1959), Anderson (1949) and Heiser (1949) who made a great contribution by illustrating the importance of hybridization as an important evolutionary mechanism. The detection and analysis of hybrids are instrumental in critically analysing character expression and to determine the homology of characters (e.g homology of 8-*O*-methyl-7-hydroxyaloin). Hybrids do however pose a problem in systematics as it is often believed that 'good' species do not hybridise. All species concepts consider the process of natural hybridization at the best to be nonexistent and at the worst to be 'bad'. (Arnold 1997). Many groups in which hybridization is evident are avoided as hybrids are considered to be deleterious and they make taxonomic treatments messy (Anderson 1997). The study of hybrids as illustrated earlier in this chapter have not been destructive in our understanding of *Aloe* evolution indicating that hybrids should not be regarded as natural 'mongrels' which lead to evolutionary cal-de-sacs. Instead, as echoed by Harrison (1990) natural hybridization acts as a window through which biologists may peer to gain more insight to what is happening in the 'natural laboratory'.

The discovery of chemical evidence to support the well known fact of rampant hybridization in *Aloe* leaves little doubt that evolution has progressed in a reticulate rather than in a neatly divergent manner. Since the cladistic method is based on the assumption of divergence, it clearly has limitations as an analytical method in genera such as *Aloe*. The prediction can be made that the limitations of the cladistic method will become more obvious as more and more taxa with reticulate phylogenies come to light.

Figure 6.16: Representatives in the 8-*O*-methyl-7-hydroxyaloin chemical group. ⇨

Photo: Reynolds 1966

Aloe niebuhriana

Photo: van Wyk & Smith 1996

Aloe mutabilis

Photo: Reynolds 1966

Aloe retrospiciens

Photo: Reynolds 1966

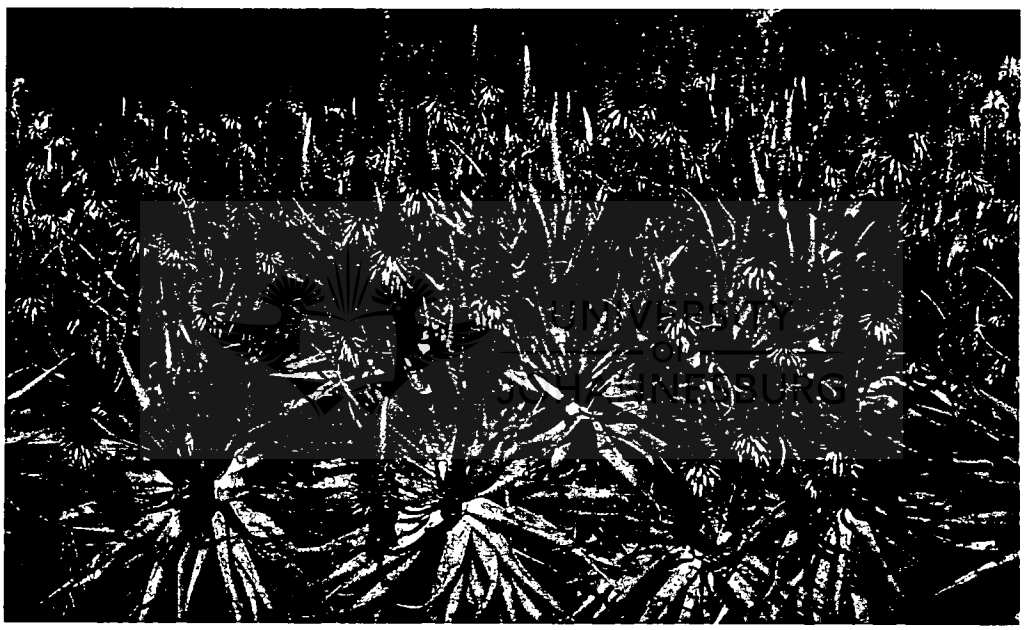
Aloe millottii

Photo: Reynolds 1966

Aloe vaombe

Photo: Reynolds 1966

Aloe tomentosa



Chapter 7

The chemotaxonomic significance of the phenyl pyrone aloenin

CHAPTER 7

THE CHEMOTAXONOMIC SIGNIFICANCE OF THE PHENYL-PYRONE ALOENIN

The phenyl-pyrones have a very restricted distribution in *Aloe* and up to date only five compounds belonging to this chemical class have been isolated from *Aloe*, with aloenin being the most prominent. This compound with its characteristic UV spectrum occurs in only 16 species, i.e. in 4.6% in a survey of 380 taxa (voucher / locality data presented in Table 7.1). Aloenin occurs in the taxonomic extremes of the genus. It is found in the tall arborescent, shrubby aloes (Group 19) and in a contrasting group of small acaulescent aloes from Tanzania (Group 5). This chapter clearly demonstrates the disadvantage of creating a 'classification system' using a single macro-morphological character. Although Reynolds' Group 5 and Group 19 are completely different with reference to habit characters, they share similarities in inflorescence and leaf characters. The presence of aloenin (always in co-occurrence with aloin) furthermore reveals a possible taxonomic alignment between these species which have previously been overlooked. It is generally accepted that the system created by Reynolds (especially his 1966 publication) is based on utility and does not necessarily reflect natural relationships between taxa. Judging by the perplexing range of morphological characters prevalent in *Aloe*, it would seem virtually impossible to suggest natural relationships between taxa without seeking additional taxonomic evidence, the leaf exudate being one such an instrumental character.

Table 7.1. Taxa, voucher details and distribution of species containing aloenin.

Species	Voucher	Distribution
A. arborescens	various samples	SA, Mozambique, Malawi, Zimbabwe
A. brachystachys	NBI 17388 (*A. schliebenii*)	S Tanzania
A. brandhamii	Carter *et al.* 2600 (type material)	S Tanzania
A. bussei	RBG, Kew 1990-1816 & ex hort Favell	NE Tanzania
A. cheranganiensis	ex hort P. Favell & ex hort B. Kemble	Uganda & Kenya
A. classenii	LEN 3910	S Kenya
A. dawei	RBG, Kew 1951-35710 & ex hort BSM	Sudan, Kenya & Uganda
A. dorotheae	RBG, Kew 295-58-29212 & NBI 17305	NE Tanzania
A. gossweileri	RBG, Kew	Angola
A. kedongensis	NBI 11210	Kenya
A. leachii	RBG, Kew 1990-1820	NE Tanzania

Aloe arborescens, the source from which aloenin was isolated (Photo: Ben-Erik van Wyk).

Species	Voucher	Distribution
A. leptosiphon	RBG, Kew 1990-1812	NE Tanzania
A. monticola	ex hort Favell	N Ethiopia
A. nyeriensis	Gil-Gil & Rumuruti	Kenya
A. secundiflora	LEN 4016 & EDS 219	Sudan, Ethiopia, Kenya Tanzania
A. tororoana	ex hort Favell	Uganda

The taxonomic arrangement of aloenin-containing species as represented in Figure 7.1: The present taxonomic distribution of the 16 aloenin-accumulating species are shown in Figure 7.1. Reynolds included six species in his large Group 19, which he defines as 'plants of shrubby growth.' Many species also included in this Group 19 contain aloin / aloinoside / microdontin and have been discussed in Chapter 5. *Aloe cheranganiensis* was later described by Carter & Brandham (1979) and they suggested that this species could be taxonomically related to *A. dawei, A. kedongensis* and *A. nyeriensis*. All three species (including *A cheranganiensis* produce aloenin). These taxa are also 'closely arranged' in the Flora treatment of Tropical East Africa (Carter 1994). It is also interesting to note that *A. nyeriensis* together with *A. elgonica* and *A. ngobitiensis* (Carter & Brandham 1979) are tetraploids (2n = 28), a rare cytological occurrence in *Aloe* (unfortunately no exudate samples of the last two species could be obtained). Two aloenin-producing species are included in Reynolds' Group 16; *A. classenii* and *A. monticola*. The other species in group 16 (Reynolds 1966) are very different and variable in terms of leaf exudate composition. The taxonomic affinities of *Aloe brachystachys* (previously described as *A. schliebenii*) remain obscure and in the description of this species Lavranos (1970) hints on a correlation with *A. seretii*, but emphasises that the relationships seems doubtful (no exudate sample could be obtained for *A. seretii*). Lavranos (1970) does however suggest that using inflorescence characters this species could occupy a position in Group 5 (Reynolds, 1966). It is meaningful to note that all the species included in Group 5 produce the phenyl-pyrone, aloenin which is also accumulated in *A. brachystachys*. *Aloe secundiflora* and *A. leachii* are both placed in Group 14 which houses all species with secund flowers. Carter (1994) suggests an affinity between *A. brandhamii* and *A. secundiflora* var. *sobolifera*, a suggestion confirmed on the chemical level. In his treatment of the Aloes of Southern Africa, Reynolds (1950) places *A. arborescens* in *Aloe* series *Arborescentes* together with three other species which are morphologically and chemically very different from one another. In his treatment of the Aloes of Tropical East Africa, *A. arborescens* is placed in

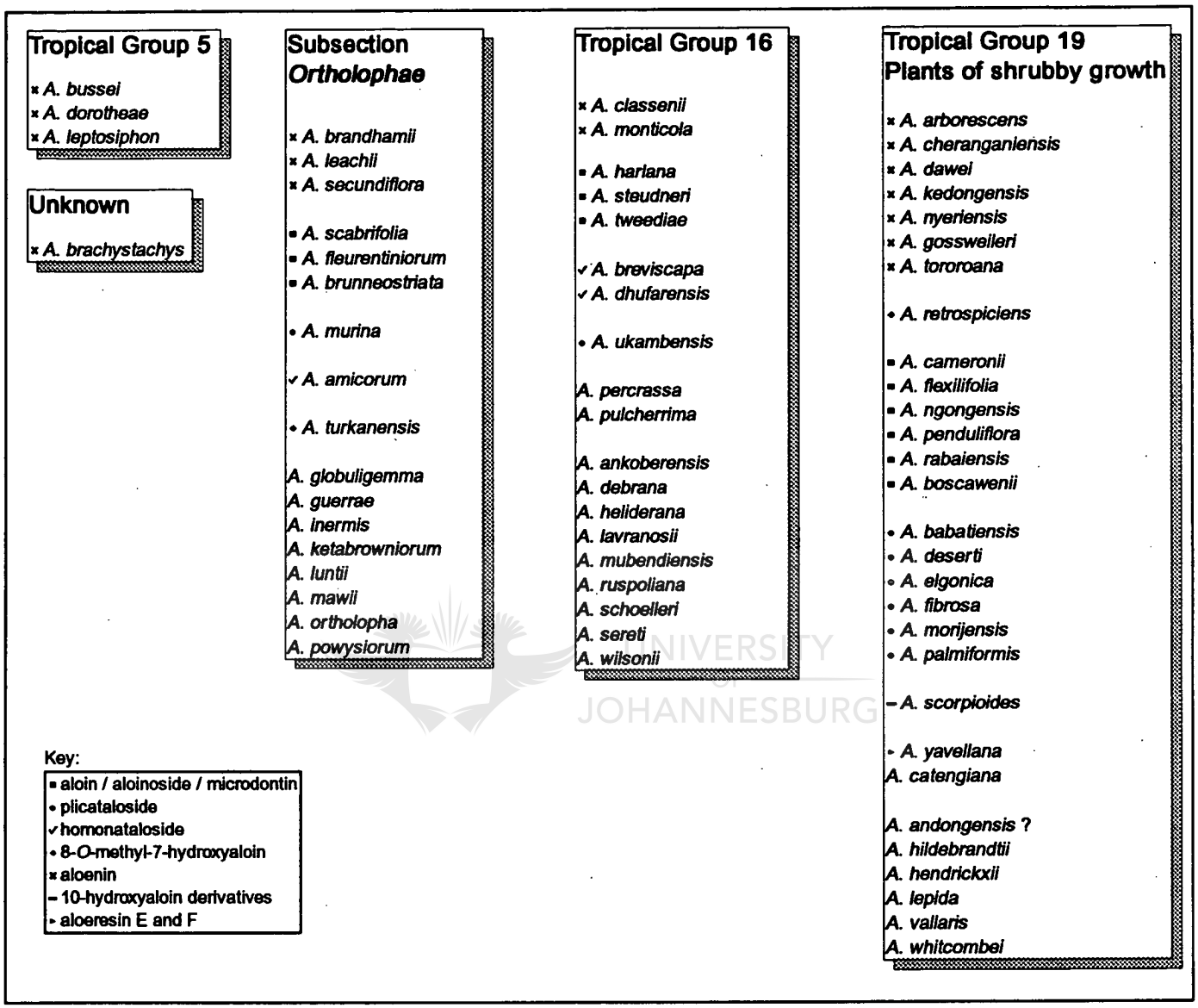


Figure 7.1: The present taxonomic position of aloenin containing species.

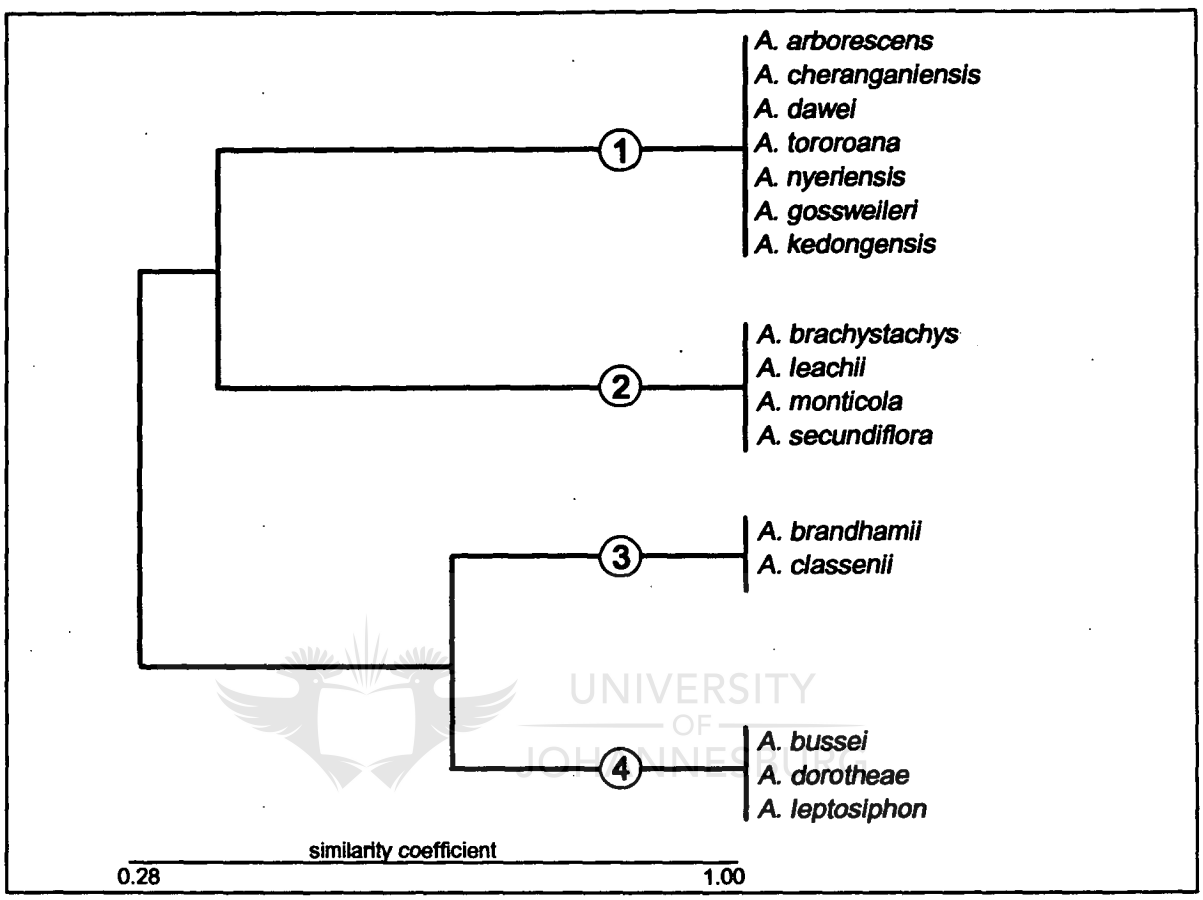


Figure 7.2. Dendrogram showing the similarity between all aloenin-containing species, using habit characters.

Group 19 (as discussed above).

The last group consists of three species which are placed in Reynolds' Group 5. This group only contains three species which are characterised by the small compact rosettes (they sucker freely to form dense groups) and the inflorescence is usually simple or sparingly branched. These three Tanzanian species, *A. bussei* (syn. *A. morogoroensis*), *A. leptosiphon* (syn. *A. greenwayi*) and *A. dorotheae* are also proposed by Carter (1994) to be very closely related.

The morphological characters which have been summarised for each species in Table 7.2 are briefly discussed below.

Habit characters (caulescence, branching and orientation): Using the habit characters as tabulated in Table 7.2, a dendrogram (Figure 7.2) was constructed showing that the 16 species allow themselves to be clustered into one of four groups:

Cluster 1 - Most species in the aloenin-containing group are distinctly caulescent, occurring in groups (arborescent) and usually not suckering from the base. This cluster represents all the species included in Group 19 (Reynolds 1966).

Cluster 2 - Four species which are usually acaulescent and solitary, suggesting that they do not form suckers and hence do not occur in dense groups.

Cluster 3 - Two species; *A. brandhamii* and *A. classenii* are usually shortly caulescent and occur in groups as a result of suckering.

Cluster 4 - The last cluster consists of three species represented in Reynolds' Group 5 (*A. bussei*, *A. dorotheae* and *A. leptosiphon*) which are usually acaulescent and form dense groups resulting from suckering.

The orientation of the stem was not used as a discriminatory character in the analysis as all species are erect or sub-erect.

Visual assessment of the grouping in Figure 7.2 are almost in complete agreement with the groups suggested by Reynolds, with the exception that the demarcated 'groups' are not considered to be taxonomically allied to one another.

In general the leaf characters seem to be of little taxonomic value. In all cases the leaves are smooth and in most cases soft except in the *A. bussei* group, where the leaves are very hard

Table 7.2 Summary of the salient morphological characters of the aloenin-producing species of *Aloe*.

species	caulescence	branching	stem orientation	leaf orientation	texture	thorns (mm)	maculation
A. arborescens	distinctly caulescent	grouped	erect	spreading / deflexed	smooth	firm 3 - 5	immaculate
A. brachystachys	shortly caulescent	solitary / grouped	-	spreading / recurved	smooth	small 3	immaculate
A. brandhamii	caulescent	grouped	suberect	spreading / recurved	smooth	sharp 2 - 3	immaculate
A. bussei	acaulescent	grouped / suckering	-	erect	smooth	cartilaginous 2 - 4	immaculate
A. cheranganiensis	distinctly caulescent	grouped	erect	spreading / apices recurved	smooth	3	immaculate
A. classenii	shortly caulescent	grouped	erect	erect / spreading	smooth	pungent 5	mostly immaculate
A. dawei	caulescent	grouped	erect	spreading / recurved	smooth	pungent 3 - 4	usually immaculate
A. dorotheae	shortly caulescent	grouped / suckering	erect	erect / spreading	smooth	4 - 5	sparsely spotted
A. gossweileri	distinctly caulescent	grouped	erect	spreading / slightly recurved	smooth	3 - 4	mostly immaculate
A. kedongensis	distinctly caulescent	grouped	erect	spreading / recurved	smooth	2 - 3	immaculate
A. leachii	mostly acaulescent	usually solitary	-	suberect / spreading	smooth	pungent 5	immaculate
A. leptosiphon	shortly caulescent	grouped / suckering	erect	spreading / recurved	smooth	pungent 2	copiously spotted
A. monticola	usually acaulescent	solitary	erect	spreading / slightly recurved	smooth	pungent 6	immaculate
A. nyeriensis	distinctly caulescent	grouped	erect	spreading / slightly decurved	smooth	pungent 3	immaculate
A. secundiflora	shortly caulescent	solitary	-	erect / spreading	smooth	4	not spotted
A. tororoana	shortly caulescent	grouped	decumbent	spreading to recurved	smooth	pungent 2 - 3	spotted

Table 7.2 cont./....

Table 7.2 cont.:

Species	inflorescence orientation	inflorescence branching	raceme shape	bract size	pedicel size	perianth shape	flower orientation
A. arborescens	erect	simple / 1 - 2 branched	conical-cylindrical	15 - 20 x 10 - 12	35 - 40	cylindrical-trigonous	nutant
A. brachystachys	erect	usually simple	cylindrical	12 - 14 x 10	16 - 22	cylindrical-trigonous	nutant
A. brandhamii	erect	branched	cylindrical / secund	12 - 15 x 5 - 7	5 - 9	cylindrical	secund
A. bussei	erect	simple / 1-4 br.	conical-cylindrical	4 - 6 x 3	8 - 10	cylindrical	pendulous
A. cheranganiensis	erect	2 - branched	cylindrical-acuminate	5 - 7 x 3	15	cylindrical-trigonous	-
A. classenii	erect	panicle	laxly cylindrical	3	8 - 10	cylindrical-trigonous (bloom)	-
A. dawei	erect	panicle	cylindrical	4 x 3-5	14	cylindric (spotted)	sub-pendulous
A. dorotheae	erect	simple	laxly cylindrical	3 x 2	6	cylindrical-trigonous	nutant
A. gosswelleri	erect	6 - 8 branched	secund / oblique	3 x 2	10	curved-cylindrical	pendulous
A. kedongensis	erect	2 - 4 branched	cylindric	5 x 5	20 - 25	cylindric-trigonous (curved)	erect
A. leachii	erect	7 - 10 branched	laxly-secund	4 x 4	6 - 8	cylindric-trigonous	secund
A. leptosiphon	erect	mostly simple	cylindric-acuminate	10 x 4 - 5	8 - 10	cylindric-trigonous	sub-pendulous
A. monticola	erect	panicle	sub-capitate	15 - 20	15 - 20	cylindric-trigonous	nutant
A. nyeriensis	erect	panicle	cylindrical-conical	5 x 7 - 3 - 4	15 - 20	cylindric-trigonous	sub-pendulous
A. secundiflora	erect	panicle	cylindric (secund)	4 x 4 - 5	8 - 10	cylindric (spotted)	secund
A. tororoana	erect	simple or 1 - 2 branched	laxly cylindrical	5 - 6 x 2.5	6 - 9	cylindrical	pendulous

and tough (Lavranos 1970). Most species in Group 16 (Figure 7.1) bear their leaves in a spreading and deflexed fashion. The majority of these species also have distinct thorns which are firm and pungent in most taxa. *Aloe bussei* and *A. brachystachys* have small teeth which are cartilaginous in the case of *A. bussei*. The leaves are mostly without marking or sculpturing. Only the leaves of *A. dorotheae*, *A. leptosiphon* and variably *A. bussei* together with *A. tororoana* are spotted.

Inflorescence and flower characters (inflorescence structure, perianth shape, perianth markings, flower orientation):

In all the species the inflorescence is erect and varies from simple to 1 - 4 branches or a much-branched panicle. The racemes are mostly cylindrical and varies from densely to laxly flowered. The species fall into two categories with reference to the length of the pedicel. Some species have a long pedicel, usually exceeding 10 mm, while an equal number of species produce a much shorter pedicel (usually shorter than 10 mm). In most cases the perianth is straight and cylindrical with the exception of *A. gossweileri* and *A. kedongensis* where the perianth is curved. In addition to the characters listed in Table 7.2, the perianth of *A. dawei* and *A. secundiflora* is spotted while the perianth of *A. classenii* has a slight surface bloom. In most species the flowers are arranged symmetrically around the floral axis except in the case of *A. secundiflora*, *A. leachii* and *A. brandhamii*, where the flowers are secund on the floral axis.

If all the diagnostic morphological characters (Table 7.2) are incorporated in a cluster analysis then the dendrogram presented in Figure 7.3 is produced. The arbitrary cut along the Y-axis shows five major clusters:

1. The first cluster contains all the species included in Reynolds' Group 19 in Figure 7.1 and corresponds to cluster 1 in Figure 7.2. Most of these species are arborescent in habit with the leaves spreading to recurved, the inflorescence is either sparingly branched or a much-branched panicle, the pedicels are fairly long and the flowers are arranged symmetrically around the floral axis.
2. *Aloe brachystachys* and *A. monticola* show a fairly high similarity coefficient as they only differ with respect to the inflorescence and pedicel characters used in the analysis.

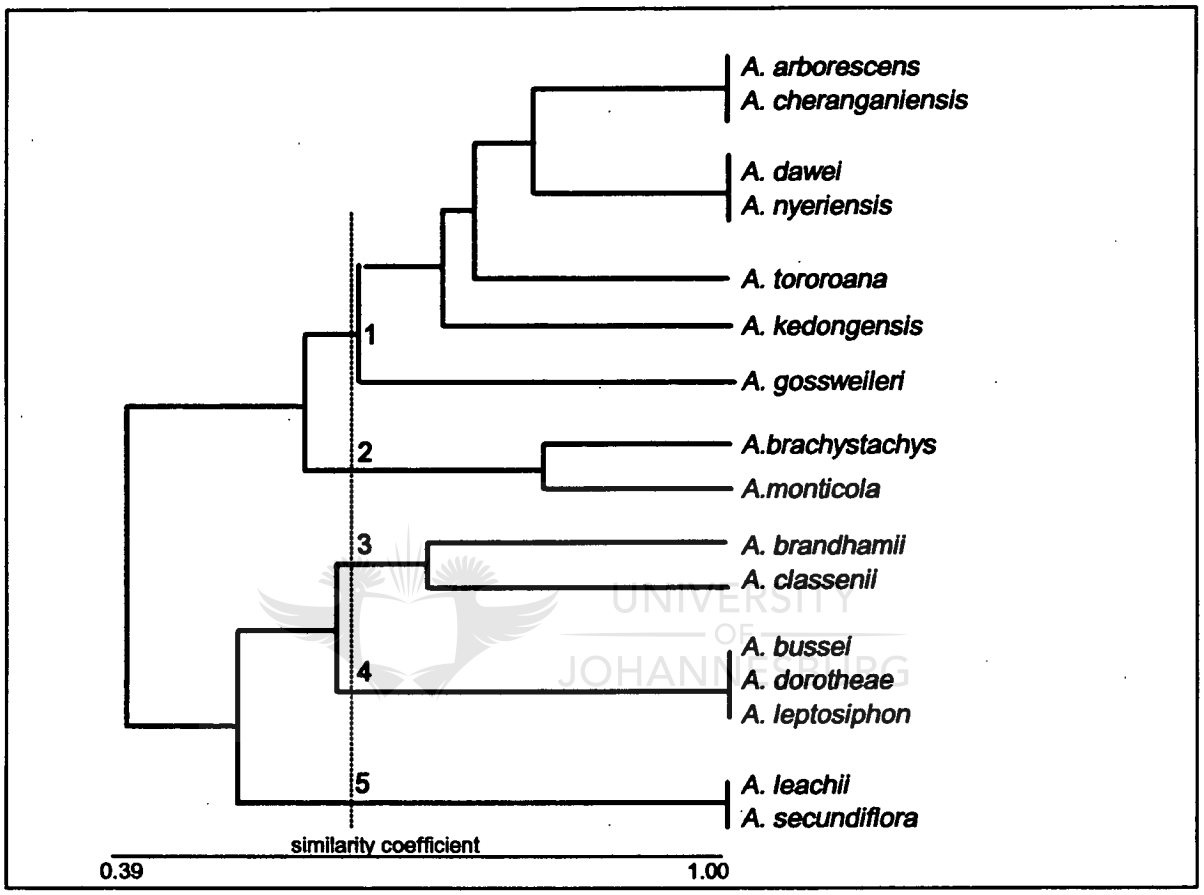


Figure 7.3. Dendrogram showing the similarity between species using all the morphological characters in Table 7.3.

3. Based on the selection of all the morphological characters in Table 7.2, *Aloe brandhamii* and *A. classenii* are shown to be similar (also shown in Figure 7.2).
4. As expected, the species included in Reynolds' Group 5 (cluster 4 in Figure 7.2) are tightly clustered together and shows a high similarity coefficient when compared to the rest of the species in this group.
5. The last cluster is represented by two species; *A. secundiflora* and *A. leachii*. Considering the morphological characters used these species are shown to be virtually identical.

The leaf exudate chemistry

The single chemical compound which represents a 'unifying chemical character' between the species is the phenyl-pyrone, aloenin. This compound is confined to a small number of species (16). Aloenin has a very characteristic UV absorbance spectrum making the identification unambiguous. The total leaf exudate composition for all the species are shown in Table 7.3 and a selection of HPLC profiles are illustrated in Figure 7.4. The chromones, aloesin and aloeresin D occur in a high number of species in this group. These compounds are very widely distributed in the genus and possibly of little taxonomic value. In all except one species the major anthrone which is accumulated is aloin A and B. The presence of nataloin A and B in *A. kedongensis* is noteworthy as this compound is restricted to only a few species in *Aloe* which seems to be erratic. It has also been demonstrated in Chapter 6 that nataloin is a 'hybrid compound' which is synthesized when an aloin and homonataloin species hybridize.

In many of the species included in this group a series of unidentified compounds have been recorded. These compounds all show the same UV absorbance spectra and have not been found in any other non-aloenin-producing species.

Aloe arborescens was widely sampled throughout the southerly part of its distributional range and three individual plants from 18 population where analysed (see Chapter 16). The results show that compounds 1 - 5 (for *A. arborescens*) are always present but only certain populations produced the late-eluting chromone which is probably a coumaroyl chromone. Reynolds and Herring (1991) used this variation to demonstrate the origin of *A. arborescens* in Gibraltar. The same variation study was carried out on *A. nyeriensis* which was collected in Kenya at two separate populations and showed no variation between and within the two populations sampled (see Chapter 16). The compound 10 (Rt = 23.61) shown in Table 7.3 co-elutes with aloin B and can only be detected by comparing the UV spectra recorded within the time of elution of this 'single' peak.

Table 7.3: Presence of major leaf exudate compounds of species in the aloenin group.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
	aloesin	7-O-methylaloesin	aloenin	unidentified compound	aloeresin A	aloeresin D	unidentified anthrone	unidentified compound	aloin B	unidentified compound	aloin A	unidentified chromone	nataloin B	nataloin A
Rt (min)	5.49	8.23	13.95	16.24	16.26	20.03	21.55	23.48	23.61	23.61	24.07	24.12	25.41	26.55
A. arborescens	■		■			■			■		■	■		
A. brachystachys	■		■						■		■			
A. brandhamii	■		■	■		■			■		■			
A. bussei	■		■						■		■			
A. cheranganiensis	■	■	■		■	■			■	■	■			
A. classenii	■		■			■			■	■	■			
A. dawei	■		■			■			■	■	■			
A. dorotheae	■		■	■					■	■	■			
A. gossweileri	■		■				■		■		■			
A. kedongensis	■	■	■					■					■	■
A. leachii	■		■	■		■			■	■	■			
A. leptosiphon	■		■						■	■	■			
A. monticola	■		■			■			■		■			
A. nyeriensis	■	■	■			■			■	■	■			
A. secudiflora			■	■					■	■	■			
A. tororoana		■	■						■	■	■			

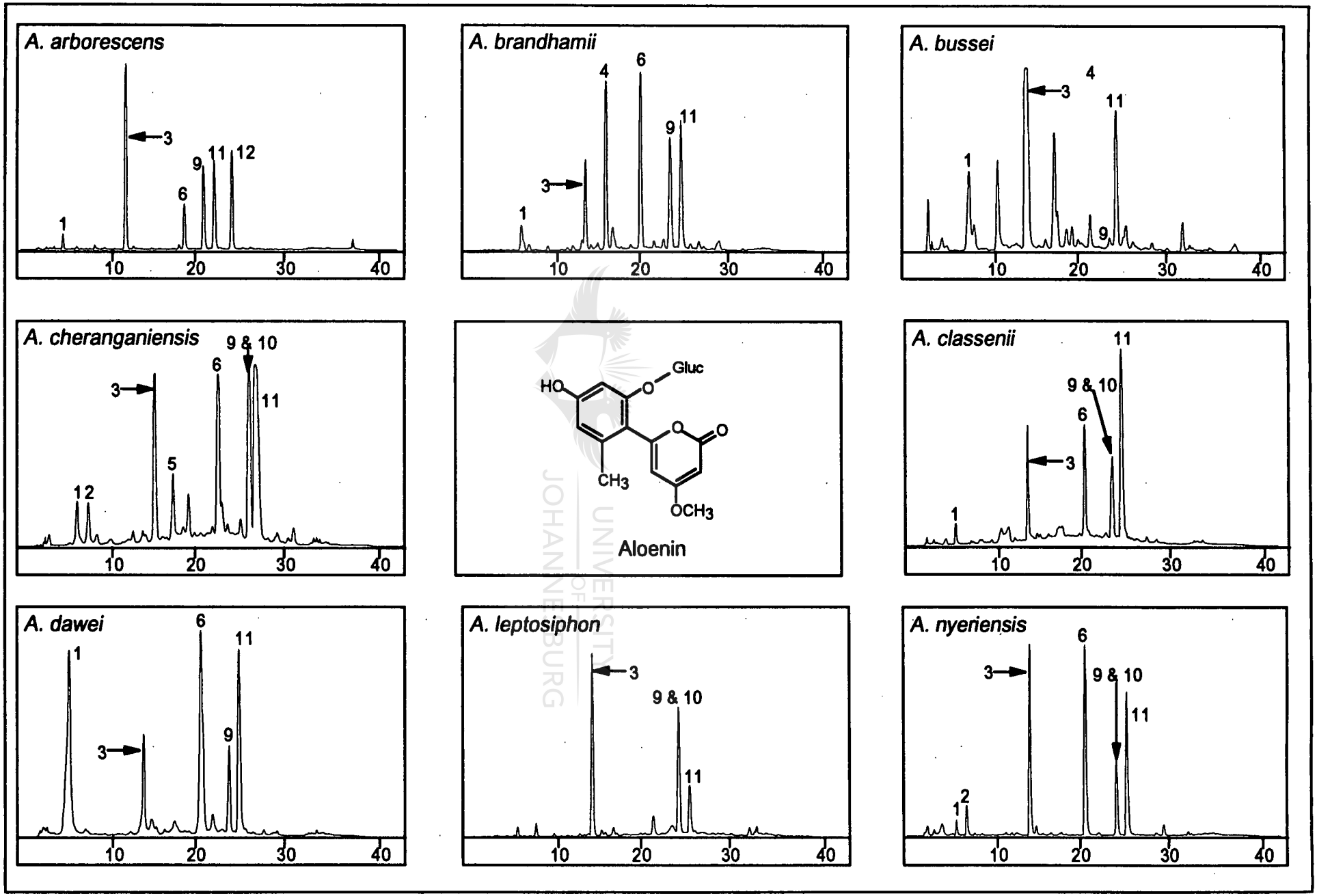


Figure 7.4: HPLC chromatograms of 8 species containing aloenin. Numbers of peaks correspond to Table 7.3. The chemical structure of aloenin is shown in the centre block.

If the leaf exudate is incorporated in Table 7.4 as a taxonomic character then the dendrogram as shown in Figure 7.5 is produced. Comparison of the dendrograms depicted in Figures 7.2 and 7.3 with the dendrogram constructed in Figure 7.5, shows that the inclusion of the 'characteristic unidentified compounds' do not influence the clustering significantly. The arborescent / shrubby aloes group together with *A. brachystachys* and *A. monticola* still forming a cluster. *Aloe classenii* is included in the *A. bussei* cluster with *A. leachii* and *A. secundiflora* forming a well defined cluster.

Figure 7.6 shows the geographical distribution of the aloenin-producing species. This distribution coincides (and is almost identical) with the distribution pattern for the aloin / aloinoside / microdontin accumulating species shown in Chapter 5. It is here also suggested that this group is of tropical origin with *A. arborescens* representing a southerly connection.

Aloe gossweileri from Angola has a very unique combination of compounds as it is the only species in this survey to accumulate both aloin and 10-hydroxyaloin B anthrone. The latter compound has been isolated from the widespread *A. littoralis* and Viljoen *et al.* (1996) illustrated that this compound is a chemotaxonomic marker for *Aloe* series *Asperifoliae* (see Chapter 9). One is tempted to explain the combination of compounds as the product of hybridization. Could there have been some exchange of genetic material between this species in the southern parts of Angola with one of the 10-hydroxyaloin-containing species of *Aloe* which are widely distributed in the south western arid parts of southern Africa? Chemical evidence exists to suggest the possible hybrid origins of *A. kedongensis* and *A. gossweileri*, implying that some species in this group may be of paraphyletic origin. The 'core group' could well be monophyletic with species participating in recent hybridization events.

It is reassuring to note the congruence in morphology and chemistry. The six species in Group 19 are obviously all related morphologically and they all contain aloenin. The three species in Group 5 form a coherent group according to morphological assessment by Carter (1994) and Reynolds (1966), this morphological consistency is confirmed with the congruency of aloenin. The alliance between the secund-flowered *A. brandhamii*, *A. leachii* and *A. secundiflora* is reinforced by the chemistry. More interesting however is the discovery that these species, in their demarcated morphological groups are related, a relatedness indicated by chemotaxonomic evidence.

Figure 7.7: Representative species in the aloenin chemical group. ⇨

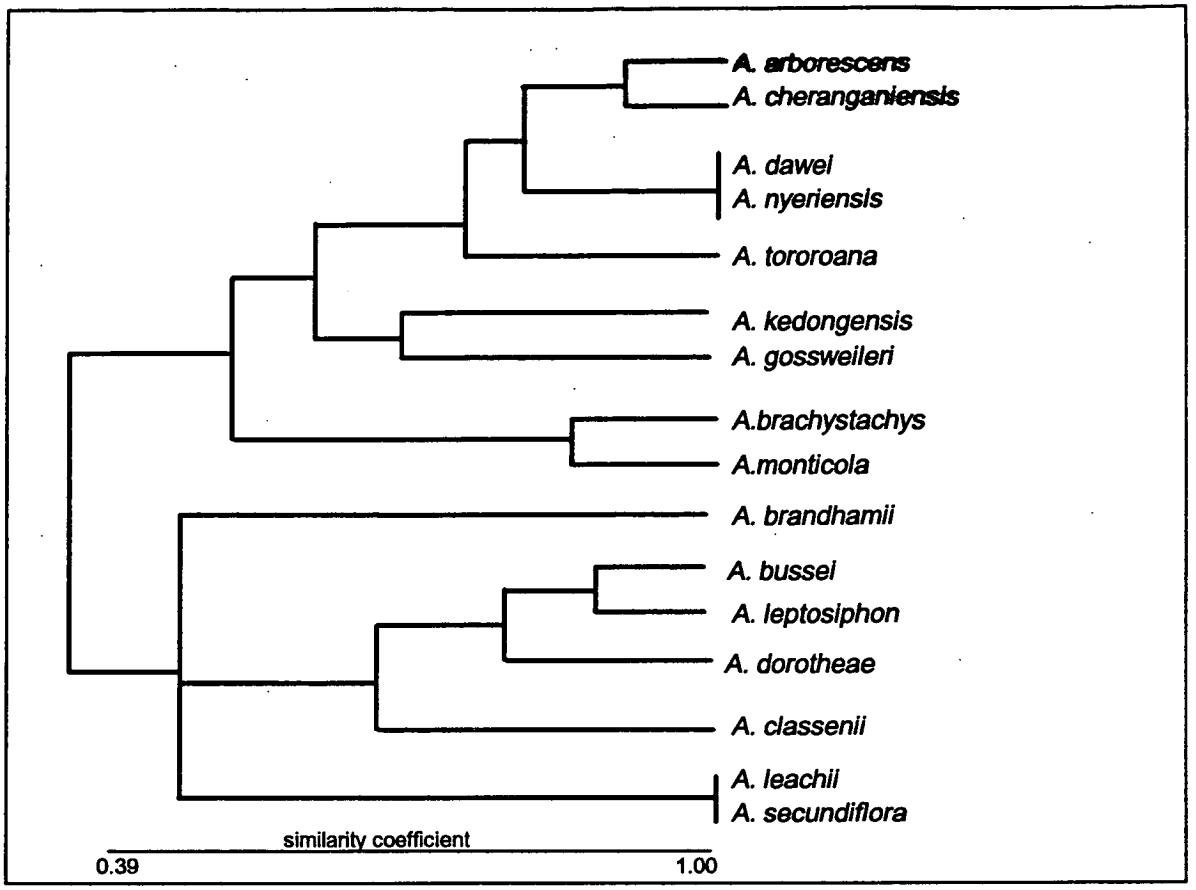


Figure 7.5. Dendrogram showing the similarity between species using all the morphological and chemical characters in Table 7.4.

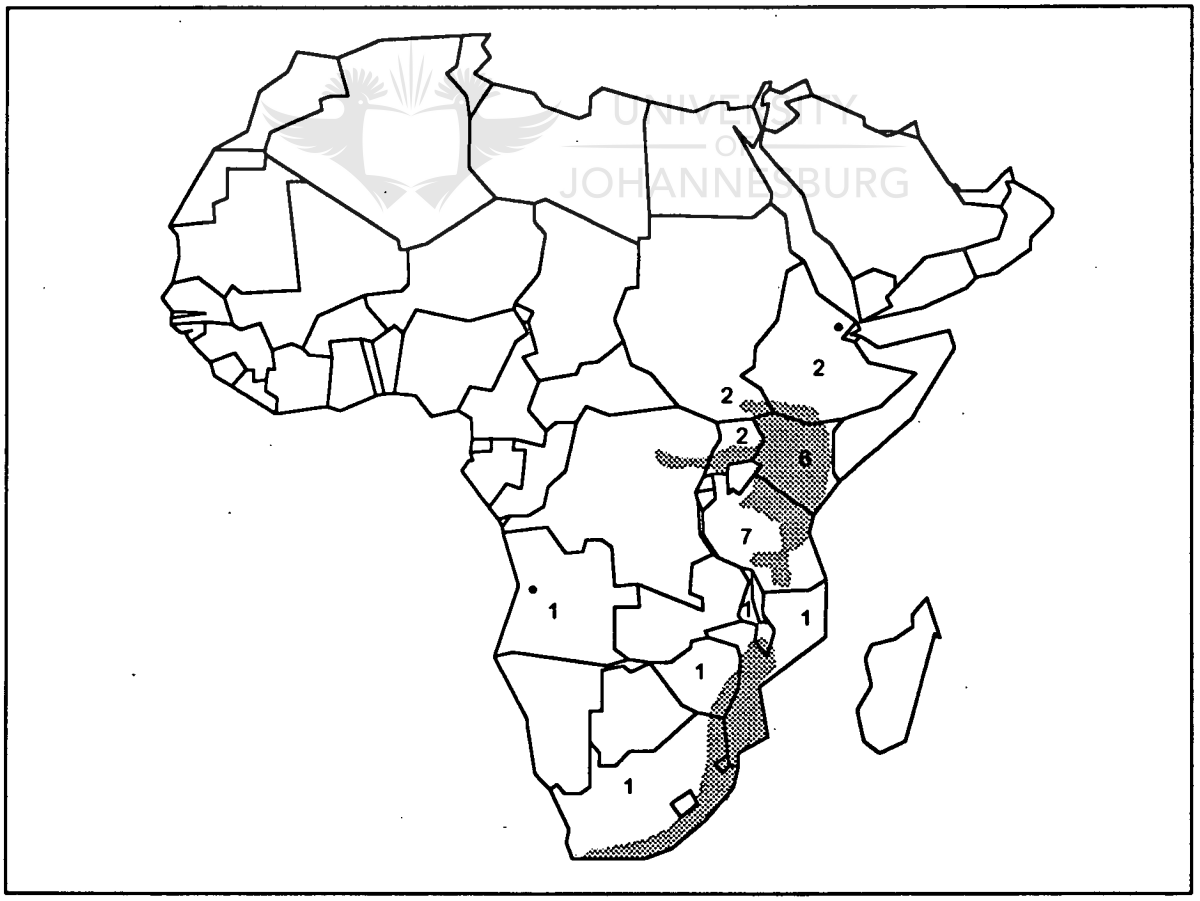


Figure 7.6: Geographical distribution of species containing aloenin. The number in each country represent the total number of species containing aloenin.

Table 7.4: Morphological (1 - 8) and chemical characters (9 & 10) used in the cluster analyses. Characters and coding of character states are shown below.

	1	2	3	4	5	6	7	8	9	10
A. arborescens	2	1	0	1	0	1	0	0	0	0
A. brachystachys	0	0	0	1	0	1	0	0	0	0
A. brandhamii	1	1	1	1	1	0	0	1	1	0
A. bussei	0	1	1	0	0	0	0	0	0	0
A. cheranganiensis	2	1	0	1	0	1	0	0	0	1
A. classenii	1	1	1	0	1	0	0	0	0	1
A. dawei	2	1	0	1	1	1	0	0	0	1
A. dorotheae	0	1	1	0	0	0	0	0	1	1
A. gossweileri	2	1	0	1	1	1	1	1	0	0
A. kedongensis	2	1	0	1	0	1	1	0	0	0
A. leachii	0	0	0	0	1	0	0	1	1	1
A. leptosiphon	0	1	1	0	0	0	0	0	0	1
A. monticola	0	0	0	1	1	1	0	0	0	0
A. nyeriensis	2	1	0	1	1	1	0	0	0	1
A. secundiflora	0	0	0	0	1	0	0	1	1	1
A. tororoana	2	1	0	1	0	0	0	0	0	1

1. *Caulescence*: acaulescent = 0, shortly caulescent = 1, distinctly caulescent = 2
2. *Branching*: solitary = 0, grouped = 1
3. *Suckering*: not suckering = 0, suckering = 1
4. *Leaf architecture*: erect to spreading = 0, spreading to recurved (or apices recurved) = 1
5. *Inflorescence structure*: simple to 1 - 4 branched = 0, much branched panicle = 1
6. *Pedicel length*: usually smaller than 10 mm = 0, usually longer than 10 mm = 1
7. *Perianth shape*: cylindrical / straight = 0, cylindrical / curved = 1
8. *Flower arrangement on floral axis*; flowers symmetrical = 0, flowers secund = 1
9. *Unidentified compound (R_f = 16.24)*: absent = 0, present = 1
10. *Unidentified compound co-eluting with aloin B (R_f 23.61)*: absent = 0, present = 1

Photo: van Wyk & Smith 1986

Aloe arborescens

Photo: Reynolds 1966

Aloe nyeriensis

Photo: Reynolds 1966

Aloe dawei

Photo: Reynolds 1966

Aloe secundiflora

Photo: Reynolds 1966

Aloe dorothea

Photo: Reynolds 1966

Aloe bussei

Chapter 8

A chemotaxonomic and morphological synopsis of *Aloe* series *Purpurascntes* and related taxa

CHAPTER 8

A CHEMOTAXONOMIC AND MORPHOLOGICAL SYNOPSIS OF *ALOE* SERIES *PURPURASCENTES* AND RELATED TAXA

This chapter aims to show the hybrid origin of *Aloe broomii*, with the one putative parent belonging to *Aloe* series *Purpurascentes* and the other belonging to *Aloe* series *Anguialoe*. The morphology and leaf exudate chemistry of both infrageneric groups will be discussed and a hypothesis on a possible phylogenetic relationship between the taxa is presented.

The present understanding of the taxonomic arrangement and suggested affinities between the taxa are diagrammatically represented in Figure 8.1. *Aloe* series *Purpurascentes* comprises five species, *A. microstigma*, *A. framesii*, *A. gariepensis*, *A. khamiesensis* and *A. succotrina* (Reynolds, 1950). The species are characterised by their spotted leaves and mostly produce an unbranched inflorescence. *Aloe pictifolia* was later described by Hardy (1976) and initially it was erroneously suggested to bear a taxonomic relationship with *Aloe* series *Echinatae*, especially to *A. krapohliana*. Laubscher (1977) however suggests a more plausible taxonomic alliance between *A. pictifolia* and *A. microstigma* stating that it is almost impossible to distinguish between juvenile plants of these two species. Reynolds (1950) included five species in *Aloe* section *Anguialoe*; *A. alooides* (syn. *A. recurvifolia*), *A. castanea*, *A. dolomitica*, *A. spicata* (syn. *A. sessiliflora*) and *A. vryheidensis*. (Some taxonomists consider *A. dolomitica* to fall within the variation described for *A. vryheidensis*). Reynolds believed that this group is sufficiently well defined by the sessile campanulate flowers and the distinct inflorescence to warrant sectional status in the taxonomic hierarchy of *Aloe* classification. In 1969 Leach described *A. tauri* from the southern part of Zimbabwe and suggested a close affinity with *A. spicata*. Lastly, Reynolds (1950) unites *A. broomii*, *A. longistyla* and *A. peglerae* into an artificial assemblage, series *Longistylae*. In 1973 Lavranos described the distinctive *A. chlorantha* from Fraserburg, postulating a taxonomic kinship with *A. broomii*.

In this chemotaxonomic survey of the genus *Aloe* it was noticed that four of the species belonging to the series *Purpurascentes* display a characteristic leaf exudate profile containing the chemotaxonomic marker microstigmin. *Aloe gariepensis* and *A. succotrina* lack the diagnostic leaf exudate compounds. *Aloe broomii* is only other species in our survey of 380 species to also contain the novel compound, microstigmin, which is characteristic of series *Purpurascentes*. More interesting, is the observation that the chromatographic profiles of species in *Aloe* section *Anguialoe* suggest a chemical alliance with both *A. broomii* and *A. chlorantha* and other species in series *Purpurascentes*. All species included in this discussion

Aloe microstigma, the species from which microstigmin was isolated (Photo: Ben-Erik van Wyk).

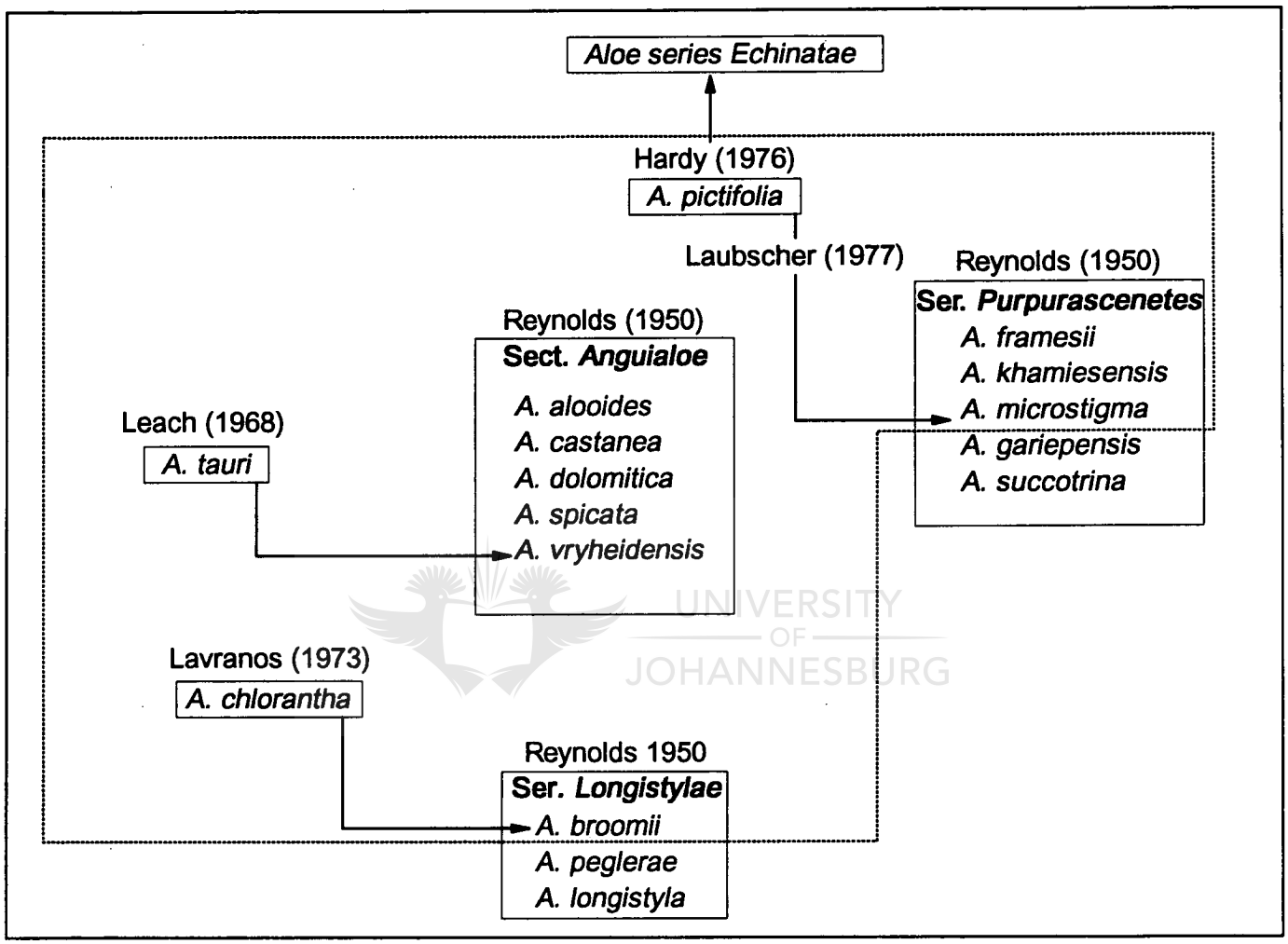


Figure 8.1: Affinity diagram showing the present taxonomic arrangement of taxa in *Aloe* section *Anguialoe*, series *Purpurascentes* and *A. broomii*.

Table 8.1. Salient morphological characters in *Aloe* section *Anguialoe*, series *Purpurascentes* and related species.

	Caulescence	Habit	Leaf orientation	Leaf maculation	Inflorescence	Bracts	pedicel	Perianth
A. aloolides	caulescent, erect	solitary	recurved	immaculate	simple	5-7 mm long	flowers sessile	cylindric-campanulate
A. broomii	short or long procumbent stem (1 m)	mostly solitary	erect	obscurely lineate	simple	longer than perianth	sub-sessile	cylindrical, slightly curved
A. castanea	caulescent, erect	solitary or arborescent	erect	immaculate	simple	12 mm long	sub-sessile	cylindric-campanulate
A. chlorantha	acaulescent or short procumbent stem	solitary or splitting into 10 rosettes	erect	striate and often spotted	simple, rarely forked	as long as perianth	shortly pedicellate	ventricose
A. dolomitica	caulescent, erect	solitary	erect, slightly incurved	immaculate	simple	8 mm long	flowers sessile	cylindric-campanulate
A. framesii	long procumbent stem	dense groups	spreading / incurved	varies from spotted to unspotted	2 - branched, rarely simple	⅔ length of pedicel	pedicellate	cylindrical trigonous
A. khamiesensis	stem erect, up to 1.5 m	solitary	erect, apex recurved	obscurely lineate and spotted	branched panicle	½ length of pedicel	pedicellate	cylindrical trigonous
A. microstigma	shortly procumbent	solitary or in small groups	erect	variable, mostly copiously spotted	simple	½ length of pedicel	pedicellate	cylindrical, slightly ventricose
A. pictifolia	shortly procumbent	pendent	deflexed	copiously spotted	simple	⅔ length of pedicel	pedicellate	cylindrical trigonous
A. spicata	caulescent, erect	solitary or shrubby	spreading / recurved	immaculate	simple	8 mm long	flowers sessile	cylindric-campanulate
A. vryheidensis	acaulescent, shortly procumbent	solitary	erect	immaculate	simple	15 mm long	flowers sessile	cylindric-campanulate
A. tauri	acaulescent	solitary	recurved	immaculate	simple	12 mm long	flowers sessile	cylindric-campanulate

are tabulated in Table 8.2 with the voucher or locality details.

Morphological characters

The salient morphological characters believed to be of diagnostic value are tabulated in Table 8.1. It has been demonstrated throughout this study that most of the groups defined by Reynolds (1950) are heterogenous assemblages of various morphological characters. This group too represents almost the entire morphological variation in *Aloe*. Within a convincingly natural clade such as the *Anguialoe*, plants could be distinctly caulescent and erect (e.g. *A. castanea* and *A. alooides*) or completely acaulescent (e.g. *A. vryheidensis* and *A. tauri*). The same degree of variation for habit characters are shown for species in series *Purpurascentes* which are mostly very shortly caulescent except for *A. khamiesensis* which develops erect stems up to 1.5 m tall. Chapter 11 has shown the same variation for the aloeresin E and F containing species where species are either completely acaulescent (e.g. *A. peglerae*) or characterised by a long procumbent stem (*A. distans*) or in the extreme case a tall erect stem over 2 m in length (e.g. *A. angelica*). With reference to leaf characters, the *Anguialoe* are characterised by immaculate leaves which are either erect or recurved. In the *Purpurascentes* the leaves are variable in maculation. At some localities the leaves of *A. framesii* are copiously spotted while at other localities the leaves are immaculate. The leaves of *A. broomii* and *A. chlorantha* are often obscurely lineate, a character shared with *A. khamiesensis* of the *Purpurascentes*. The inflorescence character is remarkably uniform in this group of species. All species but two produce an unbranched inflorescence while *A. khamiesensis* and *A. framesii* produce a panicle. The inflorescences of all the species are extremely long, much longer than the rosettes. In all species the racemes are cylindrical and densely flowered. The imbricate bracts of *A. broomii* and *A. chlorantha* are characteristic, being as long or longer than the perianth. The pedicel character has a distinct taxonomic significance in this group. The *Anguialoe* are characterised by sessile flowers which is a rare occurrence in *Aloe*. This character is only shared with a small number of species from Madagascar which do not seem to be related to the African species. The flowers of *A. broomii* and *A. chlorantha* are shortly pedicellate while in the species pertaining to the *Purpurascentes* the flowers are distinctly pedicellate. The perianth shape for the taxa in Table 8.1 is also rather invariable within each of the infrageneric groups. All species in the *Anguialoe* are characterised by the cylindric-campanulate flowers while the flowers of the *Purpurascentes* representatives are long, cylindrical trigonous flowers characteristic of *Aloe*.

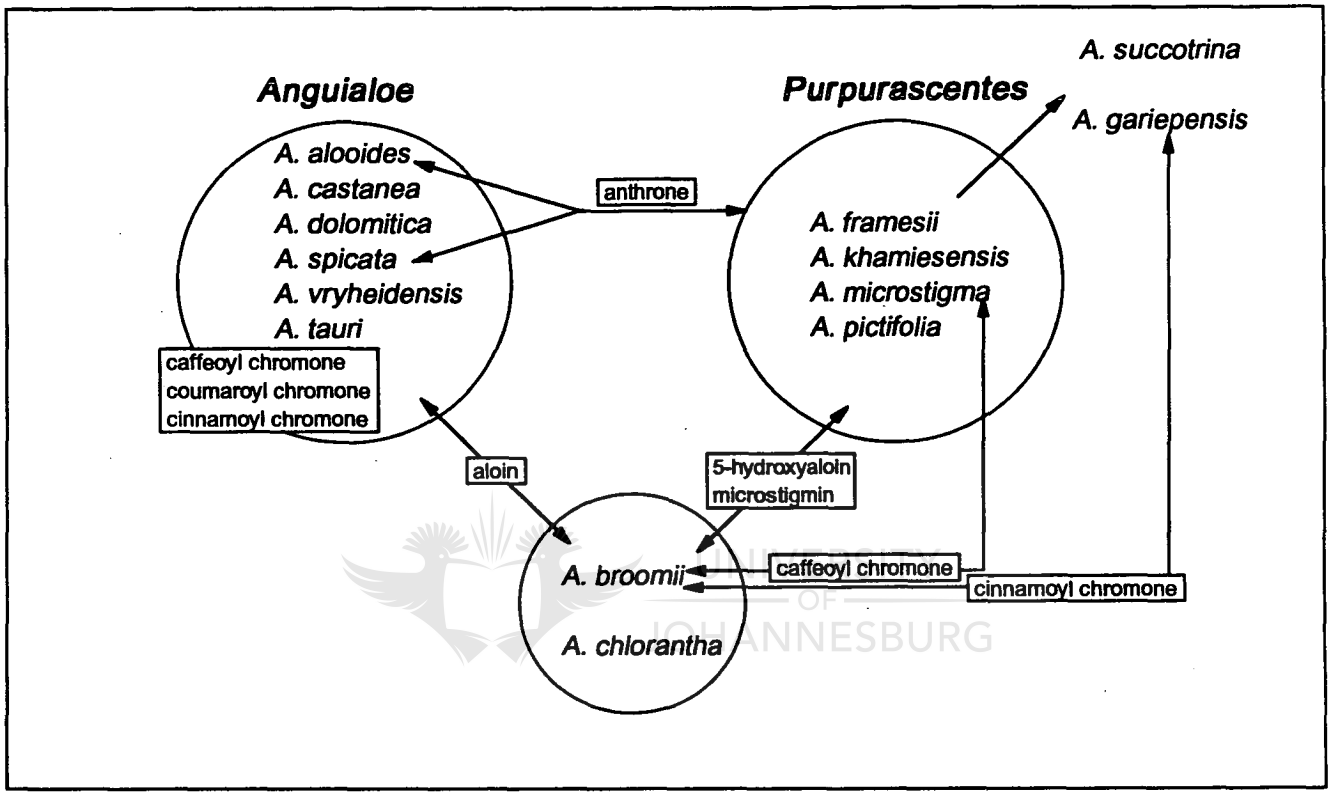


Figure 8.2: Diagrammatic representation of chemotaxonomic markers in *Aloe* section *Anguialoe*, series *Purpurascentes* and *A. broomii*

The Leaf Exudate Chemistry

Each of the three groups; series *Purpurascentes*, section *Anguialoe* and the *Aloe broomii* - *A. chlorantha* alliance produce a diagnostic exudate profile for each group with a degree of similarity between the three groups. Table 8.2 shows the presence of the leaf exudate compounds for the species. All species produce the chromone aloesin and it has been suggested through results generated in this study that this chromone probably originated early in the evolution of the genus as it is the most widely distributed leaf compound and therefor of no obvious chemotaxonomic value.

The chemotaxonomic value of the important chemical markers are discussed in relation to Figure 8.2. All the species in section *Anguialoe* are characterised by a diagnostic chemical profile. The species produce a caffeol chromone (compound 6 in Table 8.2) with a retention time of 20.6 which is usually present in trace amounts. Eluting between the aloin isomers is 6'-*O*-coumaroylaloesin, a second characteristic chromone with a coumaroyl ester group (compound 9 in Table 8.2). The last of the characteristic 'chromone-trio' is a late eluting cinnamoyl chromone (compound 15 in Table 8.2). The characteristic profile of members of the *Anguialoe* are shown in Figure 8.3 with the distinct UV spectra of the three chemotaxonomic markers. The leaf exudate of *Aloe broomii* was investigated intensively by Holzapfel *et al.* (1997) and three compounds were isolated from this species. The chromone eluting at 17.29 min is (E)-2-acetonyl-8-(2'-*O*-caffeoyl-β-D-glucopyranosyl-7-methoxy-5-methyl chromone (compound 4 in Table 8.2). This chromone is present in all three samples of *A. broomii*. Trace amounts of this chromone was also found in two of the three samples of *A. microstigma*. *Aloe broomii* shows variation with reference to the anthrone composition. One sample from Springfontein contained 5-hydroxyaloin A together with aloin A and B while two samples from different localities contained microstigmin in co-occurrence with the anthrone 5-hydroxyaloin A. The second chromone isolated from *A. broomii* is (E)-2-acetonyl-8-(2'-*O*-cinnamoyl-β-D-glucopyranosyl-7-methoxy-5-methyl chromone (compound 13 in Table 8.2). Trace amounts of a compound with the same UV spectrum and Rt was detected in *A. microstigma* (Calitzdorp), *A. gariepensis* and in *A. chlorantha*. The latter species also contains 5-hydroxyaloin A together with aloin A and B resembling the anthrone composition of *A. broomii* (Springfontein). The leaf exudate of the species belonging to series *Purpurascentes* is extremely complex. The chemotaxonomic marker, microstigmin, was isolated by Dagne *et al.* (1997) and is present in *A. microstigma*, *A. pictifolia*, *A. framesii*, *A. khamiesensis* and in two of the three populations of *A. broomii*. It is interesting to note that this compound always occurs in the absence of the

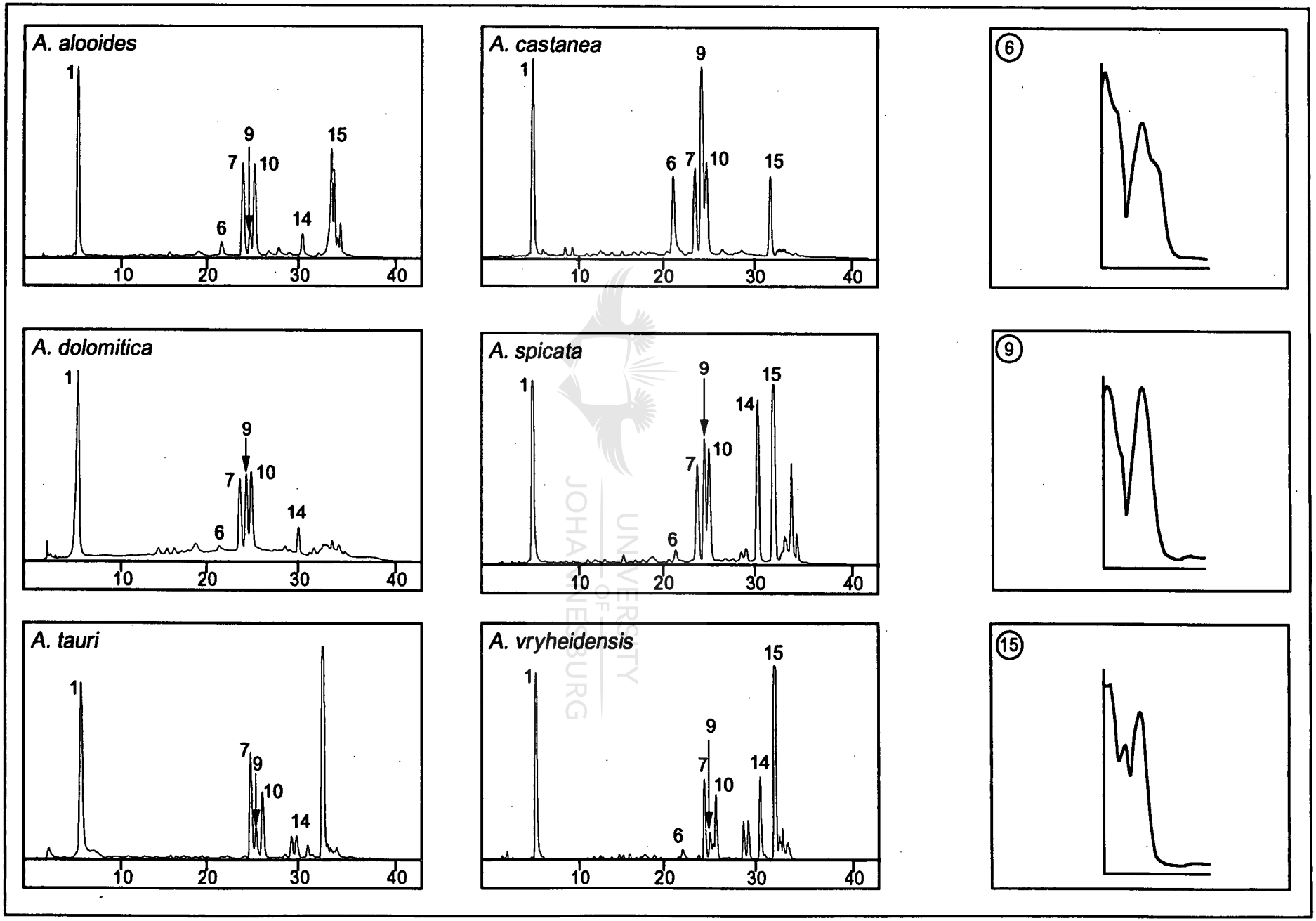
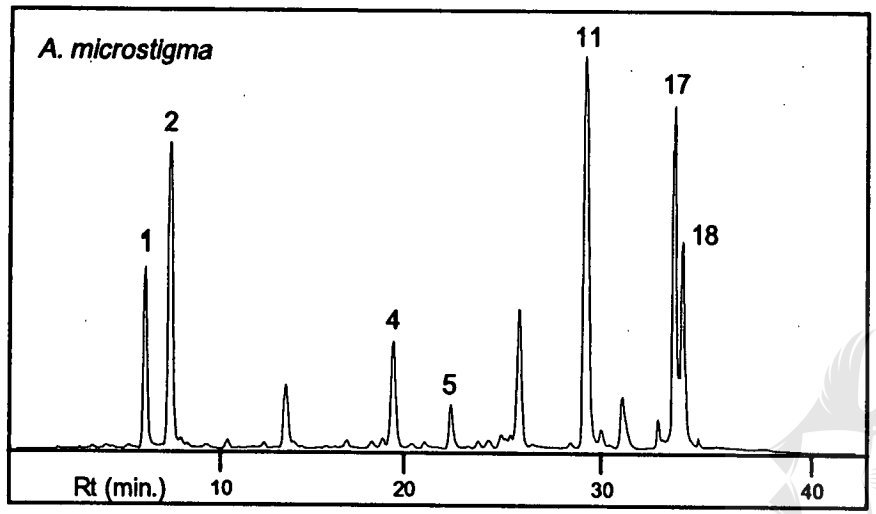
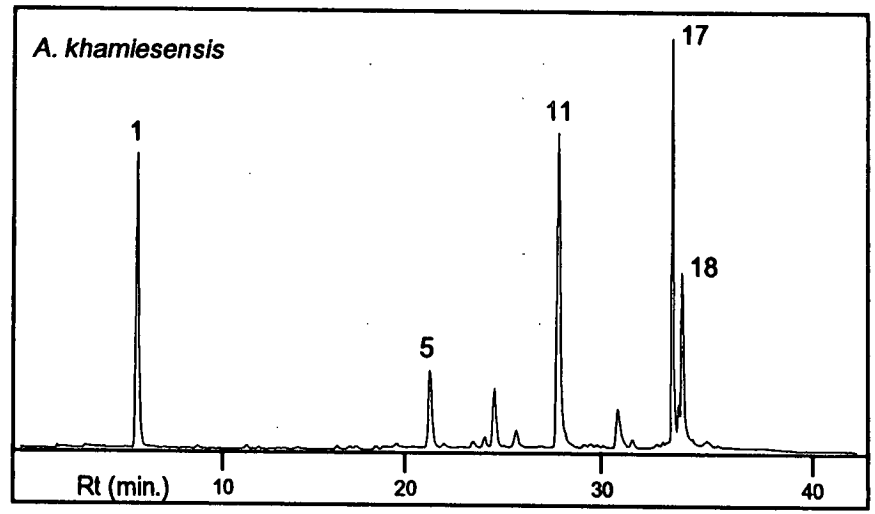


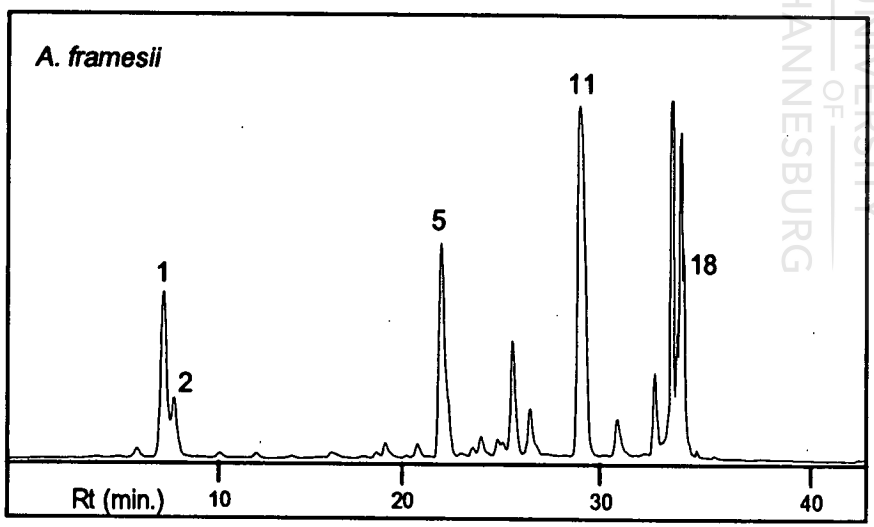
Figure 8:3: HPLC chromatograms of the 6 species in the *Anguialoe* group. The characteristic UV spectrum of the three chemotaxonomic marker compounds are also illustrated. Peak numbers correspond to the compounds in Table 8.2.

Table 8.2: The major leaf exudate compounds in Aloe section Anguialoe, series Purpurascentes and related species.

		aloesin	7-O-methylaloesin	caffeic chromone	caffeic chromone	5-hydroxyaloin	caffeic chromone	aloin B	homonataloin B	6'-O-coumaroylaloesin	aloin A	microstigmin	homonataloin A	cinnamic chromone	cinnamic chromone	cinnamic chromone	cinnamic chromone	unidentified] anthrone	cinnamic chromone
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	Retention time	5.1	7	10.7	17.2	19.4	20.6	23.3	23.6	23.7	24.7	26.3	26.4	29.9	30.3	32	33.3	33.7	33.9
A. alooides	The Bonnet	■					■	■		■	■				■	■			
A. broomii	Springfontein	■			■	■		■			■			■					■
	Graaff-Reinet				■	■						■							■
	Whitlesea	■	■		■	■						■		■					■
A. castanea	Three Rondawels	■					■	■		■	■					■			
	Elandslaagte	■					■	■		■	■								
A. chlorantha	Fraserburg	■				■		■			■			■					
A. dolomitica	Wolkeberge	■					■	■		■	■				■				
A. framesii	ex hort NBI	■	■			■						■						■	■
A. gariepensis	Keimoes	■	■						■				■	■					
A. khamiesensis	Skynshoogte Pass	■				■						■					■	■	■
A. microstigma	Robertson	■	■		■	■						■					■	■	■
	Cradock	■	■	■															■
	Calitzdorp	■		■	■							■		■					■
A. pictifolia	Patensie	■		■		■						■						■	■
A. spicata	Bourke's Luck	■					■	■		■	■				■	■			
A. tauri	WE 547	■						■		■	■				■				
A. vryheidensis	Louwsberg	■					■	■		■	■				■	■			







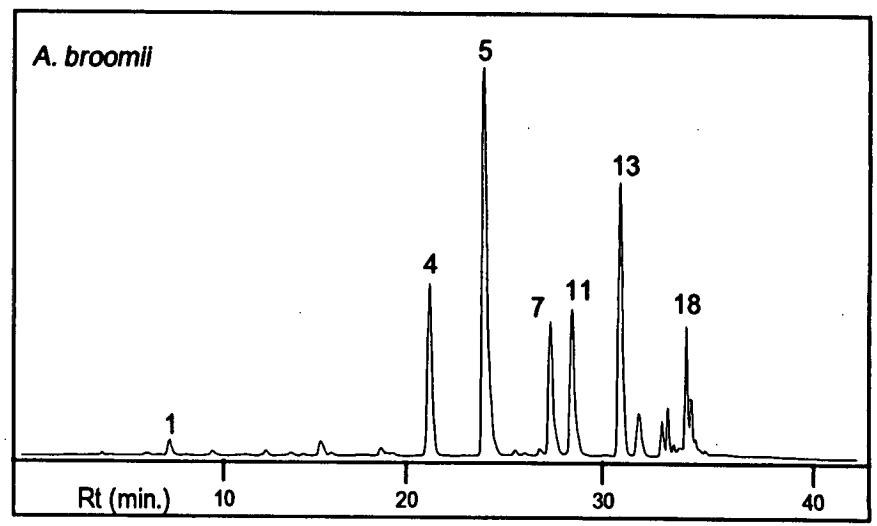


Figure 8.4: HPLC chromatograms of the microstigmin producing species. Peak numbers correspond to compounds in Table 8.2.

anthrone isomers aloin A and B. A selection of the HPLC profiles for the microstigmin-producing aloes are shown in Figure 8.4. The distribution of chemical compounds shown in Table 8.2 clearly shows the importance of extensive sampling of plant populations. Through extensive sampling procedures various patterns emerge from the data, establishing a chemotaxonomic affinity between the taxa as summarised in Figures 8.2.

Taxonomic relationships

When superimposing the chemical and morphological data on the taxonomic arrangement of the species in Figures 8.1 and 8.2, interesting congruencies and incongruencies are noted. *Aloe* section *Anguialoe* is an example where the present grouping of the species is completely supported on the chemical level. Irrespective of the specific taxonomy of this group, the distinct morphological coherence between the taxa in this group is reflected in the diagnostic and consistent leaf exudate profile as shown in Figure 8.3. What could be debated however is if this chemical and morphological distinction warrants sectional status, especially when viewed in relation to the new proposed taxonomic counterparts as shown in Figures 8.2. Of the six species included in *Aloe* series *Purpurascentes* (including *A. pictifolia*), four produce an identical exudate profile with 5-hydroxyaloin A and the recently described anthrone microstigmin, as chemotaxonomic marker compounds. *Aloe succotrina*, the type species of the *Purpurascentes* group produces leaf exudate very different from the other members of the *Purpurascentes* mentioned above. Rauwald (1986 & 1994) indicated the presence of 7-hydroxyaloin derivatives in this species, and this comprehensive survey has not detected the same combination of exudate anthrones in any other species. It has been demonstrated in Chapter 6 that 7-hydroxyaloin and derivatives thereof form readily when crossing an aloin and homonataloin producing species implicating that *A. succotrina* could be a product of hybridization of which the parents are not obvious (from a chemical and morphological perspective). The second chemical outlier included in series *Purpurascentes* is *A. gariepensis*, which follows a distribution along the western tributary of the Orange River (alternatively known as the Gariep River). This species is included by Reynolds (1950) in the series *Purpurascentes* with the following comments: "*A. gariepensis* is the only species in the series having long cylindric-acuminate racemes 35 - 50 cm long, and bracts much longer than the pedicels". In all the other species in this group the pedicels are long with the bracts always shorter than the pedicel. The leaves of *A. gariepensis* are always distinctly lineate and varies from spotted to unspotted. This plant also varies with respect to inflorescence character with the raceme being

uni- or bicoloured. The leaf exudate chemistry is completely different to any other species in the series *Purpurascentes* as it produces the anthrone isomers homonataloin A and B together with cinnamoyl chromones. The anthrones produced by all species in this complex is aloin or derivatives thereof in the presence cinnamoyl chromones. It has not been possible to establish if this specific cinnamoyl chromone also occurs in other representatives of this group although compounds with similar retention time and UV spectra have been recorded in *A. microstigma* and *A. broomii*. Cinnamoyl chromones in general have a very restricted distribution in the genus occurring only in 40 species in this survey of 380 species with most of these species distributed in South Africa (see Chapter 14). It is here suggested that *A. gariepensis* could be a product of a hybridization between a member of the *Purpurascentes* and perhaps *A. comosa*. The former parent could contribute the variable spotted leaf character and the cinnamoyl chromones while *A. comosa* could contribute the distinct inflorescence length, the leaf lineation and the larger bracts (as remarked upon by Reynolds 1950) together with the leaf exudate anthrone homonataloin.

The last assemblage in Figure 8.2 involves *A. broomii* and *A. chlorantha*. The former species is placed by Reynolds in the heterogenous group series *Longistylae* together with *A. peglerae* and *A. longistyla*. In Chapter 11 it has been shown that *A. peglerae* could possibly be related to other aloeresin E and F containing species while *A. longistyla* is both morphologically and chemically speaking anomalous. This species produces a series of unidentified anthrone derivatives resembling 5-hydroxyaloin A in UV absorbance characters. Considering the spottedness of the leaves and the presence of 5-hydroxyaloin derivatives which are both characteristic of the *Purpurascentes* one could imagine, perhaps, some ancient alliance with this group. More interesting and convincing is the taxonomic position of *A. broomii* which is best reflected by the distribution map (Figure 8.5). It is here suggested that *A. broomii* is an ancient hybrid between the *Anguialoe* and the *Purpurascentes*. With respect to morphological characters is shares with the *Anguialoe* the sessile flowers and the distinct single inflorescence up to 1.5 m tall. This resemblance is supported on the chemical level as some populations produce the same anthrone found in the *Anguialoe*, aloin A and B. *Aloe broomii* also produces various caffeoyl, cinnamoyl and coumaroyl chromones. This combination of chromones is characteristic of the *Anguialoe*. With the *Purpurascentes, A. broomii* possibly shares the spotted leaves (reduced in *A. broomii*) and obscure leaf lineation. More convincing are the chemical resemblances which includes 5-hydroxyaloin A and microstigmin which only occurs in the four other species of *Aloe* shown in Figure 8.2. The occurrence of leaf exudate

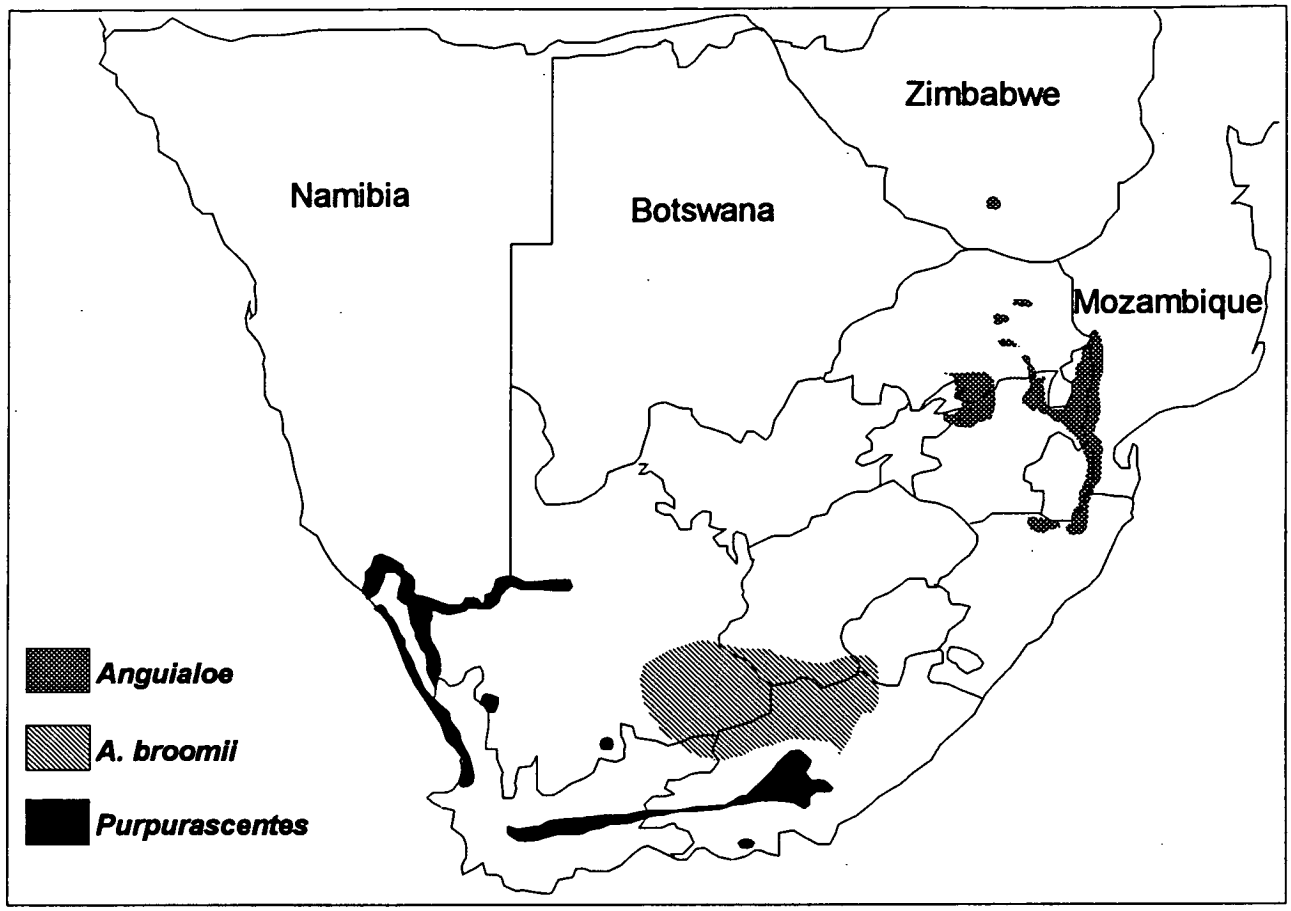


Figure 8.5: Distribution of *Aloe* section *Anguialoe* (north-eastern South Africa), *A. broomii* (central South Africa) and series *Purpurascentes* in the western parts of the country.

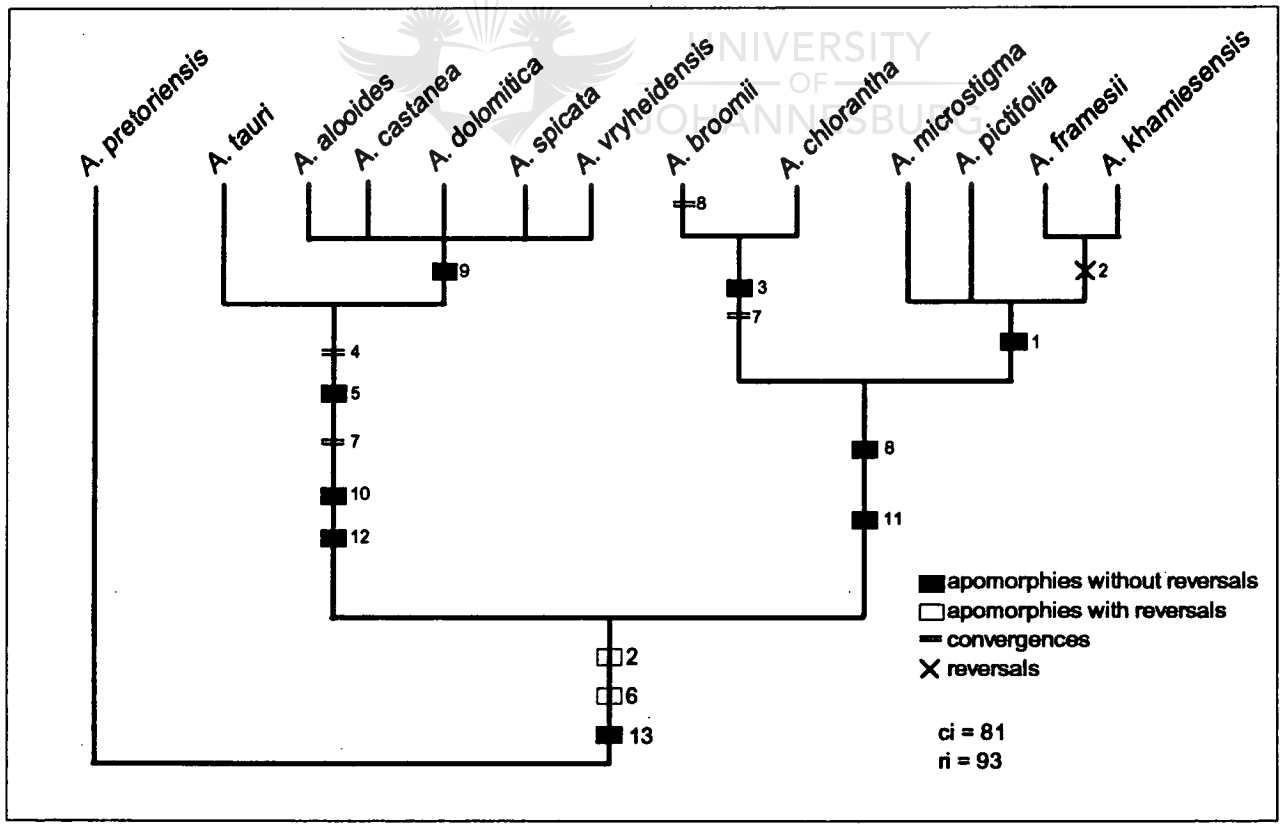


Figure 8.6: Cladogram constructed using the characters tabulated in Table 8.3. A single cladogram with 16 steps was generated using the "ie" command in Hennig 86.

Table 8.3: Characters and polarization of morphological and chemical character states.

	Characters and character states												
	1	2	3	4	5	6	7	8	9	10	11	12	13
A. pretoriensis (outgroup)	0	0	0	0	0	0	0	0	0	0	0	0	0
A. alooides	0	1	0	1	1	1	1	0	1	1	0	1	1
A. broomii	0	1	1	1	0	1	1	1	0	0	1	0	1
A. castanea	0	1	0	1	1	1	1	0	1	1	0	1	1
A. chlorantha	0	1	1	0	0	1	1	1	0	0	1	0	1
A. dolomitica	0	1	0	1	1	1	1	0	1	1	0	1	1
A. framesii	1	0	0	0	0	1	0	1	0	0	1	0	1
A. khamiesensis	0	0	0	0	0	1	0	1	0	0	1	0	1
A. microstigma	1	1	0	0	0	1	0	1	0	0	1	0	1
A. pictifolia	1	1	0	0	0	1	0	1	0	0	1	0	1
A. spicata	0	1	0	1	1	1	1	0	1	1	0	1	1
A. vryheidensis	0	1	0	1	1	1	1	0	1	1	0	1	1
A. tauri	0	1	0	1	1	1	1	0	0	1	0	1	1

1.	Leaf maculation	leaves not spotted = 0; leaves spotted = 1
2.	Inflorescence shape	inflorescence a panicle = 0; inflorescence simple = 1
3.	Bracts	bracts not imbricate = 0; imbricate bracts covering buds = 1
4.	Pedicel	sessile to sub-sessile = 0; flowers pedicellate = 1
5.	Perianth	tubular / cylindric = 0; campanulate = 1
6.	Anthrones	absent = 0; present = 1
7.	Aloin	absent = 0; present = 1
8.	5-hydroxyaloin B	absent = 0; present = 1
9.	Caffeoyl chromone (cmpd 6 in Table 8.2)	absent = 0; present = 1
10.	Coumaric chromone (cmpd 9 in Table 8.2)	absent = 0; present = 1
11.	Microstigmin	absent = 0; present = 1
12.	Cinnamic chromone (cmpd 15 in Table 8.2)	absent = 0; present = 1
13.	Flavonoids	present = 0, absent = 1

compounds in *Aloe broomii* is of special interest. Three populations were investigated; plants from the first population (Springfontein) contain aloin A and B, the major anthrone of the *Anguialoe*. The second (Graaff-Reinet) and third (Whitlesea) populations contained microstigmin and 5-hydroxyaloin A (in the absence of aloin A and B), the marker compounds of the *Purpurascentes*. This is increasing support for the hybrid origin of *A. broomii* showing the leaf exudate to resemble that of any of the two putative parents. The last species, *A. chlorantha* is undisputably closely related to *A. broomii*. It is noteworthy that in the description of the species, the author Lavranos (1973) makes the following interesting statements:

> ".....the peduncle is covered from the base up, by numerous, large sterile bracts which, like the floral ones, are rather fleshy. This character is met with in other South African species of *Aloe*, notably *A. glauca*, *A. pratensis*, *A. microstigma*, *A. comosa* etc."....."Mr Stayner suggests a certain resemblance between *A. chlorantha* and the decumbent form of *A. microstigma*.....If flowers and inflorescence be a guide, a much closer relationship may exist between our species and *A. comosa*....."

It is encouraging that independent of the chemical results the pattern of reason and suggestions of affinity as discussed in this Chapter have been put forwards by 'aloe authorities' who by their field observation also suggest a possible relationship between the species discussed and shown in Figure 8.2.

An hypothesis on the phylogenetic relationships is presented in Figure 8.6 using the chemical and morphological characters in Table 8.3. Based on previous chemotaxonomic results (Viljoen *et al.* 1997) *A. pretoriensis* is used as an outgroup as the flavonoid producing species of *Aloe* are believed to present the plesiomorphic condition in *Aloe*. *Aloe pretoriensis* also shows morphological affinities with this group of species. The cladogram shows the series *Purpurascentes* to be the derived lineage. *Aloe broomii* is basal to this most derived lineage which is congruent with the results of McDade (1992) illustrating that hybrids are often basal to the most apomorphic clade. These results are in agreement with the phylogenetic hypothesis for *Aloe* series *Asperifoliae* (Viljoen *et al.* 1996) showing a drought adapted clade derived from a more tropical group. The distribution pattern of the species shown in Figure 8.5 suggests that the arid adapted *Purpurascentes* clade is of tropical origin with the *Anguialoe* suggested to be the sister clade of this group. The intermediate distribution of *A. broomii* serves as further evidence that this species may be of hybrid origin.

The possible hybrid origin and even taxonomic affinities of *A. broomii* have eluded several taxonomists and even Reynolds himself. It is only through chemical evidence revealed in this

study that the taxonomic affiliation of *A. broomii* became apparent. But, what about several possible hybrids that defy any form of detection; morphological, chemical and genetic detection? It becomes even more evident throughout this thesis that hybridization is rive in *Aloe* which imposes a problem to present a desired neat phylogeny. It is very much in 'vogue' to produce evolutionary histories of organisms by using phylogenetic methods and even more fashionable to present well resolved cladograms which of course is possible if the taxa under investigation are 'behaving well' in evolutionary terms i.e. following a pattern of divergent speciation. One of the problem encountered in a taxonomic treatment dealing with hybrids is the method of analysis to infer phylogenies, cladistics. This algorithm requires that evolution is a divergent process and that taxa are of monophyletic origin. The reality in *Aloe* is that hybridization is an important evolutionary stimulus resulting in reticulate evolution implying that many taxa are of polyphyletic origin. The situation in *Aloe* is also defied by the statement of Hennig that in all cases involving polyphyletic origin of species, the species involved are so closely related that they could just as well be considered races of the same species. McDade (1990 & 1992) illustrated the effects of hybrids on cladistic analysis leading her to the conclusion that hybrids do not disrupt phylogenetic analysis if the taxa are closely related (as pre-empted by Hennig). Figures 6.9 and 6.10 in Chapter 6 has shown that in *Aloe* it is more, likely that disparate taxa will hybridise rather than closely related taxa. McDade's data is based on the results obtained with artificial F1 greenhouse hybrids between closely related taxa. In a study of this nature one has to be careful to extrapolate results into reality - natural hybridization. Firstly, we will often not even know what the hybrids or even the parents are as many hybrids will defy any means of detection. Secondly, it is unlikely that natural hybridization are F1 hybrids, but instead these initial hybrids will participate in successive introgression. Often the characters used in the analysis of a smaller infrageneric group become irrelevant in a greater analysis e.g that of a genus. The bract character used here in Table 8.3 is valuable at this scale, but will become meaningless in a cladistic analysis of the genus. If one wishes to establish the occurrence of hybridization not knowing what the hybrids or the parents are then an encompassing cladistic analysis of the entire genus will be required, with the possibility of excluding valuable characters not relevant at the generic level. This exercise has been followed through in this study, and as predicted by McDade (1990 & 1992) the 'taxonomic noise' added by hybrids to the analysis resulted in a total collapse of the topology.

It is evident that the awareness of hybridization is fundamental in understanding the processes regulating the evolution of the group under investigation and that greater attention should be

paid to develop more appropriate algorithms to compensate for one of the evolutionary realities in nature, hybridization.

Figure 8.7: Representatives of *Aloe* section *Anguialoe*, series *Purpurascentes* and *A. broomii*.

⇨

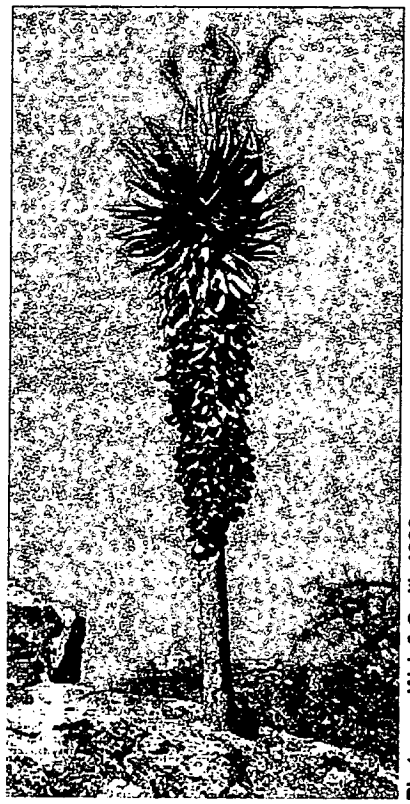


Photo: van Wyk & Smith 1996

Aloe khamiesensis

Photo: van Wyk & Smith 1996

Aloe framesii

Photo: van Wyk & Smith 1996

Aloe broomii

Photo: van Wyk & Smith 1996

Aloe microstigma

Photo: van Wyk & Smith 1996

Aloe pictifolia

Photo: van Wyk & Smith 1996

Aloe alooides

Photo: van Wyk & Smith 1996

Aloe castanea

Photo: van Wyk & Smith 1996

Aloe spicata

Photo: van Wyk & Smith 1996

Aloe vryheidensis

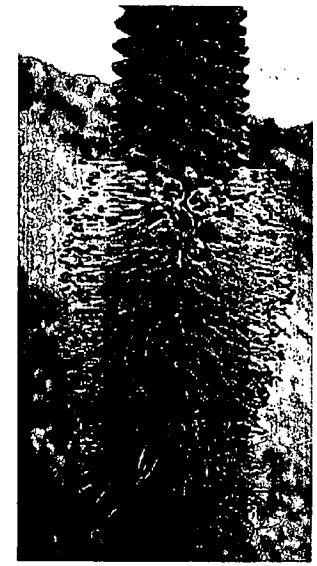


Photo: van Wyk & Smith 1996

Inflorescens of
Aloe vryheidensis

Chapter 9

The chemotaxonomic value of 10-hydroxyaloin B and the phylogeny of *Aloe* series *Asperifoliae*

CHAPTER 9

THE CHEMOTAXONOMIC VALUE OF 10-HYDROXYALOIN B AND THE PHYLOGENY OF *ALOE* SERIES *ASPERIFOLIAE*

This chapter presents a chemotaxonomic and cladistic study of *Aloe* series *Asperifoliae* and related species. The leaf exudate of most species included in, or pertaining to series *Asperifoliae* have littoraloin, deacetyllittoraloin and 10-hydroxyaloin B. *Aloe viridiflora* is shown to be misplaced in series *Asperifoliae*, as the chemical composition of the exudate and morphological characters are remarkably different from all other members of the group, but similar to the more distantly related *A. hereroensis*. *Aloe littoralis* is a logical outgroup for the series *Asperifoliae* because it is chemically identical to most members of the group. A cladistic analysis, based on chemical and morphological data, is presented, together with an interpretation of distribution patterns. These results give a new perspective on natural relationships and are consistent with the hypothesis that the *Asperifoliae* is an extremely xerophytic southern clade of tropical origin, with *A. littoralis* as the basal species.

Reynolds (1950) included five species in his delineation of *Aloe* series *Asperifoliae*; *A. asperifolia, A. pachygaster, A. falcata, A. claviflora* and *A. viridiflora*. (Figure 9.1) Since his benchmark publication, four new species of this group have been described, namely *A. argenticauda*, previously confused with *A. pachygaster* (Giess 1974), *A. corallina* (Verdoorn 1979), *A. namibensis* (Giess 1970) and *A. dewinteri* (Giess 1973). The species are all endemic to the western parts of southern Africa and occur in Namibia, the north western Cape and the Karoo (Reynolds, 1950 and Jankowitz, 1972 and 1975). Species with voucher / locality details and their distributions are given in Table 9.1. Reynolds (1950) emphasised the obvious morphological similarity between *A. asperifolia, A. pachygaster, A. falcata* and *A. claviflora*. *Aloe viridiflora* was included with comments suggesting that it should be viewed as a marginal species in the series *Asperifoliae*. A survey of the leaf exudate of 380 species in the genus *Aloe* revealed that 10-hydroxyaloin B is found only in *Aloe* series *Asperifoliae* and in *A. littoralis* and *A. esculenta*. Four oxanthrone chemotaxonomic markers have been isolated and characterized as 10-hydroxyaloin B (a in Figure 9.2) and its two nilic acid esters, littoraloin (b in Figure 9.2) and deacetyllittoraloin B, c in Figure 9.2) from *A. littoralis* (Dagne *et al.* 1996). A forth chemically related compound 10-hydroxyaloin B 6'-*O*-acetate (d in Figure 9.2) was reported by Dagne *et al.* (1998), from *A. claviflora*.

Aloe claviflora, a species containing 10-hydroxyaloin B and derivatives thereof (Photo: Aloe 34(3): 1982).

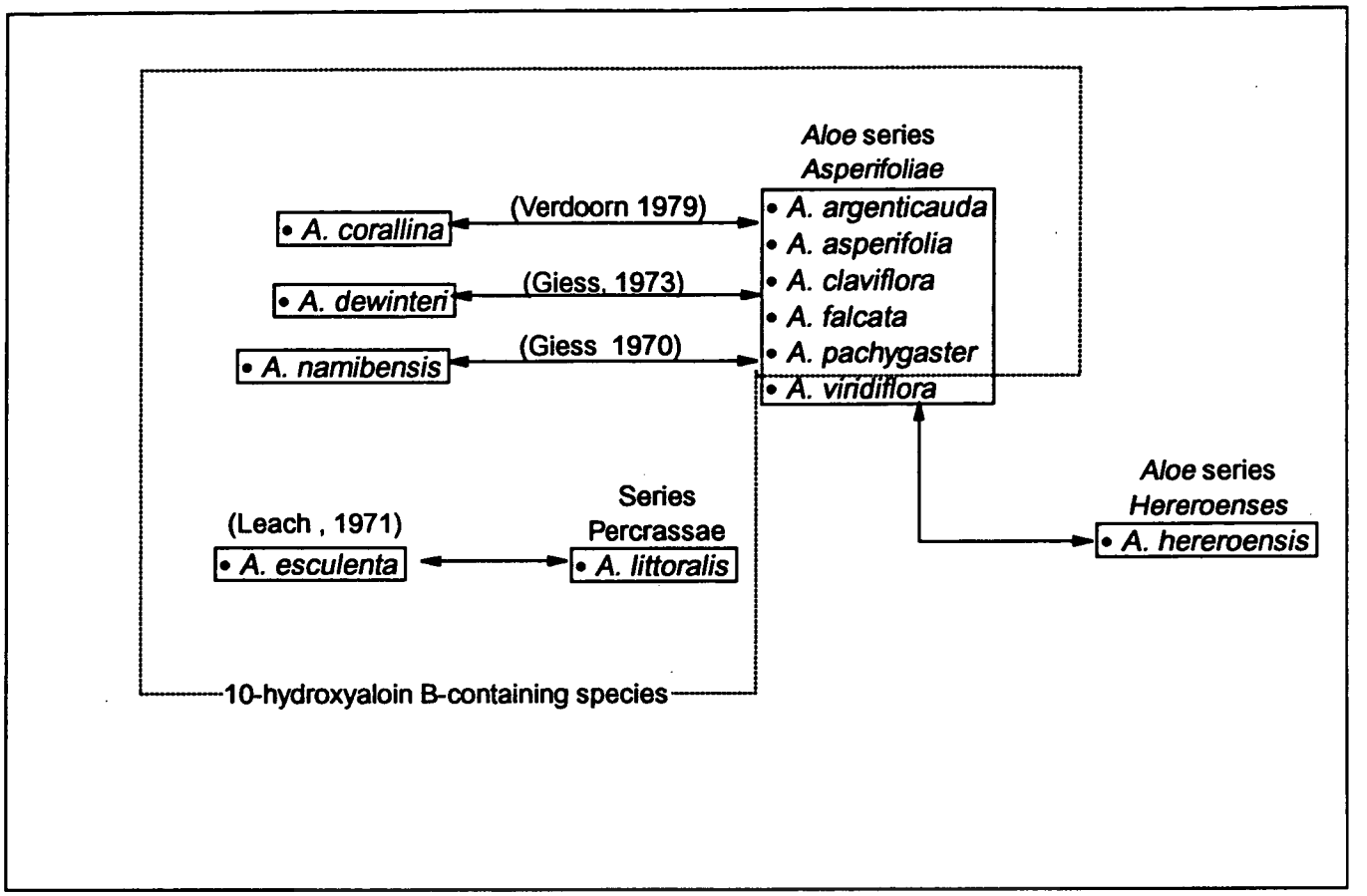


Figure 9.1: Taxonomic distribution of species containing 10-hydroxyaloin B and related anthrones.

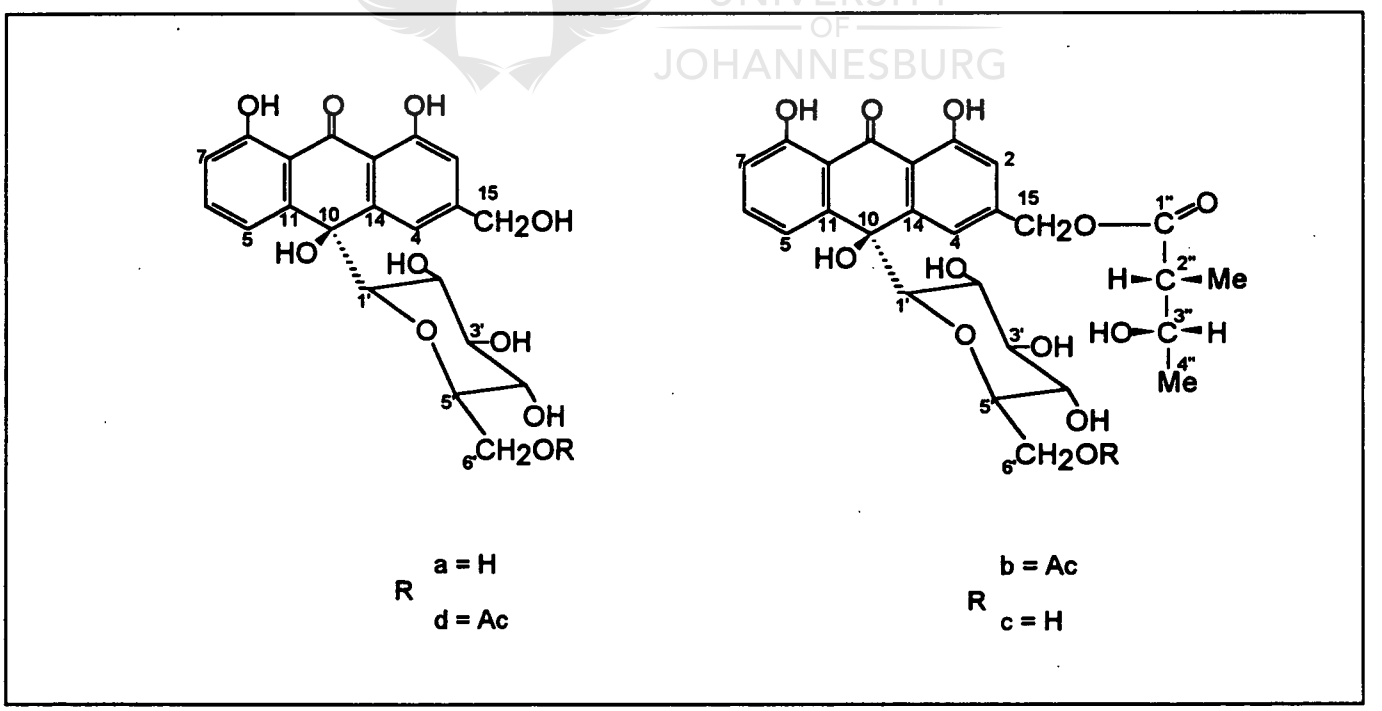


Figure 9.2. The four oxanthrone chemotaxonomic markers for series *Asperifoliae* and related taxa. a = 10-hydroxyaloin B, b = 10-hydroxyaloin B 6'-O-acetate, c = littoraloin, d = deacetyllittoraloin.

Table 9.1 Taxa, voucher details and distribution of species discussed in this Chapter.

Species	Voucher / Locality	Distribution
A. argenticauda	ex hort JBG	Namibia
A. asperifolia	EVJ 2850 & NBI 432/72 & ex hort JBG	Namibia
A. claviflora	Strydenburg & Beaufort West Graaff-Reinet & Namibia	Namibia & South Africa
A. corallina	NBI 20079	Namibia
A. dewinteri	ex hort NBG & Warmbad	Namibia
A. esculenta	NBI 27823	Namibia
A. falcata	Van Rhynsdorp	South Africa
A. hereroensis	NBI 28966 & & ex hort JBG	Namibia and South Africa
A. littoralis	Vivo, Etosha & Windhoek	Namibia, South Africa, Zimbabwe & Botswana
A. namibensis	NBI 28193	Namibia
A. pachygaster	ex hort JBG & NBG 1120/70	Namibia
A. viridiflora	NBI 28700 & ex hort JBG	Namibia

Table 9.2 gives a summary of chemical characters of the species pertaining to *Aloe* series *Asperifoliae,* together with *A. littoralis*, *A. esculenta* and *A. hereroensis*. All except two of them have 10-hydroxyaloin B in the leaf exudate, often in combination with littoraloin, deacetyllittoraloin B and 10-hydroxyaloin B 6'-O-acetate. Small amounts of aloin and an unknown derivate of aloin occur less frequently. The HPLC profiles of selected samples are shown in Figure 9.3. The combination of major chemical compounds in *A. claviflora* and *A. littoralis* are identical, and closely similar patterns are found in other species (Table 9.2). Both species produce an unknown chromone, together with compounds a to d (Figure 9.2). Namibia's rare endemic aloe, *A. viridiflora*, was included in the series *Asperifoliae* by Reynolds (1950) but the morphology and the leaf exudate chemistry now unambiguously show it to be misplaced in the section. *Aloe viridiflora* is closely allied to *A. hereroensis*, with which it shares several characters. Both species produce homonataloin as major anthrone constituent of the leaf exudate. This chemical similarity is amplified on the morphological level as both species produce a branched panicle with capitate racemes. There is also agreement in the leaf surface characters and flowering time. Various authors have mentioned the morphological similarity between the two species (Bruyns 1988, Jankowitz 1975 and Van Jaarsveld 1989), and the chemical evidence presented here establishes beyond doubt that *A. viridiflora* should be

excluded from the series *Asperifoliae*. The remaining species, together with *A. littoralis* and *A. esculenta*, are likely to be monophyletic because they share a remarkable chemical similarity. In order to find out how the interesting chemical pattern should be interpreted the various morphological characters are polarized according to the outgroup method. The interpretation of the evolution of character states is summarised in Table 9.3. A brief discussion of salient morphological features is given below.

Habit

All the species in series *Asperifoliae* are acaulescent or have a short procumbent stem. *Aloe argenticauda, A. asperifolia, A. pachygaster, A. claviflora* and *A. falcata* always form dense clusters, while the three species from northern Namibia, (*A. namibensis, A. dewinteri* and *A. corallina*) are all solitary. *A. littoralis* is generally caulescent and solitary, but a form with short stems and a clustered habit has been described as a separate species, *A. esculenta* (Leach 1971). In contrast to all the other species, *A. dewinteri* and *A. corallina* are cliff-hanging species and have pendulous stems.

Leaf Characters

As the name indicates, all the species pertaining to *Aloe* series *Asperifoliae* have a more or less granular leaf texture and the leaves have a distinct glaucous bloom. In *A. littoralis*, the leaves may be somewhat glaucous but the surface is not asperous. *Aloe argenticauda, A. pachygaster, A. asperifolia, A. claviflora, A. falcata* and *A. namibensis* are characterized by incurved leaves, while *A. littoralis, A. corallina* and *A. dewinteri* produce decurved leaves. Juvenile plants of *A. littoralis* also have incurved leaves and although generally spreading and recurved in the mature plants, some individuals occasionally have the leaves incurved (Reynolds 1966).

Inflorescence and Flower Characters

Inflorescence characters vary considerably in the series *Asperifoliae*. A simple (unbranched) inflorescence structure is characteristic of *A. argenticauda* and *A. pachygaster*. In the southern part of its distribution area, *A. claviflora* usually also produces simple racemes, while a branched panicle is more common in the northern parts of its distribution (Reynolds 1938). *Aloe falcata* and *A. littoralis* both produce a much branched panicle, laterally spreading in the former and more compressed in the latter. *Aloe asperifolia, Aloe namibensis, A. corallina*, and

A. dewinteri have a 2- to 3-branched inflorescence (rarely simple in the latter). In *A. corallina* though, the inflorescence is branched in the upper half, while in *A. dewinteri* and *A. namibens* it is branched near the base (Verdoorn 1977a). The homology of flower shape deserves further study. A clavate or subclavate perianth is characteristic of *A. claviflora*, *A. corallina*, *A. esculenta* and the unrelated *A. viridiflora*, species that otherwise do not share any obvious synapomorphies. The ventricose shape of the perianth in *A. argenticauda* and *A. pachygaster* however, is here interpreted as a shared derived character. Flower colour varies considerably. All the species have flowers with various shades of pink or red, while *A. viridiflora* (green) and *A. hereroensis* (orange or greenish) are notable exceptions. The flower colour is seemingly correlated with the equally exceptional capitate inflorescence structure of these two species.

Leaf Exudate Chemistry

If *A. viridiflora* is excluded from the series and if *A. littoralis* is included, then 10-hydroxyaloin B becomes a chemical marker for the *Asperifoliae*. *Aloe littoralis* is currently placed in group 18 of Reynolds (1966) but the leaf exudate chemistry clearly shows a relationship with the *Asperifoliae*. The chemical profiles of *A. argenticauda, A. pachygaster, A. claviflora, A. falcata* and *A. littoralis* are practically identical. All these species contain high levels of 10-hydroxyaloin B, together with littoraloin and deacetyllittoraloin (Table 9.2). *Aloe dewinteri* and *A. namibensis* have lower levels of 10-hydroxyaloin B, and produce an unique derivative of aloin (compound 8 in Table 9.2) which is also present in *A. corallina*, the only species lacking 10-hydroxyaloin B. It is interesting to note from Table 9.2 that the unknown derivative of aloin also occurs in *A. asperifolia*, and that this species also lacks littoraloin and deacetyllittoraloin, characters which emphasise its relationship with *A. namibensis* and *A. dewinteri* (Verdoorn 1977b and 1977c).

Distribution

The geographical distributions depicted in Figure 9.4 were compiled from literature (Reynolds 1950, Jankowitz 1972 and 1975) and from specimens housed in the National Herbarium, Pretoria (PRE). The species occur mainly in the Namib Desert, and in the central and north western Cape. This area is prone to warm dry conditions and periodic droughts, receiving an average rainfall of only 125 mm per annum. Jankowitz (1977) pointed out the correlation between the summer rainfall area of Namibia and the distribution area of *Aloe littoralis* and *A.*

Table 9.2. Distribution of major chemical compounds in the leaf exudate of *Aloe* series *Asperifoliae* and some other species.

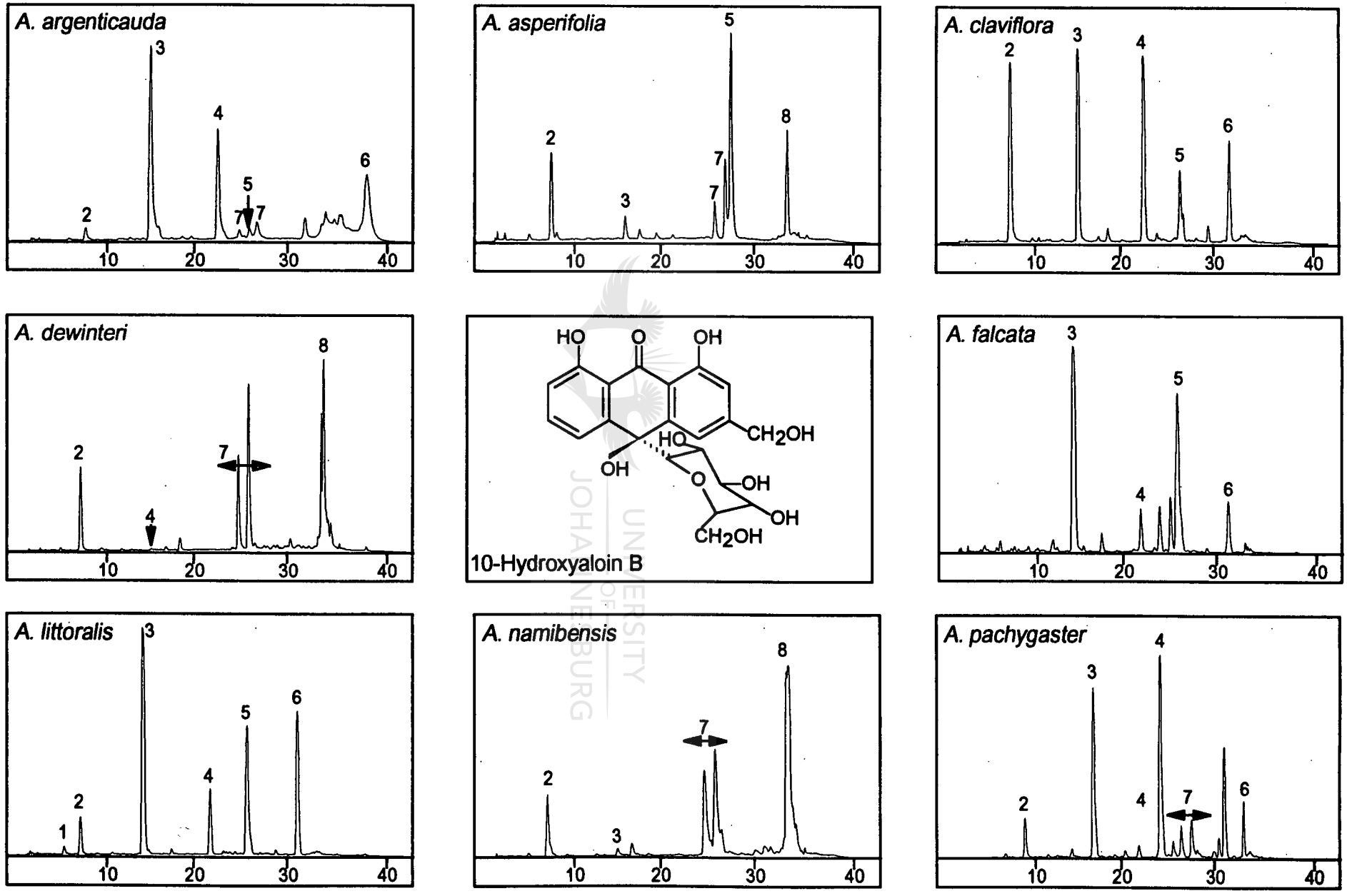


Figure 9.3: HPLC chromatograms of 8 species containing 10-hydroxyaloin B and anthrone derivatives. Numbers of peaks correspond to data in in Table 9.2. The chemical structure of the chemical marker 10-hydroxyaloin B is also shown.

Table 9.2: The occurrence of major leaf exudate compounds in *Aloe* series *Asperifoliae* and related taxa.

	1	2	3	4	5	6	7	8	9
A. argenticauda		■	■	■	■	■	tr		
A. asperifolia			■				■	■	
A. claviflora		■	■	■	■	■	■	tr	
A. corallina	■						■	■	
A. dewinteri		■	■				■	■	
A. falcata			■	■	■	■	tr		
A. namibensis		■	■				■	■	
A. pachygaster	■	■	■	■		■	tr		
A. viridiflora	■								■
A. hereroensis	■	■							■
A. littoralis	■	■	■	■	■	■			
A. esculenta	tr		■	■	■	■	tr		

1. Aloesin
2. 7-*O*-methylaloesin
3. 10-hydroxyaloin B
4. 10-Hydroxyaloin B 6'-*O*-acetate
5. Deacetyllittoraloin
6. Littoraloin
7. Aloin A & B
8. Unidentified derivative of aloin
9. Homonataloin A & B

claviflora, while *A. pachygaster* is always associated with dolomite and limestone. *Aloe littoralis* has a wide distribution range extending from Angola in the north, southwards to southern Namibia and eastward to the northern Transvaal. *Aloe corallina, A. dewinteri* and *A. namibensis* are geographically localized and the sympatric distribution of the latter species with *A. asperifolia* supports their chemical and morphological similarity. We propose that the present-day distributions reflect allopatric evolutionary changes in response to the extremely arid conditions of the western part of southern Africa.

Cladistic Analysis

Figure 9.5 shows the single, fully resolved cladogram of hypothetical relationships in the *Asperifoliae*, based on the morphological and chemical characters listed in Tables 9.2 and 9.3. *Aloe littoralis* is shown to be basal to the group, with *A. falcata* basal to the *Asperifoliae sensu stricto*. *Aloe littoralis* and *A. falcata* are similar in inflorescence structure and flower morphology, and the leaf exudate chemistry of the two species are identical. *Aloe pachygaster* and *A. argenticauda* form a well-defined clade based on inflorescence structure and flower morphology. This is not unexpected, as *A. argenticauda* has been confused with *A. pachygaster* (Reynolds 1950) and later described by Giess (1974) as a distinct species. Both species produce an unbranched inflorescence, with ventricose flowers and long bracts. *Aloe claviflora* and *A. asperifolia* are also very similar, but the leaf exudate chemistry revealed notable differences. As expected, *A. namibensis, A. corallina* and *A. dewinteri* form a well supported clade. The latter two species are considered to be more closely related as they

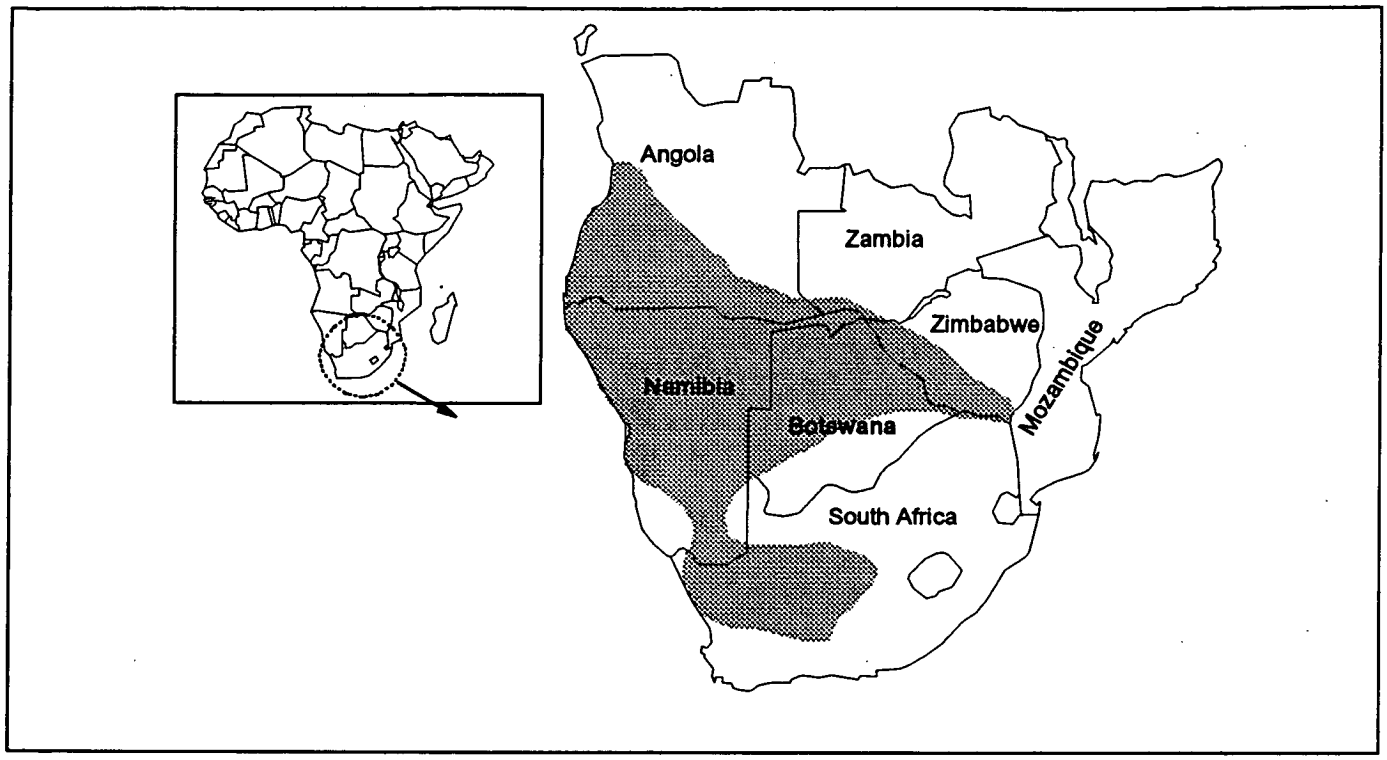


Figure 9.4: Geographical distribution of species containing 10-hydroxyaloin B and related anthrones.

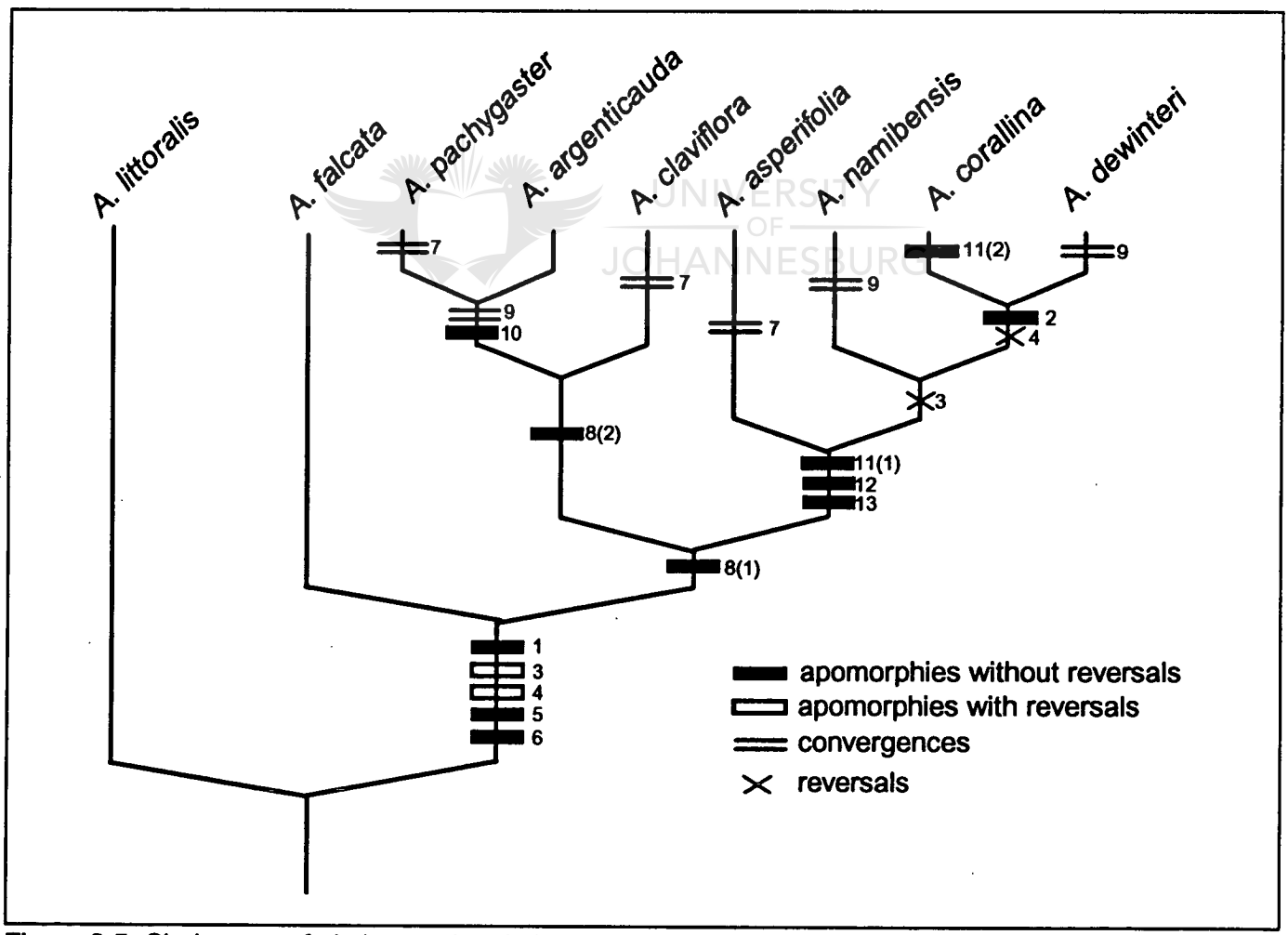


Figure 9.5. Cladogram of phylogenetic relationships in *Aloe* series *Asperifoliae,* based on data in Table 9.3. A single resolved cladogram with 21 steps and consistency index of 71 was obtained, using the 'ie' command of HENNIG 86.

Table 9.3: Characters and polarization of morphological and chemical character states in *Aloe* series *Asperifoliae*.

	Characters and character states												
Species	1	2	3	4	5	6	7	8	9	10	11	12	13
A. argenticauda	1	0	1	1	1	1	0	2	1	1	0	0	0
A. asperifolia	1	0	1	1	1	1	1	1	0	0	1	1	1
A. claviflora	1	0	1	1	1	1	1	2	0	0	0	0	0
A. corallina	1	1	0	0	1	1	0	1	0	0	2	1	1
A. dewinteri	1	1	0	0	1	1	0	1	1	0	1	1	1
A. falcata	1	0	1	1	1	1	0	0	0	0	0	0	0
A. namibensis	1	0	0	1	1	1	0	1	1	0	1	1	1
A. pachygaster	1	0	1	1	1	1	1	2	1	1	0	0	0
A. littoralis	0	0	0	0	0	0	0	0	0	0	0	0	0

1	Caulescence	caulescent = 0; acaulescent or short procumbent stem = 1
2	Stem	erect or procumbent = 0, hanging = 1
3	Habit	solitary = 0; clustered = 1
4	Leaf orientation	decurved = 0; incurved = 1
5	Leaf maculation	spotted = 0; immaculate = 1
6	Leaf texture	smooth = 0; asperous = 1
7	Inflorescence orientation	erect = 0; oblique = 1
8	Inflorescence structure	much-branched panicle = 0; invariably 2- or 3-branched = 1; usually single racemes = 2
9	Bract length	bracts much shorter than the flowers = 0, bracts as long as the flowers = 1
10	Perianth shape	cylindrical = 0; ventricose = 1
11	10-Hydroxyaloin B	present in high quantities = 0; low quantities = 1; absent = 2
12	Littoraloin and B Deacetyllittoraloin	present = 0; absent = 1
13	Derivative of aloin (compound 8 in Table 9.2)	present = 0; absent = 1

are both cliff-hanging species with pendulous stems and both have the leaves decurved in the upper half.

Based on all the data presented, *A. asperifolia* could be viewed as somewhat intermediate between the *Asperifoliae sensu stricto* (as described by Reynolds 1950) and the three species more recently described from the north. It is particularly similar, both chemically and morphologically, to the sympatric *A. namibensis* . The cladogram supports the notion that the *Asperifoliae* developed from a geographically widespread basal species (*A. littoralis*), with subsequent adaptive radiation from south to north. Note the remarkable correlation between the sequence of branching in the cladogram, and the geographical replacement of species from south to north.

A rigorous comparison of morphological and chemical characters have resulted in a new and improved understanding of natural affinities within the series *Asperifoliae* and related species. The leaf exudate chemistry is relatively conservative and shows that the circumscription of the series should be modified to exclude *A. viridiflora* but to include *A. littoralis.*

A. viridiflora was clearly misplaced and should be grouped with *A. hereroensis*. These two species are morphologically and chemically very similar (both produce homonataloin) and lack the defining synapomorphies of the *Asperifoliae*.

The inclusion of *A. littoralis* would result in a chemically uniform group and would be consistent with our hypothesis that the *Asperifoliae* represents a southern, drought-adapted clade of tropical origin, with *A. littoralis* as the basal species. Adaptive radiation and allopatric speciation seems to have occurred in a northerly direction along the dry western parts of southern Africa.

Figure 9.6: Representatives of the 10-hydroxyaloin B containing species. ⇨

Photo: Aloe 19 (2) 1982

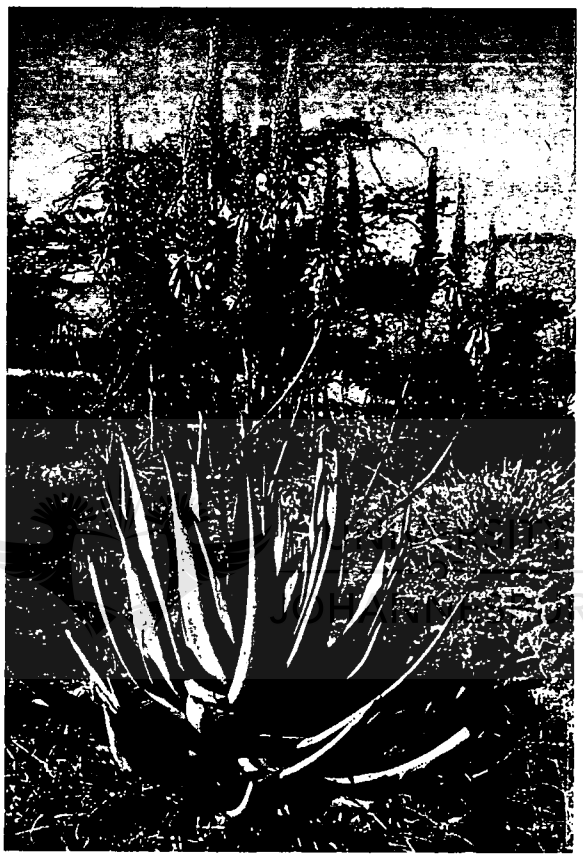
Aloe claviflora

Photo: van Wyk & Smith 1996

Aloe falcata

Photo: van Wyk & Smith 1996

Aloe littoralis



Chapter 10

The chemotaxonomic value of homonataloside B

CHAPTER 10

THE CHEMOTAXONOMIC VALUE OF HOMONATALOSIDE B

The unique anthrone, homonataloside B, the only diglucoside anthrone known from *Aloe*, was detected in 14 species. This compound was isolated from *A. lutescens* (van Heerden *et al.* 1997) and with the exception of a single species it is always associated with the homonataloin isomers. The presence of this compound illustrates how the chemical patterns encourage a reinvestigation of morphological similarities, often with convincing support for the chemical similarities between species. The distribution of the homonataloside B producing species is in agreement with other chemogeographical patterns that are repeated several times in this study i.e. a group of tropical origin with drought adapted species in the southern parts of Africa. This chapter shows the taxonomic distribution of the homonataloside B producing species, followed by an evaluation of the morphology and concludes with suggestions on relationships as indicated by chemical and morphological characters.

Table 10.1: Taxa, voucher details and distribution of species containing homonataloside B.

Species	Voucher	Distribution
A. abyssicola	NBI 15813	South Yemen
A. amicorum	LEN 3217	Kenya
A. bargalensis	NBI 16949	N Somalia
A. breviscapa	NBI 17034	NBI 17034
A. citrina	ex hort P. Favell	Somalia, Ethiopia & Kenya
A. cryptopoda	WE 8 & ex hort NBI	SA, Botswana, Zimbabwe, Malawi & Mozambique
A. dhufarensis	RBG, Kew 409-77	Oman
A. erensii	RBG, Kew 29558	Sudan & Kenya
A. krapohliana	Lavranos 29442	South Africa
A. lutescens	JBG 855332 & Kingskloof	South Africa
A. mendesii	NBI 11992	Angola
A. molederana	NBI 11194	N Somalia
A. tomentosa	RBG, Kew 305-70-02870 & NBI 21758	Yemen & Somalia
A. wickensii	ex hort NBG & JBG 855336	South Africa

Aloe cryptopoda, a species containing homonataloside B (Photo: Ben-Erik van Wyk).

Taxonomic arrangement and affinities between homonataloside B-containing species as represented in Figure 10.1.

Visual assessment of the distribution of homonataloside B superimposed on the present classification is erratic and not confined to any infrageneric groups using the system of Reynolds (1950 & 1966). This could partly be ascribed to the fact that many species containing this unique dianthrone was described after the publication of Reynolds (1966) hence they have not been 'taxonomically arranged'. The taxonomic distribution and affinities between the species will be discussed starting with the *Latebracteatae* group and moving in an anticlockwise direction (Fig. 10.1). All three the species placed in series *Latebracteatae* accumulate the characteristic anthrone. It has been debated strongly in the past if these taxa should enjoy species status as the distinction between the taxa seems to be very vague considering the clinal geographical variation (Bullock 1974 & Kamstra 1975). In his monograph on the tropical aloes Reynolds (1966) creates a Group 11 (Series *Latebracteatae pro parte*). Two species, *A. macrosiphon* and *A. compacta* which are included in this group were analysed. They were found to be virtually identical in leaf exudate composition when compared to one another yet they produced a completely different exudate profile compared to that of the *A. lutescens* - *A. wickensii* complex (Reynolds 1950).

Aloe krapohliana is placed together with *A. humilis* and *A. melanacantha* in series *Echinatae*. All three species in this group have very different chemical profiles. *Aloe krapohliana* shows a leaf exudate composition virtually identical to that of *A. lutescens* with which it also shares the presence of peculiar transverse bands which are often found on the leaves of these two species (see Figure 10.6). *Aloe humilis* is a flavonoid producing species (Chapter 12) while *A. melanacantha* accumulates aloeresin E and F (Chapter 11).

In his species description of *Aloe bargalensis* (Lavranos 1973) does not suggest any taxonomic relationships. He regards the leaf character to be unique and characteristic of this Somalian species. *Aloe mendesii* is a pendent species, hence its placement by Reynolds (1966) in Group 10 which houses all the pendent to semi-pendent species. Reynolds suggests the closest ally of this species to be *A. veseyi* from Zambia, the leaf exudate of the latter species is very different from that of *A. mendesii*. *Aloe breviscapa* occupies a position in Group 16 (Reynolds 1966), a group containing plants with 'compact rosettes'. Reynolds includes comments, that based on habit and growth characters this species resembles *A. tomentosa*. The latter species also contains homonataloside B, but is placed in Group 9 with all the aloes having a pubescent to tomentose perianth. Lavranos (1967) hints on a resemblance of the

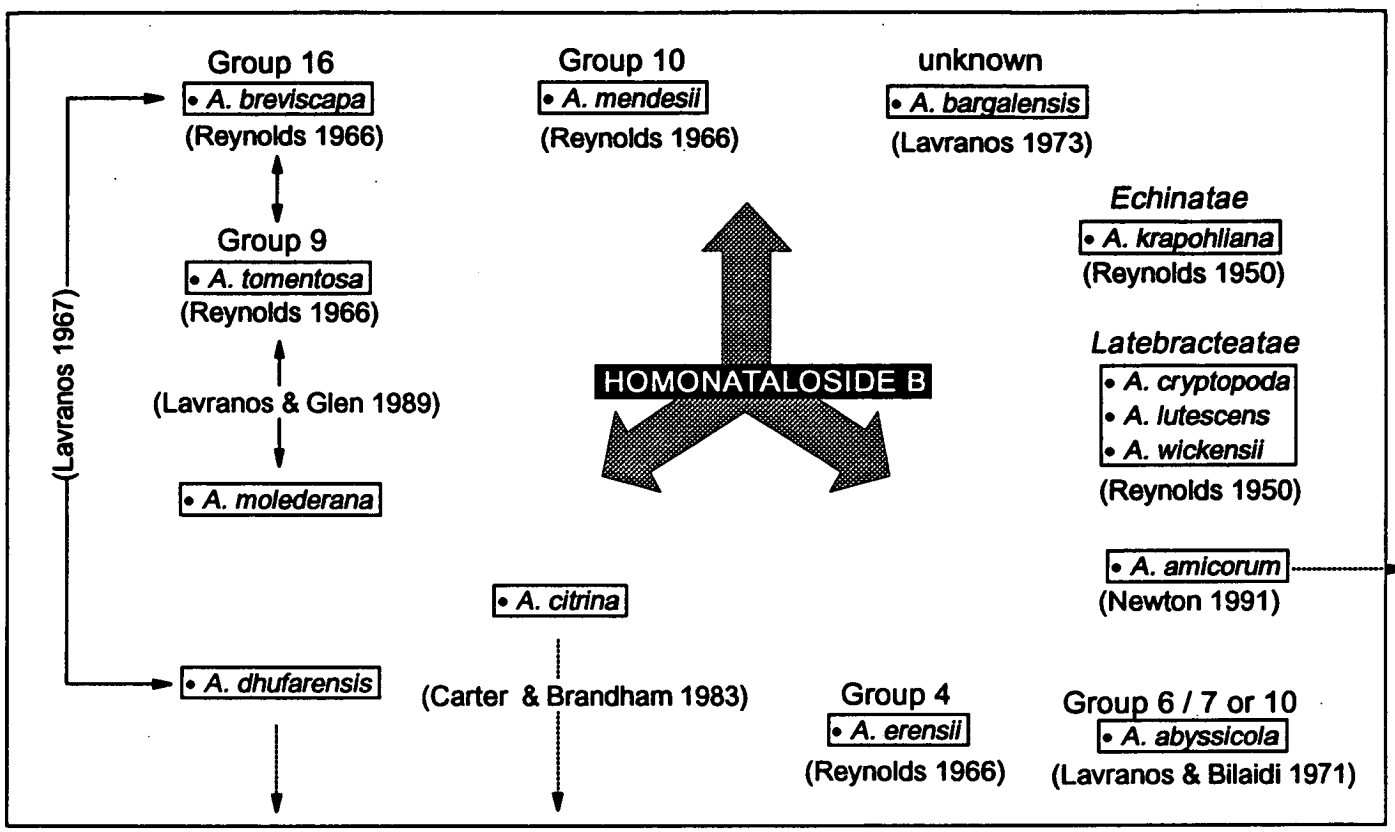


Figure 10.1: Taxonomic distribution and affinities of the homonataloside-containing species.

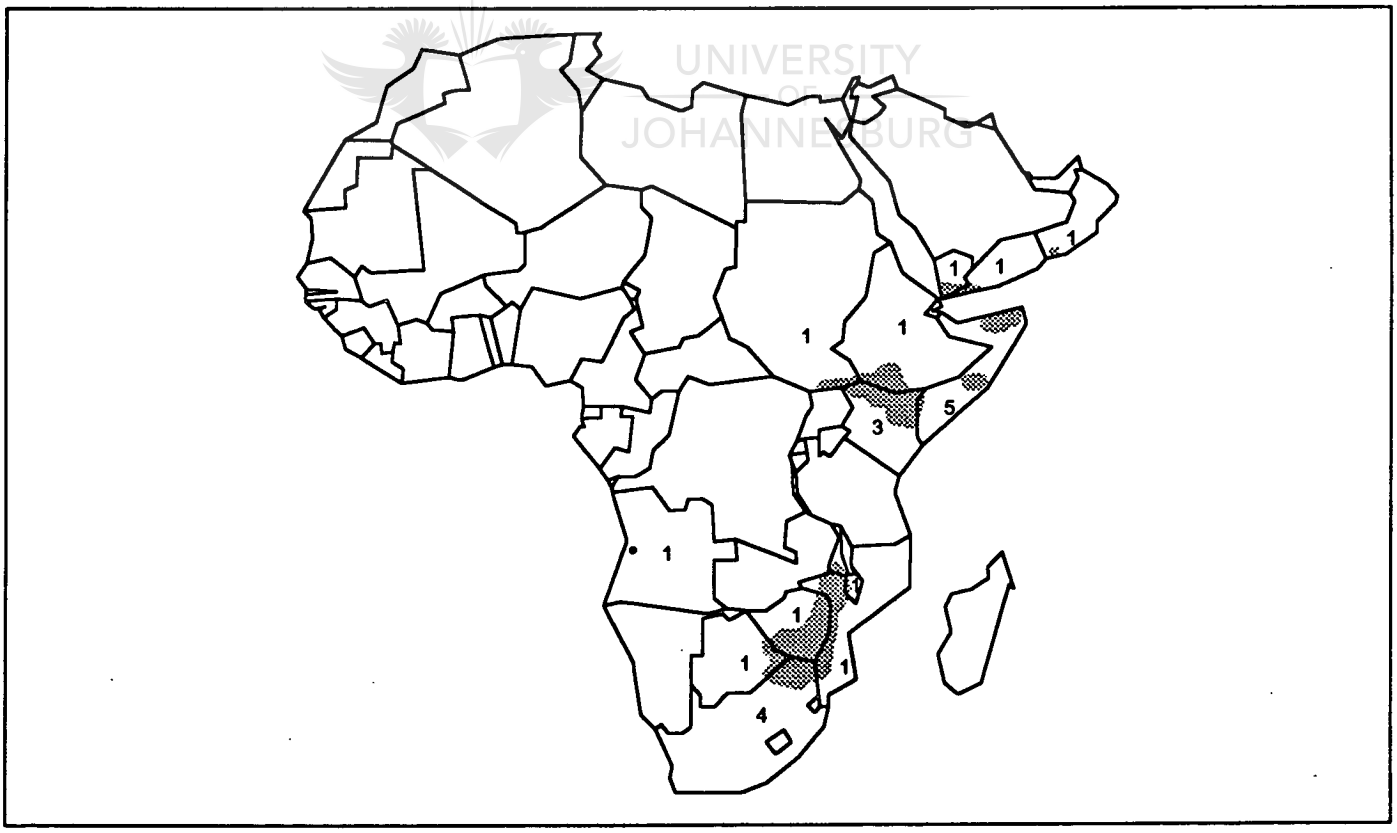


Figure 10.5: Geographical distribution of species containing homonataloside B. The number in each country represent the total number of species with the characteristic chemical compound.

floral characters between *A. dhufarensis* and *A. breviscapa*. He also suggests a possible relationship between *A. dhufarensis* and *A. ukambensis*, the latter species is a plicataloside-accumulating species which places it in the chemical group discussed in Chapter 13. The Somalian species, *A. molederana* is suggested by Lavranos & Glen (1989) to be distantly related to another homonataloside containing species, *A. tomentosa*. This taxonomic relationship is based on the hairy perianth which is also characteristic of *A. citrina*. The latter species was described by Carter & Brandham (1983) suggesting that it is closely allied to *A. trichosantha*, a relationship based on the pubescent perianth. *Aloe erensii*, with the striped flowers are placed in group 4 together with all other species of which the perianth is distinctly or obscurely striped. Most members of Group 4 produce an exudate profile which has placed them in chemical group 1 (Chapter 5). *Aloe abyssicola*, another pendent species from Yemen was described by Lavranos & Bilaidi (1971) with the comment ..."we find it difficult to assign precise affinities to *A. abyssicola* as indeed none are obvious." The authors do however suggest that this species could find a place in Group 10 (Reynolds 1966) using the pendent habit as diagnostic character. Newton (1991) described another pendent species, *A. amicorum* from Mount Kulal in Kenya with comments that this species could be related to *A. inermis*. This comment is based on the inflorescence and flower characters which is described as '...quite distinct from other known pendulous species...' In summary, assessing Figure 10.1 it is obvious that the distribution of this compound is taxonomically diverse. Being the only dianthrone glucoside known in *Aloe* it seems necessary to search for some measure of taxonomic coherence between the leaf exudate chemistry and morphology before simply dismissing the occurrence of this unique anthrone as a chemotaxonomic coincidence.

The morphological characters are summarised for each species in Table 10.2 and briefly discussed below.

Habit characters (caulescence, branching and orientation):
A wide range of habit characters are represented in this morphologically heterogenous group. The three pendent species (*A. abyssicola, A. amicorum* and *A. mendesii*) usually hang from rock faces. In the case of *A. amicorum* the stem is very long while the other two species produce much shorter stems. None of the species in this group produce tall, erect stems with the plants occurring as single individuals. Some of the species occur in groups, while *A. bargalensis* and rarely *A. citrina* form dense groups as a result of suckering.

Table 10.2: Salient morphological features of the homonataloside B producing species.

species	caulescence	branching	stem orientation	leaf orientation	texture	thorns (mm)	maculation
A. abyssicola	shortly caulescent	solitary	pendent	-	smooth	1	immaculate
A. amicorum	caulescent (1 m)	grouped	pendent	erect / spreading	rough	1	mostly immaculate
A. bargalensis	acaulescent or shortly caulescent	grouped (suckering)	erect	suberect	furrowed	rigid, 1 -2	striated / irregularly spotted
A. breviscapa	shortly caulescent	grouped	decumbent	erect / incurved	smooth	entire or 1 - 2	immaculate
A. citrina	acaulescent	solitary or grouped	-	erect	smooth	small, 1 - 2	copiously spotted
A. cryptopoda	acaulescent	usually solitary	erect	erect	smooth	pungent, 2	immaculate
A. dhufarensis	acaulescent	solitary	-	erect / incurved	smooth / soft	margin entire	immaculate
A. erensii	acaulescent	solitary	-	erect / incurved	smooth	small, 1 - 5	striate / spotted
A. krapohliana	mostly acaulescent	solitary	-	arcuate-erect	smooth	small	transverse bands
A. lutescens	acaulescent	solitary	decumbent	erect	smooth	deltoid, 2	immaculate / often with transverse bands
A. mendesii	caulescent (1 m)	?	pendent	erect	smooth	blunt, 1 - 2	lineate
A. molederana	shortly caulescent	grouped	decumbent	suberect	smooth	margin entire	immaculate
A. tomentosa	shortly caulescent	grouped	decumbent	erect	smooth	blunt / entire	immaculate
A. wickensii	mostly acaulescent	solitary	-	erect / incurved	smooth	pungent 2	immaculate

Table 10.2 cont./..

Table 10.2 cont..

Species	inflorescence orientation	inflorescence branching	raceme shape	bract size	pedicel size	perianth shape	flower orientation
A. abyssicola	erect / terminal recurved	simple	laxly cylindrical	7 - 8 x 3	8 - 9	cylindrical	?
A. amicorum	erect	6 branched	laxly secund	3.5 x 2.5	8	cylindrical / ovary inflated	secund
A. bargalensis	erect	simple	laxly cylindrical	15 x 5	5 - 7	cylindric	pendulous
A. breviscapa	erect	branched panicle	cylindric	6 x 3	10 - 14	cylindric-trigonous (bloom)	nutant
A. citrina	erect	2-6 branched	cylindric	12 x 4	10	cylindric (pubescent)	erect / pendent
A. cryptopoda	erect	branched panicle	conical-cylindrical	20 x 12	15 - 20	cylindric-trigonous	pendulous
A. dhufarensis	erect	simple, 1 - 2 br.	cylindric	12	12 - 15	cylindric-trigonous	pendulous
A. erensii	erect	6 - 7 branched	cylindric	6	8 - 9	cylindrical (bloom)	sub-secund
A. krapohliana	erect	mostly simple	sub-dense	15 x 5	20	cylindric	pendulous
A. lutescens	erect	3 branched	cylindric	15 x 15	15	cylindric-trigonous (curved)	erect / pendulous
A. mendesii	arcuate-ascending	3 - 4 branched	cylindric	12 x 5	18 - 20	cylindric / slightly ventricose	sub-pendulous
A. molederana	erect	4 branched	cylindric	7 - 8 x 3 - 4	6 - 9	cylindric-trigonous (pubescent)	sub-pendulous
A. tomentosa	erect	branched	cylindric	7 x 4	6 - 9	cylindric-trigonous (pubescent)	nutant
A. wickensii	erect	branched	cylindric	20 x 16	20 x 25	cylindric	pendulous

Leaf characters (orientation, texture, thorns and maculation):

Almost all species bear their leaves in an erect or spreading manner. In some species the leaves are somewhat incurved (e.g. *A. breviscapa*). No species produces leaves which are strongly deflexed and canaliculate. For most species the leaves are smooth with the exception of *A. amicorum* where the leaves have a rough texture and *A. bargalensis* in which the leaves are characteristically furrowed. With the exception of the *Latebracteatae*-group, these aloes generally lack the prominent large pungent thorns characteristic for many species of *Aloe*. In some species the leaf margin is completely entire (e.g. *A. molederana*, *A. tomentosa*, *A. dhufarensis* and *A. breviscapa*). The leaves are mostly immaculate except for *A. erensii* and *A. citrina* where the leaves are copiously spotted.

Inflorescence and flower characters :

In all species the peduncle is erect except for the pendent species where it is arcuate-ascending. The inflorescence branching varies from simple (e.g. *A bargalensis*) to much branched (e.g. *A. erensii*). In most species the raceme is cylindrical. *Aloe amicorum* and to a lesser extent, *A. erensii*, are exceptions as the flowers are secundly disposed. The bracts and pedicels of these species are generally small except for the species pertaining to series *Latebracteatae* (including *A. krapohliana*) where the bracts and pedicels are larger than the average for this group of species. The flowers vary from being glabrous (e.g. series *Latebracteatae*) to those where they perianth is covered in a conspicuous bloom (e.g. *A. erensii* and *A. breviscapa*) to those with a prominent pubescent perianth surface (e.g. *A. tomentosa*, *A. citrina* and *A. molederana*).

Leaf exudate chemistry:

The HPLC profiles of a selection of species accumulating homonataloside B are shown in Figure 10.2 with the exudate compounds tabulated in Table 10.3. Homonataloside B, 3'-*O*-coumaroylaloesin and 3',6'-di-*O*-coumaroylaloesin were isolated and described from *A. lutescens* (Van Heerden *et al.* 1997). Initially 3'-*O*-coumaroylaloesin was incorrectly designated as aloeresin A, but NMR data showed the coumaroyl ester to be attached to the 3' position of the glucose and not to the 2' position as reported for aloeresin A. The UV spectra and the R_t of these two compounds, as expected, are virtually identical. This was only established after 3',6'-di-*O*-coumaroylaloesin was isolated from *Aloe lutescens* (which was designated as an 'unidentified chromone' during initial screening). It was thought to be unlikely that the mono-

glucoside would have a coumaroyl group attached to the 2' position of the glucose.
Aloe amicorum and *A. dhufarensis* also show the presence of aloeresin A (based on R_t and UV absorbance). It could be speculated that this could well be 3'-*O*-coumaroylaloesin, but as 3',6'-di-*O*-coumaroylaloesin is not present in these two species it would be at least provisionally correct to identify this compound as aloeresin A. All species in this group, except for *A. molederana* contain the anthrone isomers homonataloin A and B.

Table 10.3: Distribution of major leaf exudate compounds co-occurring with homonataloside B.

	1	2	3	4	5	6	7	8	9
A. abyssicola			■					■	
A. amicorum			■	■		■		■	
A. bargalensis			■			■		■	
A. breviscapa	■	■	■			■		■	
A. citrina	■	■	■			■		■	
A. cryptopoda	■		■		■			■	■
A. dhufarensis	■		■	■				■	
A. erensii		■	■			■		■	
A. krapohliana	■		■					■	
A. lutescens	■		■		■			■	■
A. mendesii	■		■				■	■	
A. molederana	■	■	■			■	■		
A. tomentosa	■	■	■			■		■	
A. wickensii	■		■		■			■	■

1. Aloesin
2. 7-*O*-methylaloesin
3. Homonataloside B
4. Aloeresin A
5. 3'-*O*-coumaroylaloesin
6. Aloeresin D
7. Aloin A & B
8. Homonataloin A & B
9. 3',6'-di-*O*-coumaroylaloesin

The rare exception of aloin co-occurring with homonataloin is found in *A. mendesii*. Homonataloside B, the defining compound for this group is the only diglucoside anthrone reported from *Aloe*, a chemical peculiarity implying an obvious taxonomic relevance.
Species in the *Latebracteatae*-group are closely related and all species in this group produce the same leaf exudate profile. The anomalous *A. krapohliana* which is obviously is misplaced in *Aloe* series *Echinatae* shows an chemotaxonomic affinity with this group. The chemical similarity is enhanced on the morphological level by the characteristic transverse bands on the leaves of *A. krapohliana* which have also been discovered in *A. lutescens* (See Figure 10.6). No attempt has been made to suggest a taxonomic position for *A. bargalensis* from Somalia. The anomaly of this species suggested by the morphological characters is defied by the chemistry as 13 other species share the same chemistry of which four possible allied species

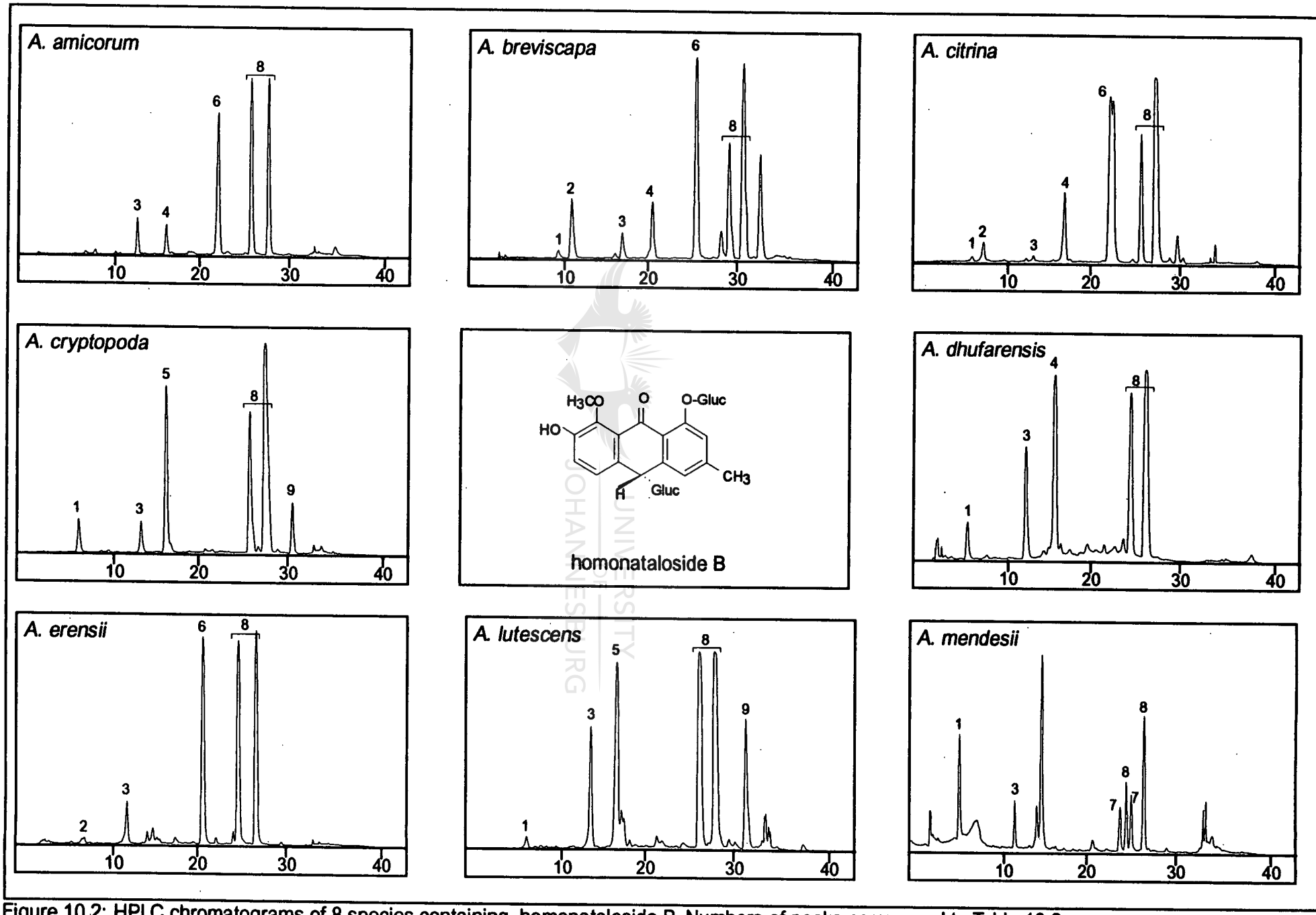


Figure 10.2: HPLC chromatograms of 8 species containing homonataloside B. Numbers of peaks correspond to Table 10.3.
The chemical structure of homonataloside B is shown in the centre block.

occur in Somalia.

Phenetic and cladistic analysis

The phenetic analysis was performed on the data presented in Table 10:4 to produce the dendrogram illustrated in Figure 10.3.

Table 10.4: Morphological (1 - 12) and chemical characters (13 - 15) used in the cluster analyses.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
A. abyssicola	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0
A. amicorum	1	1	1	0	0	0	0	1	0	0	0	1	0	0	0
A. bargalensis	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0
A. breviscapa	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0
A. citrina	0	0	0	0	0	1	0	1	0	0	1	0	0	0	0
A. cryptopoda	0	0	0	0	1	0	0	1	1	1	0	0	1	0	0
A. dhufarensis	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. erensii	0	0	0	0	0	1	0	1	0	0	0	1	0	0	0
A. krapohliana	0	0	0	0	0	0	1	0	0	1	0	0	0	0	0
A. lutescens	0	0	0	0	1	0	1	1	1	1	0	0	1	0	0
A. mendesii	1	1	0	0	0	0	0	1	0	1	0	0	0	0	1
A. molederana	0	0	0	0	0	0	0	1	0	0	1	0	0	1	0
A. tomentosa	0	0	0	0	0	0	0	1	0	0	1	0	0	0	0
A. wickensii	0	0	0	0	1	0	0	1	1	1	0	0	1	0	0

1. caulescence, 2. pendent, 3. leaves rough, 4. leaves furrowed, 5. thorns pungent, 6. leaves copiously spotted, 7. transverse bands on leaves, 8. inflorescence a panicle, 9. bracts large, deltoid, 10. pedicel long, 11. perianth pubescent, 12. flowers secund, 13. 3'-*O*-coumaroylaloesin present, 14 only aloin present, 15. aloin and homonataloin present.

The analysis produced three major clusters. All the pendent species are united in a single cluster A. The three species with a tomentose perianth are grouped in cluster B with *A. breviscapa* and *A. erensii* peripherally associated with this group. The four South African representatives are assembled in cluster C. As mentioned by their respective authors, the affinities of *A. bargalensis* and *A. dhufarensis* are obscure, also here reflected in the phenetic analysis.

A cladistic analysis on the data in Table 10:5 produced the cladogram depicted in Figure 10:4. The widespread *A. trichosantha* is the most likely outgroup species based on the presence of the tomentose perianth. It is here suggested that this group evolved from an ancestor with a hairy perianth. *Aloe molederana*, like *Aloe trichosantha* produces aloin as the major anthrone

while all other species in this group accumulate homonataloin as the major anthrone.

Table 10.5: Morphological (1 - 12) and chemical characters (13 - 16) used in the cladistic analysis (Figure 10.4). Character states and polarisation of characters are indicated below.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
A. trichosantha	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A. abyssicola	1	0	1	1	0	0	1	0	0	0	1	0	0	1	1	1
A. amicorum	1	1	1	1	0	0	0	0	0	0	1	1	0	1	1	1
A. bargalensis	0	1	0	1	0	0	1	1	0	0	1	0	0	1	1	1
A. breviscapa	0	1	0	1	0	0	0	0	0	0	1	0	0	1	1	1
A. citrina	0	0	0	1	1	0	0	0	0	0	0	0	0	1	1	1
A. cryptopoda	0	0	0	0	0	1	0	1	1	1	1	0	1	1	1	1
A. dhufarensis	0	0	0	1	0	0	1	0	0	0	1	0	0	1	1	1
A. erensii	0	0	0	1	1	0	0	0	0	0	1	1	0	1	1	1
A. krapohliana	0	0	0	1	0	1	1	1	0	1	1	0	0	1	1	1
A. lutescens	0	0	0	0	0	1	0	1	1	1	1	0	1	1	1	1
A. mendesii	1	0	1	1	0	0	0	0	0	0	1	0	0	0	1	1
A. molederana	0	1	0	1	0	0	0	0	0	0	0	0	0	0	0	1
A. tomentosa	0	1	0	1	0	0	0	0	0	0	0	0	0	1	1	1
A. wickensii	0	0	0	0	0	1	0	1	1	1	1	0	1	1	1	1

Characters:

1. Stem: acaulescent (or very shortly caulescent) = 0, distinctly caulescent = 1
2. Dispersion of plants in a population: solitary = 0, grouped / clustered = 1
3. Habit: erect = 0, pendent = 1
4. Leaf margin: pungent thorns = 0, margins entire or minutely dentate = 1
5. Leaf maculation: immaculate = 0, distinctly spotted = 1
6. Leaf markings: transverse bands absent = 0, transverse bands present = 1
7. Inflorescence: a panicle = 0, simple = 1
8. Bract length: bracts short = 0, bracts long = 1
9. Bract shape: long and slender = 0, deltoid = 1
10. Pedicel length: pedicel short = 0, pedicel long = 1
11. Perianth surface: tomentose = 0, glabrous = 1
12. Flower orientation on floral axis: symmetrical = 0, secund = 1
13. 3'-coumaroylaloesin: absent = 0, present = 1
14. Aloin: present = 0, absent = 1
15. Homonataloin: absent = 0, present = 1
16. Homonataloside: absent = 0, present = 1

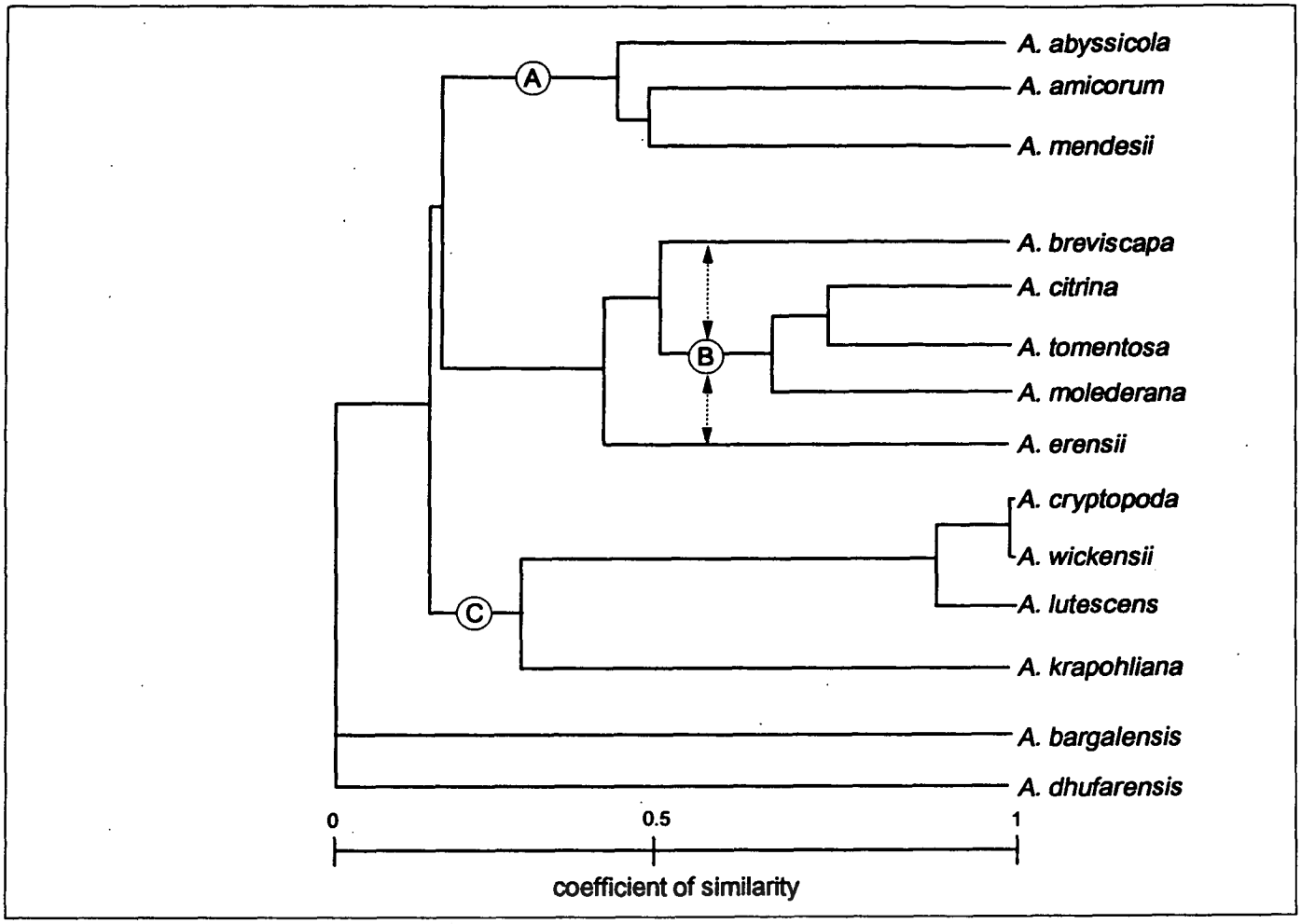


Figure 10.3. Dendrogram constructed from the data in Table 10.4.

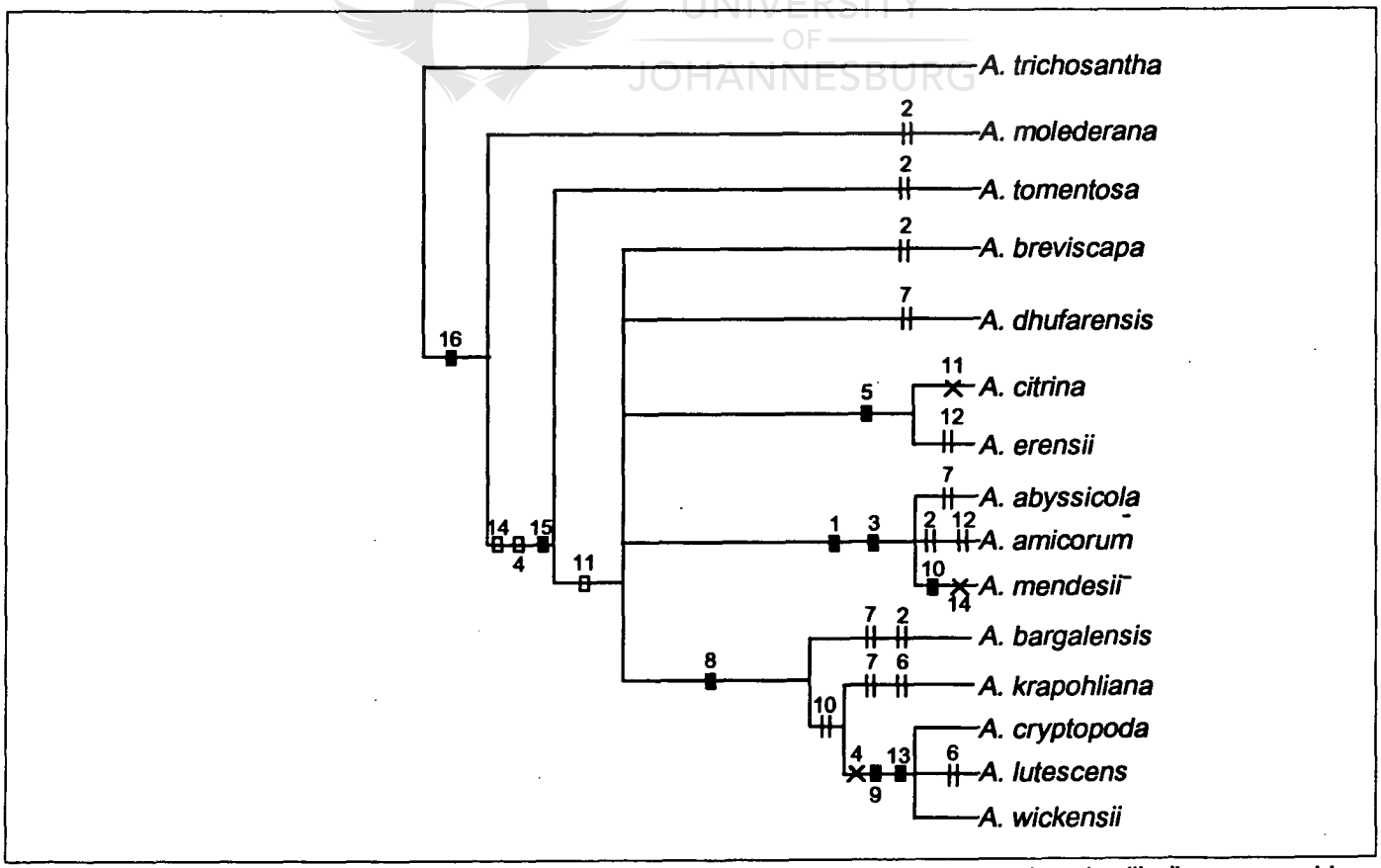


Figure 10.4: Consensus cladogram constructed from the data in Table 10.5 using the "i.e" command in Hennig 86. Steps = 29, ci = 55 and ri = 62.

The presence of aloin together with the tomentose perianth gives *A. molederana* the basal position in the analysis. Considering the data presented in Tables 10.2 and 10.5 one is inclined to predict excessive homeoplasy in any cladistic analysis as none of the salient morphological characters seem to be correlated. The three pendent species united in the cluster analysis are retained as a clade in the cladistic analysis with two correlated habit characters being apomorphies for this group. This study has shown that habit characters are not always reliable taxonomic characters. A more convincing relationship could be presented as all three pendent species are here shown to produce homonataloside B. The four South African species, together with the Somalian *A. bargalensis* represents the most derived lineage. Besides the observation that the cladogram in Figure 10:4 is riddled with homeoplasy it shows some similarities and differences when compared to the phenetic analysis. In the cladistic analysis the species with a tomentose perianth are not united in a single clade. It is here suggested that the three species with a distinct tomentose perianth and the presence of homonataloside B (*A. citrina*, *A. molederana* and *A. tomentosa*) are related. The hairy perianth is only restricted to a small number of species in the genus. It is unlikely that a hairy perianth together with the diglucoside anthrone, homonataloside B, would have evolved independently in these three species. Although this morphologically unique character (hairy perianth) probably only evolved once it would be presumptuous to suggest that all the species (not discussed here) are related. Being guided by the total leaf exudate composition for these species there is reason to believe that some species with a hairy perianth have been involved in hybridization events obscuring relationships. This is also clearly demonstrated in Chapter 16 where the presence of the hybrid compound 8-*O*-methyl-7-hydroxyaloin has been detected in *Aloe pubescens* (the specific epithet indicative of the hairy perianth).

On the topic of hybridization, leaf exudate of one of the species, *A. mendesii* immediately draws attention to caution. It is illustrated in Chapter 16 that the co-occurrence of homonataloin and aloin could be indicative of a previous hybridization event. These two compounds are mutually exclusive as they are probably formed via two different biochemical pathways (see Chapter 6). Hybridizing an aloin-producing species with a homonataloin-producing species would result in a 'species' accumulating both anthrones. The degree of homeoplasy in the analysis (ci 56) further emphasises the evolutionary pattern in *Aloe* ie; hybridization resulting in reticulate evolution rather than divergent speciation.

It is proposed that this group has its origin in north-east Africa (Kenya / Somalia) from where

speciation took place towards the south. The present geographical distribution of these species are shown in Figure 10.5 and is congruent with several biogeographical patterns that have emerged from this study. A disjunct north / south Africa distribution is shown for many other chemical compounds e.g. plicataloside, aloinoside, aloenin and aloeresin E and F. These general patterns have assisted in defining arguments to suggest taxonomic relationships between species of *Aloe* not previously thought to be even remotely related.

Figure 10.6: Representatives of the homonataloside B-producing species of *Aloe*. ⇨

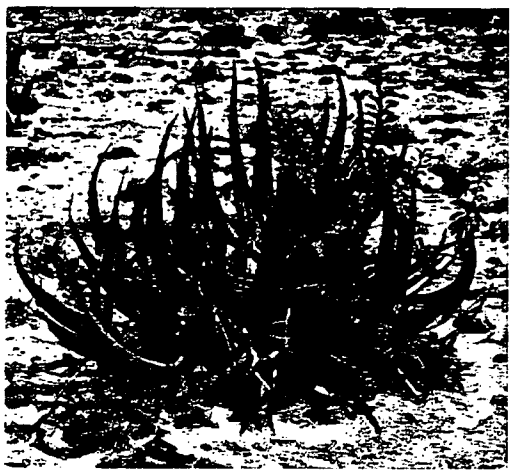


Photo: Reynolds 1966

Aloe breviscapa

Photo: Newton 1991

Aloe amicorum

Photo: van Wyk & Smith 1996

Aloe cryptopoda

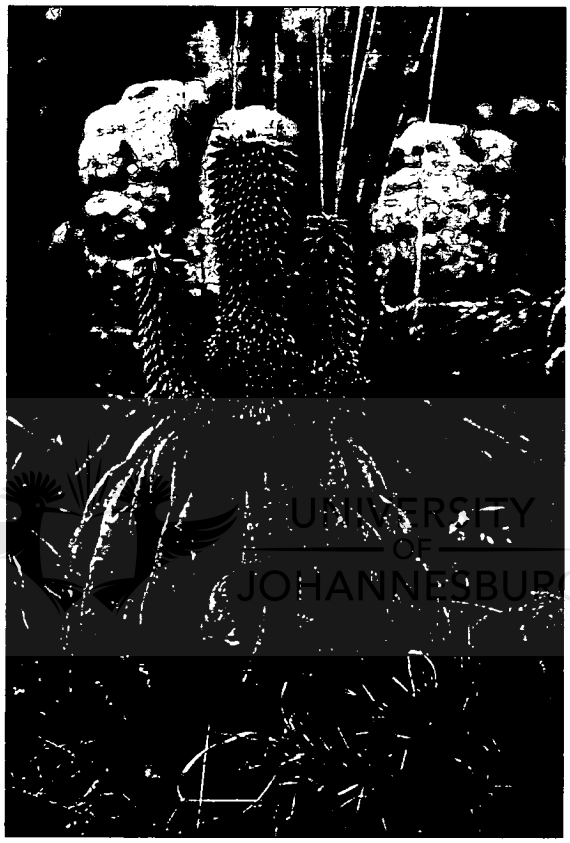
Photo: Reynolds 1966

Aloe tomentosa

Aloe lutescens

Photo: Reynolds 1966

Aloe erensii



Chapter 11

The chemotaxonomic value of the cinnamoyl chromones aloeresin E and F

CHAPTER 11

THE CHEMOTAXONOMIC VALUE OF THE CINNAMOYL CHROMONES ALOERESINS E AND F IN *ALOE*

This study indicated a remarkable quantitative and qualitative similarity in leaf exudate composition between twelve species. This diagnostic leaf exudate profile serves as a "fingerprint", repeated in all the representatives of this group - a combination of homonataloin A and B with either one or both of two recently described cinnamoyl chromones, aloeresin E and F, together with various coumaroyl chromones. A taxonomic assessment of the morphological and chemical data is presented in this chapter. Chemical evidence supports the transfer of *Aloe pearsonii*, previously misplaced in *Aloe* series *Macrifoliae*, to *Aloe* series *Mitriformes*. The other species which display the diagnostic chemical pattern characteristic of the *Mitriformes*-group are *Aloe peglerae*, *A. melanacantha*, *A. erinacea*, *A. angelica* and *A. yavellana*. The last-mentioned species from Ethiopia is another example of the chemogeographical links between the southern and east African species of *Aloe*.

The species belonging to the series *Mitriformes* are characterised by an unique leaf exudate composition which is virtually identically represented in six other species not previously associated with *Aloe* series *Mitriformes*. Aloeresin E and F producing species together with voucher / locality details are presented in Table 11.2 Leaf exudate chemistry in itself is not a unifying taxonomic character but when considered in concordance with morphological characters it leads to a more convincing taxonomic congruence. References to literature and results from a broader study on *Aloe* indicate that constructing a natural phylogeny for *Aloe* is a daunting challenge as there seems to be almost no correlation between morphological characters. Furthermore it is believed that hybridization has played an important role in the evolution of *Aloe*, obscuring the taxonomic relationships between most species. The leaf and root chemistry seem to be conservative characters of considerable taxonomic value, as is clearly demonstrated in the group discussed here.

Morphological characters

The morphological characters of this group is detailed in Reynolds (1950); we therefore only provide a rigorous summary and comparison of the most reliable diagnostic characters in Table 11.1. With regards to habit characters the species represent almost the entire range of character variation present in *Aloe*. Plants are either distinctly caulescent or acaulescent.

Aloe peglerae, the species from which aloeresin E and F was isolated (Photo: Ben-Erik van Wyk).

Table 11.1: Salient macromorphological characters for aloeresin E and F accumulating species.

species	caulescence	branching	stem orientation	leaf orientation	texture	thorns (mm)	maculation
A. angelica	distinctly caulescent	usually simple	erect	recurved	smooth	pungent 2 - 3	immaculate
A. arenicola	caulescent	grouped	procumbent	erect	smooth	small 0.5	distinctly spotted
A. comptonii	caulescent	grouped	procumbent	erect / decurved	smooth	blunt 2 - 3	immaculate
A. dabenorisana	shortly caulescent	solitary or grouped	pendent	recurved	smooth	small 2 x 1	obscurely lineate
A. distans	caulescent	grouped	procumbent	erect / spreading	smooth	3 - 4 deltoid	spotted
A. erinacea	mostly acaulescent	solitary / grouped	erect	erect / spreading	smooth	5 - 9 (also on keel)	immaculate
A. meyeri	caulescent	solitary / grouped	pendent	erect / spreading	smooth	small 2	striate
A. melanacantha	shortly caulescent	grouped	erect	erect / incurved	smooth	10 (also on keel)	immaculate
A. mitriformis	caulescent	grouped	procumbent	erect / slightly incurved	smooth	4 - 6 deltoid	immaculate
A. pearsonii	caulescent	grouped	erect	deflexed	smooth	1 - 2	obscurely lineate
A. peglerae	acaulescent	mostly solitary	-	incurved	smooth	6 (also on keel)	immaculate
A. yavellana	distinctly caulescent	grouped	procumbent	spreading	smooth	2 - 3	obscurely spotted

Table 11.1: Cont./...

Table 11.1: Cont.:

species	inflorescence orientation	inflorescence branching	raceme shape	bract size	pedicel size	perianth shape
A. angelica	erect	branched panicle	capitate	8 - 10	25	cylindric-trigonous-ventricose
A. arenicola	erect	simple / 1 - 2 branched	capitate	10 x 3 - 4	35	cylindric and slightly curved
A. comptonii	erect	branched panicle	capitate	7 x 3	30 - 35	cylindric and slightly curved
A. dabenorisana	pendulous-recurved	2 - 4 branched	conical	7 x 2	20 - 28	cylindrical-subclavate-curved
A. distans	erect	3 - 4 branched	capitate	8 x 5	30 -40	cylindric and slightly curved
A. erinacea	erect	simple	cylindrical	25 - 27 x 4.5	18 - 19	cylindrical-subventricose
A. meyeri	pendulous-recurved	mostly simple	capitate	3 x 5	20	cylindrical-subclavate-curved
A. melanacantha	erect	simple	cylindrical	25 x 7	15	cylindric and slightly curved
A. mitriformis	erect	2 - 5 branched	capitate	10 x 5 - 6	40 - 45	cylindric and slightly curved
A. pearsonii	erect	2 - 3 branched	cylindric	6 - 6 x 3	20	cylindric
A. peglerae	erect	simple	cylindric	16 x 7	2 - 4	cylindric-ventricose
A. yavellana	erect	branched	capitate	3 x 2	10	cylindric

When present, the stem usually develops a characteristic sprawling habit as in the case of *A. mitriformis* where the procumbent stem could reach up to 1 m, with only the apical part being foliate. In many species the stem initially remains erect, but topples over with an increase in length (e.g. *A. yavellana*). *Aloe erinacea*, *A. melanacantha*, and *A. peglerae* are acaulescent or very shortly caulescent. The species are equally variable in leaf characters. The leaf orientation varies from erect and spreading (e.g *A. erinacea*) to incurved (e.g. *A. peglerae*) or decurved (e.g. *A. angelica)*. In all species the leaf surface is smooth in texture and could be immaculate, spotted or striate. The marginal thorns are pale-coloured and blunt in most species of the *Mitriformes*-group while they are black and distinctly pungent in *A. erinacea*, *A. melanacantha* and *A. peglerae*. These three species also produce prominent black pungent surface thorns along the keel of the leaf. The inflorescence characters prove to be reliable and diagnostic within this group. In all species the inflorescence is erect except in the two closely related pendent species, *A. dabenorisana* and *A. meyeri* where it is pendulous and recurved. Most species pertaining to the *Mitriformes* group produce a branched panicle with capitate racemes. The other species in this group produce a single inflorescence with a cylindrical raceme. The bracts of most taxa are relatively short with the exception of *A. peglerae, A. erinacea* and *A. melanacantha* which have much longer bracts. Most members of the *Mitriformes* group are also characterised by the flowers with exceptionally long pedicels (± 30 mm) while the pedicel is extremely short in the case of *A. peglerae*. The perianth is mostly cylindrical and slightly curved, but subclavate in *A. meyeri* and *A. dabenorisana.*

Taxonomic affinities

The present taxonomic arrangement and affinities between the taxa are diagrammatically represented in Figure 11.1. In his taxonomic treatment of the genus *Aloe*, Reynolds (1950) delineates the series *Mitriformes* to include *A. mitriformis*, *A. arenicola*, *A. comptonii* and *A. distans*. Since the work of Reynolds two additions have been made: *A. meyeri* (Van Jaarsveld, 1981) and *A. dabenorisana* (Van Jaarsveld, 1982). Most members of this group are characterised by a procumbent stem with the apical section being foliate. The pedicel is long and slender being longer or as long as the perianth. The distribution pattern of the species generally agree with the winter rainfall region in South Africa (Figure 11.2). With the exception of *A. arenicola* which is an inhabitant of sandy places, all the other species grow on rocky areas or rock faces. The remarkable morphological similarity between the species has led to ill defined taxa in the *Mitriformes* group and raised the question as to whether it is sensible to recognise different species which seem to be mere local variations of geographical variable

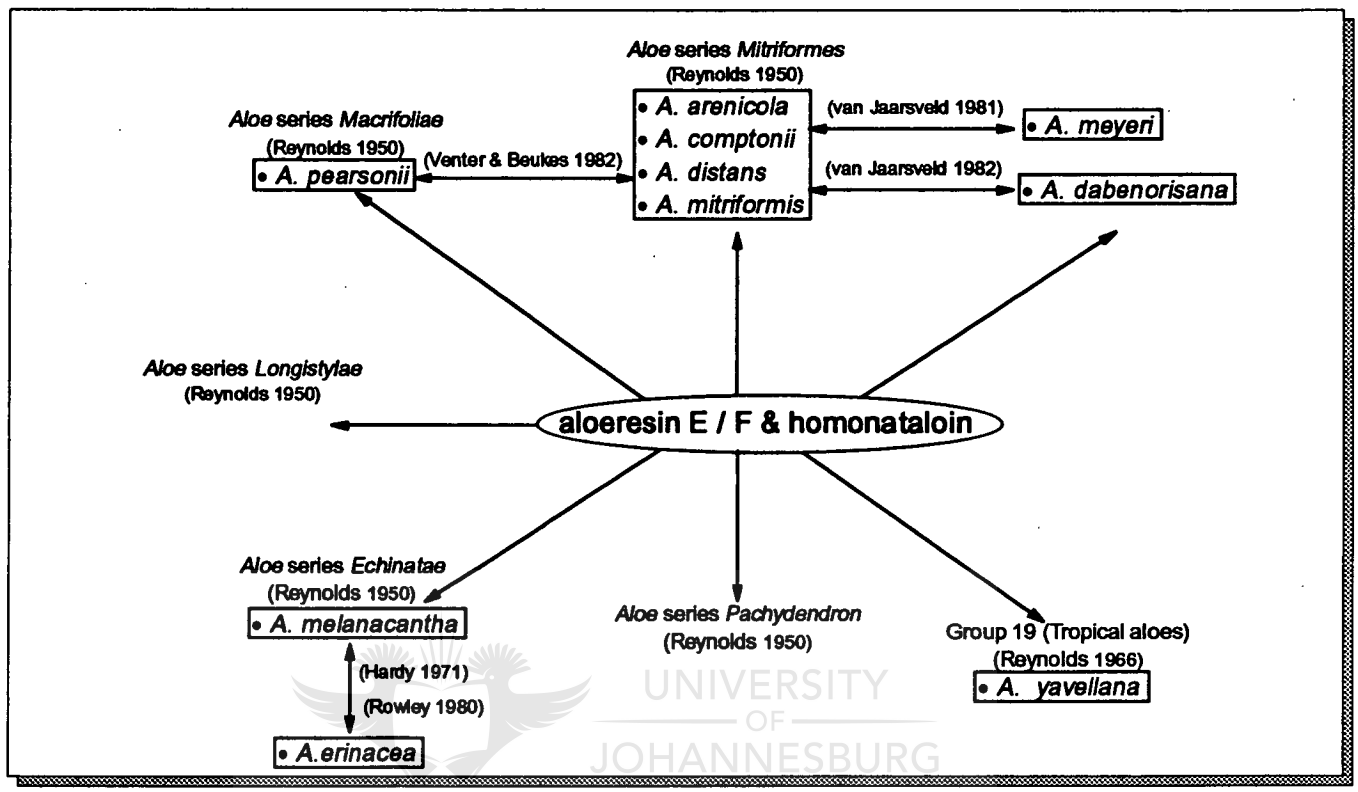


Figure 11.1: Taxonomic distribution and affinities between species containing aloeresin E and / or F, usually in the presence of homonataloin.

and widespread taxa. The species of the *Mitriformes* group have been studied extensively, with various authors debating the specific status of the taxa defined by Reynolds (1950). *Aloe distans* and *Aloe mitriformis* for example are distinguished only on the basis that *A. mitriformis* is a smaller plant with smaller flowers and pedicels when compared to *A. distans*. A detailed study of these two species (Marais, 1980) concluded that *A. mitriformis* varies with regards to quantitative characters only and found the "typical" *A. distans* to be more closely related to *A. mitriformis* than are certain of the proposed varieties of *A. mitriformis*. The morphological study by Marais (1980) clearly shows that the characters suggested to distinguish between *A. comptonii*, *A. mitriformis* and *A. distans* are ambiguous. *Aloe distans* falls well within the range of morphological variation described for *A. mitriformis* and/or *A. comptonii*. *Aloe arenicola* however, is distinguished from its allies by the leaves which are copiously spotted. The two more recently discovered species *A. meyeri* and *A. dabenorisana*, are both pendulous in habit, hanging from vertical rock faces and differ from other species also in floral character (they both have a subclavate perianth). In his description of *A. dabenorisana*, Van Jaarsveld (1982) suggests this species to be morphologically intermediate between the series *Mitriformes* and *Macrifoliae*. In terms of morphological characters this statement seems evident as *A. dabenorisana* with its conical raceme bears subclavate flowers not typical of the *Mitriformes* group.

A. pearsonii, erroneously placed in the series *Macrifoliae* by Reynolds (1950), bears deflexed leaves which are obscurely lineate. *Aloe dabenorisana* is the only other species in which the leaves are deflexed. Although not explicitly stated, it can be assumed that Reynolds also thought the *Macrifoliae* to be phylogenetically allied to the series *Mitriformes*, which is suggested in his taxonomic placement of *A. pearsonii*. Although *A. pearsonii* shares morphological characters with the rest of the series *Macrifoliae* (slender erect stems and conical racemes), the morphological characters conflicting with the status quo in the *Mitriformes* group does not necessarily warrant its omission from this group. The chemical evidence presented here gives convincing support for the transfer of *A. pearsonii* to the series *Mitriformes*, as suggested by Venter & Beukes (1982) . It is also interesting to note that both the series *Mitriformes* and *Macrifoliae* lack the diagnostic 1-methyl-8-hydroxyanthraquinone pathway characteristic of the root chemistry of the genus *Aloe* (Van Wyk *et al.* 1995). The sporadic absence of this pathway in various infrageneric groups is however speculated to be due to secondary loss and it would be advisable to investigate additional characters to confirm or dismiss the possible taxonomic alliance between these groups. The leaf exudate pattern, however, unambiguously shows that species belonging to *Aloe* series *Macrifoliae* have a

different leaf chemistry. Firstly, the members of the *Macrifoliae* produce little of no exudate and the leaf extracts contain flavonoids such as isovitexin rather than the more usual anthrone and chromone derivatives (Chapter 12 & Viljoen *et al.* 1998).

More interesting, however, are the five species which have not previously been associated with the taxa discussed above. *Aloe peglerae* is placed in *Aloe* series *Longistylae,* together with *A. longistyla* and *A. broomii.* The leaf exudate of the latter species suggests it to be of hybrid origin between species in *Aloe* series *Anguialoe* and series *Purpurascentes* (Chapter 8). The morphological anomaly of *Aloe longistyla* is supported on the chemical level as it produces a leaf exudate different from all other species of *Aloe.* The latter aside, as we rather which to emphasise the chemical similarity between the coveted Magaliesberg endemic, *A. peglerae* with other members included in this group, *A. erinacea* and *A. melanacantha.* Table 11.2 shows the occurrence of leaf exudate compounds and Figure 11.3 illustrates the HPLC profiles of various representatives of this group. *Aloe melanacantha* is placed in series *Echinatae* together with *A. krapohliana* and *A. humilis. Aloe krapohliana* is chemically identical to *Aloe* series *Latebracteatae* (Chapter 10) while *A. humilis* is a flavonoid-producing species (Chapter 12). *Aloe erinacea* was described by Hardy (1971) with comments drawing on a relationship with *A. melanacantha.* Rowley (1980) believes that *A. erinacea* is merely a geographical form of *A. melanacantha* while Rossouw (1980) demonstrates that the distinction in floral characters between the two species warrants specific status for these two taxa. No attempts have yet been made to suggest any taxonomic alignment between these two species and other species of *Aloe.* Within this group, *A. peglerae* is the closest morphological relative, as it also has dark pungent thorns on the leaf margin and keel, a single inflorescence, large bracts and an acaulescent to very shortly caulescent habit.

Aloe angelica is placed in *Aloe* section *Pachydendron* (Reynolds 1950) with the following comments by the author ..."*A. angelica* does not fit well into any series or section. It is a very distinctive species with its much branched inflorescence of bicoloured capitate racemes." The branched panicle and capitate racemes are shared with members of the *Mitriformes* (e.g. *A mitriformis*). With regards to its habitat preferences for the dense bushveld of the Soutpansberg, it may be speculated that the development of a tall, erect stem could be a survival strategy to project above this dense bush.

Aloe yavellana represents an equally interesting situation. This species occupies a taxonomic position in Group 19 (Reynolds, 1966). It is obvious that the system of classification used by Reynolds (1966) is one based on utility rather than reflecting phylogenetic relationships. In his description of *Aloe yavellana,* Reynolds states: "another peculiarity of *A. yavellana* is that it

Table 11.2: Occurrence of major chromones and anthrones. 1 = aloesin, 2 = aloeresin A, 3 = aloeresin E, 4 = aloeresin F, 5 = homonataloin B, 6 = homonataloin A, 7 = nataloin B, 8 = nataloin A. Structures of relevant compounds are shown in Figure 11.3.

	Voucher / Locality	1	2	3	4	5	6	7	8
A. angelica Evans	Waterpoort	+	++	+++	++	+	+++		
A. arenicola Reynolds	ex hort JBG	++	+++	-	+++	++	++		
A. arenicola	NBI 1283/92	++	+++	-	++	+	++		
A. comptonii Reynolds	NBI 29356	++	-	+	+++	++	++		
A. comptonii	Perdepoort	++	+	-	+++	++	++		
A. dabenorisana Van Jaarsveld	Pellaberg	+	-	++	+++	+	++		
A. distans Haworth	Saldanah	+	++	++	+++	+	++		
A. erinacea Hardy	NBI 13426	+	++	+++	+			+	+
A. erinacea	NBI 24391	+	++	+++	+			+	+
A. melanacantha Berger	JBG 835440	+	-	+	+++				
A. meyeri Van Jaarsveld	Roesyntjieberg	+	-	+	+++	+	++		
A. mitriformis Miller	Du Toitskloof	++	+	++	+++	+	++		
A. mitriformis	Nieuwoudtville	++	++	-	+++	+	++		
A. mitriformis	Kogmanskloof	++	+++	+	+++	+	++		
A. pearsonii Schonland	Helskloof	++	-	+++	++	+	++		
A. pearsonii	NBI 29382	+	-	+++	++	+	++		
A. peglerae Schonland	Kingskloof	+	++	++	++	++	++		
A. peglerae	Scheerpoort	+	-	++	++	++	++		
A. yavellana Reynolds	RBG (Kew) 19744192	+++	-	+	++	++	++		
A. yavellana	ex hort L. Newton	++	-	+	++	++	++		

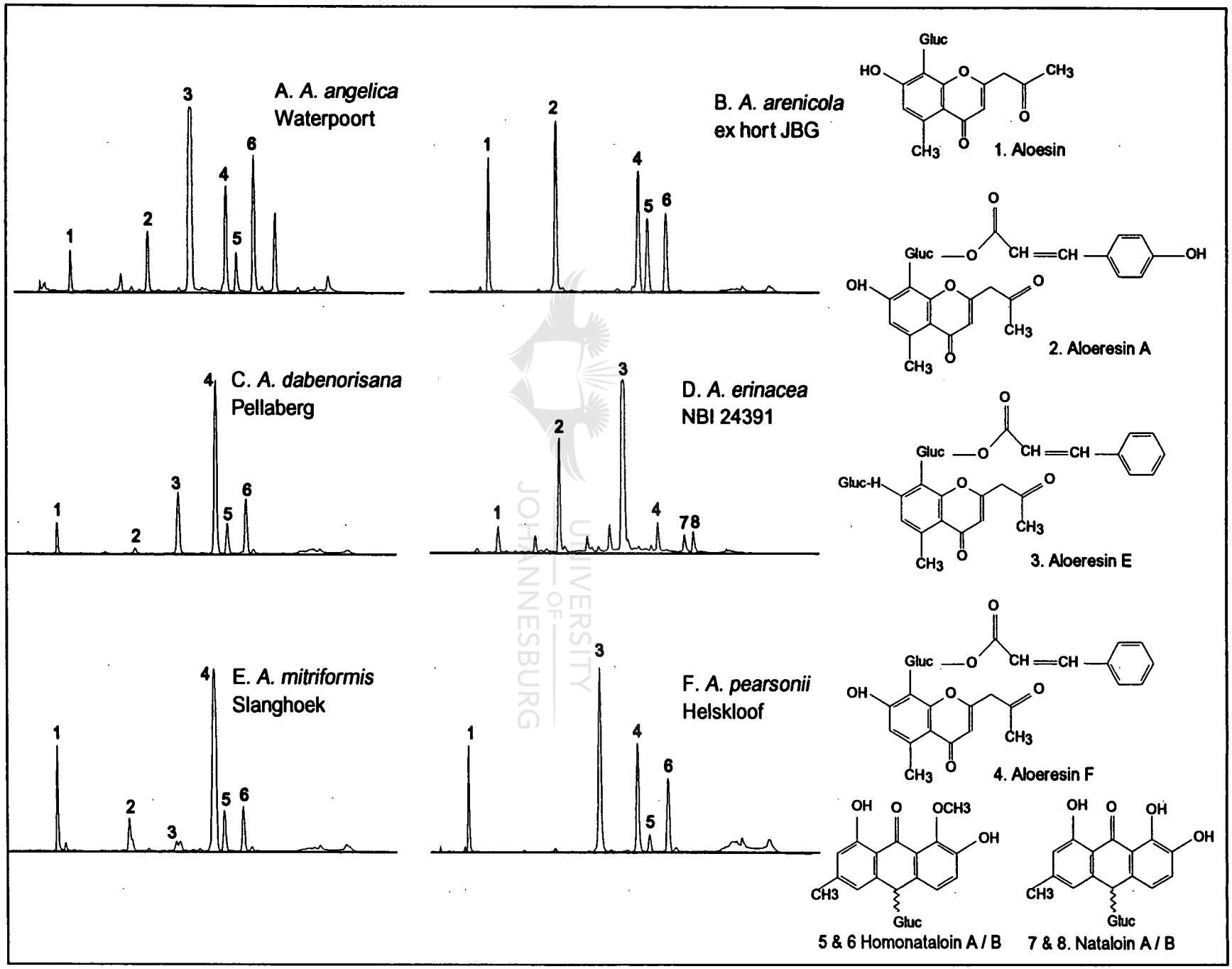


Figure 11.3: Chromatograms of various species showing the presence of the major anthrones and chromones. The peak numbers correlate to the adjacent structures and to the compounds in Table 11.2.

forms fairly compact shrubs when stems are erect and not exceeding 1 m in length, but with development stems topple over and form sprawling shrubs with stems 2 - 3 m long, especially on steep slopes, with the foliate portion ascending". This description is identical to that of many of the species in *Aloe* series *Mitriformes*, and together with the resemblances in the inflorescence structure, suggest an affiliation with the *Mitriformes* group. This chemotaxonomic survey of the genus *Aloe* has shown many examples of a 'chemical relationship' between species in South Africa and east Africa which has previously been reported by De Winter (1971) and Newton (1980) in broader floristic analyses.

A cladistic analysis of the data summarised in Table 11.3 shows the *A. melanacantha*-clade to be sister to series *Mitriformes sensu lato* (i.e. including *A. yavellana*, *A. angelica* and *A. pearsonii*) (Figure 11.4). The tropical *A. yavellana*, is suggested to be ancestral to series *Mitriformes* sensu stricto. This agrees with results of Holland (1978) on the biogeography of *Aloe* suggesting that species in north-east Africa are ancestral to the species in southern Africa. While the coherence of the clade as a whole is based on a single chemical character (12 in Table 11.3), the broadened circumscription of series *Mitriformes* to include *A. yavellana* and *A. angelica* is more convincing.

Aloe series *Mitriformes* and related species are characterised by an unique leaf exudate profile. A rigorous morphological and chemical analysis supports the notion that *A. pearsonii* should be included in the *Mitriformes* group. No substantial evidence can be presented to support the assumption of a phylogenetic affinity between *Aloe* series *Mitriformes* and *Aloe* series *Macrifoliae*. *Aloe yavellana* presents an interesting example of chemical and biogeographical links between the aloes of South Africa and east Africa. The taxonomically problematic *A. angelica* is chemically identical to the species in the *Mitriformes*-complex, and the branched panicle bearing capitate racemes is in agreement with the chemical pattern. The two closely related xerophytic species, *A. erinacea* and *A. melanacantha* prove to be closely related to *A. peglerae*. The affinities of *A. melanacantha*, *A. erinacea*, *A. peglerae*, *A. yavellana* and *A. angelica* have hitherto been a mystery. A hypothesis of relationships is therefore a small but noteworthy advance towards a natural classification system for the genus *Aloe*.

Table 11.3: Characters and polarization of morphological (1 - 10) and chemical (11 & 13) character states.

Taxa	Characters and character states												
	1	2	3	4	5	6	7	8	9	10	11	12	13
Macrifoliae	0	0	0	0	0	0	0	0	0	0	0	0	0
A. angelica	0	0	0	0	0	2	1	0	1	0	1	1	1
A. arenicola	0	1	1	0	0	1	1	0	1	1	1	1	1
A. comptonii	0	1	1	0	0	2	1	0	1	1	1	1	1
A. dabenorisana	0	2	1	0	1	1	1	0	1	1	1	1	1
A. distans	0	1	1	0	0	2	1	0	1	1	1	1	1
A. erinacea	1	1	0	1	0	0	0	2	0	0	0	1	1
A. melanacantha	1	1	0	1	0	0	0	2	0	0	0	1	1
A. meyeri	0	2	1	0	1	1	1	0	1	1	1	1	1
A. mitriformis	0	1	1	0	0	2	1	0	1	1	1	1	1
A. pearsonii	0	0	1	0	0	1	1	0	1	1	1	1	1
A. peglerae	1	0	1	1	0	0	0	1	0	0	1	1	1
A. yavellana	0	1	0	0	0	2	1	0	0	0	1	1	1

1. Caulescence: distinctly caulescent = 0, ± acaulescent = 1
2. Stem orientation: erect = 0, procumbent = 1, pendulous = 2
3. Leaf shape: narrow triangular to oblong = 0, broadly triangular = 1
4. Thorn colour: white, blunt and harmless = 0, black and pungent = 1
5. Inflorescence orientation: erect = 0, pendulous-recurved = 1
6. Inflorescence branching: simple = 0, few-branched = 1, paniculate = 2
7. Raceme: cylindrical = 0, capitate to sub-capitate = 1
8. Bract length: short (< 10 mm) = 0, intermediate (± 15 mm) = 1, long (< 18 mm) = 2
9. Pedicel length: short = 0, long (± as long as the perianth) = 1
10. Flower shape: relatively broad = 0, narrow, slender = 1
11. Homonataloin: absent = 0, present = 1
12. Aloeresin E and F: absent = 0, present = 1
13. Flavones: present = 0, absent = 1

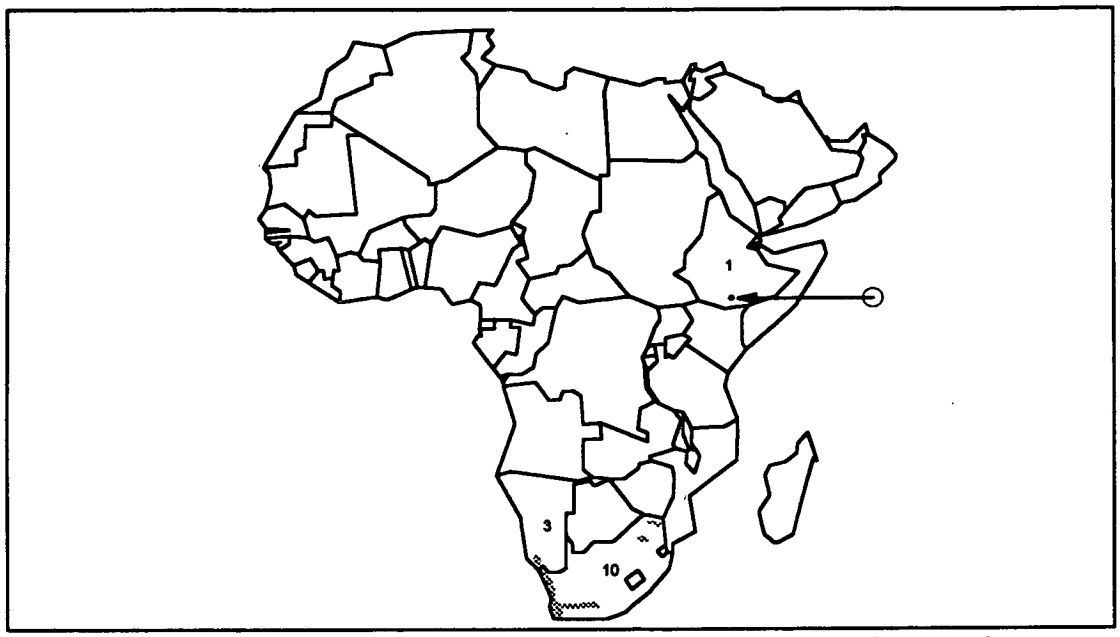


Figure 11.2: Geographical distribution of species containing the cinnamoyl chromones; aloeresin E / aloeresin F, both compounds usually co-occur with homonataloin. The number in each country represents the total number of species with the characteristic chemical compound.

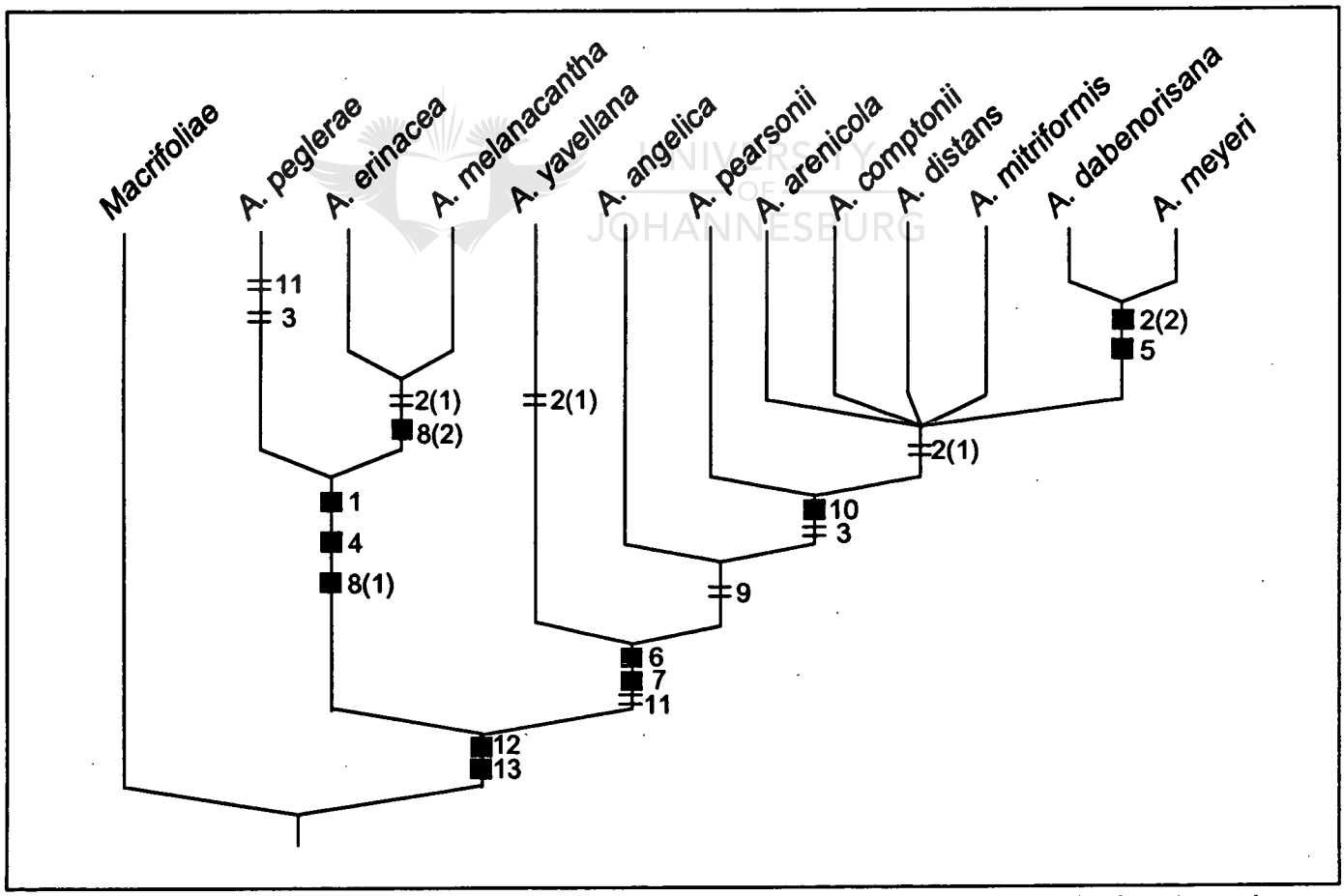


Figure 11.4. Cladogram of phylogenetic relationships in *Aloe* series *Mitriformes* and related species based on the data presented in Table 11.3. A fully resolved cladogram with 18 steps and a consistency index of 71 was obtained using the "i.e" command in HENNIG 86.

Aloe pearsonii

Photo: van Wyk & Smith 1996

Aloe angelica

Photo: van Wyk & Smith 1996

Aloe peglerae

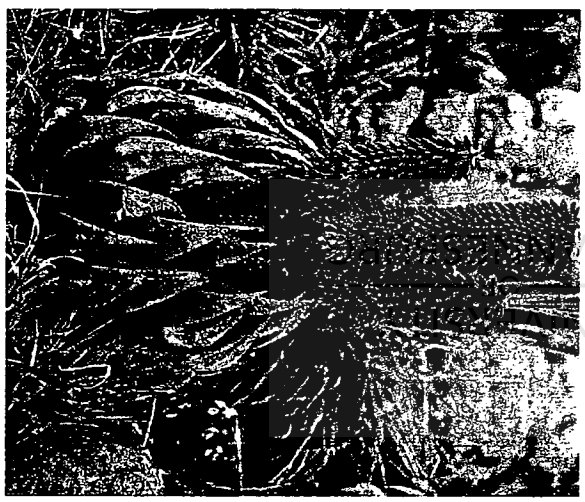


Photo: van Wyk & Smith 1996

Aloe comptonii

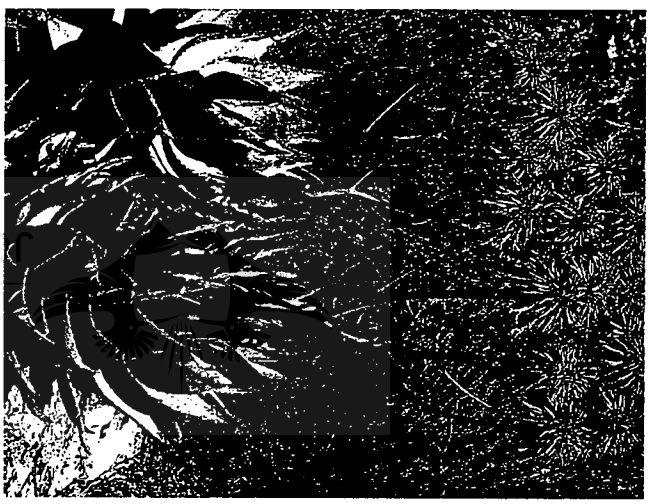


Photo: van Wyk & Smith 1996

Aloe yavelliana

Photo: Reynolds 1968

Aloe melanacantha

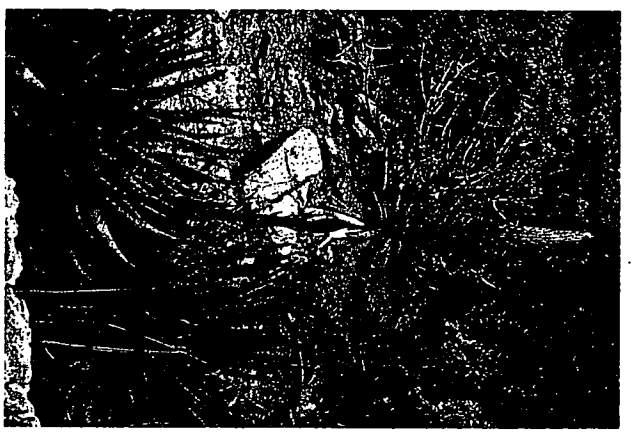


Photo: van Wyk & Smith 1996

Chapter 12

The distribution and chemotaxonomic significance of flavonoids in *Aloe*

CHAPTER 12

THE DISTRIBUTION AND CHEMOTAXONOMIC SIGNIFICANCE OF FLAVONOIDS IN *ALOE*

This chemotaxonomic study of practically all the species of the genus *Aloe* showed that flavonoids occur as major compounds in 31 out of a total of 380 species investigated. Flavanones and dihydroflavonols are present in the exudate of species in *Aloe* series *Rhodacanthae* and *Superpositae* and also in a number of the endemic species from Madagascar. Flavones occur as the only major compound in the leaf extracts of the sections *Leptoaloe* and *Graminialoe*. In the series *Macrifoliae* and in *Lomatophyllum*[1], isovitexin co-occurs with the *C*-glucosylanthrone aloin. The chemotaxonomic implication of these results together with the significance of the taxonomic and chemogeographical distribution of flavonoids in the genus *Aloe* are illustrated in this chapter. With a few rare exceptions, the leaf compounds from two different biogenetic pathways (polyketide pathway and flavonoid pathway) are mutually exclusive. Since flavonoids are restricted to the basal groups in *Aloe*, it is conclude that flavonoids are plesiomorphic characters in *Aloe* reflecting ancient phylogenetic and biogeographic links.

Flavonoids are neglected chemotaxonomic characters in the genus *Aloe*. With the exception of the work of Williams (1975) nothing is known on the occurrence of these compounds in the genus. Her broad-based screening for kaempferol, apigenin, quercetin and luteolin in the Liliaceae included only 18 species of *Aloe* and trace amounts of the above mentioned flavonoids were reported in eight of these species. The lack of flavonoid data for *Aloe* can mainly be ascribed to the fact that the preponderant chemotaxonomic studies on the genus *Aloe* (Reynolds 1985, 1986, 1990) has concentrated on the chromone, anthrone, phenyl pyrone and to a lesser extent the alkaloid (Dring *et al.* 1984) content of the leaves. These compounds usually occur in high concentration and are readily detected by TLC and HPLC methods. The apparent absence of flavonoids in *Aloe* is perhaps also due to the fact that most of the flavonoid-containing species are either difficult to obtain (grass-like aloes and Malagasy endemics) or they do not perform well under cultivation once transplanted from nature.
Flavonoids were detected as major compounds in 31 species out of the total of 380 species investigated (Table 12.1). Only four major flavonoid markers occur in *Aloe*: one flavanone, naringenin; one dihydroflavonol, dihydroisorhamnetin and two flavones, apigenin and

[1]Since completion of this thesis the genus *Lomatophyllum* has been subsumed under *Aloe* as *Aloe* section *Lomatophyllum*

Aloe kraussii, a grass aloe containing the flavone isovitexin (Photo: Ben-Erik van Wyk).

Table 12.1: The occurrence and taxonomic distribution of chromones, anthrones and flavonoids in all flavonoid-containing groups of the genus *Aloe*.

1. isovitexin (flavone); 2. apigenin (flavone); 3. naringenin (flavanone); 4. dihydroisorhamnetin (dihydroflavonol); 5. unidentified flavanone/dihydroflavonol (due to sample limitations, flavonoid 5 could not yet be isolated and identified); 6. aloesin (chromone); 7. aloeresin A (chromone); 8. aloin A and B (anthrone); 9. homonataloin A and B (anthrone); 10. nataloin A and B (anthrone); 11. 7-hydroxyaloin (anthrone);

U = leaf exudate, T = leaf extract; tr = compounds in trace amounts only.

		U	T	1	2	3	4	5	6	7	8	9	10	11
Detected in hydrolysed (h) or unhydrolysed (uh) extracts				uh	h	h	h	h	uh	uh	uh	uh	uh	uh
Retention times				19.5	30	26	18	22	6.5	16	24	25	28	17.5
Locality/Voucher specimen														
Section *Graminialoe*														
A. minima.	The Brook		+	+										
A. saundersiae	Melmoth		+	+										
Section *Leptoaloe*														
A. boylei.	Piet Retief		+	+										
A. chortolirioides	Barberton		+						+				+	+
A. chortolirioides	Sabie	+	+						+		+			+
A. ecklonis	Middelburg District		+	+										
A. hlangapies	Piet Retief		+	+										
A. inconspicua	E of Escort		+	+										
A. inyangensis	ex hort NBI		+	+										
A. kraussii.	Mooi River Falls		+	+										
A. linearifolia	Margate		+	+										
A. linearifolia	Oribi Gorge		+	+										
A. nubigena	God's Window		+	+										
A. parviflora	Bothas Hills		+	+										
A. soutpansbergensis	Letjume		+	+										
A. thompsoniae	NBI 29456		+	+										

		U	T	1	2	3	4	5	6	7	8	9	10	11
Detected in hydrolysed (h) or unhydrolysed (uh) extracts				uh	h	h	h	h	uh	uh	uh	uh	uh	uh
Retention times				19.5	30	26	18	22	6.5	16	24	25	28	17.5
A. verecunda	The Wilds		+	+										
A. verecunda	Melville Koppies		+	+										
A. vossii	Soutpansberg		+	+										
Series *Macrifoliae*														
A. cilianis.	NBI 10674		+	+					+					
A. commixta	NBI 29455		+	+										
A. striatula	ex hort JBG		+						+		+			
A. tenuior	ex hort NBI (Grahamstown)		+	+							+			
A. tenuior	ex hort NBI (Transkei)		+	+										
A. tenuior	ex hort NBI (Cape Town)		+	+										
A. tidmarshii	ex hort JBG		+	+										
Series *Superpositae*														
A. christianii	Zambia (North)	+										+		
A. christianii	Zambia (South)	+							+			+		
A. christianii	ex hort NBI		+						+			+		
A. pretoriensis	NBI 2483	+	+				+							
A. pretoriensis	ex hort NBI (Waterberg)	+	+			+								
A. pretoriensis	Soutpan	+	+				+							
A. suprafoliata	East of Vryheid		+							+		+		
A. thorncroftii	NBI 28651		+			+								
A. thorncroftii	ex hort NBG		+			+								
Series *Rhodacanthae*														
A. glauca	ex hort NBI (Worcester)	+	+			+	+							
A. glauca	Bonnievale	+	+			tr		+						
A. lineata	Vaalkranz	+				+								
A. lineata	Annsvilla	+					tr							

		U	T	1	2	3	4	5	6	7	8	9	10	11
Detected in hydrolysed (h) or unhydrolysed (uh) extracts				uh	h	h	h	h	uh	uh	uh	uh	uh	uh
	Retention times			19.5	30	26	18	22	6.5	16	24	25	28	17.5
A. lineata	Tipper's Creek	+				+								
A. pratensis	ex hort JBG	+						+						
A. polyphylla	Lesotho		+										+	
Series *Echinatae*														
A. humilis	NBI 27971	+	+			+	+	+						
Species from Madagascar														
A. bakeri	NBI 31548		+				+							
A. bellatula	NBI 16648		+											
A. suzannae	ex hort NBI	+		+	+	+								
A. vaotsanda	ex hort Hardy	+				+	+		tr		+			
Lomatophyllum														
L. aldabrense	NBI 3519		+	+							+			
L. lomatophylloides	ex hort NBI		+	+							+			
L. occidentale	NBI 10853		+	+						+	+			
L. orientale	NBI 19481		+	+					tr		+			
L. purpureum	NBI 81155		+	+					tr		+			

isovitexin. Several unknown flavanones co-occurred with naringenin, and some flavones occasionally co-occur with isovitexin. However, these compounds are sporadic in their occurrence and have not been isolated and identified.

The absence of flavonoids in most aloes is not due to masking by high concentrations of anthrones. This possibility was investigated and flavonoids were found to be totally absent from those species not listed in Table 12.1 even when large amounts of leaves were extracted. Table 12.1 shows that isovitexin is present in the unhydrolysed extracts of sections *Graminialoe* and *Leptoaloe*, *Aloe* series *Macrifoliae* and in the genus *Lomatophyllum*.

This compound is a major metabolite in almost all of these species, as can be seen in Table 12.1 and in the selected HPLC profiles in Figure 12.1.

Species pertaining to the sections *Graminialoe* and *Leptoaloe*, the grass aloes, are unique in that the leaf extract contained only isovitexin as the major constituent while anthrones were absent (Figure 12.1). The only species of this group to deviate from this pattern is *A. chortolirioides var. chortolirioides* and *A. chortolirioides* var. *wooliana*. In *A. chortolirioides* var. *chortolirioides*, 7-hydroxyaloin and nataloin were detected, while 7-hydroxyaloin together with aloin was observed in *A. chortolirioides* var. *wooliana*. The latter is one of the rare examples of a species in *Aloe* where the two anthrones co-occur. *Aloe chortolirioides* and its varieties are the only species in the *Leptoaloe* which produce a visible amount of exudate. It is furthermore interesting to note that chromones, which are widely and abundantly distributed in *Aloe*, are totally absent in species of this group.

In the series *Macrifoliae*, *Aloe striatula* and *A. tenuior* (Figure 12.1) also produce the anthrone aloin in addition to isovitexin. This combination is also repeated in the genus *Lomatophyllum* (Figure 12.1), where higher concentrations of aloin are present. In contrast to *Graminialoe* and *Leptoaloe*, *Lomatophyllum occidentale* and certain species belonging to the *Macrifoliae* also produce the chromones aloesin and aloeresin A.

The leaf exudate of certain species pertaining to series *Superpositae*, *Rhodacanthae* and Malagasy *Aloe* species contain complex mixtures of dihydroflavonols and flavanones (Table 12.1). Acid hydrolysis of the crude extracts yielded mixtures which were equally complex and variable and this extreme complexity intricate the task of selecting flavanone markers. In most species, naringenin was produced after hydrolysis (Figure 12.2). Dihydroisorhamnetin occurs in hydrolysates of *A. pretoriensis*, *A. lineata*, *A. glauca*, *A. humilis*, and the two Malagasy endemics, *A. bakeri* and *A. vaotsanda*. From Table 12.1 it is interesting to note that the flavonoid-containing species belonging to the series *Rhodacanthae* and *Superpositae* only

produce flavanones and dihydroflavonols in the exudate and are totally devoid of anthrones. *Aloe vaotsanda* from Madagascar is the only flavanone-containing species where high levels of aloin have been observed, with trace amounts of aloesin. Chromones are absent from all other flavanone containing species listed in Table 12.1.

Isovitexin (compound 1 in Table 12.1 and Figure. 12.1).

In this chemotaxonomic survey of 380 *Aloe* species the flavone isovitexin was found to be a chemotaxonomic marker restricted to the grass-like aloes (*Graminialoe* and *Leptoaloe*), the *Macrifoliae* and the sister genus of *Aloe*, *Lomatophyllum*. Remarkably, the anthrone aloin, which occurs in approximately 60% of all *Aloe* species, is absent from virtually all of the species of *Graminialoe*, *Leptaloe* and *Macrifoliae*. In *Lomatophyllum*, however, aloin invariably co-occurs with isovitexin. In the case of *L. occidentale*, the chromones aloesin and aloeresin A were present in high concentrations in the leaf extract. This information supports the notion that *Lomatophyllum* is closely allied to the genus *Aloe* (Smith & Van Wyk 1991; Newton 1973; Van Wyk *et al.* 1995), and that the fleshy berry-like fruit do not necessarily warrant its separation from the genus *Aloe*.

The uniform pattern in the *Graminialoe* and *Leptoaloe* is disrupted by the presence of anthrones in *A. chortolirioides*, forcing one to speculate on the possibility of (1) hybrid origin from a species containing aloin, or (2) parallel evolution of the biochemical pathway. Our study of the leaf exudate patterns in concordance with morphological evidence indicates that hybridization must have played a very important role in the evolution of *Aloe*. The overall pattern in Table 12.1 leads us to propose that flavonoids originated early in the genus *Aloe* or in its ancestors, that is to say if we support the notion that the grass-like aloes and also the *Macrifoliae* represent the basal lineages in the evolution of *Aloe*, as is evidenced by their less succulent leaf consistency and the absence of pungent thorns. It would seem functional to produce bitter tasting anthrones as antifeedents to deter herbivores. Anthrone-bearing species would in time displace those with flavonoids as a result of this selective advantage.

A morphological coherence between the flavone-containing species (those containing isovitexin) supports our results on the chemical level. The *Graminialoe*, *Leptoaloe*, *Macrifoliae* and even *Lomatophyllum* bear leaves which are linear-lanceolate, thin and only slightly fleshy with minute marginal teeth. The inflorescence is usually single and unbranched with the racemes rather laxly flowered. Many of the grass-like aloes also have the tendency to produce robust stems (e.g. *A. chortolirioides*) similar to the more sarmentose-scandent species

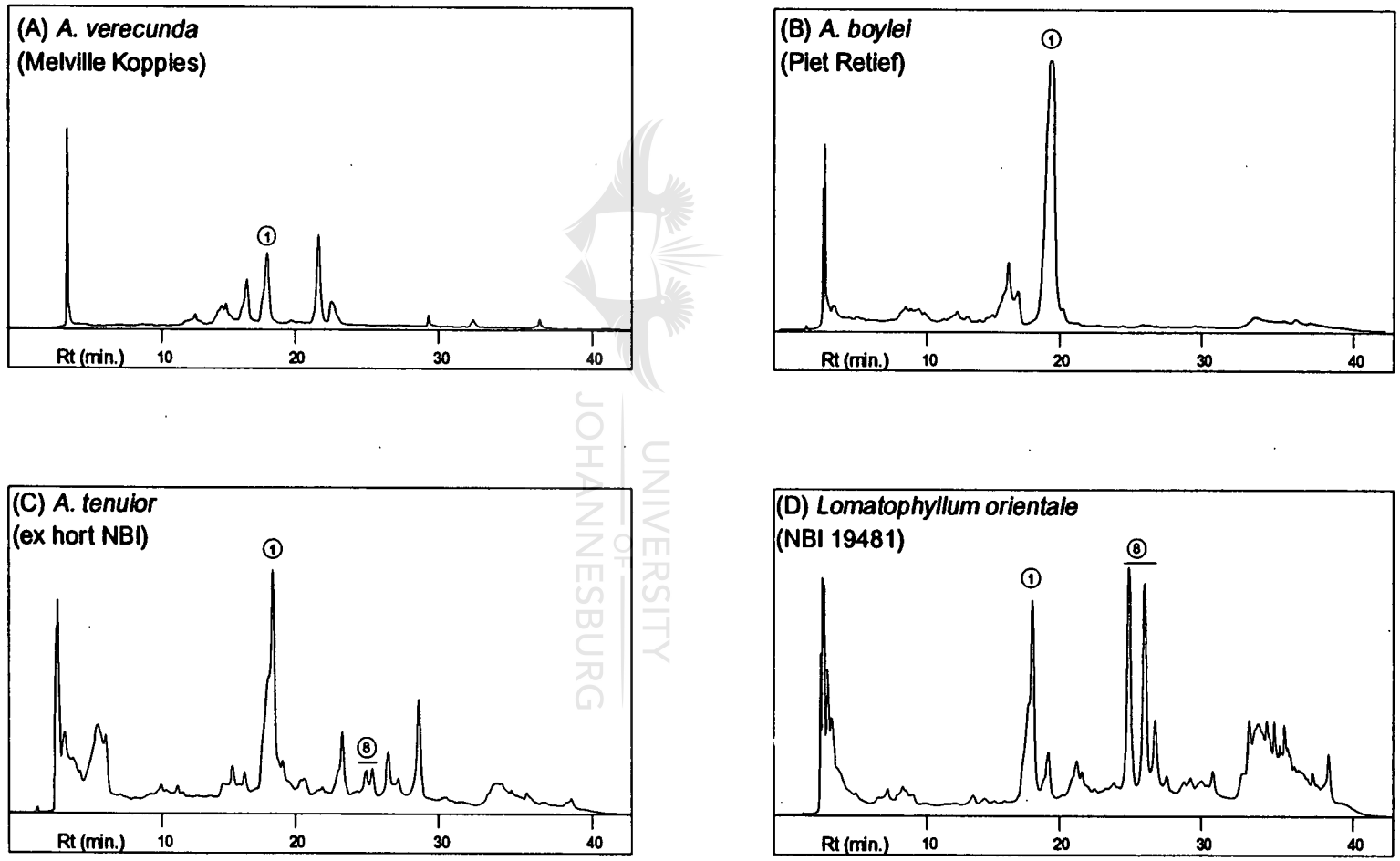


Figure 12.1: HPLC profiles of flavone containing species.

belonging to the series *Macrifoliae*.

Flavones, and specifically isovitexin occur sporadically in low concentrations in a few Malagasy species not related to the taxonomic groups above. These species (*A. acutissima*, *A. ibityensis* and *A. suarezensis*) are also characterized by the absence of anthrones.

Dihydroisorhamnetin (compound 4 in Table 12.1 and Figure 12.2) and naringenin (compound 3 in Table 12.1 and Figure 12.2).

Dihydroisorhamnetin (a dihydroflavonol) and naringenin (a flavanone) occur in *Aloe* series *Superpositae*, *Rhodacanthae* and some Malagasy endemics (Table 12.1 and Figure. 12.2). With the exception of *A. suzannae* , flavones (isovitexin, apigenin) and flavanones (naringenin) were found to be mutually exclusive in our survey (Figure. 12.3). This departure from the general pattern does not come as any surprise as *A. suzannae* has numerous oddities. The nectar sugar composition was found to be different from all other species (Van Wyk, unpublished), the leaf exudate chemistry could in its simplest be described as unique (Herbst, in prep.) and the morphological characters are well documented as being peculiar (Reynolds 1950; Glass & Foster 1983; Swartz 1995).

The occurrence of flavanones (naringenin) and dihydroflavonols (dihydroisorhamnetin) in the genus *Aloe* has a pronounced taxonomic bearing (Table 12.2 and Figure 12.4). Flavanone-derived compounds (various glycosides of naringenin) have a very limited taxonomic distribution in the genus, only occurring in 10 of the 380 species studied. We do not believe that this biochemical pathway originated independently and it would seem more realistic to suggest an affiliation, however distant it may be, amongst the flavanone-containing species. The chemical similarity (flavanone-containing leaf exudate) of the species belonging to series *Superpositae* and *Rhodacanthae* demands elaboration. In his treatment of the genus *Aloe*, Reynolds (1950) grouped *A. glauca*, *A. lineata*, *A. pratensis* and *A. polyphylla* together under series *Rhodacanthae*. Reynolds, however, includes statements suggesting that *A. polyphylla* does not fit well in this series. As in the case of *A. chortolirioides*, *A. polyphylla* contains anthrone compounds (nataloin and derivatives thereof) in the leaf exudate. This species, endemic to the highlands of Lesotho, is often referred to as an unique and morphologically curious *Aloe* (Pillans 1934; Reynolds 1950), and although the taxonomic position of *A. polyphylla* in the genus *Aloe* seems to be enigmatic, the leaf exudate chemistry unambiguously shows it to be different when compared to the other members of series *Rhodacanthae*. More interesting however, is that should one consider *A. polyphylla* to be allied to its

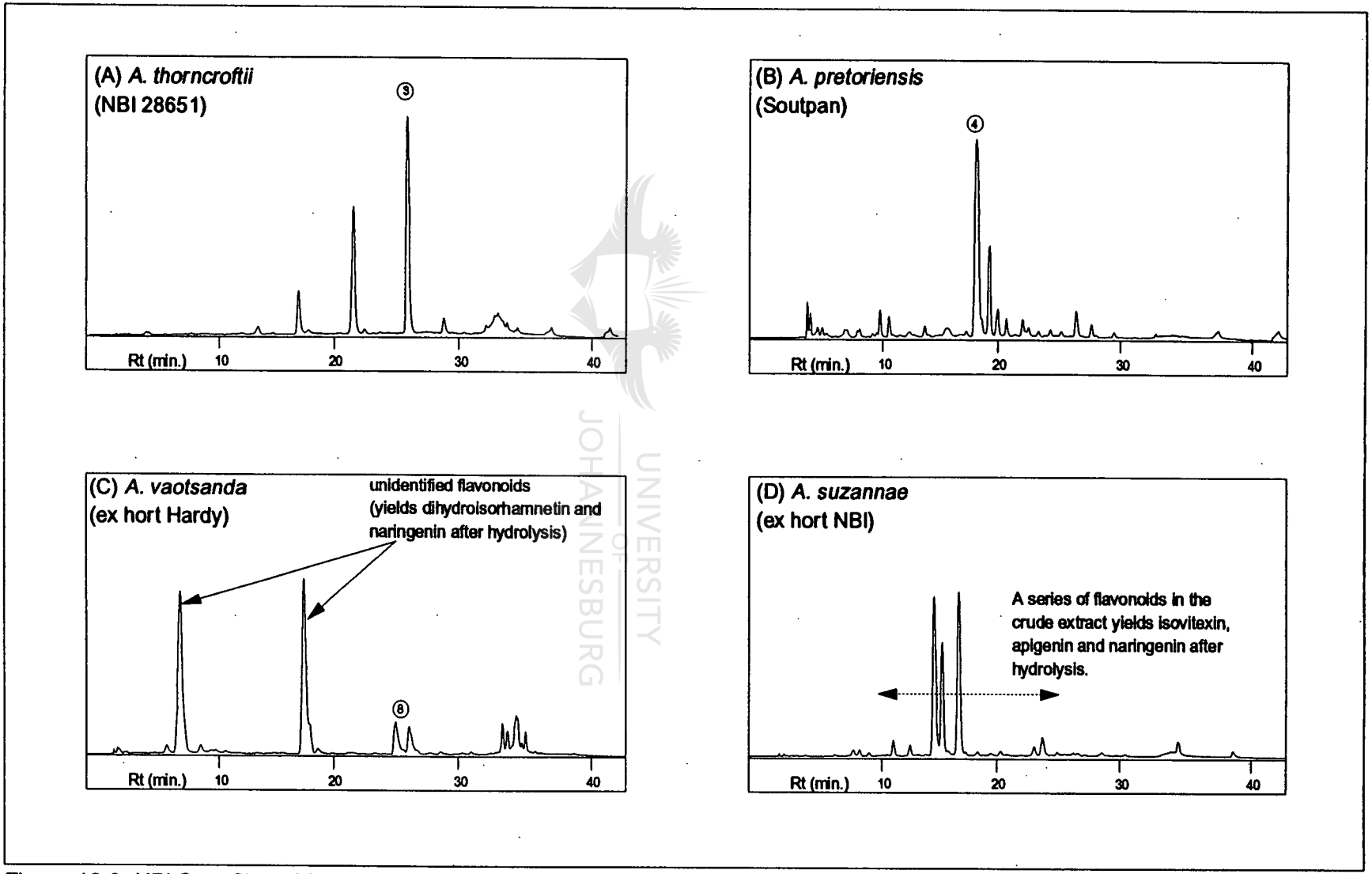


Figure 12.2: HPLC profiles of flavanone containing species.

Rhodacanthaean counterparts as suggested by Reynolds (1950) and Pillans (1934), then the debate reopens as discussed in the case of *A. chortolirioides*. *Aloe chortolirioides* is chemically a misfit in the flavone-containing complex, because it also produces nataloin and 7-hydroxyaloin in addition to isovitexin. The chemical deviant in *Aloe* series *Rhodacanthae* also has the biochemical pathway producing nataloin. In the light of its sporadic occurrence it would not be premature to suggest that nataloin and its derivatives (Sigler & Rauwald 1994) are without any chemotaxonomic value except as autapomorphies for some species. The chemical anomaly of these two species could also be ascribed to possible hybridization events. In Chapter 6 it has been illustrated the nataloin and 7-hydroxyaloin form when homonataloin and aloin producing species are hybridized.

According to Reynolds (1950) *Aloe* series *Superpositae* includes four species; *A. suprafoliata*, *A. christianii*, *A. pretoriensis* and *A. thomcroftii*. Table 12.1 shows that *A. pretoriensis* and *A. thomcroftii* both contain the flavanone aglycone naringenin after hydrolysis of the leaf exudate, while *A. christianii* and *A. suprafoliata* both contain the anthrone homonataloin as major compound in the leaf exudate. Morphologically, *A. pretoriensis* and *A. thomcroftii* have obscurely lineate leaves (Reynolds 1950). *Aloe pretoriensis* studied and collected at Soutpan indeed have leaves which are distinctly lineate. Both species also bear undifferentiated cylindrical flowers as is the case in the flavanone-containing species pertaining to series *Rhodacanthae* (i.e. those with naringenin and the unidentified dihydroflavonol / flavone). It is interesting to note that Glen and Hardy (1987) found juvenile plants of *A. thomcroftii* to be tuberculate, becoming smooth in the adult plant, a characteristic shared with *A. pretoriensis*. These similarities encourages one to speculate on the taxonomic position of *A. humilis*. This flavanone-containing species (with glycosides of naringenin) is tuberculate in the adult stage and it is clear that *A. humilis* is misplaced in the artificial group, series *Echinatae*. In our opinion an affiliation of *A. humilis* with *A. pratensis*, as suggested by Baker (1883), should be reconsidered.

To suggest the omission of *A. suprafoliata* and *A. christianii* from the flavanone-containing complex would be premature. The fact that they are both homonataloin- and chromone-producing species do not justify their transfer to any other taxonomic group, as this chemical combination in the leaf exudate is a general pattern in a large percentage of species investigated in our survey. The emphasis is rather placed on the interesting discovery that the leaf exudate of certain species in series *Superpositae* and *Rhodacanthae* have a unique and complimentary chemical composition of which implications on taxonomic level are summarized

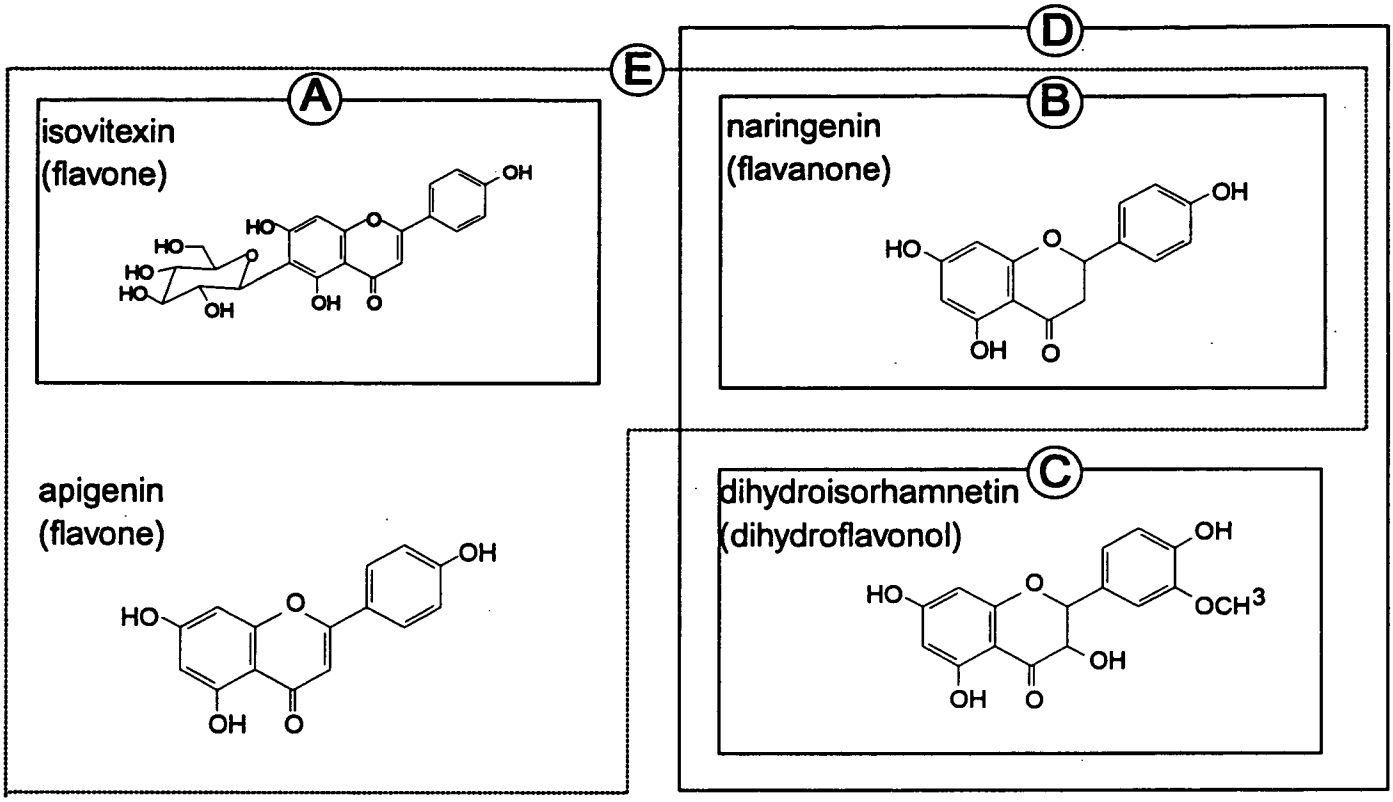


Figure 12.3: The four flavonoid chemotaxonomic markers in the genus *Aloe*.
The following patterns of occurrence are recognised:
A. isovitexin only; *Aloe* section *Leptoaloe* and *Graminialoe*, series *Macrifoliae* and the genus *Lomatophyllum*
B. naringenin only; *Aloe pretoriensis*, *A. thorncroftii* and *A. lineata*
C. dihydroisorhamnetin only; *Aloe pretoriensis*, *A. lineata* and *A. bakeri*
D. naringenin and dihydroisorhamnetin; *Aloe glauca*, *A. humilis* and *A. vaotsanda*
E. isovitexin, apigenin and naringenin; *Aloe suzannae*

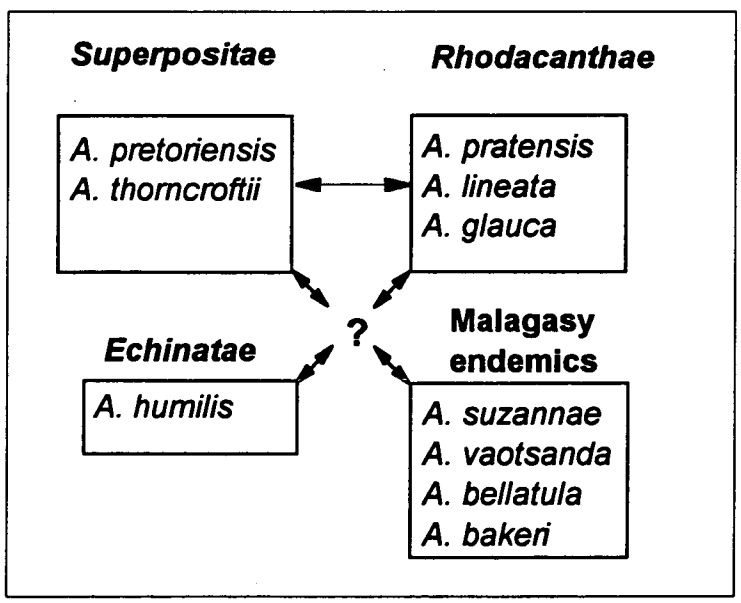


Figure 12.4: The taxonomic distribution of flavanones and / or dihydroflavonols in the *Aloe* spp. and possible taxonomic links.

in Table 12.2 and Figure 12.4.

Table 12.2: Summary of the distribution of flavonoids in the various flavonoid-bearing sections and series of the genus *Aloe*.

	flavones	dihydroflavonols	flavanones
Section *Graminialoe*	isovitexin	-	-
Section *Leptoaloe*	isovitexin	-	-
Series *Macrifoliae*	isovitexin	-	-
Series *Superpositae*	-	dihydroisorhamnetin	naringenin
Series *Rhodacanthae*	-	dihydroisorhamnetin	naringenin
Series *Echinatae*	-	dihydroisorhamnetin	naringenin
Madagascar species	isovitexin & apigenin	dihydroisorhamnetin	naringenin
Genus *Lomatophyllum*	isovitexin	-	-

In view of the unspecialised morphology of all these species, it seems reasonable to assume that flavanones (naringenin derivatives) and dihydroflavonols (e.g. dihydroisorhamnetin) are plesiomorphic characters. The species in Figure 12.4 appear to be relicts from an era when these compounds were more widely distributed in the genus *Aloe*.

The taxonomic distribution of flavanones in the genus *Aloe* (Figure 12.4) could not be dismissed as a chemotaxonomic coincidence. We propose that the restricted distribution (both taxonomically and geographically) of flavanone-containing species, (with special reference to the *A. lineata*, *A. glauca*, *A. thomcroftii*, *A. pretoriensis*, *A. suzannae* and *A. vaotsanda* alliance) establishes a clear chemogeographical link between the *Aloe* species of Africa and Madagascar.

Reynolds (1966) speculates on the absence of aloaceous counterparts between Africa and Madagascar. Certain groups are thought to have evolved independently (e.g. the *Saponariae*, which have no representatives on Madagascar) and the grass-like aloes (which are restricted

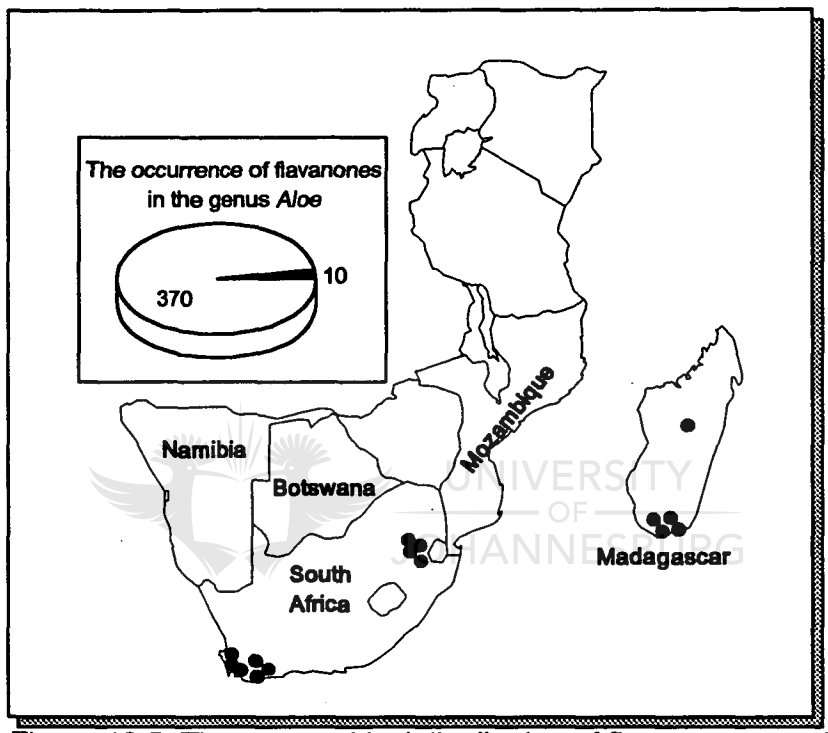


Figure 12.5: The geographical distribution of flavanone-containing species in the genus *Aloe*.

to Africa, mainly South Africa and Zimbabwe). As illustrated by Holland (1978), there is no biogeographical link between the species of Africa and Madagascar (based on the absence of a communal species between Africa and Madagascar). However, all six life forms as defined by Holland occur in the South Africa and in Madagascar. Although the palaeo-geological kinship of Madagascar in relation to its Gondwanaland neighbours is a much debated topic (Smith & Hallam 1970; Darracott 1974; Embleton & McElhinny 1975; Agrawal *et al.* 1992), the information presented here supports the numerous alliances in the geology, fauna and flora of Madagascar and Africa (Figure 12.5).

This chemotaxonomic survey of the genus *Aloe* is the first to show that flavonoids are major compounds in some infrageneric groups. Four distinct flavonoid markers are reported for the first time from *Aloe* (Figure 12.3):

A. The flavone isovitexin, which is restricted to the *Leptoaloe*, *Graminialoe*, *Macrifoliae* and the genus *Lomatophyllum*. Isovitexin could therefore be considered a plesiomorphic chemotaxonomic marker for these taxonomic groups; B. the flavanone naringenin and C. the dihydroflavonol dihydroisorhamnetin, which have a very limited taxonomic distribution, indicating a definite alliance between *Aloe* series *Rhodacanthae* and *Superpositae*. The restricted geographical distribution of these two compounds furthermore emphasises a geographic-taxonomic correlation between *Aloe* species of Africa and Madagascar; D. the flavone apigenin, which was only detected in *Aloe suzannae*, where it co-occurs with the flavanone naringenin and the flavone isovitexin.

Flavonoids are clearly plesiomorphic characters restricted to various basal groups within *Aloe*. Their taxonomic distribution reflects ancient links, not only between species within the genus, but also biogeographic links between southern Africa and Madagascar.

Figure 12.6: Representatives of flavonoid containing species. ⇨

Photo: van Wyk & Smith 1996

Aloe verecunda

Photo: van Wyk & Smith 1996

Aloe krausii

Photo: van Wyk & Smith 1996

Aloe chortolirioides

Photo: van Wyk & Smith 1996

Aloe commixta

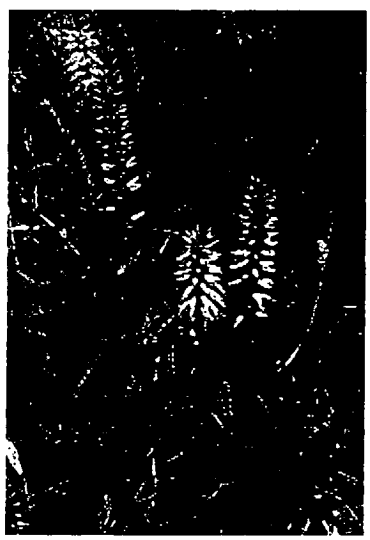


Photo: van Wyk & Smith 1996

Aloe tenuior

Photo: van Wyk & Smith 1996

Aloe gracilis

Photo: Reynolds 1966

Aloe bakeri

Photo: van Wyk & Smith 1996

Aloe humilis

Photo: van Wyk & Smith 1996

Aloe lineata

Photo: van Wyk & Smith 1996

Aloe pratensis

Photo: van Wyk & Smith 1996

Aloe pretoriensis

Photo: Reynolds 1966

Aloe suzannae

Chapter 13

Plicataloside in *Aloe* - a chemotaxonomic appraisal

CHAPTER 13

PLICATALOSIDE IN *ALOE* — A CHEMOTAXONOMIC APPRAISAL

In a chemical survey of 380 taxa of *Aloe*, 20 species were found to contain the naphthalene derivative plicataloside as the major phenolic in the leaf exudate. Most of these species are restricted to East Africa (Kenya, Uganda & Tanzania). Only three species (*A. chabaudii, A. palmiformis, A. plicatilis*) in southern Africa contained this compound while the Malagasy endemics studied were found to be devoid of plicataloside. A comparison of the macromorphology of the species are presented in an attempt to search for other characters common to the species, and taxonomic affinities are assessed. Previous studies have suggested some of the taxa defined by this unique chemical compound to be taxonomically related, while many of the taxa have not previously been associated together.

As discussed in Chapter 1 and 2 various studies have been undertaken to assess chromatographic patterns in the genus *Aloe* (Reynolds, 1985, 1986, 1990; and Cutler *et al.*, 1980) but the chemotaxonomic utility of chemical characters at the level of infrageneric taxa has not been fully explored. The present classification system for the genus *Aloe*, which is largely artificial, emphasises the need for additional characters to be studied in a multidisciplinary approach. The leaf exudate chemistry is only additional to various other forms of taxonomic evidence that could be used to explore possible natural relationships.

Leaf exudate chemistry

Plicataloside was first isolated from *A. plicatilis* (Wessels *et al.*, 1996) and initially it was thought that this unique compound is restricted to this anomalous species in the monotypic section *Kumara*. As the study progressed and 380 taxa of *Aloe* were analysed 20 species (Table 13.1) were found to have plicataloside in the leaf exudate.

In most of the 20 species it was found that this is the only phenolic compound in the exudate detected under the analysing parameters. In some species this compound co-occurred with trace amounts of the other compounds characteristic of *Aloe* (the chromones and anthrones) or together with unidentified compounds (Figure 13.1). Previous phytochemical work on *Aloe* reported the presence of a dark purple staining zone (P35), which most probably correlates to plicataloside (methods given in Reynolds 1985). This zone was reported in *A. plicatilis, A. otallensis*, *A babatiensis* and *A. deserti* (Reynolds, 1985) and also in *A. palmiformis* and *A. fibrosa* (Reynolds, 1990). Our survey confirmed that plicataloside is present in these species.

Aloe plicatilis, the species from which plicataloside was isolated (Photo: Ben-Erik van Wyk).

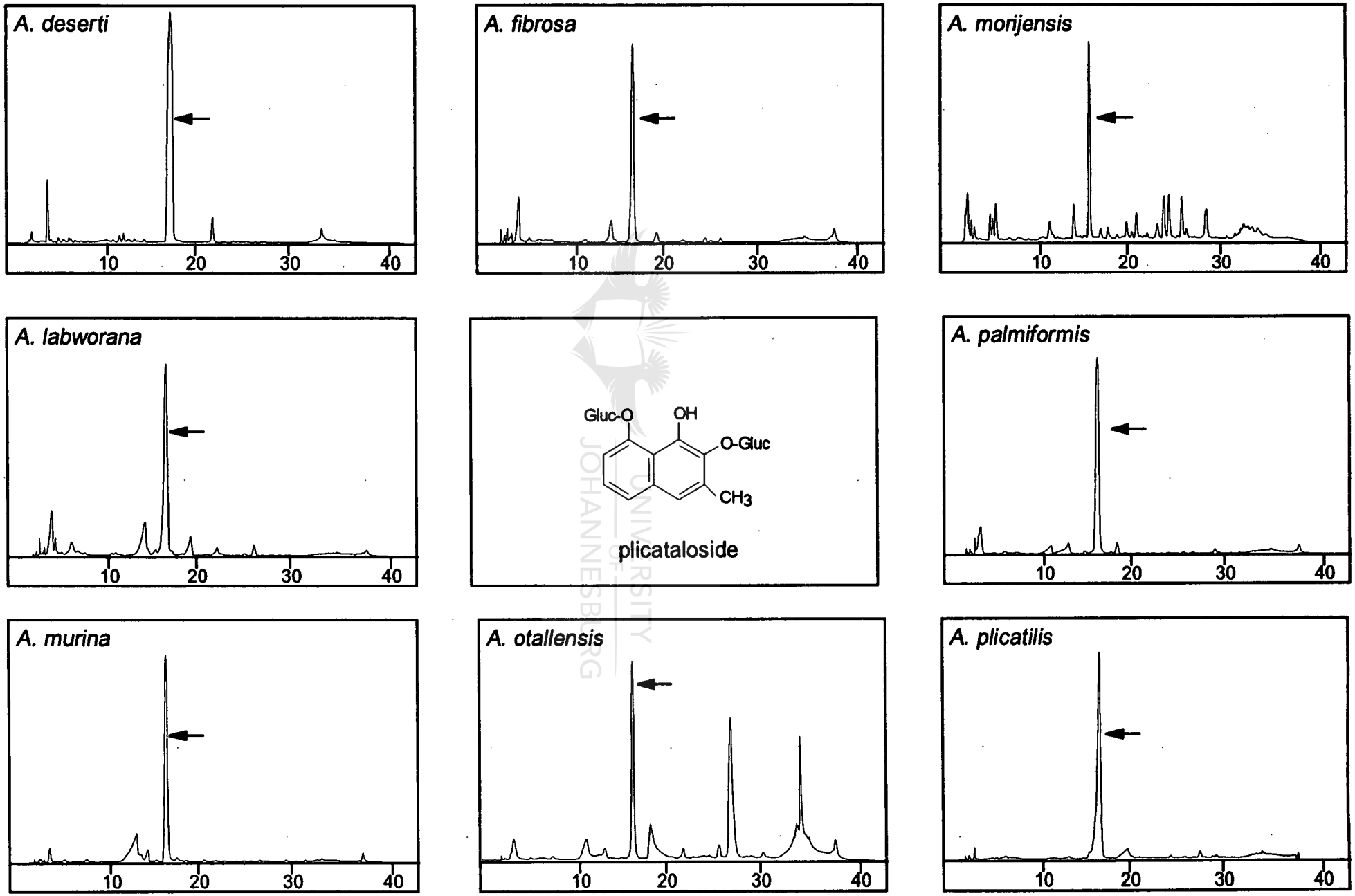


Figure 13.1: A selection of plicataloside containing species showing the unique exudate profile. Plicataloside has a retention time of 17.8 min and is denoted by an arrow. The structure of plicataloside is also included.

Table 13.1: Plicataloside-containing species of *Aloe* and corresponding voucher details.

Species	Voucher / Locality
A. archeri Lavranos	Newton 3118 (neotype plant) (K, EA)
A. babatiensis Christian & Verdoorn	RBG 1974-4463
A. chabaudii Schönland	Ellert 32 (ex Zimbabwe)
A. deserti Berger	Newton 3608 (type locality)
A. fibrosa Lavranos & Newton	ex hort P. Favell
A. francombei Newton	Newton 4130 (type plant) (K, EA)
A. labworana (Reynolds) S. Carter	RBG 295-58-2921
A. morijensis S. Carter & Brandham	Newton 3661 (K)
A. multicolor Newton	Newton 4133 (type plant) (K, EA)
A. murina Newton	Newton 2497 (type plant) (K, EA)
A. otallensis Baker	RBG 194-09-012941
A. palmiformis Baker	RBG 224-94-020-95
A. parvidens Gilbert & Sebsebe	RBG 1985–4219 & Newton 4384
A. plicatilis (L.) Miller	NBG 19503
A. pustuligemma Newton	Newton 3739 (type plant) (K, EA)
A. rugosifolia Gilbert & Sebsebe	Sebsebe 22
A. schweinfurthii Baker	ex hort NBI
A. tugenensis Newton & Lavranos	Newton 3514 (type plant) (K, EA, MO)
A. ukambensis Reynolds	NBI 20505
A. wredfordii Reynolds	RBG 1977-4192

Other characters

After the group of plicataloside-containing species had been identified, descriptions of these species were examined to see if there are other characters common to members of the group. A brief description of the salient morphological features of each species is presented, together with information relating to the taxonomic status and distribution. The information elaborated below is partly summarised in Table 13.2.

Aloe archeri was originally described by Lavranos (1977). The description was based on plants that he thought were from the Nguruman escarpment, southern Kenya. In his species description Lavranos also refers to plants collected at Kichich, further north in Kenya, suggesting that they resemble the aloes from Nguruman. After studying plants from the stated type locality of *A. archeri*

Newton (1992) concluded that they did not fit the species description, whereas plants from Kitich and some other northern localities did. He showed unambiguously that the Nguruman plants and the northern plants are not conspecific. Newton (1992) suggested that Lavranos received plants from Kitich but was misinformed about their source. The original description of Lavranos (1977) was amended by Newton (1992), reflecting a difference in growth habit. This species is characterised by the long decumbent stems (up to 4 m), spreading and slightly decurved leaves with a rough texture, and the inflorescence is a panicle. The bracts are large (12–15 mm) and cover the young flower buds. The cylindrical trigonous flower is approximately 20–22 mm in length. *Aloe archeri* occurs in the Rift Valley Province of Kenya.

Aloe babatiensis is a dense shrub with erect or decumbent stems up to 1 m long. The densely arranged leaves are spreading and recurved, and armed with pungent thorns. The inflorescence is a 2–4 branched panicle. The ovate bracts are 20–30 mm and envelope the young buds. The cylindrical perianth is 20–40 mm in length. This species is known only from the Masai District in north-east Tanzania.

Aloe chabaudii is mostly acaulescent or rarely develops a short stem and suckers to form groups. The leaves are erect and obscurely lineate. The inflorescence is a panicle with the racemes mostly cylindrical to acuminate. The decurved perianth is constricted above the ovary and conspicuously trigonously indented. This species is widely distributed throughout southern Africa.

Aloe deserti develops an erect or sprawling stem up to 1 m in length. The leaves are slightly rough, spreading and become decurved with age. The racemes of the panicle are initially limp and drooping, becoming stiff and erect as the flowers mature. The imbricate bracts are conspicuously white. The perianth is 28–35 mm long. *A. deserti* is found in southern Kenya and northern Tanzania.

A. fibrosa has a shrubby habit with stems erect or decumbent (up to 2.5 m). The leaves are spreading and sometimes recurved at the tips. The erect inflorescence is mostly simple but rarely 2–3-branched. The buds are enveloped by the whitish bracts. The perianth is 30–35 mm in length, cylindrical and restricted above the ovary. As indicated by the epithet, this species is conspicuously identified by the tough fibres in the leaf parenchyma. *A. fibrosa* is only known from southern Kenya and the Moshi District in Tanzania.

Aloe francombei develops an erect stem approximately 40 cm long. The compactly arranged leaves are erect and distinctly rough to touch. The inflorescence is a panicle, racemes cylindrical. The imbricate bracts are whitish-scarious and 10–12 cm long. The trigonous-cylindrical perianth is 25 mm long. This species is known only from the Mukutan Gorge in the Laikipia District of Kenya.

Aloe labworana was originally described as a variety of *A. schweinfurthii* (Reynolds 1956). Carter (1994) considered the variety to differ distinctly from *A. schweinfurthii*, hence the specific rank. This species is acaulescent and suckering from the base. The leaves are spreading with the apices recurved. The leaves are armed with pungent marginal teeth and are spotted on both sides. The inflorescence is a panicle. The bracts are small, clasping the pedicel. This species is found on the Labwor Hills in Uganda and northwards across the border in Sudan.

Aloe morijensis is a shrubby aloe developing slender sub-erect stems up to 1 m long. The leaves are spreading and recurved with distinct internodes. The inflorescence is mostly simple but rarely 1–2-branched. This species is known from the south-west Kenya and north Tanzania.

Aloe multicolor is shrubby with stems erect or decumbent and could reach 2 m in length. The leaves are spreading and recurved with pungent marginal teeth and are sparsely spotted at the base of the lower surface. The erect inflorescence has 5–8 branches. The imbricate bracts are 10–13 mm long. The perianth is clavate. This species has a disjunct distribution with one population on Mount Kulal in Kenya and the other on Forole, on the border between Kenya and Ethiopia.

A. murina is the Nguruman plant discussed under *A. archeri*. Plants are acaulescent or with a very short procumbent stem. The leaves are spreading with pungent marginal teeth and rough to the touch. The inflorescence is a panicle bearing flowers that are secund in the bud stage. This species is only known from the Nguruman escarpment in southern Kenya.

A. otallensis is solitary or occurs in small clumps, and is mostly stemless. The leaves are erect or slightly recurved. The glaucous inflorescence is a panicle bearing 12 racemes. The perianth is cylindrical to clavate with a conspicuous papillose midrib. This species is distributed in the southern parts of Ethiopia.

A. palmiformis is shrubby in growth with stems erect, 1–1.5 m tall. The leaves are spreading-recurved with prominent marginal teeth. The inflorescence is simple or 2–3-branched. The species is found in the Huila District in the southern part of Angola.

A. parvidens is a stemless aloe that is usually solitary. The leaves are spreading and recurved. The tall inflorescence is 4–8-branched. *Aloe parvidens* is widely distributed in Kenya, Tanzania, Somalia and Ethiopia.

A. plicatilis, with its tree-like appearance, has a distinct growth form. The robust stem is dichotomously branched. The leaves are arranged in a distichous (fan-like) cluster, unspotted and without marginal teeth. The inflorescence is single and the racemes are laxly flowered. This species is restricted to the mountainous areas of the south-western Cape in South Africa.

Table 13.2: Summary of salient morphological characters for the plicataloside-containing species of *Aloe*.

Species	Habit	Suckering	Leaf orientation	Leaf surface	Bracts (mm)	Inflorescence	Perianth	Exudate chemistry
A. archeri	long decumbent stem	No	spreading and recurved	unspotted rough	12 - 15	6–12-branched panicle	cylindrical trigonous	only plicataloside
A. babatiensis	erect or decumbent	No	spreading and recurved	unspotted smooth	20 - 30	2–4-branched panicle	cylindrical trigonous	plicataloside and unidentified cmpds
A. chabaudii	mostly acaulescent	Yes	leaves erect	obscurely lineate sometimes with a few spots	3 - 5	6–12-branched panicle	decurved, trigonously indented	plicataloside and unidentified cmpds
A. deserti	erect / sprawling stem	No	spreading becoming decurved	with or without spots rough	15 mm, deflexed	3–8-branched panicle	cylindrical trigonous	only plicataloside
A. fibrosa	stem erect or decumbent	No	erect apices often recurved	unspotted smooth	12 - 18	simple or 1–2-branched	cylindrical, slightly restricted above ovary	only plicataloside
A. francombei	shortly caulescent	No	erect	spotted rough	10 - 12	up to 8-branched panicle	cylindrical trigonous	plicataloside and traces of aloin
A. labworana	acaulescent	Yes	spreading, apices recurved	densely spotted smooth	1.5 - 3	10–12-branched panicle	cylindrical trigonous	plicataloside and traces of aloin
A. morijensis	suberect, stem 1 m	No	spreading to recurved	spotted smooth	10 - 15	simple or 1–2-branched	cylindrical trigonous	only plicataloside
A. multicolor	erect or decumbent	No	spreading and recurved	sparsely spotted beneath smooth	10 - 13	5–8-branched panicle	clavate	only plicataloside

Species	Habit	Suckering	Leaf orientation	Leaf surface	Bracts (mm)	Inflorescence	Perianth	Exudate chemistry
A. murina	acaulescent	No	spreading	unspotted rough	5 - 6	up to 13-branched panicle	cylindrical trigonous	plicataloside and traces of aloin
A. otallensis	acaulescent	No	erect, slightly recurved	sometimes spotted smooth	12 mm	up to 12-branched panicle	cylindrical to clavate and papillose	only plicataloside
A. palmiformis	stem 1 - 1.5 m long	No	spreading and recurved	usually spotted beneath smooth	2 - 3	simple or 2—4-branched	cylindrical trigonous	plicataloside and traces of aloin
A. parvidens	acaulescent	No	spreading and recurved	spotted smooth	5 -6	2—10-branched panicle	cylindrical trigonous	plicataloside and an unidentified cmpd
A. plicatilis	distinctly caulescent	No	distichous	unspotted smooth	8 mm	simple	cylindrical trigonous	only plicataloside
A. pustuligemma	stems erect or decumbent	No	spreading and recurved	unspotted rough	11 -13	8—9-branched panicle	cylindrical and papillose	only plicataloside
A. rugosifolia	acaulescent	Yes	erect and slightly incurved	spotted rough	9 -11, deflexed	8—10-branched panicle	cylindrical trigonous	only plicataloside
A. schweinfurthii	acaulescent	Yes	spreading and recurved	usually spotted near base smooth	4 -7	8—10-branched panicle	cylindrical trigonous	only plicataloside
A. tugenensis	decumbent stem - 1m	No	spreading and recurved	unspotted rough	10 -12	up to 12-branched panicle	cylindrical trigonous	plicataloside and unidentified compounds
A. ukambensis	acaulescent	Yes	erect and slightly incurved	striate smooth	7 - 10	simple or 1—3-branched	cylindrical trigonous	plicataloside and unidentified compounds
A. wrefordii	acaulescent	No	erect, apices recurved	obscurely lineate smooth	9 -12	up to 16-branched panicle	cylindrical-clavate	only plicataloside

A. pustuligemma is a sprawling shrub with stems erect or decumbent and 1.5 m long. Leaves are spreading-recurved, rough and armed with deltoid pungent teeth. The inflorescence is a panicle. This species is known only from a small area in northern Kenya.

A. rugosifolia is solitary and acaulescent, suckering from the base. The rugose leaves are erect and slightly incurved. The inflorescence is a panicle. The scarious bracts are whitish and deflexed. The species is restricted to northern Kenya.

A. schweinfurthii is acaulescent or suckering from the base and has a short procumbent stem. The compact leaves are spreading and recurved, bearing pungent marginal teeth. The inflorescence is 4–8-branched. The species is widely distributed, occurring in central and west Africa.

A. tugenensis is shrubby in habit with stems ascending or decumbent reaching 1.2 m in length. The leaves are spreading and slightly recurved, dull green and somewhat rough to the touch. The inflorescence is a panicle. The whitish bracts envelop the buds. This species is only known from the Baringo District in Kenya.

A. ukambensis is acaulescent, suckering to form dense groups. The leaves are erect and slightly incurved, and conspicuously striate. The inflorescences are simple or 1–2-branched. The racemes are sub-capitate and densely flowered. This species is usually found on exposed rocky outcrops in southern Kenya.

A. wrefordii is acaulescent, usually solitary or in dense groups. The leaves are erect, spreading with the apices recurved, and with pungent marginal teeth. The inflorescence is a panicle, rarely simple. The racemes are sub-capitate bearing flowers of which the perianth is cylindrical-clavate. This species has been recorded in Uganda, Kenya and Sudan.

Evaluation of characters:

1. Habit. Several growth forms found in the genus *Aloe* are represented in the group. The basic habit forms are:

1.1 Acaulescent or with a short procumbent stem: *A. chabaudii*, *A. labworana*, *A. schweinfurthii*, *A. rugosifolia*, *A. ukambensis*, *A. murina*, *A. otallensis*, *A. parvidens*, and *A. wrefordii*. The first five species listed above form dense groups due to suckering from the base. The other species are all solitary or occur in small groups.

1.2 Most species in this chemical group produce long stems that are initially erect but become decumbent as the length of the stem increases. *Aloe archeri* is the extreme situation where the decumbent stem could reach lengths of 4 m long. Longer stems of *A. deserti*, *A. fibrosa* and *A.*

morijensis are frequently supported by surrounding shrubs. The other species in this category are: *A. babatiensis*, *A. multicolor*, *A. palmiformis*, *A. pustuligemma* and *A. tugenensis*.

1.3 A completely different growth form is presented by the South African species *Aloe plicatilis*, which develops a robust, dichotomously branched stem that remains erect, giving this aloe a tree-like appearance.

2. Leaf characters. Most species (14 out of 20) represented in this group bear their leaves in a spreading manner with the leaf deflexed or in some case only the apices are recurved. This applies to *A. archeri*, *A. babatiensis*, *A. deserti*, *A. fibrosa*, *A. labworana*, *A. morijensis*, *A. multicolor*, *A. otallensis*, *A. palmiformis*, *A. parvidens*, *A. pustuligemma*, *A. schweinfurthii* and *A. tugenensis*. In *A. chabaudii*, *A. francombei*, *A. murina* and *A. plicatilis*, the leaves are erect and not decurved. *Aloe plicatilis* once again represents a distinctive difference as the leaves are distichously arranged while all other species have the leaves arranged in rosettes. In *A. rugosifolia* and *A. ukambensis* the leaves are slightly incurved. The latter species has leaves that are conspicuously striate; the only other species in this group with lineate markings is *A. chabaudii*. Most species in this group have leaves spotted on the upper or lower leaf surface or on both. With the exception of a few species the leaf margin is armed with large deltoid pungent teeth. The leaf surface is usually smooth, with the exception of *A. archeri*, *A. deserti*, *A. francombei*, *A. murina*, *A. rugosifolia* and *A. tugenensis*, all of which have a somewhat asperous leaf surface.

3. Bracts. Based on quantitative measurements two 'size groups' are recognised within this group. Those species in which the bracts are very small (3–7 mm) are *A. chabaudii*, *A. labworana*, *A. murina*, *A. palmiformis*, *A. parvidens*, *A. plicatilis* and *A. schweinfurthii*. In all the other species the bracts are fairly large, ranging in length from 10 to 30 mm. The bracts of *A. deserti* and *A. rugosifolia* are distinctly white and deflexed.

4. Inflorescence and raceme. With the exception of the following species, most species in the group have a panicle with cylindrical racemes. *Aloe deserti* presents the unique phenomenon where the racemes are initially drooping and limp and become stiff and erect with maturity. In *A. fibrosa*, *A. morijensis*, *A. palmiformis*, *A. plicatilis* and *A. ukambensis* the inflorescence is not a much-branched panicle but mostly simple or 2–3-branched in some cases. *Aloe ukambensis* is the only member of this group that has a sub-capitate raceme. *A. murina* is also unique in the group as the developing buds are secund.

5. Perianth. Most species pertaining to this group have a perianth that is cylindrical-trigonous in shape. The following species deviate from this general pattern. *Aloe chabaudii* has a decurved perianth, which is restricted above the ovary, where it is trigonously indented. A sub-clavate to clavate perianth is characteristic of *A. otallensis*, *A. wrefordii* and *A. multicolor*. *Aloe pustuligemma*, *A. francombei* and *A. otallensis* are characterised by the pustulate perianth surface.

6. Distribution. As shown in Figure 13.2, most species in this group are distributed in Tropical East Africa (Uganda, Tanzania and Kenya). The arm extending into West Africa represents only *A. schweinfurthii*. The highest number of plicataloside species (13) occur in Kenya. The two geographical 'outliers' are *Aloe plicatilis* (South Africa) and *A. palmiformis* (Angola), which have localised distributions in their areas. Most species in this group have specific and localised distributions. *Aloe chabaudii*, *A. labworana*, *A. parvidens*, *A. schweinfurthii* and *A. ukambensis* deviate from the norm as they are widely distributed in comparison with the other species in this group.

Relationships

The 'affinity diagram' (Figure 13.3) is a summary of previously reported relationships between species in this group. All species contained in the solid block are characterised by possession of the naphthalene-like compound plicataloside, which is the unifying character for all the taxa.

In her Flora treatment of the Aloes of Tropical East Africa, Carter (1994) states that due to the absence of morphological characters indicating phylogeny, the species are not arranged in any phylogenetic sequence. She does however suggest that although the species are numerically arranged following the concept of Reynolds (1966), where species are basically arranged in terms of habit characters 'from smallest to biggest', species that she thinks 'belong together' are listed together (pers. comm.), though her list is not divided into groups. All the species in block A are closely arranged in the Flora treatment. The same applies for those species in block B. Yet, reference to literature shows that these two groups of species (block A and B) have not previously been associated with one another. Of the species listed in block A, many have been related to one another. Newton (1994) assessed the morphological relationships of some of these species. He remarks on the similar growth habit of *A. pustuligemma*, *A. archeri* and *A. tugenensis*, all having rough and unspotted leaves.

In the protologue of *A. tugenensis* (Newton & Lavranos, 1990), it is suggested that this species is closely related to *A. compacta* (now *A. macrosiphon* — unfortunately no exudate material of this

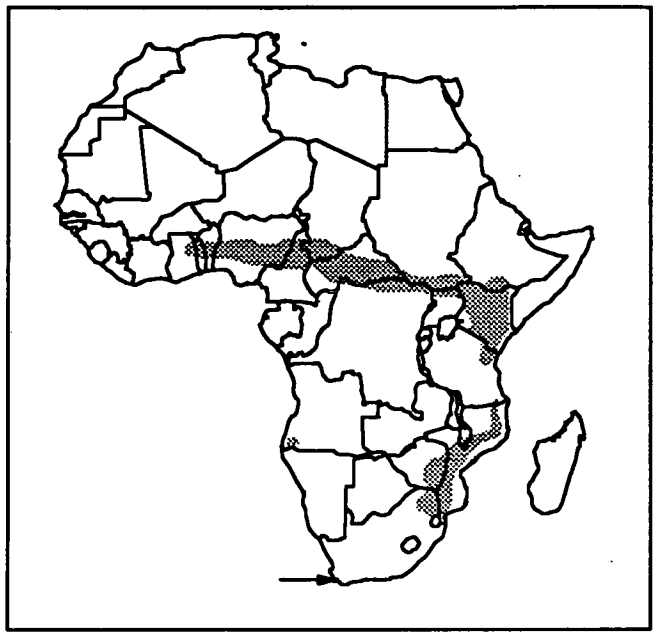


Figure 13.2. Geographical distribution of plicataloside containing species of *Aloe*.

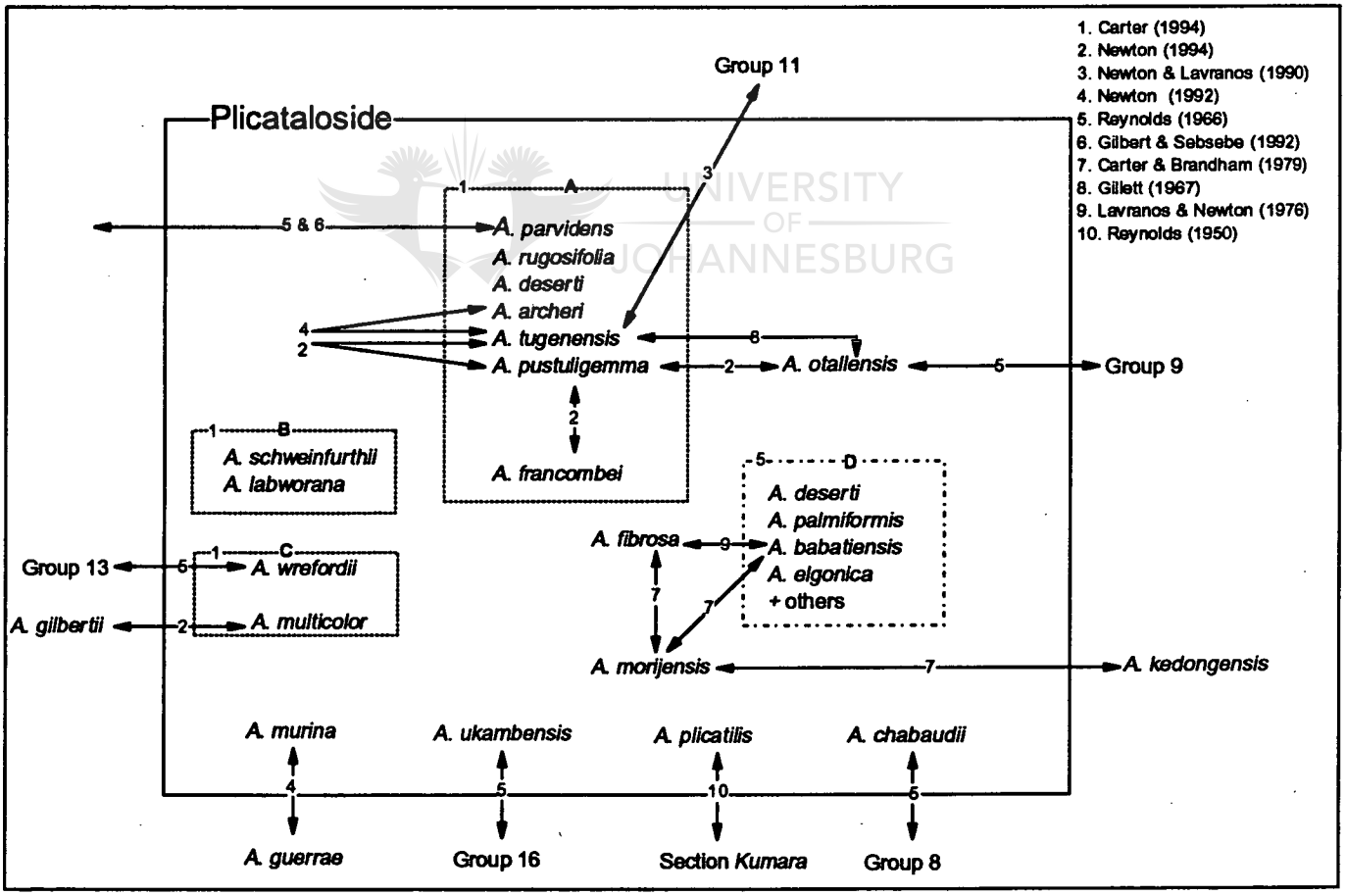


Figure 13.3. A. taxonomic 'affinity-diagram' showing possible relationships between the taxa as previously suggested. Numbers correspond to literature references where these relationships between the taxa have been discussed.

species could be obtained). The authors speculate that the Group 11 created by Reynolds (1966) could include other species with large floral bracts that are imbricate and cover the flower buds, e.g. *A. deserti*. The latter species also contains plicataloside. In the amended species description of *A. archeri* (Newton, 1992) a correlation is drawn between *A. tugenensis* and *A. archeri* as both species have imbricate bracts, and they are similar in growth and habit. Three species in this plicataloside group (block A) are characterised by a pustulate perianth surface *(A. pustuligemma, A. otallensis and A. francombei)* and it has been suggested by Newton (1994) that it seems unlikely that this 'unique character' would evolve more than once in the very small geographical area where all three species occur. Reynolds (1966) never saw *A. otallensis*, and as the other two allied species were described recently not too much emphasis should be placed on the present taxonomic position of this species, which places it in Group 9. *Aloe rugosifolia* was previously known as *A. otallensis* var. *elongata*. After assessing the identity of *A. otallensis*, Gilbert and Sebsebe (1992) raised this variety to specific rank and renamed it. As suggested by the new epithet, the leaves of this species are somewhat rugose. Rough leaves are also characteristic of *A. archeri*, *A. deserti, A. francombei*, *A. murina* and *A. tugenensis*. Another character placing *A. rugosifolia* close to *A. deserti* is the whitish, deflexed bract that is characteristic of both species.

Block B in Figure 13.3 contains two species that are closely arranged in Carter 1994. *A. labworana* was previously described as a variety of the widespread *A. schweinfurthii*, hence the expected similarity.

A. wrefordii and *A. multicolor*, shown as block D in Figure 13.3, also appear close together in Carter's account. *A. wrefordii* is placed by Reynolds (1966) in Group 13 as it has a clavate perianth. In this plicataloside group, two other species, *A. multicolor* and *A. otallensis*, have sub-clavate perianths. Newton (1994) suggests *A. multicolor* is most closely related to *A. gilbertii*. Although these two species differ in growth habit, leaf and bract characters this similarity is suggested on the basis of perianth shape.

The last significant group in the affinity diagram is contained in block D. Reynolds (1966) created Group 19 to house all species with a shrubby growth form. Four of the plicataloside species are included in this large group. Based on habit and inflorescence characters, *A. fibrosa* is suggested to be most closely related to *A. babatiensis* (Lavranos & Newton 1976). Both these species are in their turn suggested to be closely allied to *A. morijensis*, while the latter species also shows a morphological resemblance to the non-plicataloside species, *A. kedongensis* (Carter & Brandham,

1979). The multi-disciplinary study by Cutler *et al.* (1980) on the morphology, anatomy, cytology and chemistry of a large group of species suggests an affinity between *A. fibrosa*, *A. morijensis* and *A. babatiensis*. The hypothesis is also put forward that *A. morijensis*, through chromosome doubling, could have given rise to the tetraploid species (*A. dawei* and *A. elgonica*). *A deserti* is placed in Group 19 by Reynolds (1966), but all the species with which it is associated in Block A, based on Carter (1994), were published after 1966.

All the species discussed above show some degree of morphological coherence with other plicataloside-containing species. Three of the four 'peripheral' species have not previously been regarded as even distantly related to any other plicataloside-containing species. Newton (1992) suggests an affinity between *A. murina* and the Angolan endemic, *A. guerrae*. Unfortunately no leaf exudate sample could be obtained from this species. The only other species in Angola to contain plicataloside is *A. palmiformis*.

Reynolds (1966) places *A. ukambensis* in Group 16 of the tropical aloes. This is the only species in the 'plicataloside-group' with a sub-capitate raceme. All the other species have cylindrical racemes. Together with *A. chabaudii*, these two species are also unique in that they are the only two species in which the leaves are striate. *Aloe chabaudii* is placed in Group 19, which contains all species in which the perianth is trigonously indented. *Aloe parvidens* (syn. *A. pirottae* sensu Reynolds) is included in Group 4 of the tropical aloes (Reynolds, 1966), which is defined as a group containing all species with 'more-or-less' striped flowers. The last and most fascinating in terms of geographical isolation is the South-African endemic *A. plicatilis*, which is morphologically unique; hence its position in the monotypic section *Kumara* (Reynolds, 1950).

It would be presumptuous to suggest any evolutionary or phylogenetic hypotheses on the data presented. The presence of this interesting chemical compound in the 20 species, and the absence of the chromones and anthrones (characteristic of *Aloe*), encourages some speculation on the possibility that this could be a monophyletic group. However, this statement is not convincing as there is only one single chemical apomorphy for this group, and no morphological character could be found to re-enforce the chemical coherence shown by the leaf exudate chemistry. This comes as no surprise as it is known that taxonomic research on *Aloe* is always confronted by the reality that the genus has relatively few morphological apomorphies at the infrageneric level. This is best represented in the work of Reynolds (1966), where an utilitarian approach was followed to group

'morphologically similar' species together, which obviously does not necessarily reflect or predict natural relationships. It is not intended that chemical characters should enjoy preference over the morphological characters as all problems (e.g. convergence) encountered with morphological characters are prevalent for chemical characters. However, the presence of this unique compound should not be completely dismissed as chemotaxonomic coincidence, and the possibility of taxonomic affinity between these plicataloside-containing taxa should at least be explore further.

Figure 13.4: Representatives of the plicataloside-producing aloes. ⇨

Photo: Newton 1994

Aloe multicolor

Photo: Newton 1994

Aloe pustuligemma

Photo: Newton 1994

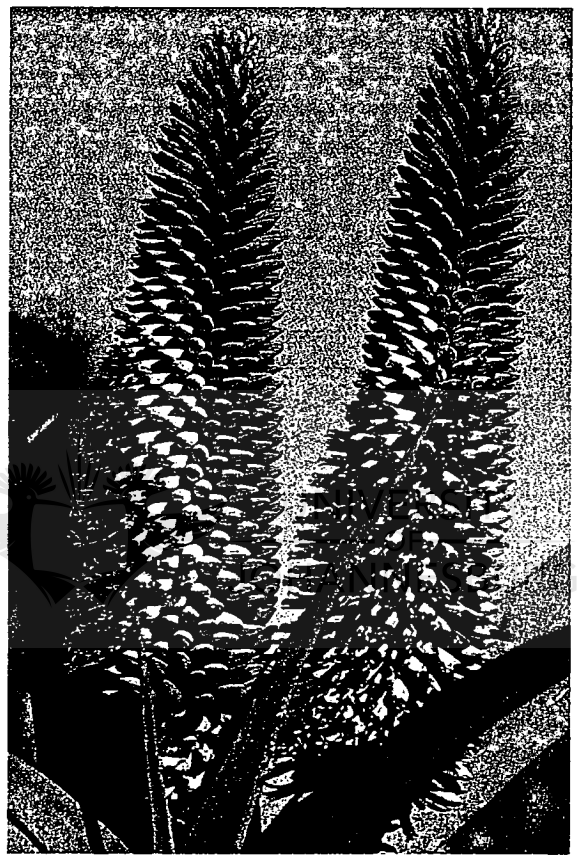
Aloe multicolor (flower)

Photo: van Wyk & Smith 1996

Aloe chabaudii

Photo: van Wyk & Smith 1996

Aloe plicatilis



Chapter 14

The occurrence and taxonomic distribution of chromones and anthrones in *Aloe* - an overview

CHAPTER 14

THE OCCURRENCE AND TAXONOMIC DISTRIBUTION OF CHROMONES AND ANTHRONES IN *ALOE* - AN OVERVIEW

This chapter will summarise the occurrence and the taxonomic distribution of the main leaf compounds which have not been discussed Chapters 5 - 13. The two major classes of phenolic compounds in the leaves of *Aloe* (exudate and / or leaf extracts) are the chromones (e.g. aloesin) and the anthrones (e.g. aloin). Other classes of phenolic compounds which have a more restricted representation in the genus are benzene and naphthalene derivatives (e.g. plicataloside), coumarins (e.g. feralolide), phenyl pyrones (e.g. aloenin), alkaloids (e.g. γ-coniceine) and flavonoids (e.g. isovitexin).

CHROMONES

The chromones constitute the highest percentage of the total volume of leaf exudate. Usually only one pair of anthrone c-glucoside isomers are present (e.g. aloin A / B or homonataloin A / B), while various chromone derivatives may occur in a single species. The distribution of the chromones will firstly be discussed followed by a summary on the distribution of aloeresin A and D after which the broad categories based on the ester group attached to the chromone will be mentioned.

During this study 380 taxa have been analysed and chromones have positively been identified in 153 (44 %) of all species. The taxonomic distribution of the chromones are superimposed on the present classification system for *Aloe* in Figure 14.2. A key to the interpretation of the diagram is shown in Figure 14.1. Studying the first hierarchy (i.e. sectional level) it is interesting to note that chromones are absent in 'taxonomic extremes' of the genus. In the grass-like aloes (*Leptoaloe* and *Graminialoe*) which comprises *ca.* 38 species only three species contain these chromones; *A. dominella*, A. *chortolorioides* var. *chortolorioides* and A. *chortolorioides* var. *wooliana* . Chapter 12 elaborates on the observation that the two latter species deviate from the chemical norm for the grass aloes as they contain both chromones and anthrones generally absent in this group. The tree-like aloes also do not accumulate chromones. Both section *Lomatophyllum* and series *Macrifoliae* contain species where chromones have been detected in trace amounts. These two groups together with the grass-like aloes are believed to represent a basal lineage in *Aloe*.

The general observation could be made that the chromones are mostly accumulated in the 'true aloes' - the latter term has been modified to include all species with the general

The inflorescence of *Aloe speciosa*, a homonataloin containing species (Photo: Leo Thamm).

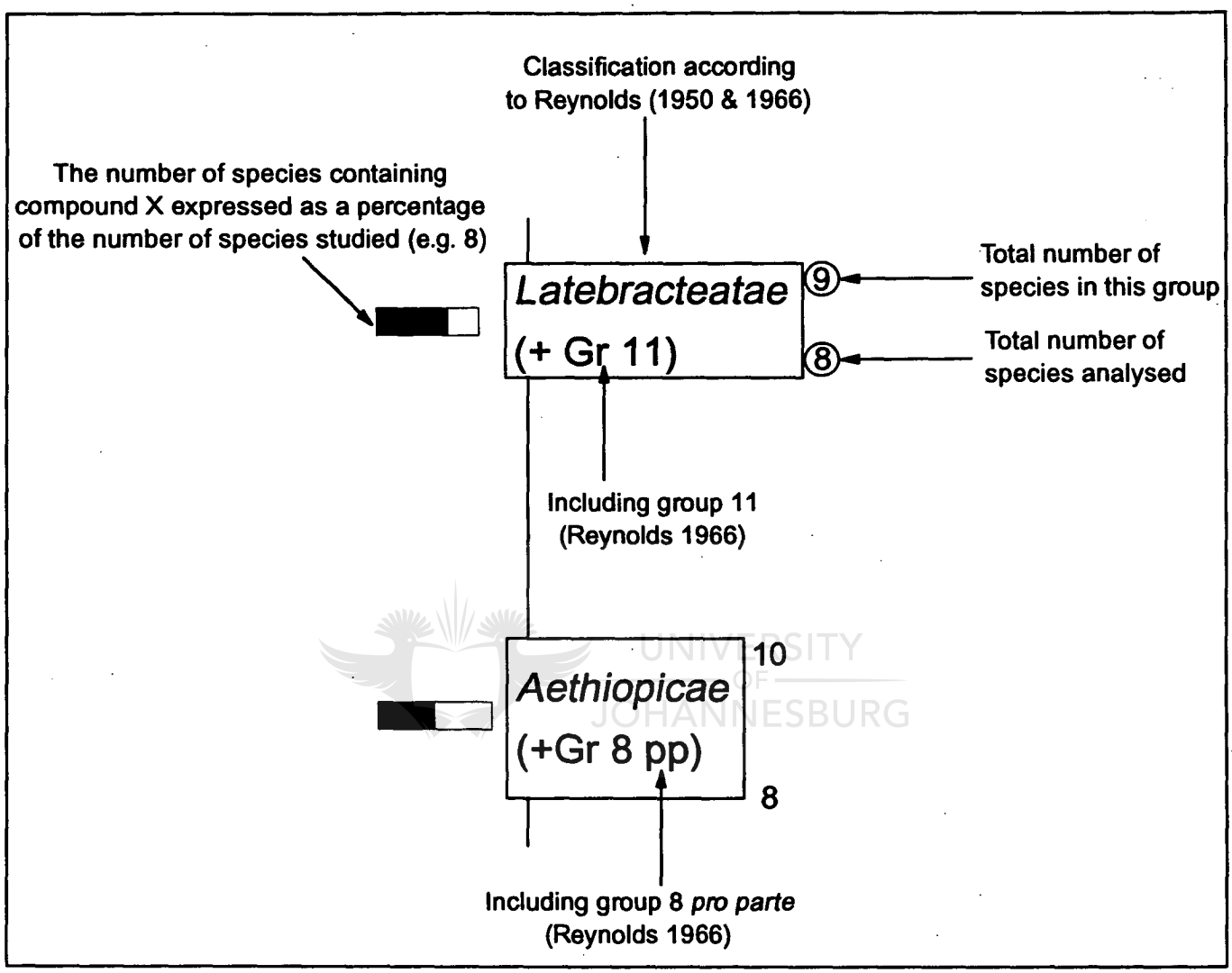


Figure 14.1: Key diagram for the interpretation of Figures 14.2, 14.3, 14.5, 14.12, 14.13.

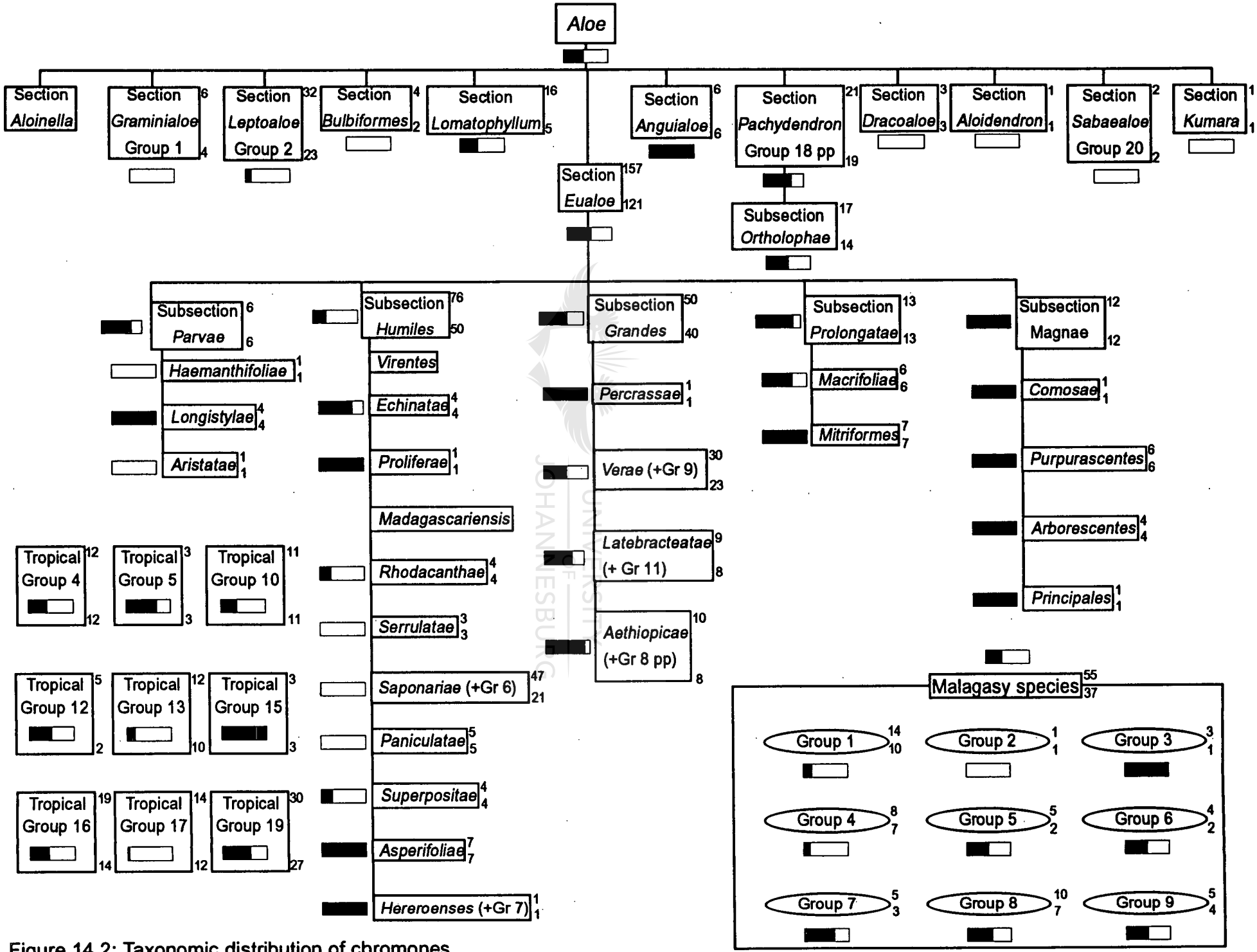


Figure 14.2: Taxonomic distribution of chromones.

appearance associated with this group (including *Latebracteatae*, *Hereroenses*, *Superpositae*, and *Purpurascentes*), *Pachydendron* (including *Ortholophae*) and *Arborescentes* (including Group 19). It is noteworthy that the widely-distributed chromones are only detected in 14 species of the 37 Malagasy species studies. This is in agreement with the general pattern for the Malagasy endemics which are very different in exudate composition when compared to African counterparts.

The expansive distribution of chromones which are almost present in every infrageneric group suggests that these compounds have been present since the early evolution of *Aloe* and that the mosaic pattern of distribution could be ascribed to; 1. The absence of the biochemical pathway responsible for chromone production (e.g. grass-like aloes), 2. A secondary loss of these exudate compounds (e.g. tree-like aloes).

Aloesin

Of all the leaf compounds aloesin is the most widely spread in the genus. As early as 1967 McCarthy & Haynes reported aloesin in 19 species of *Aloe* and in 1971 Holdsworth detected this compound in another five species. An extensive TLC survey by Reynolds (1985) showed aloesin to be present in 35 % of the 240 species studies. Rauwald *et al.* (1991) calculated aloesin in 46 % of 183 species studied. This study has positively identified aloesin in 131 species (i.e. 39 %). As all chromone-producing species usually contain aloesin the discussion above for chromones in general is relevant to this compound. This implies that aloesin is the 'precursor' chromone from which the other chromones have their origin. In some cases aloesin is believed to be totally transformed into analogue compounds (e.g 7-*O*-methylaloesin), while in most cases at least trace amount of aloesin are detected together with other compounds which are structural modifications of this basic compound.

Aloeresin A

Aloeresin A is a *p*-coumarate ester of aloesin esterfied on the C_2 of the sugar moiety (Gramatica *et al.* 1982). The structure and UV spectrum is shown in Chapter 12. The taxonomic distribution of aloeresin A is shown in Figure 14.3. This compound is restricted to members of series *Pachydendron* (including *Ortholophae*) and in several species from tropical Africa. Aloeresin A could not be detected in any of the Malagasy species. The aloeresin A producing species have been extracted from Figure 14.3 and are diagrammatically represented in Figure 14.4. The co-occurrence of other exudate compounds in these species are shown

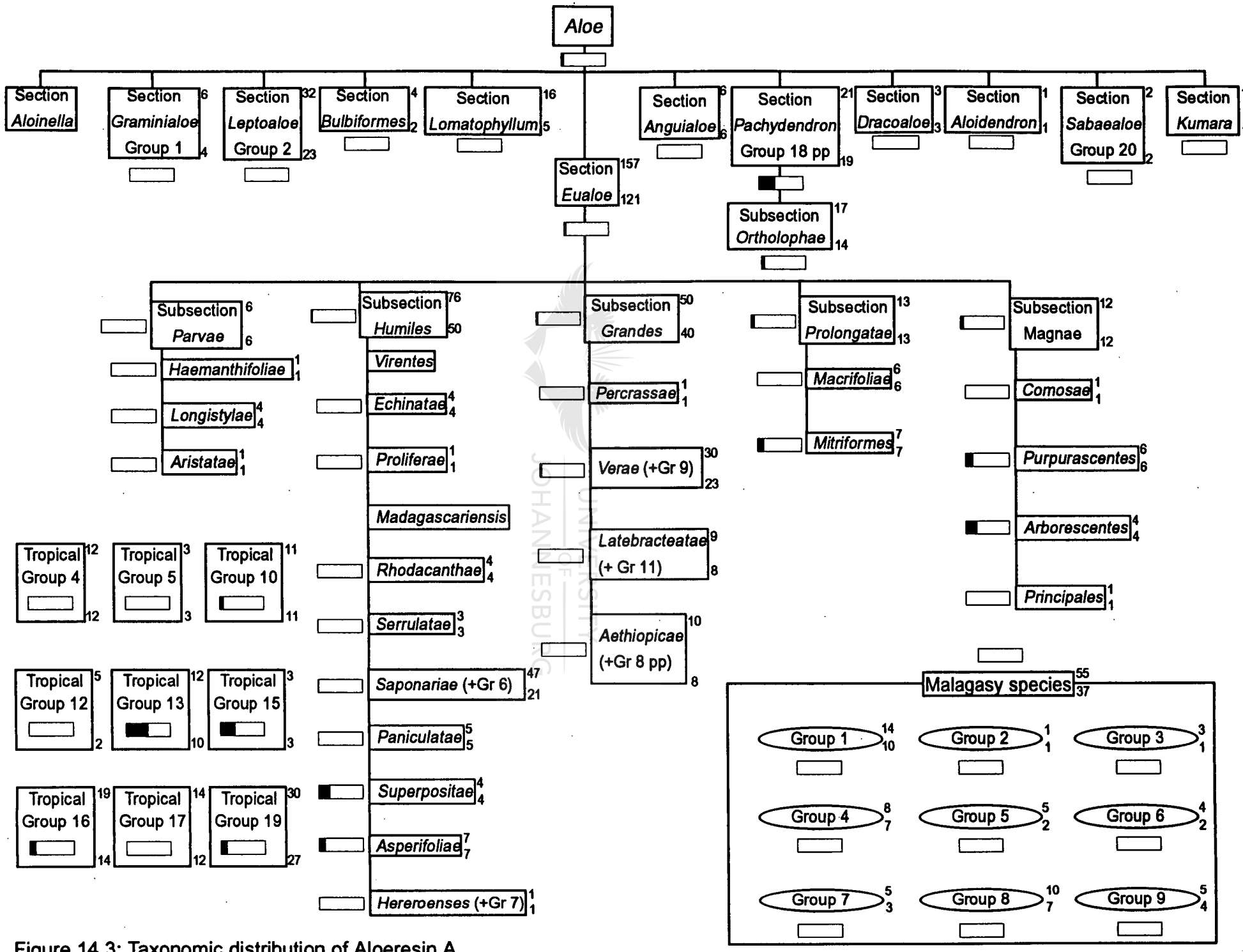


Figure 14.3: Taxonomic distribution of Aloeresin A.

in Table 14.1.

The highest number of species containing aloeresin A are grouped in *Aloe* series *Pachydendron*. This infrageneric group is an assemblage of species in which the habit resembles that of a 'thick-tree' although it also contains species which are very shortly caulescent (e.g. *A. reitzii* and *A. petricola*). A recent study on the leaf exudate of this group (Reynolds 1997) concluded that it is a chemically heterogenous group.

Table 14.1: The occurrence of exudate compounds in Aloeresin A containing species.

	1	2	3	4	5	6	7	8	9	10
A. amicorum		■		■		■		■		
A. angelica	■			■	■			■		■
A. arenicola	■			■	■			■		
A. breviscapa	■	■		■		■		■		■
A. cameronii	■			■		■	■		■	
A. catengiana	■			■				■		
A. cheranganiensis	■		■	■		■	■			
A. citrina	■	■		■		■		■		
A. corallina	■			■			■			
A. cremnophila	■			■				■		
A. decurva	■			■		■	■			
A. dhufarensis	■	■		■				■		
A. excelsa	■			■		■	■			
A. ferox	■			■			■		■	
A. forbesii	■			■			■			
A. hardyi	■			■				■		
A. hildebrandtii	■			■			■			
A. marlothii	■			■		■	■	■		
A. petricola	■			■			■			
A. reitzii	■			■			■			
A. suprafoliata	■			■				■		
A. volkensii	■			■				■		

1. Aloesin
2. Homonataloside B
3. Aloenin
4. Aloeresin A
5. Aloeresin E / F
6. Aloeresin D
7. Aloin A & B
8. Homonataloin A & B
9. Aloinosides A / B
10 Cinnamoyl chromones

These results are in agreement with those reported by Reynolds (1997) with the exception that the presence of aloeresin A could not confirmed in *A. rupestris* and *A. thraskii*. The taxonomic 'misfit' in *Pachydendron*, *A. angelica* is suggested to be more closely allied to the series *Mitriformes* with which it shares several chemical and morphological characters (Chapter 11). The only other member of the *Mitriformes* containing Aloeresin A is *A. arenicola*. This compound further reinforces the close taxonomic affinity between *A. ferox* (syn. *A.*

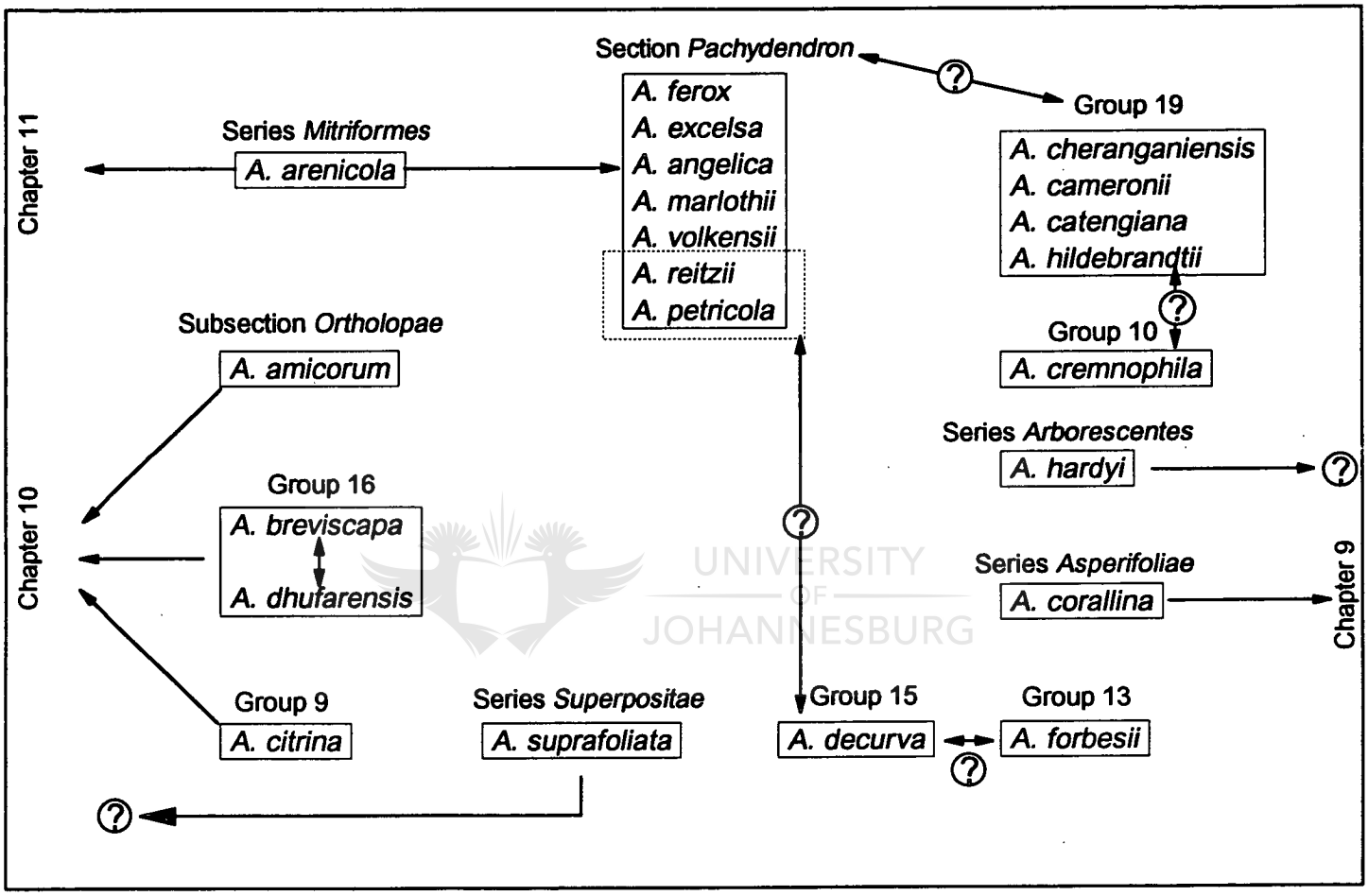


Figure 14.4: Taxonomic arrangement of aloeresin A containing species.

candelabrum, Viljoen *et al.* 1996), *A. excelsa* and *A. marlothii* (syn. *A. spectabilis*). The presence of aloeresin A also indicates a taxonomic affinity between species in *Aloe* section *Pachydendron* and species included in Group 19 of the tropical aloes (Figure 14.4). This has been discussed in Chapter 5 where the occurrence of aloinosides and microdontin indicates a definite relationship between these two groups. In Chapter 5 it has been suggested that the shared characters between *A. africana* and *A. cameronii* (aloinosides and curved perianth) could be indicative of this relationship. Here, it is interesting to note the chemical similarity between *A. cameronii* and *A. ferox*. The latter species is believed to be a close relative of *A. africana*.

The cliff-dwelling *A. hildebrandtii* is also included by Reynolds (1966) in Group 19. A multi-disciplinary study on the cremnophilous aloes (Brandham *et al.* 1994) suggested a close affinity between *A. cremnophila* and *A. jacksonii*. The phytochemistry of the latter species has been extensively researched by Conner *et al.* (1988 & 1990) and the unique exudate profile shown in Appendix 2 is not matched by any other species of *Aloe*. Another species included in their study group was *A. hildebrandtii*, which like *A. cremnophila* contains aloeresin A. Three other aloeresin A containing species have a habitat preference for steep rocky areas; *A. amicorum*, *A. corallina*, *A. hardyi*. *Aloe amicorum* is suggested to be more closely related to other homonataloside B containing species (Chapter 10) and it would suffice to mention that four homonataloside B containing species (*A. breviscapa*, *A. dhufarensis*, *A. amicorum* and *A. citrina*) are included in this group of which possible taxonomic relationships have been discussed in Chapter 10. Although *Aloe corallina* does not contain the chemical apomorpy for *Aloe* series *Asperifoliae* (Chapter 9) is shares more chemical and morphological characters with members of the *Asperifoliae* group than with any other group. *Aloe hardyi* is placed in *Aloe* series *Arborescentes* (Glen 1987). The *Arborescentes*-group contains four species and it is doubtful if they are related in any way. *Aloe suprafoliata* is placed in series *Superpositae*. The taxonomic coherence of this group could not be justified as its members have diverging biochemical pathways. *Aloe thomcroftii* and *A. pretoriensis* accumulate flavonoids (Chapter 12) while *A. christianii* contains the aloin isomers and 8-*O*-methyl-7-hydroxyaloin (Chapter 6). *Aloe suprafoliata* accumulates homonataloin A and B and coumaroyl chromones.

Aloe decurva is placed in Group 15 of the tropical aloes together with other shortly pedicellate species e.g. *A. aculeata*. The latter species is closely related to *A. reitzii* and *A. petricola*, which are also produce aloeresin A and are placed in section *Pachydendron*, together with *A. aculeata* (Reynolds, 1950). The last species in this group occupies a position in Group 13

which is defined by plants with clavate perianths. *Aloe decurva* has a distinct clavate perianth which together with their identical leaf chemistry suggests a degree of similarity between these two species (Figure 14.4).

In summary on the chemotaxonomic value of aloeresin A it is clear that this compound is rather erratic in its taxonomic distribution. This pattern clearly demonstrates that the exudate composition of species have become 'entangled' resulting in a chemical mosaic. This is shown by the four homonataloside B containing species which share this compound yet their closest chemical relatives are very different. The occurrence of aloeresin A is a further support of the notion that many of the shrubby aloes (Group 19) are closely related to species in section *Pachydendron*.

Aloeresin D

Aloeresin D is also a *p*-coumarate ester of aloesin esterfied on the C_2 of the sugar moiety and with methylation at the C_7 position (Speranza *et al.* 1986). The structure and UV spectrum is shown in Chapter 2. The taxonomic distribution of aloeresin D is shown in Figure 14.5. This compound is absent in the dwarf and grass-like aloes as well as in the tree aloes. The taxonomic distribution as depicted in Figure 14.5 also reflects the interesting geographical distribution of this chromone shown in Figure 14.6. Aloeresin D is mostly present in aloes of north and east Africa and in some species on the Arabian Peninsula. Series *Verae* (11 aloeresin D containing species), *Aethiopicae* (4), Group 16 (4), Group 19 (10) and subsection *Ortholophae* (4) are groups which contain most of the aloeresin D accumulating species, all of these groups only have representatives in Tropical Africa. It is speculated that this compound had its origin in the tropical region of the distributional range of *Aloe* and that it has mostly remained restricted to the species in these areas. Only three species in South Africa (*A. comosa*, *A. arborescens* and *A. marlothii*) show high levels of aloeresin D. The remaining 40 species are all found in north east Africa with the high number of species distributed in Kenya, Somalia and Tanzania. The disjunction in distribution (in number) from north to south has also been shown in Chapter 13 for *A. plicatilis*. It is interesting to note that this pattern is repeated in this group with *Aloe comosa* being the geographical outlier. In his treatment Reynolds (1950) creates a monotypic series for *A. comosa*. Indeed, this species has distinctive morphological features, but judged by the chemical profile it is suggested that the closest taxonomic relatives of *A. comosa* could be found in the tropics.

The present taxonomic arrangement of aloeresin D containing species are diagrammatically

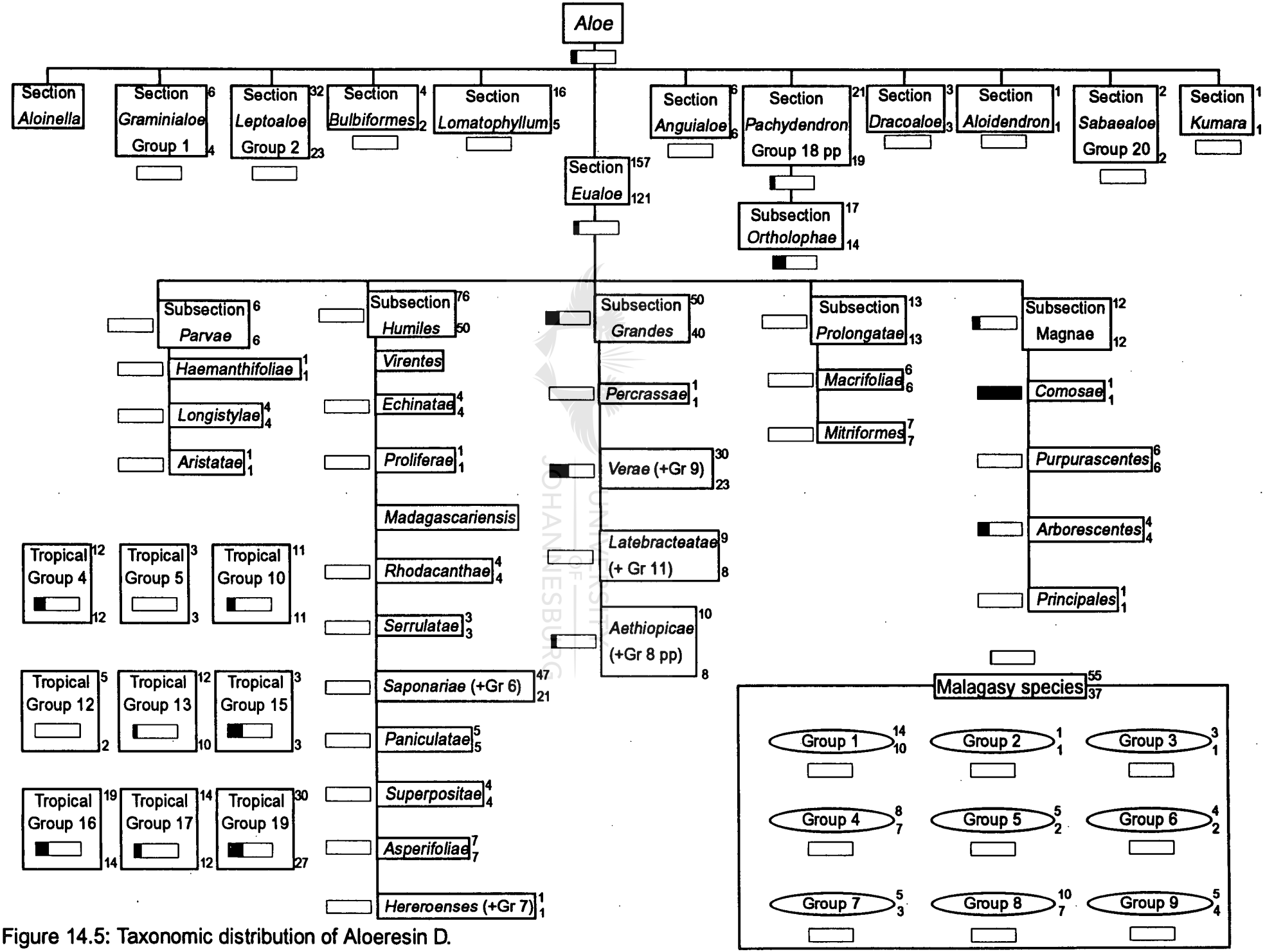


Figure 14.5: Taxonomic distribution of Aloeresin D.

Table 14.2: The occurrence of exudate compounds in Aloeresin D containing species.

	1	2	3	4	5	6	7	8	9	10
A. aageodonta						■		■	■	
A. amicorum		■			■	■	■			
A. arborescens	■		■			■		■		
A. bargalensis		■			■	■	■			
A. bella						■		■		
A. brandhamii	■		■			■		■		
A. breviscapa	■	■			■	■	■			
A. cameronii	■				■	■		■	■	
A. canarina	■					■		■	■	■
A. cheranganiensis	■		■		■	■		■		
A. chrysostachys						■		■	■	
A. citrina	■	■			■	■		■		
A. classenii	■		■			■		■		
A. comosa	■					■	■			
A. confusa						■				
A. dawei	■		■			■		■		
A. decurva	■				■	■		■		
A. erensii		■				■	■			
A. excelsa	■				■	■		■		
A. flexilifolia	■					■		■	■	
A. kulalensis	■					■		■		
A. leachii	■		■			■		■		
A. marlothii	■				■	■	■	■		
A. massawana						■		■		
A. mcloughlinii	■					■		■	■	
A. menachensis	■			■		■		■		
A. mendesii	■	■				■	■	■		
A. monticola	■		■			■		■		
A. ngongensis						■		■	■	■
A. niebuhriana				■		■		■		
A. nyeriensis	■		■			■		■		
A. officinalis	■			■		■		■		
A. peckii	■					■		■	■	
A. pubescens	■			■		■	■	■		
A. rabaiensis						■		■	■	
A. retrospiciens				■		■	■	■		
A. rigens	■					■	■			
A. secundiflora			■			■		■		
A. splendens	■				■	■	■			
A. squarrosa	■	■				■	■			
A. tomentosa	■	■		■		■	■	■		
A. vera	■					■		■		
A. wilsonii	■					■	■			

1. Aloesin
2. Homonataloside B
3. Aloenin
4. 8-O-Me-7-OH-aloin
5. Aloeresin A
6. Aloeresin D
7. Homonataloin A & B
8. Aloin A & B
9. Aloinosides A & B
10 Microdontin A & B

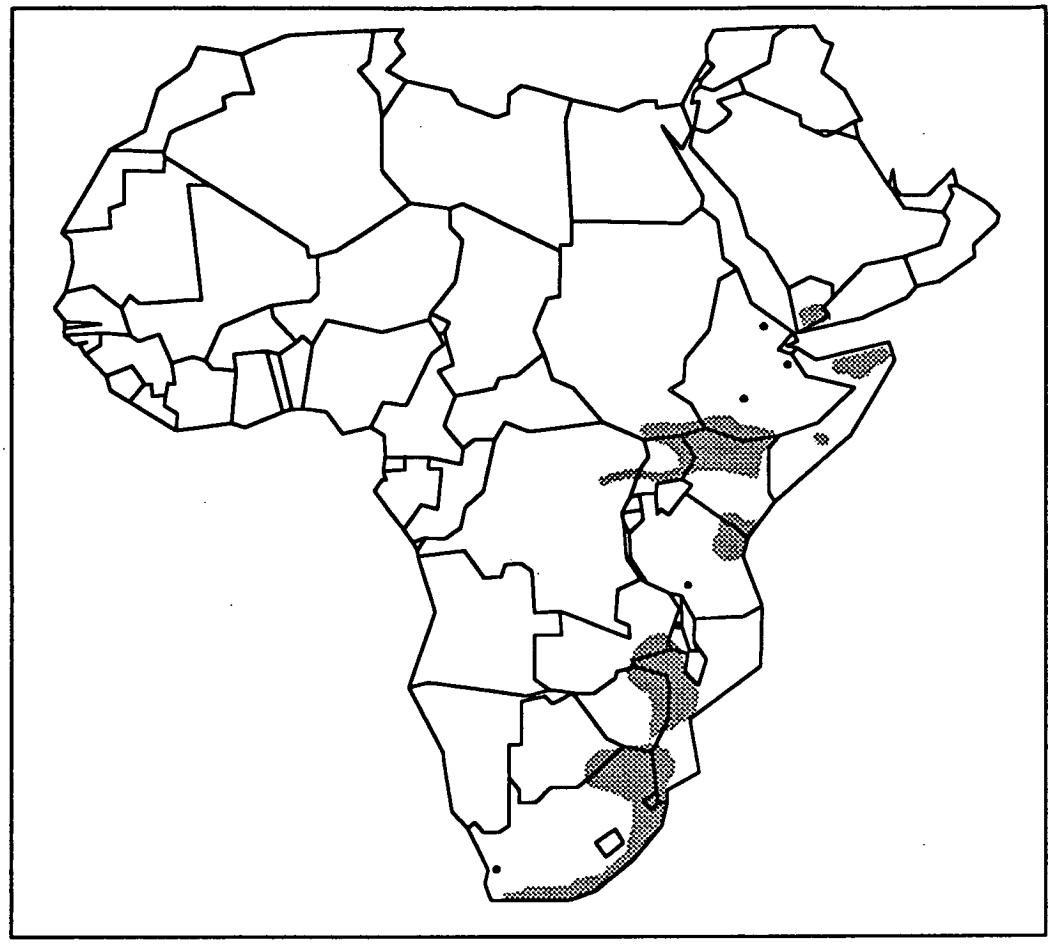


Figure 14.6: The geographical distribution of aloeresin D containing species.

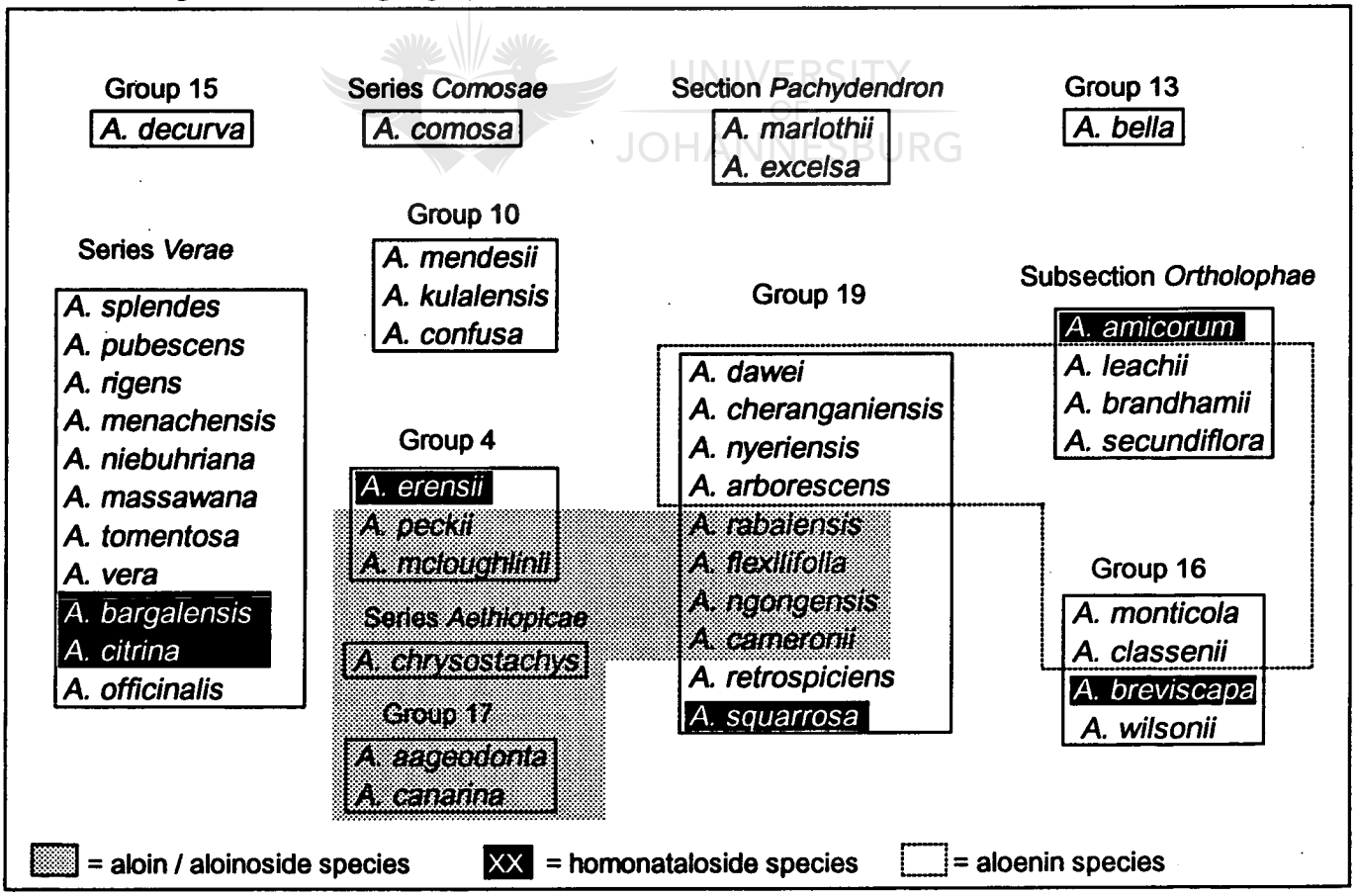


Figure 14.7: Taxonomic arrangement of aloeresin D containing species. The three distinct chemical patterns have been superimposed (see text for explanation).

represented in Figure 14.7 with the co-occurrence of exudate compounds in these species shown in Table 14.2. The impression created in Figure 14.7 is that the distribution of aloeresin D is well correlated to various of the larger groups created by Reynolds (e.g. series *Verae* and Group 19). Although all these species contain aloeresin D it has to be emphasised that this chromone is here used as a marker compound and that the entire exudate compliment has to be examined to explore more convincing chemotaxonomic correlations. If one should only use a single chemical character then the approach would be similar to that used by Reynolds in his groupings of species where single morphological character were used to suggest relationships between species (e.g clavate perianths, secund flowers etc.). The species contained in each of the groups in Figure 14.7 are chemically divergent and this is shown by assessing the distribution of these species in the predefined groups as reflected on the dendrogram in Figure 14.8. The dendrogram was constructed using all the exudate compounds as possible grouping characters (Table 14.2). Although aloeresin D could be used to suggest relationships between species, it does not imply that all aloeresin D containing species are closely related. For example; *Aloe secundiflora* contains aloeresin D and aloenin, the latter is a phenyl pyrone with obvious chemotaxonomic value (discussed in Chapter 7), *A. nyeriensis* and *A. arborescens* are two closely related species which also contain aloenin but on the basis of habit they are placed in a group defined by its 'shrubby growth'. Therefore, the cluster as shown in the dendrogram (Figure 14.8) has grouped all the aloenin-accumulating species together suggesting a relationship between other members in this complex of 40 species. Another example would be *Aloe amicorum* which bears its flowers in a secund fashion, a character placing the species in subsection *Orthlophae*. Yet, it contains homonataloside B which is the only known anthrone diglucoside in *Aloe* and only occurs in 14 other species of *Aloe* (Chapter 10). Within this aloeresin D containing complex there are five homonataloside B producing species which firstly implies a relationship between these five species and a possibly taxonomic alliance with some of the other 38 species in this aloeresin D group.

The arbitrary cut along the y-axis in Figure 14.8 shows two distinct groups which are correlated on the basis of the anthrone isomers produced. Species united in cluster A produces aloin and derivatives thereof (e.g. aloinosides and microdontin) while species in cluster B represents the homonataloin producing species. Two major groupings are defined in A1. A large number of species produce aloin together with aloinosides and in the case of *A. canarina* and *A. ngongensis*, microdontin A and B are formed as a further modification of the anthrone. This group and suggestions on possible relationships have been discussed in Chapter 5. The third

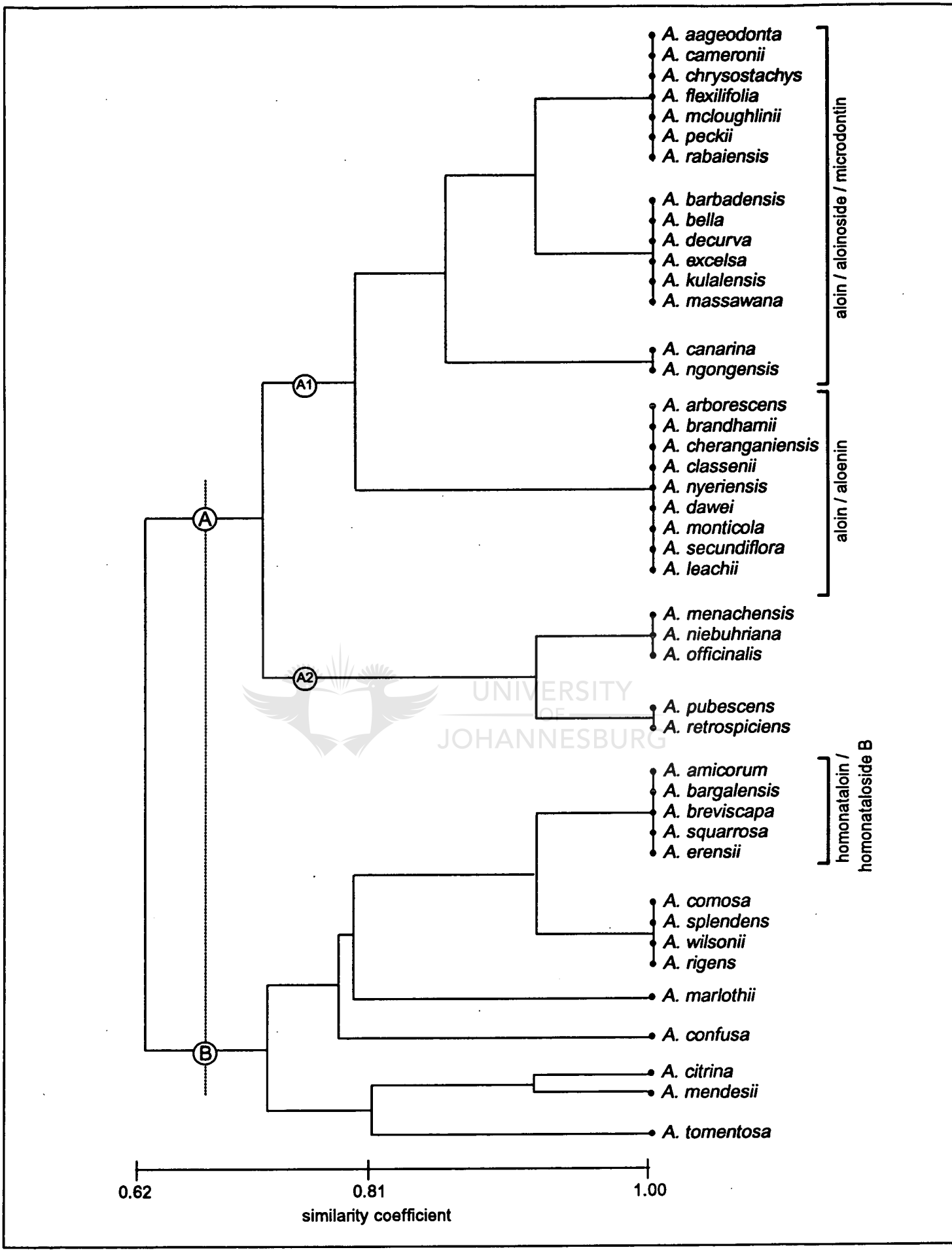


Figure 14.8:. Dendrogram constructed from chemical data in Table 14:2.

cluster (containing *A. arborescens*) is a group of species which accumulate the aloin isomers and the phenyl pyrone aloenin. Thoughts on the chemotaxonomy of this group are given in Chapter 7. The A2 cluster represents the species which produce 8-*O*-methyl-7-hydroxyaloin. The taxonomic distribution of this 'hybrid compound' is dealt with in Chapter 6. *Aloe pubescens* and *A. retrospiciens* are unique in exudate composition as aloin and homonataloin co-occur. This co-occurrence has also been found in *A. mendesii* and *A. mutabilis*. The B cluster represents a heterogenous batch of species where homonataloin A and B are produced. Species in the *A. amicorum*-complex all contain homonataloside B of which the taxonomic implications have been mentioned in Chapter 10. The *A. comosa* complex all produce homonataloin in the presence of aloeresin D. It is interesting to note that *A. comosa* is nested within this group with tropical species as closest chemotaxonomic neighbours. Although the association with these particular species are not convincing, it emphasises a possible relationship between *A. comosa* and species of tropical origin. *Aloe marlothii* could be described as the 'chemical crazy mutant' in *Aloe*. A wide survey of this species has shown immense chemical variation within and between populations (see Chapter 16). The levels of exudate compound in *A. confusa* were extremely low and aloeresin D was detected with two unidentified anthrones. *Aloe citrina* would be better placed in the *A. amicorum*-cluster based on the presence of homonataloside B. The latter cluster however has homonataloin as the major anthrone while *A. citrina* accumulates the aloin anthrone. *Aloe tomentosa* seems to be as variable as *A. marlothii* as various samples of this species was studied with very different and unique chemical profiles (see Appendix 2). To extract meaningful chemotaxonomic value from the occurrence and taxonomic distribution of aloeresin D one needs to establish consensus between Figure 14.7 and the dendrogram represented in Figure 14.8. These results suggest a possible taxonomic nexus between various species with secund flowers placed in subsection *Orthlophae* (e.g. *A. secundiflora*, *A. brandhamii*) with various species placed in Group 19 which houses all aloes with a shrubby habit (e.g. *A. nyeriensis* and *A. dawei*). This is indicated by the presence of aloenin in both taxonomic groups. Newton (1993) questioned the circumscription of subsection *Orthlophae* and suggested that the secund flowers have evolved independently in different groups. These results support the view of Newton as the exudate chemistry of the species included in subsection *Orthlophae* have complex and different exudate compositions. It could be considered that the secund-flowered aloes which accumulate aloenin should be viewed as a group within the aloenin-group of species. This suggestion would be based on two character states and not a single morphological character

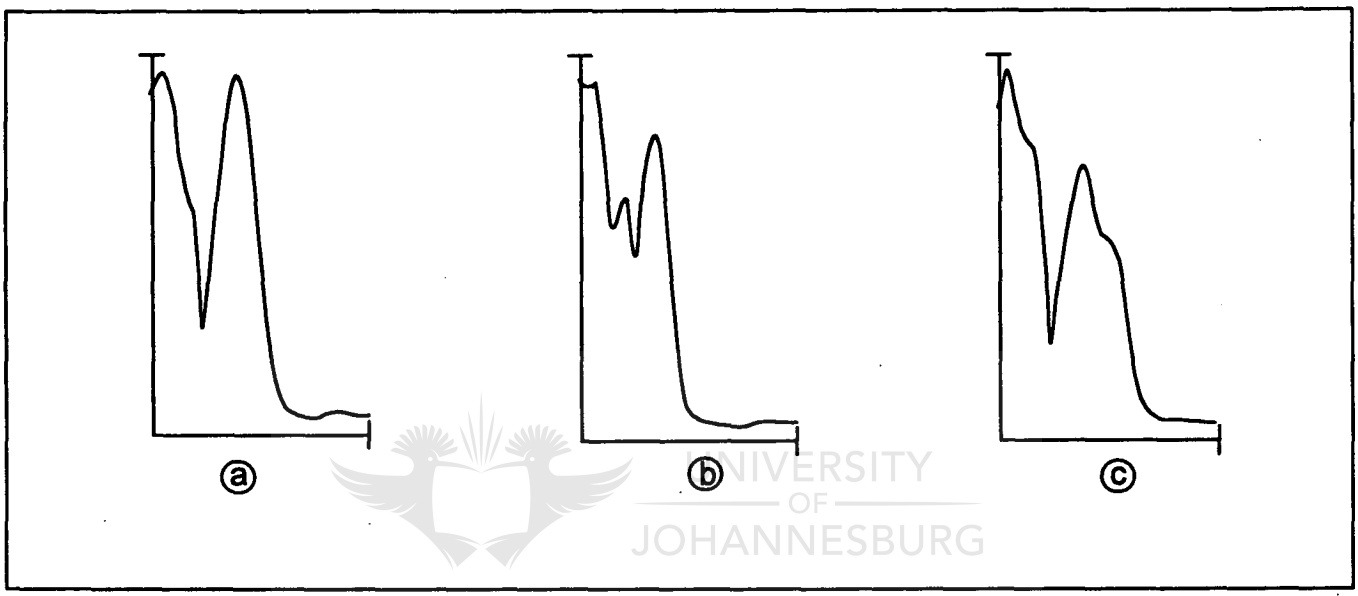


Figure 14.9: Comparison of UV spectra for three classes of chromones.
a. coumaroyl chromones b. cinnamoyl chromones c. feroyl and caffeoyl chromones

as suggested by Reynolds.

Cinnamoyl Chromones

All samples have been studied using an HPLC equipped with diode array UV detector and the UV scans of all compounds have been recorded and compared. This proved to be exceptionally useful to distinguish between the chromones as the degree of acylation has a remarkable influence on the UV spectrum. The adjacent Figure 14.9 (a - c) shows the diagnostic UV scan recorded for a. coumaroyl chromones (e.g aloeresin A), b. cinnamoyl chromones (e.g. aloeresin E) and c. feroyl or caffeoyl chromones (e.g. compound from *A. broomii*).

The coumaroyl chromones display the general pattern discussed for aloesin. The feroyl or caffeoyl chromones have a very restricted distribution in *Aloe*. The cinnamoyl chromones have a wider representation in *Aloe* and the chemotaxonomic value of two of these cinnamoyl chromones (aloeresin E and F) has been detailed in Chapter 11. Table 14.3 shows all the species which contain cinnamoyl chromones in the leaves. Most of these chromones have not yet been identified, hence this group is rather described by this class of chromone which is present. The dendrogram (Figure 14.10) has been constructed from the compounds tabulated in Table 14.3. Three distinct groupings are shown: All species in the section *Anguialoe* are tightly clustered as the leaf exudate composition of these species are almost identical. This group has been discussed in detail in Chapter 8. The second grouping is mostly constituted by series *Mitriformes* and related species. This group consisting of 12 species is dealt with in Chapter 11. The third group contains species placed in *Aloe* series *Purpurascentes* and this study has suggested a taxonomic affinity between series *Purpurascentes* with section *Anguialoe* through *A. broomii* (see Chapter 8). This is one of the chemical groups which shows a direct correlation with the groups created by Reynolds (1950). The groupings as shown on the dendrogram are superimposed on the present classification system for *Aloe* (Figure 14.11). Chapter 11 has elaborated on the inclusion of *A. peglerae*, *A. melanacantha*, *A. erinacea*, *A. angelica* and *A. yavellana* in the *Mitriformes* group. Another species, *A. retrospiciens* placed in Group 19 also accumulates cinnamic acid ester chromones. Although aloeresin E and F (the diagnostic compounds for the *Mitriformes*-group) have not been detected in this species, its inclusion in this group should be considered. The inflorescence which is a branched panicle with capitate racemes is reminiscent of *A. yavellana*, and indeed for most of the species in the *Mitriformes* group. This species is also distinctly caulescent and the leaf architecture (long and

Table 14.3: The occurrence of exudate compounds in species producing cinnamoyl chromone derivatives.

	1	2	3	4	5	6	7	8	9	10	11	12
A. alooides	■						■				■	■
A. angelica	■							■		■		
A. arenicola	■							■		■		
A. barbadensis	■		■		■						■	
A. bella					■						■	
A. breviscapa	■	■			■					■		
A. broomii	■					■			■		■	
A. bukobana	■									■		
A. castanea	■						■				■	■
A. chlorantha	■					■					■	
A. citrina	■	■			■					■		
A. comptonii	■							■		■		
A. dabenorisana	■							■		■		
A. distans	■							■		■		
A. dolomitica	■										■	■
A. erensii		■			■					■		
A. erinacea	■							■				
A. fragilis	■											
A. gariepensis	■									■		
A. khamiesensis	■					■			■			
A. mawii	■									■		
A. melanacantha	■							■				
A. meyeri	■							■		■		
A. microstigma	■								■			
A. mitriformis	■							■		■		
A. pearsonii	■							■		■		
A. peglerae	■							■		■		
A. percrassa	■		■								■	
A. pictifolia	■								■			
A. pubescens	■			■	■					■	■	
A. retrospiciens				■	■					■	■	
A. rubroviolacea	■											
A. spicata	■						■				■	■
A. splendens	■				■					■		
A. tauri	■										■	■
A. tomentosa	■			■	■						■	
A. vanbalenii	■										■	
A. vryheidensis	■						■				■	■
A. wilsonii	■				■					■		
A. yavellana	■							■		■		

1. Aloesin
2. Homonataloside B
3. 7-hydroxyaloin
4. 8-*O*-Me-7-OH-aloin
5. Aloeresin D
6. 5-hydroxyaloin
7. Unindentified chromone
8. Aloeresin E and / or F
9. Microstigmin
10. Homonataloin A & B
11. Aloin A & B
12. Unidentified chromone

reflexed) bears a similarity with *A. angelica*. The anomalous co-occurrence of aloin and homonataloin in *A. retrospiciens* could be indicative of a previous hybridisation event (Chapter 6). *Aloe pubescens* which is morphologically very different from *A. retrospiciens* shows the same leaf exudate composition. *Aloe pubescens* also produces aloin together with homonataloin. To conclude the discussion on the *Mitriformes*-group and related species the position of *A. mawii* needs to considered. The leaf exudate of this species is very similar to that of the members in the *Mitriformes* group. This species with its divaricately branched inflorescence on which the flowers are secundly arranged is placed in subsection *Ortholophae*. Newton (1993) proposed that this is not a natural group and that species in which the flowers are secund have evolved several times in the genus. The most striking resemblance that *A. mawii* shows with *A. peglerae* are the flowers which are distinctly clavate, very shortly pedicellate and the black exerted anthers (see Figure 14.16). The second group (indicated by a dotted line) in Figure 14.11 is the *Anguialoe*, *Purpurascentes* and *Longistylae* complex. The relationships in this group has been discussed in Chapter 8. The diagram does however suggest that the *Mitriformes*-group (shaded grey) and the *Anguialoe*-group (dotted frame) could form a species complex. It is suggested that *A. peglerae* could be a 'bridging species' between these two groups. With the *Mitriformes*-group it is identical in leaf exudate composition, and with the *Anguialoe* and *A. broomii* it shares the presence of cinnamoyl chromones, the shortly pedicellate flowers (flowers sessile in *Anguialoe*) and the dense cylindrical racemes.

Aligning the peripheral species (on the right in Figure 14.11) is a daunting task. *Aloe rubroviolacea* has a very distinct exudate composition showing the presence of anthrone compounds with UV spectra identical to that of 7-hydroxyaloin and nataloin. These compounds have a very restricted distribution in *Aloe* and it is illustrated in Chapter 6 that these compounds form when a homonataloin-producing species is hybridized with an aloin-producing species. Three species in Figure 14.11 also produce 7-hydroxyaloin related compounds: *A. barbadensis*, *A. percrassa* and *A. melanacantha*. The latter species has been suggested to be closely related to *A. peglerae* (Chapter 11). As in *A. peglerae*, the flowers of *A. rubroviolacea* is shortly pedicellate, clavate and the anthers are exerted. This is another example of chemical congruence between species in the north (*A. rubroviolacea* is found in Yemen) and species in South Africa. Five species in series *Verae* also contain cinnamoyl chromones. Three species, *A. citrina*, *A. pubescens* and *A. tomentosa* are characterised by the hairy perianth, a unique character in *Aloe*. In much the same way as Newton (1993)

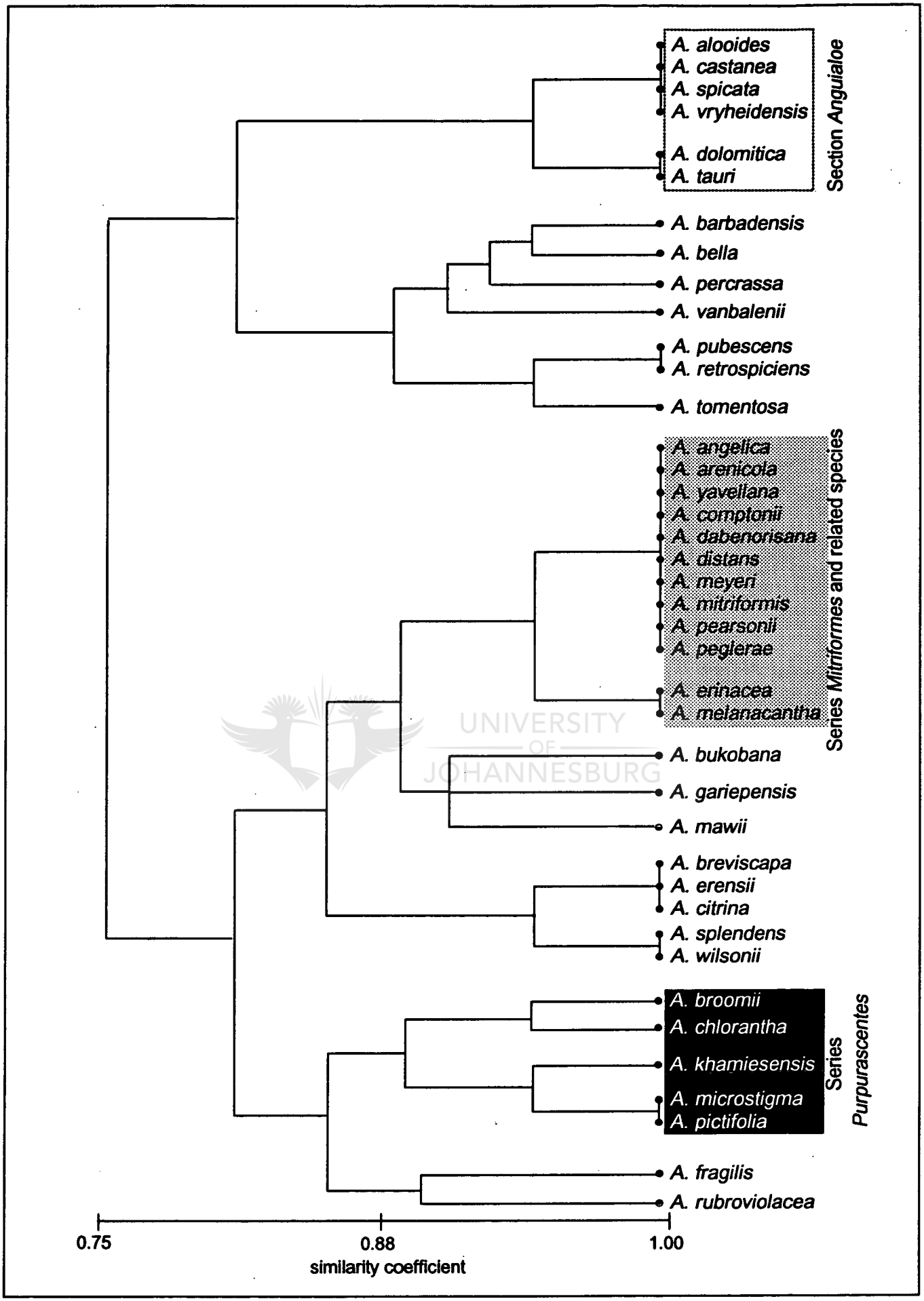


Figure 14.10: Dendrogram constructed for the cinnamoyl producing species using the data in Table 14.3.

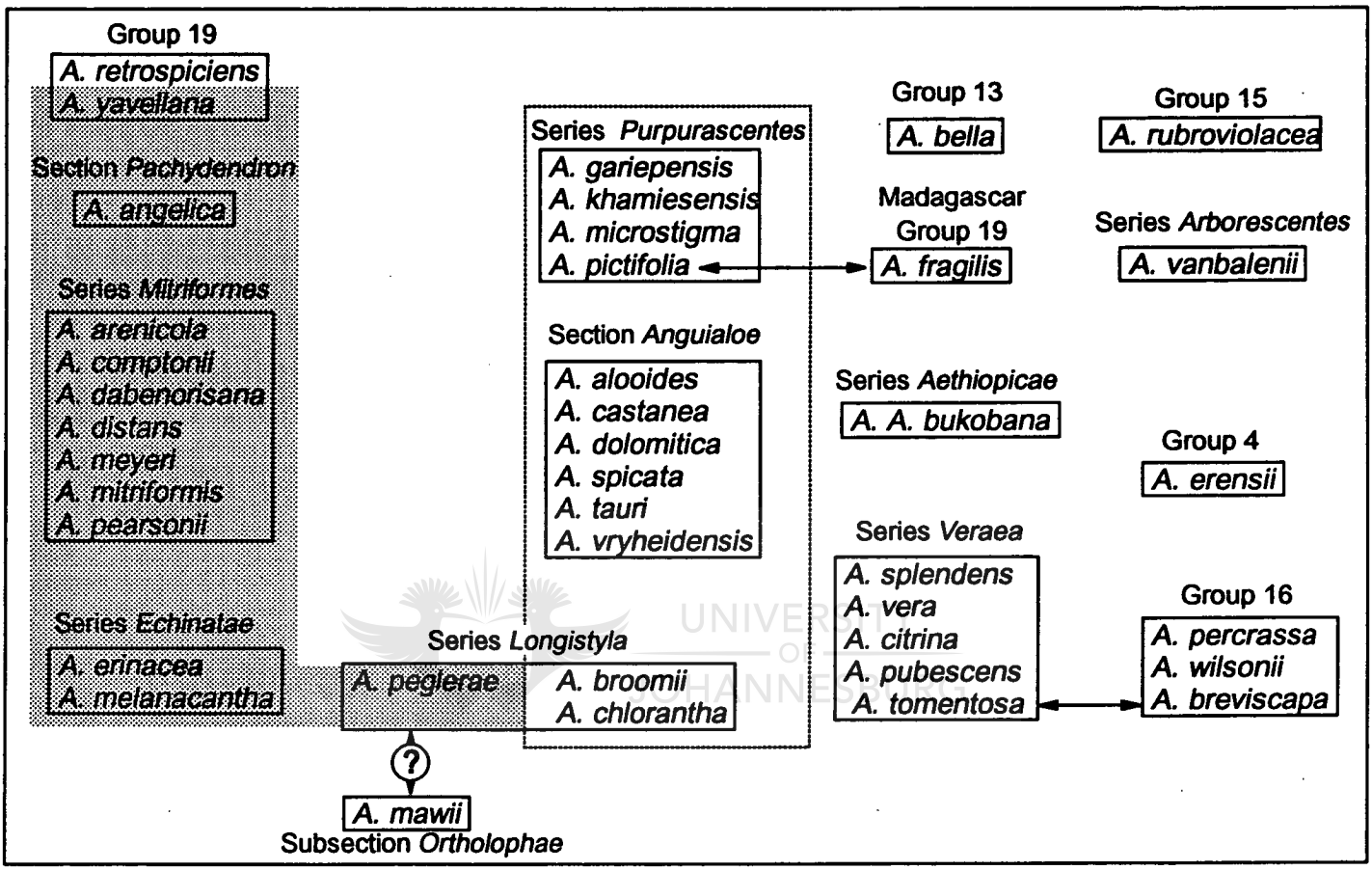


Figure 14.11: Taxonomic arrangement of cinnamoyl chromone containing species.

suggested that the secund flowered aloes do not represent a monophyletic group it could be suggested that the character of a hairy perianth has also originated more than once in *Aloe*. This argument stems from assessing the leaf exudate composition from these species which are very different. It is however evident from these results that *A. citrina*, *A. pubescens* and *A. tomentosa* are closely related but not necessary related to the other species with a pubescent perianth. *Aloe breviscapa* bears a striking resemblance with *A. tomentosa* (which was noted by Reynolds). This species has a distinct bloom on the perianth - a character shared with *A. splendens* and *A. percrassa*. It is here hypothesised that the species from the north of the African continent (*A. rubroviolacea*, the five species in series *Verae* and the three in Group 16) are taxonomically related to their southern cinnamoyl producing counterparts through *A. mawii*. In habit characters, and especially in leaf characters *A. mawii* is similar to the species from the north (leaves erect to spreading and never incurved). *Aloe erensii* is placed in Group 4 (striped perianth) and is also characterised by a distinct bloom on the perianth surface. The leaves of this species are also copiously spotted as described for *A. citrina*. Reynolds (1950) places *A. vanbalenii* in series *Arborescentes* together with *A. arborescens* and *A. mutabilis*. Chemically and to a large extent morphologically, this group is an heterogenous assemblage. *Aloe vanbalenii* produces a characteristic leaf exudate which has not been recorded in any other species. Reynolds does however remark on the similarity this species bears with its strongly recurved and canaliculate leaves with the juvenile form of *A. alooides* which also contains cinnamoyl chromones and is placed in *Aloe* section *Anguialoe*. The last species in this group, *A. fragilis*, has recently been described from Madagascar and is the only Malagasy species in the chemical group. In his description (Lavranos 1994) suggests *A. guillaumettii* to be the closest relative. The latter is chemically very different from *A. fragilis* which has been found to share chemical characters with *A. pictifolia*. This is another example where Malagasy species are found to share rare chemical compounds with African species.

ANTHRONES

The anthrones are widely represented in *Aloe*. This group of compounds are not as diverse as the chromones. They usually occur in pairs as diastereomeric *C*-glucosides. The major anthrones detected in *Aloe* are aloin A and B, aloinoside A and B, microdontin A and B, and homonataloin A and B. Anthrones of less wide distribution are nataloin A and B, 7-hydroxyaloin, 5-hydroxyaloin, 10-hydroxyaloin, homonataloside B, microstigmin A and 8-*O*-methyl-7-hydroxyaloin. The chemotaxonomic value of these anthrones have been discussed

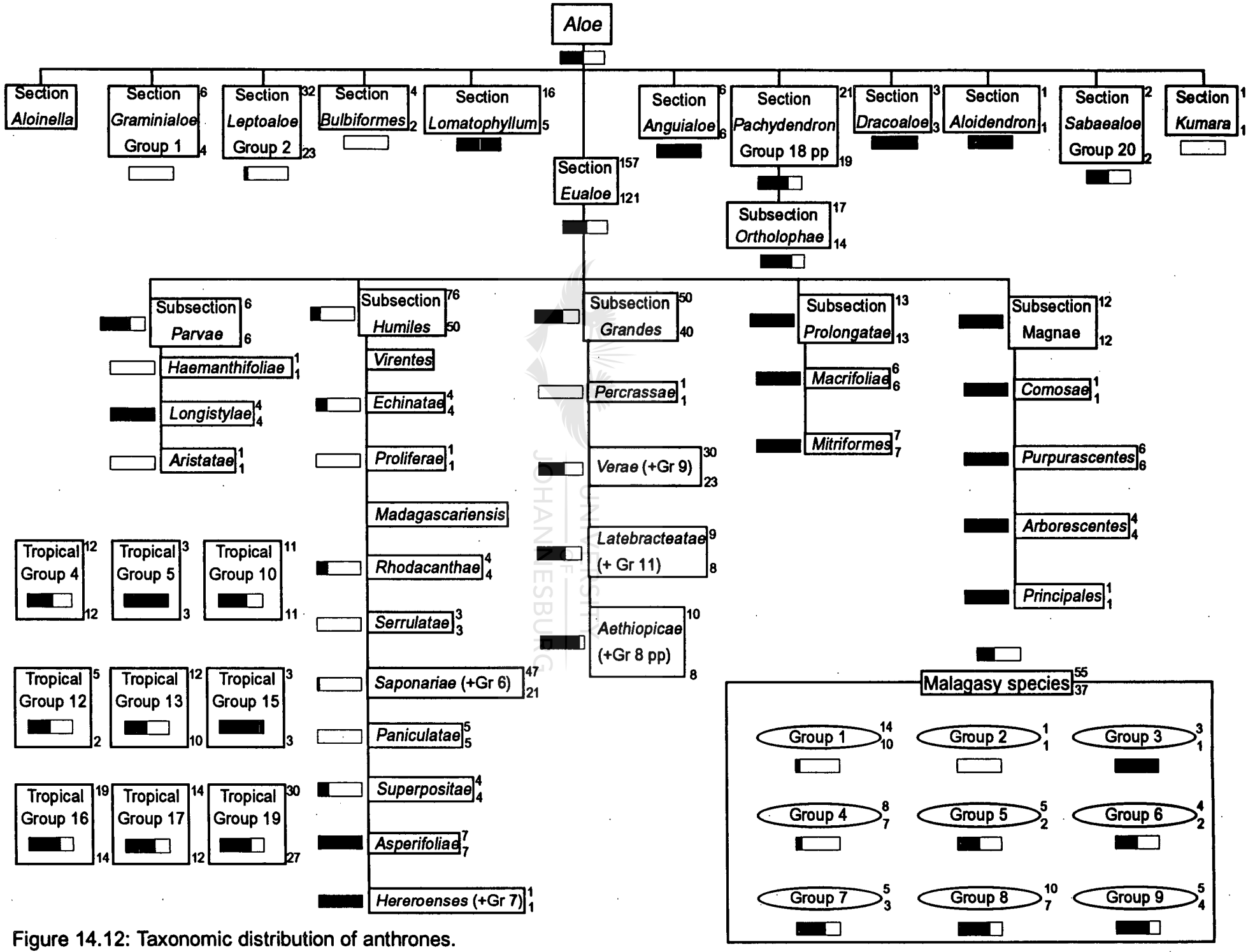


Figure 14.12: Taxonomic distribution of anthrones.

as follows; aloin, aloinoside and microdontin in Chapter 5, homonataloin in Chapter 14, 10 hydroxyaloin in Chapter 9, homonataloside B in Chapter 10, microstigmin in Chapter 8 and 8-O-methyl-7-hydroxyaloin in Chapter 6. Figure 14.12 is a diagrammatic summary of the distribution of anthrones in the genus. With the exception of three grass aloes, anthrones are generally absent in the *Graminialoe* and *Leptoaloe*. Species in the two latter groups are flavonoid-producers (Chapter 12) and anthrones and flavonoids were found to be mostly mutually exclusive. A large number of Malagasy species were also found to be devoid of anthrones. These compounds with their bitter-tasting principles are believed to be responsible for the antifeedant properties of aloes. It could be speculated that there is an ecological explanation to offer for the occurrence of anthrones. Madagascar is not home to any higher grazing mammals, hence it could be reasoned that there has been no selective pressure on aloes to produce these compounds. The aloes of Madagascar generally lack the pungent thorns which is possibly another deterrent to many herbivores. Furthermore, the aloes on Madagascar are small with only a few species producing tall erect stems, another strategy to be 'out of reach' of herbivores. On the African continent, rich in herbivorous mammals, the aloes mostly produce copious amounts of exudate, the leaves are mostly armed with pungent thorns and a large number of species are distinctly caulescent. This pattern of vegetative adaptation is especially correlated with the drier habitats e.g. *Aloe dichotoma* and *A. pillansii* occur in arid regions in southern Africa, in these conditions a succulent becomes extremely attractive to foraging herbivores. The species in desert environment also produce an elaboration of the general anthrone structures. e.g. *A. littoralis* produces a series of anthrones instead of a single pair of anthrone isomers.

From a chemotaxonomic point of view it is meaningful to note that these compounds are absent in the grass-like aloes and it is suggested here that this pathway never evolved in these species. The plicataloside-accumulating species (Chapter 13) only produce this single compound in the absence of the chromones and anthrones. Although plicataloside is also formed along the polyketide pathway is here suggested that the part of the pathway leading to the production of anthrones should be interpreted as a secondary loss.

The anthrone aloin is so widely and taxonomically diversely distributed throughout the genus that many of the arguments presented above are also applicable to aloin. The discussion below will thus be restricted to an interpretation of the chemotaxonomic value of homonataloin

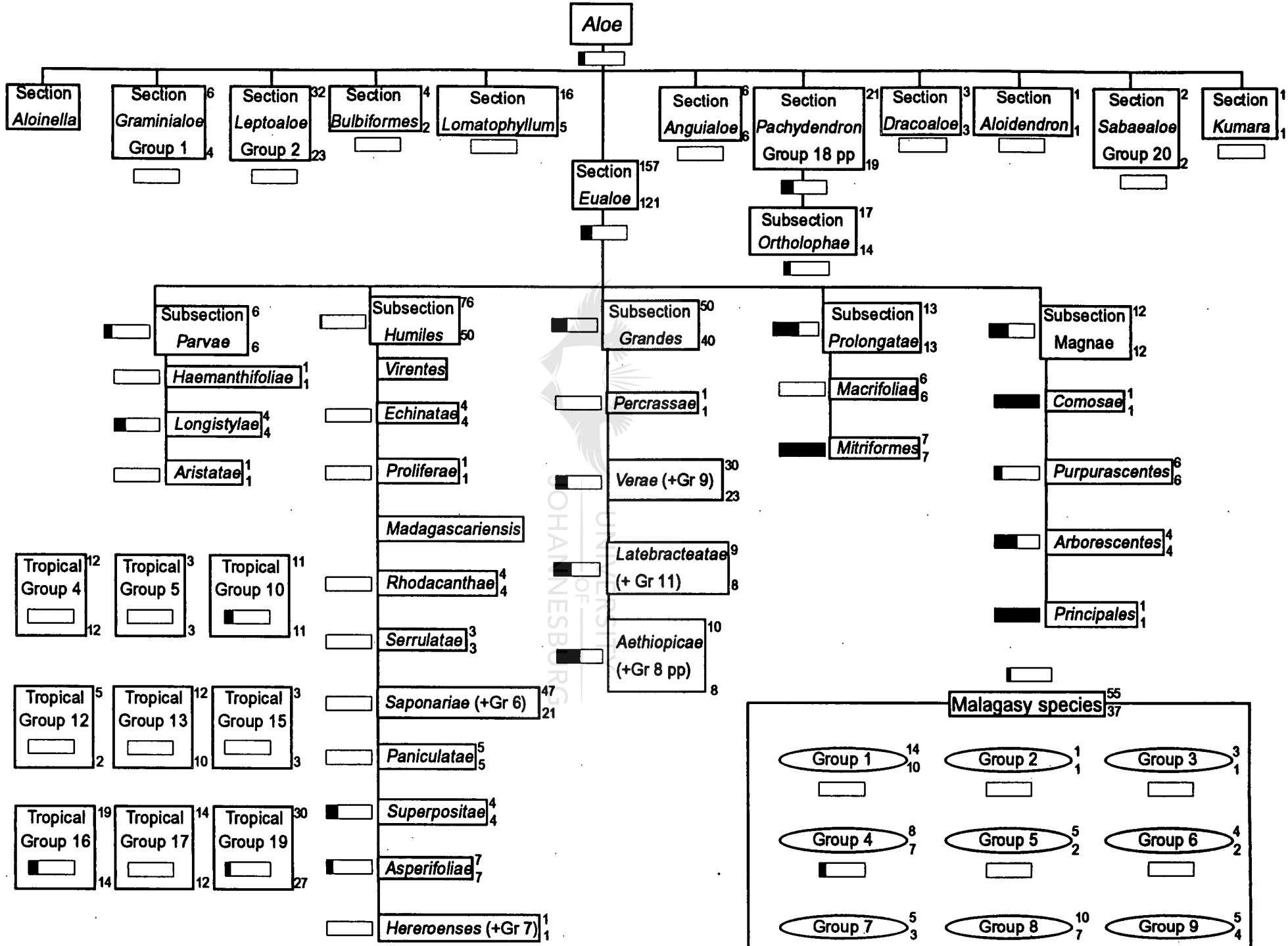


Figure 14.13: Taxonomic distribution of homonataloin.

Table 14.4: The occurrence of the main exudate compounds in homonataloin producing species.

	1	2	3	4	5	6	7	8
A. abyssicola		■				■		
A. amicorum		■		■		■		
A. angelica	■				■	■		
A. arenicola	■				■	■		
A. bargalensis		■		■		■		
A. breviscapa	■	■		■		■		
A. bukobana	■					■		
A. citrina		■		■		■		
A. comosa	■			■		■		
A. comptonii	■				■	■		
A. congdonii	■					■		
A. cremnophila	■					■		
A. cryptopoda	■	■				■		■
A. dabenorisana	■				■	■		
A. dhufarensis	■	■				■		
A. distans	■				■	■		
A. gariepensis	■					■		
A. hardyi	■					■		
A. hereroensis	■					■		
A. isaloensis	■		■			■		
A. krapohliana	■	■				■		■
A. lutescens	■	■				■		■
A. marlothii	■			■		■		
A. mawii	■				■	■		
A. mayottensis	■					■		
A. meyeri	■				■	■		
A. mitriformis	■				■	■		
A. munchii	■					■		
A. mutabilis	■		■			■		
A. mzimbana	■					■		
A. pearsonii	■				■	■		
A. peglerae	■				■	■		
A. pubescens	■		■	■		■	■	
A. retrospiciens			■	■		■	■	
A. rigens	■			■		■		
A. speciosa						■		
A. splendens	■			■		■		
A. squarrosa	■	■		■		■		
A. suffulta	■					■		
A. suprafoliata	■					■		
A. thraskii	■					■		
A. tomentosa	■	■	■			■	■	
A. viridiflora	■					■		
A. volkensii	■					■		
A. wickensii	■	■				■		■
A. wilsonii				■		■		
A. yavellana	■				■	■		

1. Aloesin
2. Homonataloside B
3. 8-O-Me-7-OH-aloin
4. Aloeresin D
5. Aloeresin E and / or F
6. Homonataloin A & B
7. Aloin A & B
8. 3',6'-di-O-coumaroyl aloesin

Homonataloin

Figure 14.13 shows the taxonomic distribution of the 47 homonataloin-containing species. This anthrone has not been found in any of the grass-like aloes, *Lomatophyllum*, *Macrifoliae* or the tree-like aloes. The groups showing the most chemical, and to a certain extent morphological resemblance with the grass-like aloes are the *Macrifoliae* and *Lomatophyllum*. The anthrone aloin has been detected in representatives of these groups and it has been suggested earlier that aloin probably originated very early in the evolution of *Aloe*. Homonataloin, with its more restricted distribution could be viewed as a more recent development in the evolutionary history of *Aloe*. The earlier evolution of aloin (preceding that of homonataloin) is further evident from the co-occurrence of aloin with flavonoids. The flavonoids are considered to represent the plesiomorphic state in *Aloe*. Secondly, many derivatives of aloin are known, structural modifications which have possibly evolved over a greater length of time. The only known derivative of homonataloin is homonataloside suggesting that 'chemical speciation' of homonataloin is more recent.

Homonataloin is primarily found in the subsections *Prolongatae*, *Magnae*, *Grandes*, section *Pachydendron* and various other species in the tropics. The homonataloin accumulating species are shown in Table 14.4 together with the major exudate constituents of these species. A dendrogram (Figure 14.14) has been constructed based on all exudate compounds as recorded for each of the species (see Appendix 2). Three major clusters are shown in Figure 14.14. The first grouping (A) is an assemblage of all homonataloside B-containing species. This group is dealt with in Chapter 10. The second cluster (B) defines all species which accumulate homonataloin and cinnamoyl chromones. This group has been dealt with in Chapter 11. Attention is drawn to the large number of species in cluster C and hypotheses would be presented here relating these species to each other or to species contained in clusters A and B. The homonataloin group represents a species complex with a perplexing range of morphological characters. As has been the norm in this study it is very difficult to find a set of characters which are completely correlated and in taxonomic agreement with each other. Although homonataloin is here considered to be a valuable unifying taxonomic character for this group, the morphological characters in this group represents almost the entire variation of a single character in the genus. For example to consider habit characters: species could be distinctly caulescent and erect (e.g. *A. muchii*), caulescent and sprawling (e.g. *A. mitriformis*), caulescent and pendent (e.g. *A. amicorum*) or acaulescent (e.g. *A. bukobana*). The encouraging aspect is that species which have been taxonomically problematic are here shown

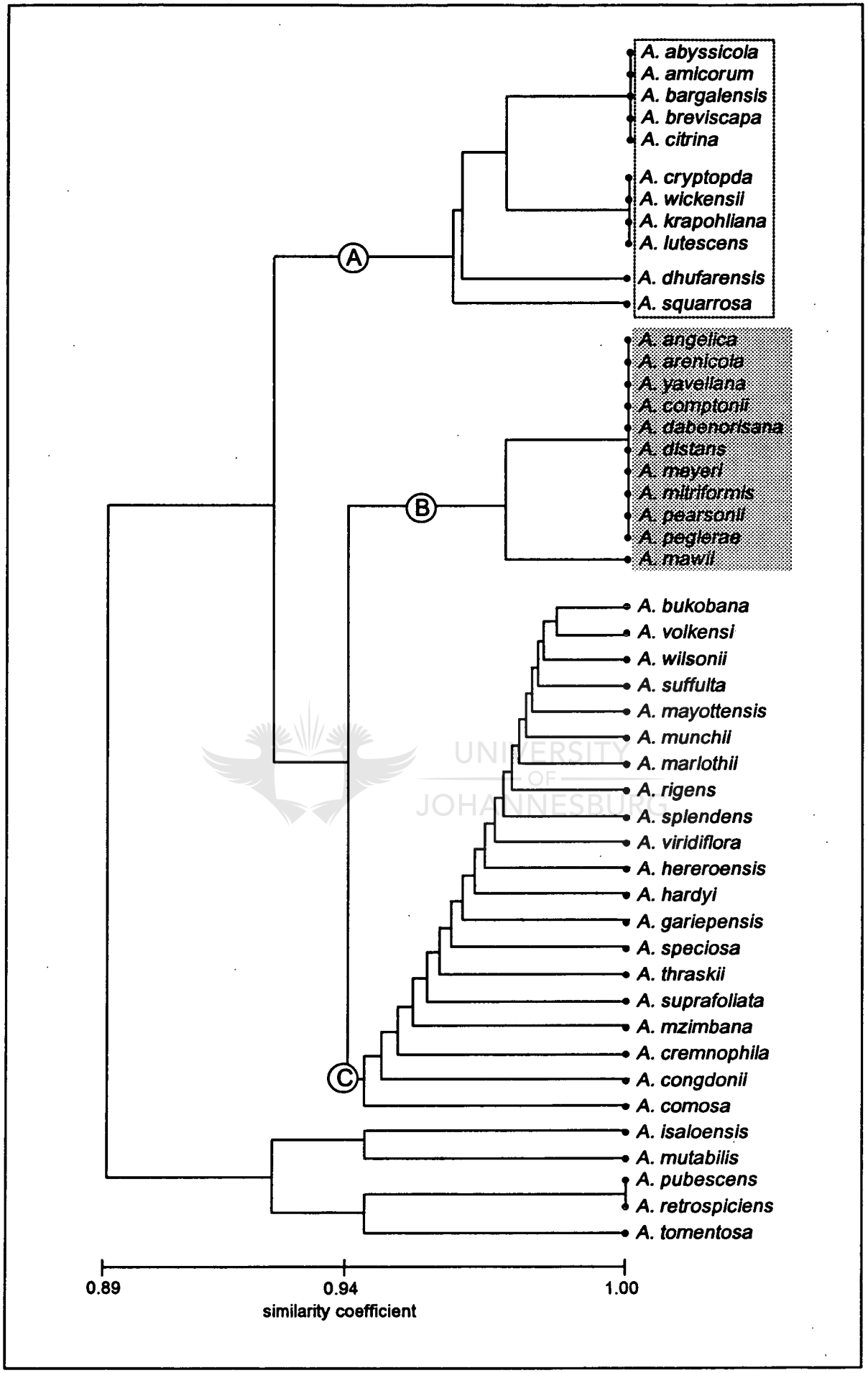


Figure 14.14: Dendrogram constructed using chemical characters in homonataloin containing species.

to be chemically related as the chemical similarity initiates a search for a possible correlation in character states. It is evident that well defined groups in *Aloe* are scarce and that species should rather be viewed in mosaic species complexes. This supports the notion that hybridization has been an important evolutionary driving force in *Aloe* as morphological and chemical characters are entangled, presenting an enigmatic taxonomic arrangement of species as illustrated in Chapter 6. The *Mitriformes*-group has been discussed at great length in Chapter 11 where it was suggested that *A. peglerae*, *A. yavellana* and *A. angelica* should be included in this group as they produce identical leaf exudates. It has also been suggested earlier that *A. retrospiciens* is closely allied to *A. angelica* using the inflorescence and habit characters. Evaluating the species in Figure 14.15 it is here suggested that *A. munchii* should also be considered part of this species complex. This distinctly caulescent species too produces a panicle with capitate racemes as in *A. angelica*. This implies that *A. munchii* and *A. retrospiciens* should be considered peripheral species in the *Mitriformes* species complex. The same argument applies to *A. viridiflora* and *A. hereroensis*. Reynolds (1950) places the former species in the series *Asperifoliae* with comments that it does not fit well in this group. In Chapter 9 it has been shown that *A. viridiflora* is chemical very different from the rest of the species pertaining to the *Asperifoliae* group. Here, *A. viridiflora* and *A. hereroensis* with their capitate racemes, longer pedicels and the presence of homonataloin show resemblances with the *Mitriformes*-group. It is further interesting to note that older plants of *A. hereroensis* could develop procumbent stems up to 1 m in length which is a characteristic feature of the *Mitriformes*-complex. The monotypic series, *Hereroenses* is thus suggested to be incorporated into the *Mitriformes* group together with *A. viridiflora*. The latter species could represent a 'transition' species between this group (*Mitriformes*) and the *Asperifoliae* perhaps through *A. claviflora* with which it shares the distinctly clavate perianth. The taxonomic account for *Aloe mzimbana* (Reynolds, 1966) fits the features of many *Mitriformes* species. This variable species produces a panicle with sub-capitate racemes. The perianth is long and slender and the pedicel (16 mm) resembles that of the *Mitriformes*-group. The same motivation would be relevant to a close relative, *A. congdonii* which is also placed in series *Aethiopicae*. Considering macromorphological characters, these two species (*A. mzimbana* and *A. congdonii*) could be related to *A. viridiflora* / *A. hereroensis* and all four species should be placed peripherally at least, within the *Mitriformes*-group.

The occurrence of a very distinct morphological character in this group indicates the 'network' of relationships prevalent in *Aloe*. A clavate / ventricose flower, which is shortly pedicellate and

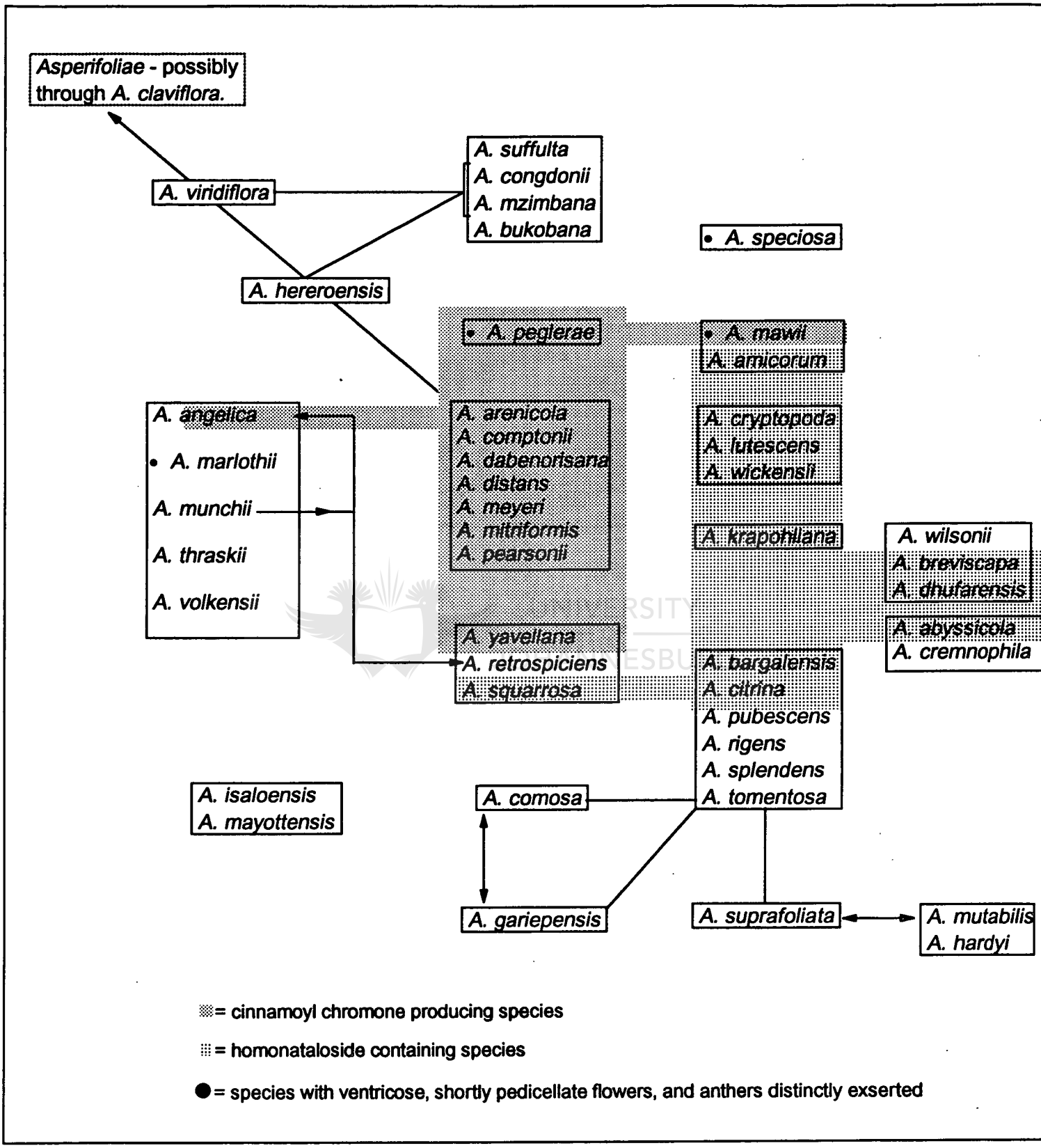


Figure 14.15: Taxonomic arrangement of homonataloin-producing species. Suggested affinities have been superimposed.

the anthers which are conspicuously exerted is characteristic for *Aloe mawii*, *A. speciosa*, *A. peglerae* and *Aloe marlothii*. (Figure 14.16). *Aloe mawii* is placed in subsection *Ortholophae* which is a group containing all plants in which the flowers are secund. The only other member in Figure 14.15 which bears secund flowers is *A. marlothii*. *Aloe marlothii* is extremely variable in terms of exudate composition. The close relative of this species *A. spectabilis* is believed to be conspecific with *A. marlothii* as it shows the same degree of chemical variation (see Chapter 16). During an extensive population study (see Chapter 16) on both taxa, population were visited where it was impossible to positively identify the inhabitants as *A. marlothii* or *A. spectabilis*. In some individuals it was also noted that the flowers were not secund but symmetrically arranged around the floral axis. This made the expression of this character doubtful as it was more prominent is some populations than in others. *Aloe speciosa* is placed in a monotypic series *Principales*. This species shares with *A. mawii* the distinct caulescence which is somewhat arborescent, the loosely deflexed leaves, the compact racemes and the shortly pedicellate flowers with exerted anthers. The inflorescence of *A. speciosa* is described as being acuate-ascending which could be a poor character expression of an oblique raceme reminiscent of *A. mawii*. In floral and raceme characters *A. peglerae* shows an affinity with *A. speciosa*. The inflorescence is always simple, cylindrical, and bicoloured. The flowers are shortly pedicellate, cylindric-ventricose with exerted anthers. In habit characters *A. peglerae* resembles members of the *Mitriformes*-group (which includes *A. melanacantha* and *A. erinacea*).

The other major grouping in the homonataloin-group are the homonataloside B-containing species which are shown in cluster A and the dotted-shading in Figure 14.15. The similarity with the *Aloe cryptopoda* group has been illustrated in Chapter 10. The hypothesis is here presented that *A. pubescens*, *A. rigens*, *A. splendens* and *A. tomentosa* form part of this species-complex. These species which are mostly acaulescent, bearing erect to spreading leaves and producing a sparingly branched panicle with acuminate-cylindrical racemes bear striking resemblances to the *A. wickensii* species complex. These species (series *Verae*) are characterised by an hairy perianth and the variable *A. tomentosa* also contains homonataloside B, thus forming a chemical link between the other homonataloin-producing species with a hairy perianth in this species complex. Peripheral but included in this group should be four species from South Africa. In Chapter 8 the exclusion of *A. gariepensis* from the *Purpurascentes* has been motivated. On page 402 Reynolds (1950) notes: "....*A. gariepensis* is the only species in this series (*Purpurascentes*) having long cylindrical-

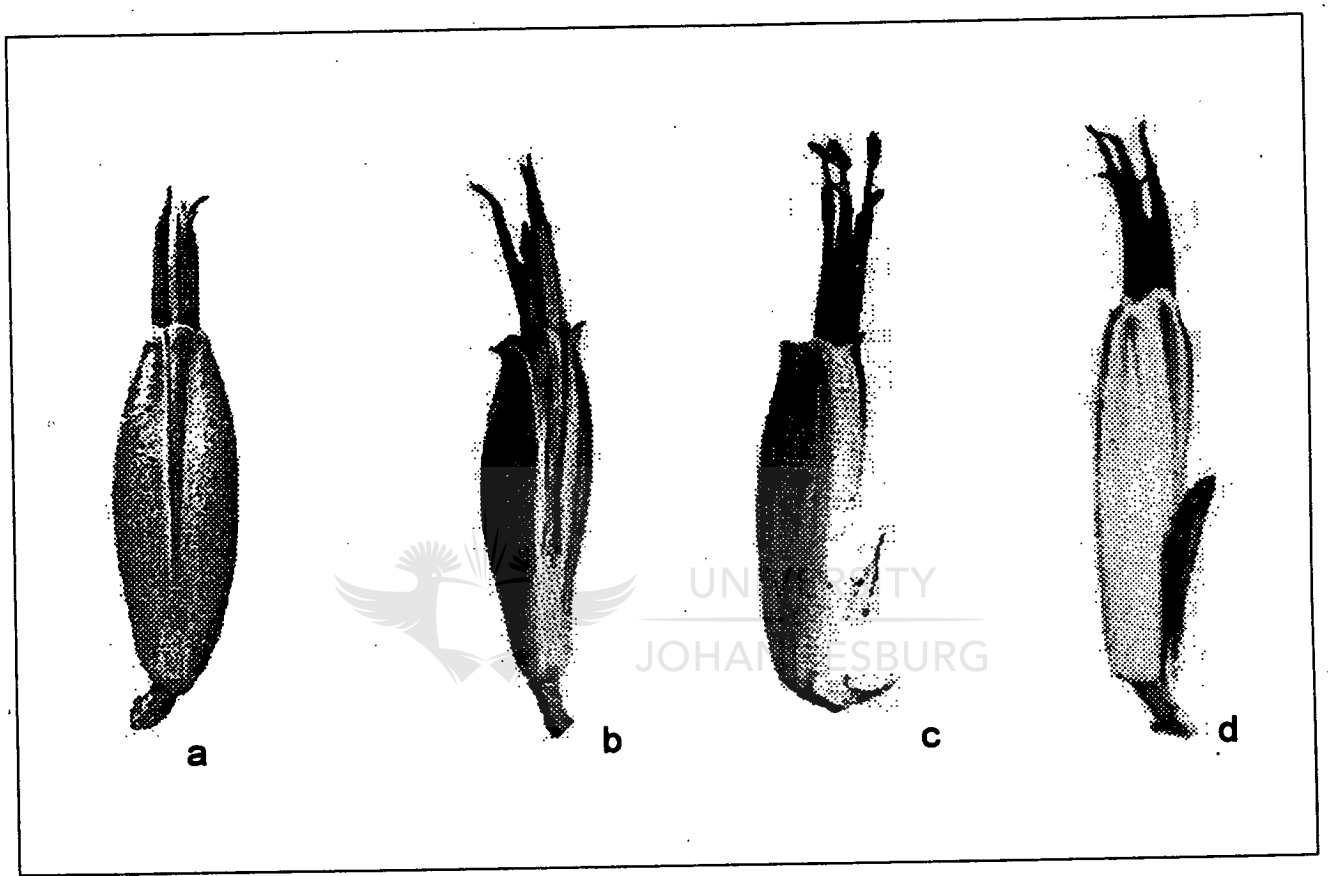
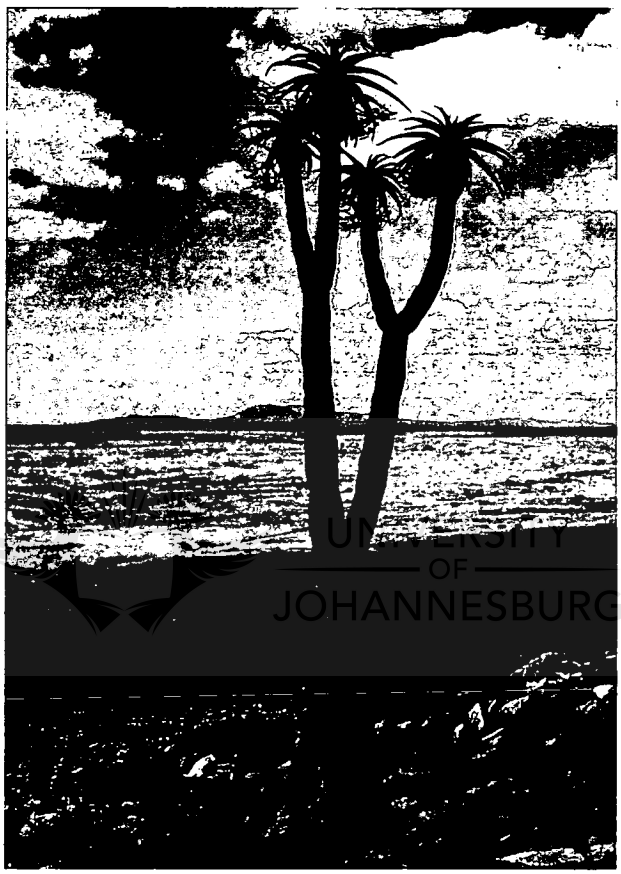


Figure 14.16: Flowers of a) *A. mawii*, b) *A. marlothii*, c) *A. peglerae* and d) *A. speciosa* (Reynolds 1950 & 1966).

acuminate racemes, pedicels only 15 - 20 mm long and bracts much longer than their pedicels." *Aloe comosa* is placed in a monotypic series *Comosae*. This species is characterised by the tall, bicoloured inflorescence and the flowers which are pressed against the floral axis and the presence of long imbricate bracts. Thus with *A. comosa*, *A. gariepensis* shares the following: a very tall bicoloured, raceme, large imbricate bracts (longer than the pedicels), leaves obscurely lineate and the presence of homonataloin. The chemotaxonomic contribution here is that *A. comosa* does not have to be taxonomically isolated in a monotypic series but that there is strong evidence that it has close relatives in the homonataloin-producing species complex. Chapter 12 has dealt with the exclusion of *A. suprafoliata* and other species in series *Superpositae*. *Aloe suprafoliata* and *A. mutabilis* are suggested on the basis of their single, acuminate-cylindrical inflorescence, deflexed and obscurely lineate leaves and the presence of homonataloin to be associated with one another. *Aloe mutabilis* does not contain the characteristic phenyl-pyrone aloenin found in *A. arborescens* which is an aloin-accumulating species. *Aloe hardyi* also seems somewhat misplaced in series *Arborescentes*. In habit characters this species shows a remarkable resemblance with the pendent *A. amicorum*, *A. dabenorisana* and *A. meyeri*. The exact position of *A. hardyi* within this group is uncertain as morphological features could place it comfortably in the *Mitriformes* or in the homonataloside B group.

Although just as complex as the variable morphology of the genus, the presence of certain leaf compounds act as indicators of possible taxonomic relationships. Some compounds (e.g. aloesin) are of little taxonomic importance while others e.g homonataloin are more reliable taxonomic markers. The taxonomic information reflected by the exudate compounds is often obscured by possible hybridization events, secondary loss of a pathway or even the apparent loss of the ability to produce exudate.



Chapter 15

The chemotypes in *Aloe* - Transforming chemical data into taxonomic information

Chapter 15

CHEMOTYPES IN *ALOE* - TRANSFORMING CHEMICAL DATA INTO TAXONOMIC INFORMATION

"There seems to be no constancy of species, no fixation of characters, no relative stability, and nature refuses to be forced into the fetters of a man-made precise system."
(Reynolds 1950)

"The relationships within the genus Aloe are often obscure and I have frequently experienced much difficulty in deciding upon the true affinities of certain species..."
(Lavranos 1973)

"Attempting to assess the relationships of the last two species demonstrates the problem of trying to find combinations of characters to define infrageneric groups" (Newton 1994)

"It has proved virtually impossible to arrange the species of the Flora in a sensible phylogenetic sequence. There are no characters, ..." (Susan Carter 1994)

"Firstly the existing infra-generic classification of the genus Aloe is far from satisfactory, and it is in need of revision. There are several species whose affinities within the genus are obscure..." (Newton 1998)

In this Chapter I will aim to summarise all the data presented in the foregoing chapters and with this integration of the data I will assess the utility of the chemotaxonomic evidence in an hypothesis of chemical relationships within the genus. As mentioned in Chapter 1, and echoed through the quotations above, the present classification system for *Aloe* is to a large extent unsatisfactory. The chemical data has provided us with profound new insights into possible relationships within the genus. Firstly, I will summarise the chemical data by discussing the well defined chemotypes that have emerged in this study. There are many species which have not been discussed in the foregoing chapters as they lack diagnostic chemotaxonomic markers which would exclude them from any of the chemical groups. These species will be placed (peripherally al least) into the chemical groups created in this study. After all species have been assigned to various chemotypes or chemical categories, an attempt will be made to convert the chemical data into taxonomic information, as it is this transformation which is the essence of chemotaxonomy.

Figure 15.1 illustrates a summary of the major chemical groups or chemotypes defined in this study and shows three broad categories:

A - The flavonoid-containing species - separated into five chemotypes

Aloe pillansii (Photo: Ben-Erik van Wyk).

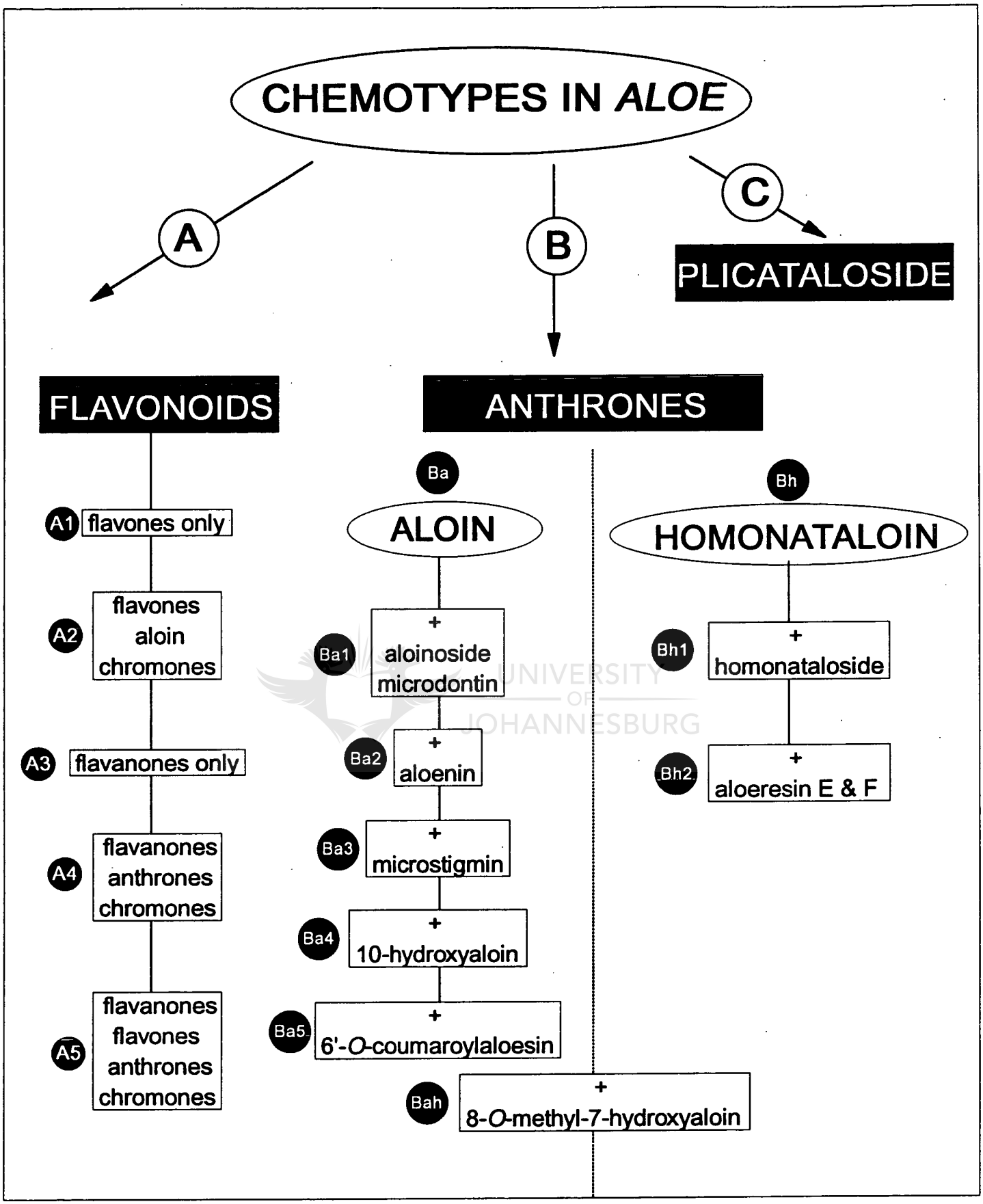
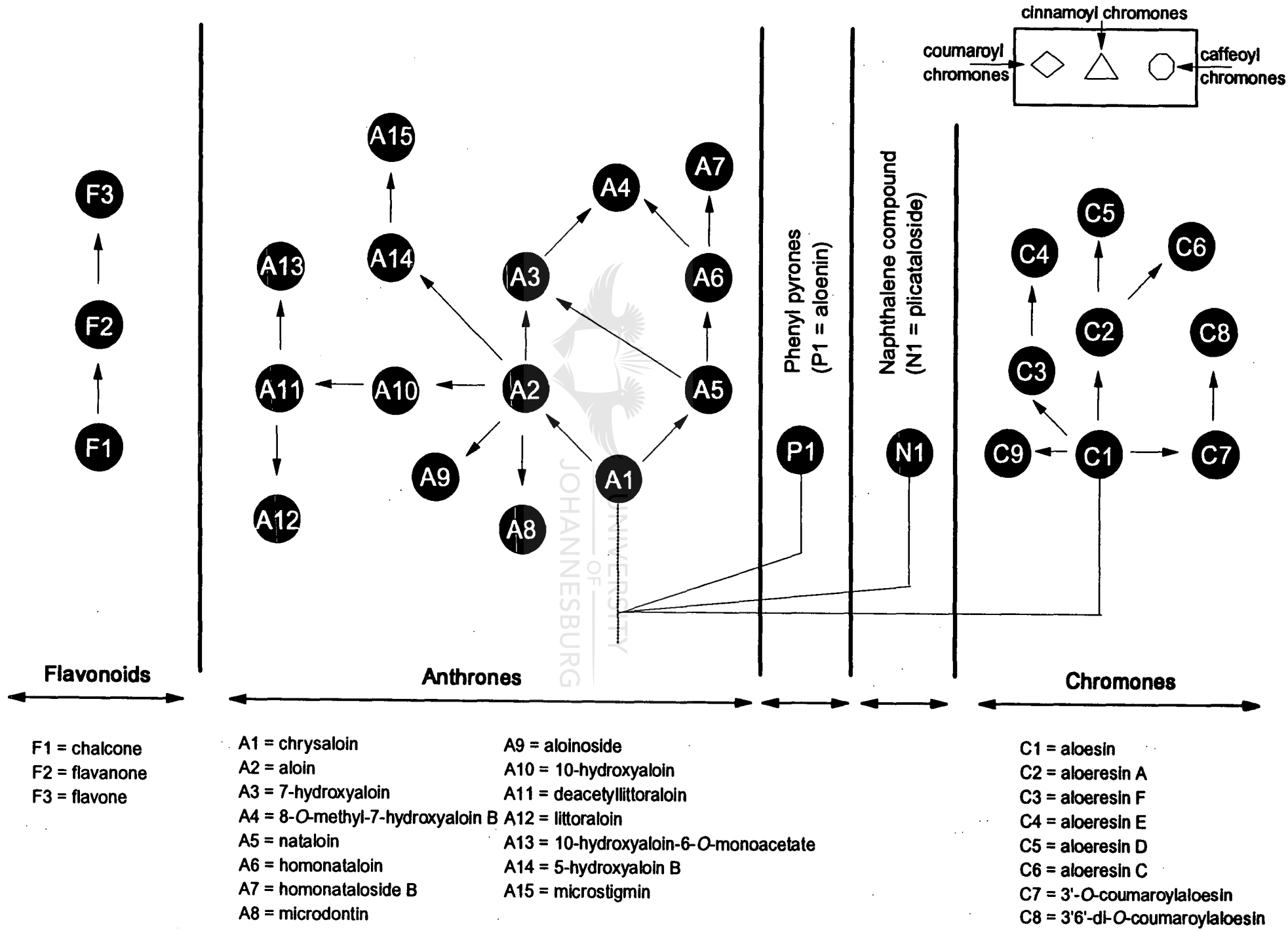


Figure 15.1: Summary of chemotypes discussed in Chapter 15.



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F3 = flavone

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A5 = nataloin
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A7 = homonataloside B
A8 = microdontin
A9 = aloinoside
A10 = 10-hydroxyaloin
A11 = deacetyllittoraloin
A12 = littoraloin
A13 = 10-hydroxyaloin-6-*O*-monoacetate
A14 = 5-hydroxyaloin B
A15 = microstigmin

C1 = aloesin
C2 = aloeresin A
C3 = aloeresin F
C4 = aloeresin E
C5 = aloeresin D
C6 = aloeresin C
C7 = 3'-*O*-coumaroylaloesin
C8 = 3'6'-di-*O*-coumaroylaloesin
C9 = 6'-*O*-coumaroylaloesin

Figure 15.2: Hypothesis of the biochemical pathways active in *Aloe*.

B - The anthrone containing species - separated into two sub-categories:

Ba - The aloin-accumulating species with five chemotypes

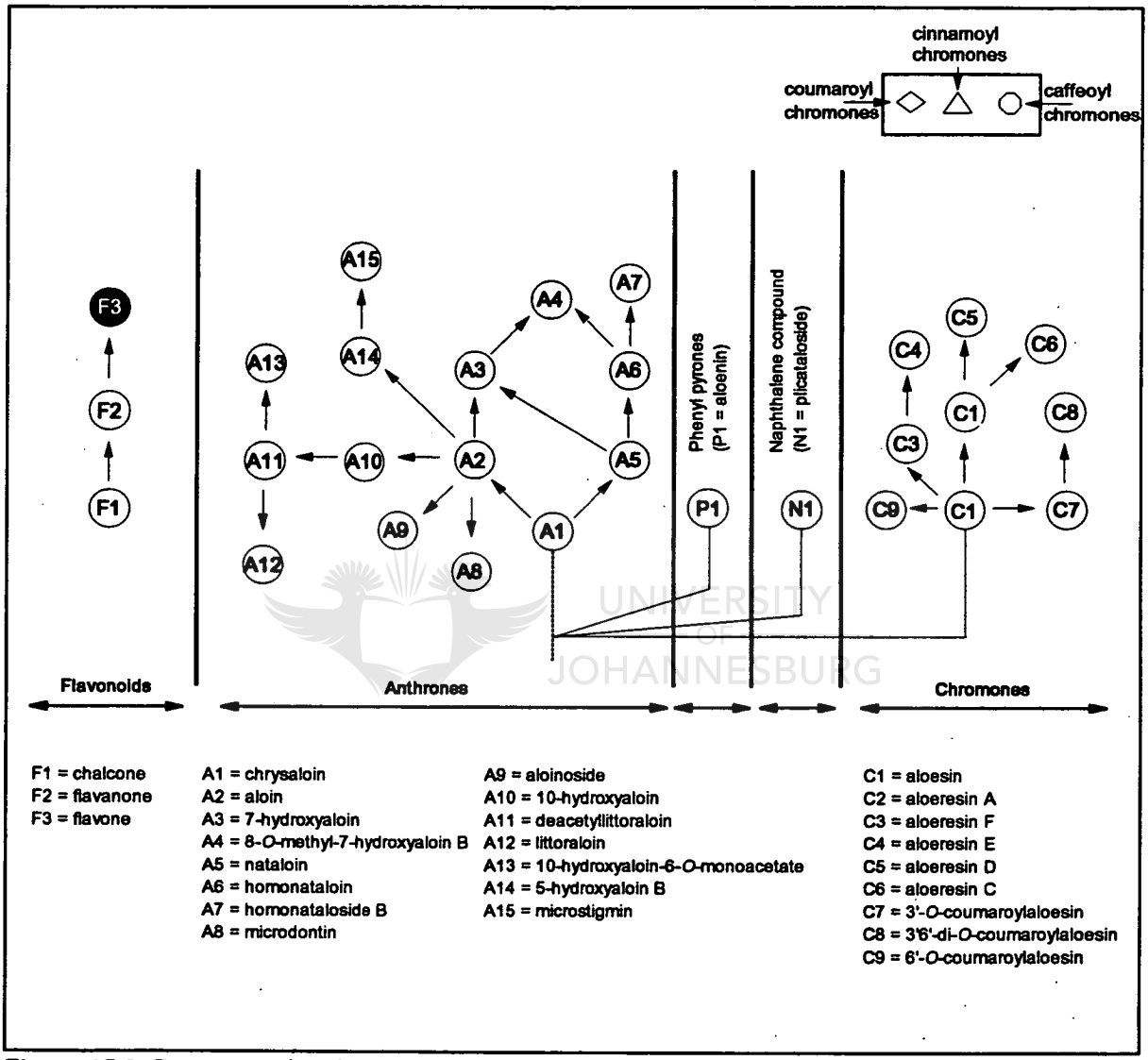
Bh - the homonataloin-accumulating species with two chemotypes

The Bah Chemotype represents an intermediate between the Ba and Bh Chemotypes.

C - The plicataloside accumulating species.

Although there is a 'partial overlap' in the categories this grouping provides the most rigorous and logical summary of the chemotypes. For example, in exceptional cases a plicataloside accumulating species may also produce aloin, or a aloin species may also produce homonataloin. These exceptions have been discussed in the foregoing chapters and I would here, for the sake of simplicity, prefer to concentrate on the general pattern.

Figure 15.2 should be interpreted together with Figure 15.1 which represents a simplified illustration of the chemical patterns. This diagram will be presented for each of the chemotypes summarised in the chapter and will allow for the visual assessment of the occurrence and co-occurrence of exudate compounds in the group as a whole. The flavonoid pathway is illustrated on the left in Figure 15.2 and stands alone as flavonoids follow their own biochemical pathway while the other compounds (anthrones and chromones etc) are formed via the polyketide pathway. From a chemotaxonomic perspective it is important to not merely evaluate the absence or presence of the end products but the absence or presence of an entire biochemical pathway. Although chalcones (F1) have not been detected in the leaf exudate they are included in Figure 15.2 as the known precursors for the flavanones (F2) which in turn are the precursors of the flavones. The flavonoid pathway has enjoyed much attention and the biochemical pathway for these compounds have been mapped as summarised by Stafford (1990). The polyketide pathway shown in Figure 15.2 is an hypothetical representation based on 'chemical prediction' rather than on results obtained from labourious biogenetic studies. Not all compounds reported from *Aloe* have been included in the scheme, as I have only incorporated compounds with chemotaxonomic relevance and compounds which have been detected in the leaf exudate in this study. Compounds which have a restricted distribution and are species specific have not been included. The anthrones (A1 - A15) are proposed to have their origin from chrysaloin (or a similar compound) from



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C7 = 3'-*O*-coumaroylaloesin
C8 = 3'6'-di-*O*-coumaroylaloesin
C9 = 6'-*O*-coumaroylaloesin

Figure 15.3: Presence of leaf compounds in the A1 Chemotype.

where the pathway branches divaricately into the aloin pathway (A2) and the homonataloin pathway (A6). Aloin undergoes further modifications (A8 - A15) while homonataloin undergoes one 'chemical alteration' to produce homonataloside B (A7). The phenyl pyrone aloenin is represented by P1 which is suggested to form independently along the polyketide pathway. The same 'biochemical independence' is suggested for plicataloside (N1). The chromones are a large and variable group of compounds here represented by C1 to C9. These compounds are of limited chemotaxonomic value. The classes of chromones, based on the type of acid attached (e.g. coumaric acid) is also included in Figure 15.1 as this information has proven to be of chemotaxonomic value.

CHEMOTYPE A - FLAVONOIDS

CHEMOTYPE A1 (FLAVONES ONLY)

The significance of the discovery that some aloes accumulate flavonoids has been expressed in Chapter 12. The first chemotype in this flavonoid group denoted by A1 represent all species which accumulates flavones (e.g. isovitexin) and are tabulated in Table 15.1. These species are devoid of anthrones and chromones except for *A. chortolorioides* var. *chortolorioides* and *A. chortolorioides* var. *wooliana* which were found to contain low concentrations of anthrones and chromones. The biochemical pathways activated in these species are shown in Figure 15.3.

Table 15.1: Species constituting Chemotype A1.

Species	Position in Reynolds' classification
A. boylei	section *Leptoaloe*
A. chortolirioides	section *Leptoaloe*
A. dominella	section *Leptoaloe*
A. ecklonis	section *Leptoaloe*
A. fouriei	section *Leptoaloe*
A. hlangapies	section *Leptoaloe*
A. inconspicua	section *Graminialoe*
A. integra	section *Leptoaloe*
A. kniphofioides	section *Leptoaloe* ../cont.

Species	Position in Reynolds' classification
A. kraussii	section *Leptoaloe*
A. leedalii	section *Leptoaloe*
A. linearifolia	section *Leptoaloe*
A. minima	section *Graminialoe*
A. modesta	section *Leptoaloe*
A. nubigena	section *Leptoaloe*
A. saundersiae	section *Graminialoe*
A. soutpansbergensis	section *Leptoaloe*
A. thompsoniae	section *Leptoaloe*
A. verecunda	section *Leptoaloe*
A. vossii	section *Leptoaloe*

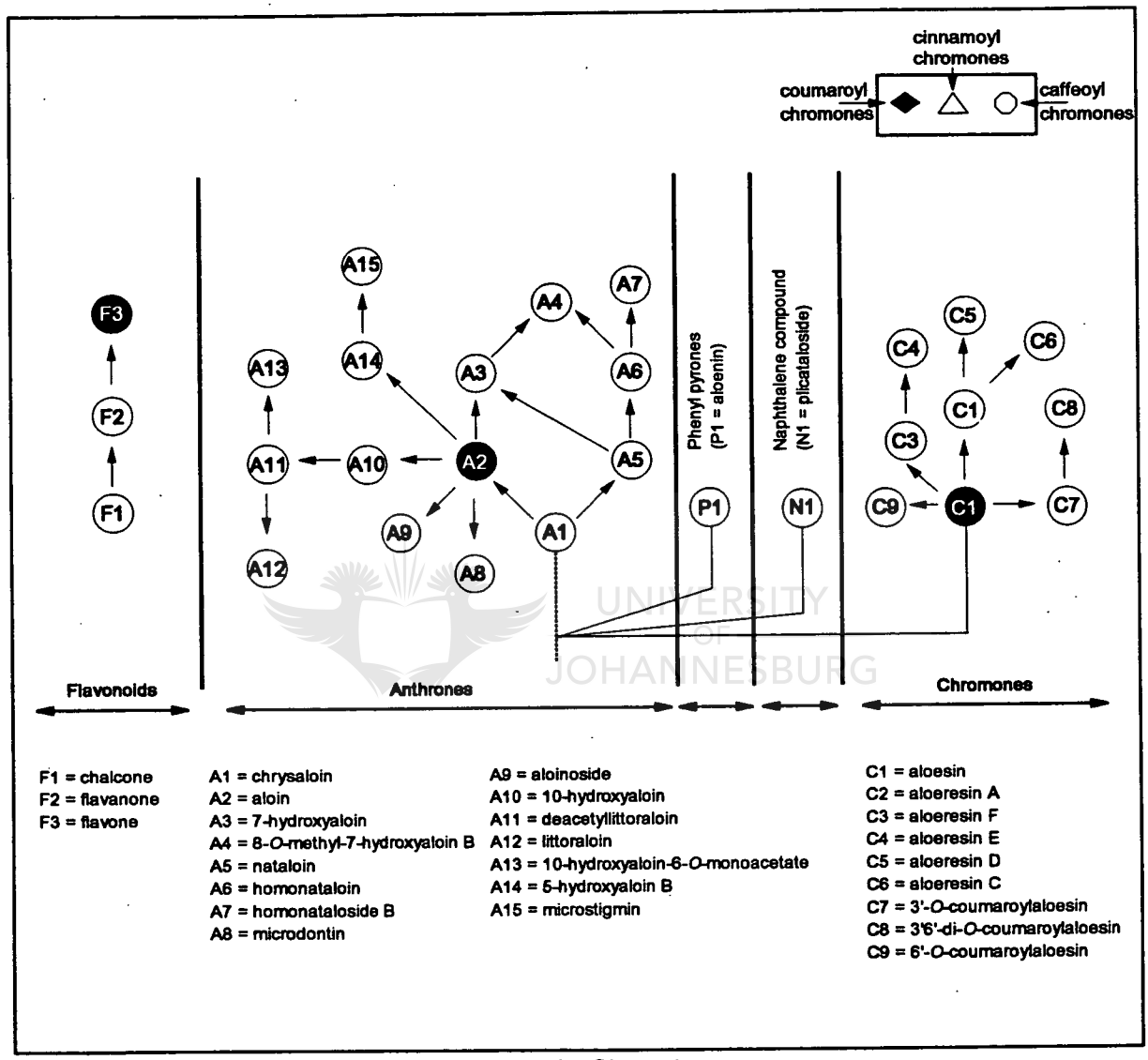
From Table 15.1 it is evident that this chemotype is clearly correlated with the present taxonomic position of these species. Flavones only (mostly isovitexin) occurs in all the grass-like aloes (sections *Graminialoe* and *Leptoaloe*). The species in this group are characterised by plants of which the leaves are soft and thin, margins with soft cartilaginous thorns (or entire), the inflorescence is mostly simple and varies from capitate, sub-capitate to cylindrical with flowers laxly arranged and symmetrical around the floral axis.

CHEMOTYPE A2 (FLAVONES, ANTHRONES & CHROMONES)

Two distinct infrageneric groups are included in this chemotype; all members of *Aloe* sect. *Eualoe* subsect. *Prolongatae* series *Macrifoliae* (Table 15.2) and the berried aloes in *Aloe* sect. *Lomatophyllum*. Both groups have been discussed in Chapter 12.

Table 15.2: Species included in the A2 Chemotype.

Species	Position in Reynolds' classification
A. ciliaris	series *Macrifoliae*
A. commixta	series *Macrifoliae*
A. gracilis	series *Macrifoliae*
A. striatula	series *Macrifoliae*
A. tenuior	series *Macrifoliae*



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C2 = aloeresin A
C3 = aloeresin F
C4 = aloeresin E
C5 = aloeresin D
C6 = aloeresin C
C7 = 3'-*O*-coumaroylaloesin
C8 = 3'6'-di-*O*-coumaroylaloesin
C9 = 6'-*O*-coumaroylaloesin

Figure 5.4: Presence of leaf compounds in the A2 Chemotype.

Species	Position in Reynolds' classification
A. aldabrensis	section *Lomatophyllum*
A. lomatophylloides	section *Lomatophyllum*
A. occidentalis	section *Lomatophyllum*
A. orientalis	section *Lomatophyllum*
A. purpurea	section *Lomatophyllum*

As in the case in Chemotype A1 there is a good correlation between the present taxonomic placement of the species and chemotaxonomic data. The leaf exudate composition of this chemotype could be seen as transitional between the grass-like aloes (Chemotype A1) and the true aloes which are mostly included in Chemotype B (Figure 15.1). Although not all species produce chromones this absence could be ascribed to concentration and / or sample limitations. Although very similar in their exudate, it would have been preferable to include more representatives of the section *Lomatophyllum* as only five of the recognised 15 taxa in this group have been studied.

The similarity in exudate composition of these two infrageneric groups does not warrant a taxonomic amalgamation of the *Macrifoliae* with *Lomatophyllum* as the distinct apomorpy, the berried fruit of *Lomatophyllum* justifies sectional status separate from the *Macrifoliae*. The presence of the leaf compounds in species belonging to this chemotype is shown in Figure 15.4

CHEMOTYPE A3 (FLAVANONES ONLY)

The two classes of flavonoids were detected in *Aloe*; the flavones and flavanones (dihydroflavonols are here included under flavanones as it was not possible to distinguish between the two classes by diode array detection). The presence of flavanones in *Aloe* is an unique occurrence. Only eight species in this entire survey produce flavanones / dihydroflavonols in the absence of chromones and anthrones (Figure 15.5). It is not convincing to suggest that all species represented in Table 15.3 are related as it is possible that the distribution of flavanones represent a paraphyletic distribution. Morphological evidence does however exist to unite *A. glauca, A. lineata* of the *Rhodacanthae* with *A. pretoriensis* and *A. thomcroftii* of the *Superpositae*. The four remaining species are 'dwarf' aloes, probably ancient relicts from a time when these compounds were more widely distributed in *Aloe*.

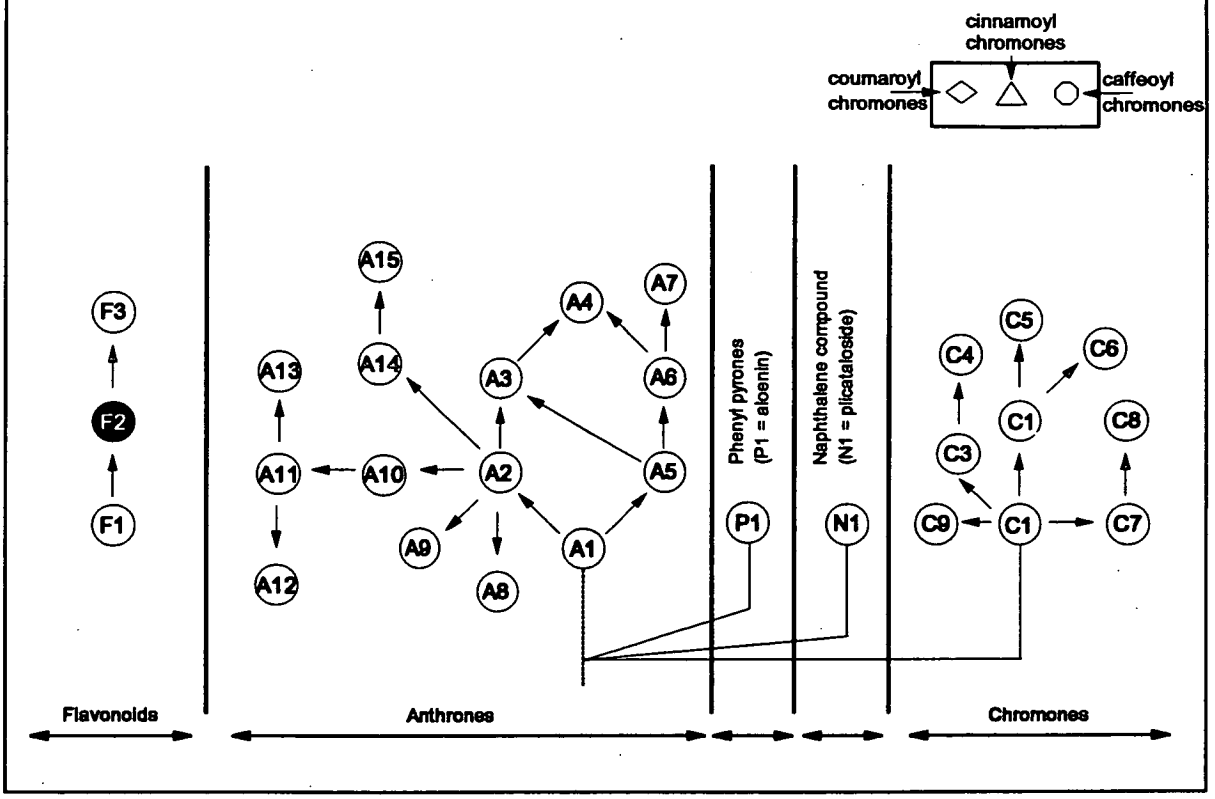


Figure 15.5: Presence of leaf compounds in the A3 Chemotype.

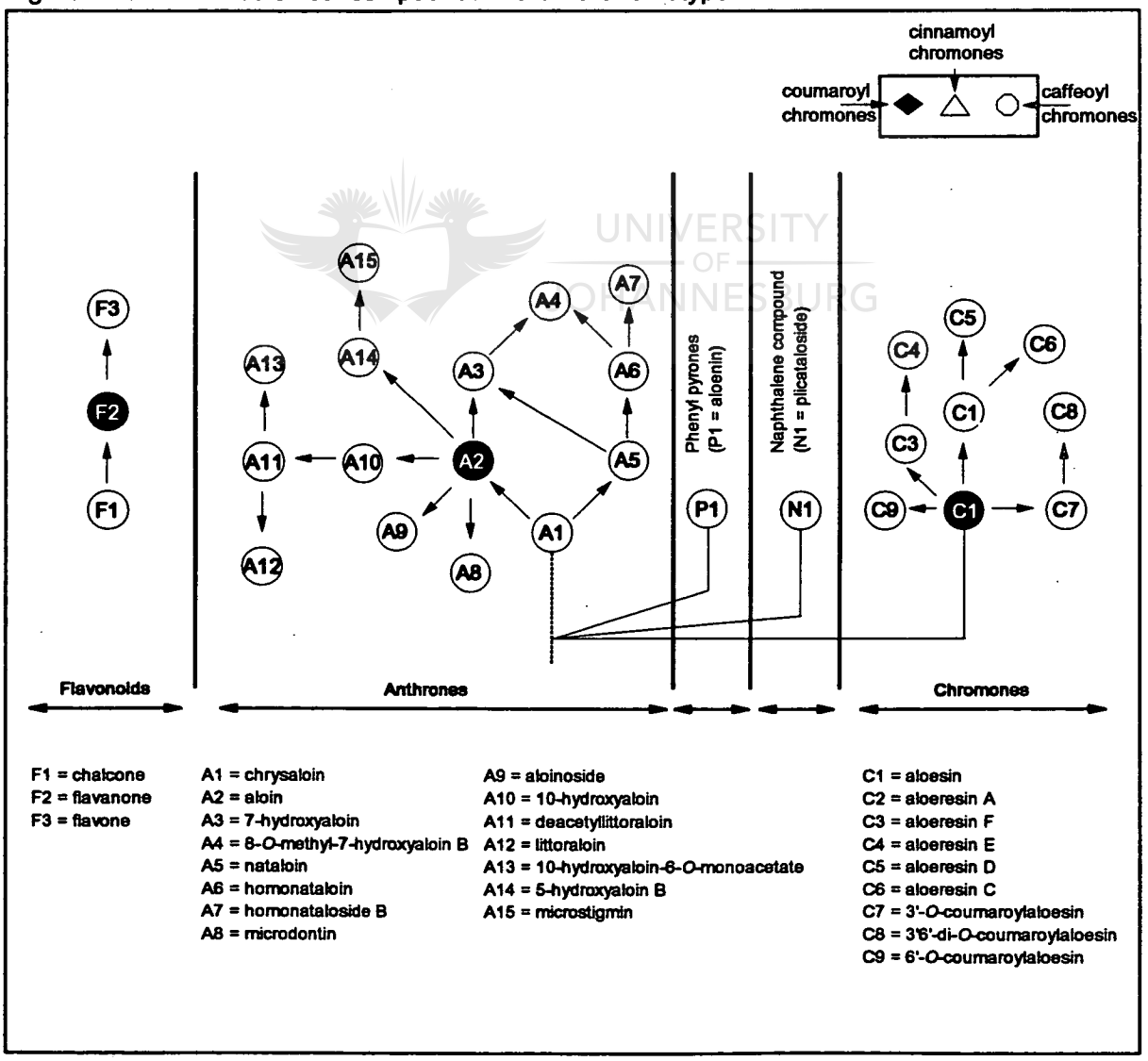


Figure 15.6: Presence of leaf compounds in the A4 Chemotype.

Table 15.3: Species included in the A3 Chemotype.

Species	Position in Reynolds' classification
A. glauca	series *Rhodacanthae*
A. lineata	series *Rhodacanthae*
A. pretoriensis	series *Superpositae*
A. thomcroftii	series *Superpositae*
A. humilis	series *Echinatae*
A. pratensis	series *Echinatae*
A. bakeri	Madagascar Group 1
A. bellatula	Madagascar Group 1

CHEMOTYPE A4 (FLAVANONES, ANTHRONES AND CHROMONES)

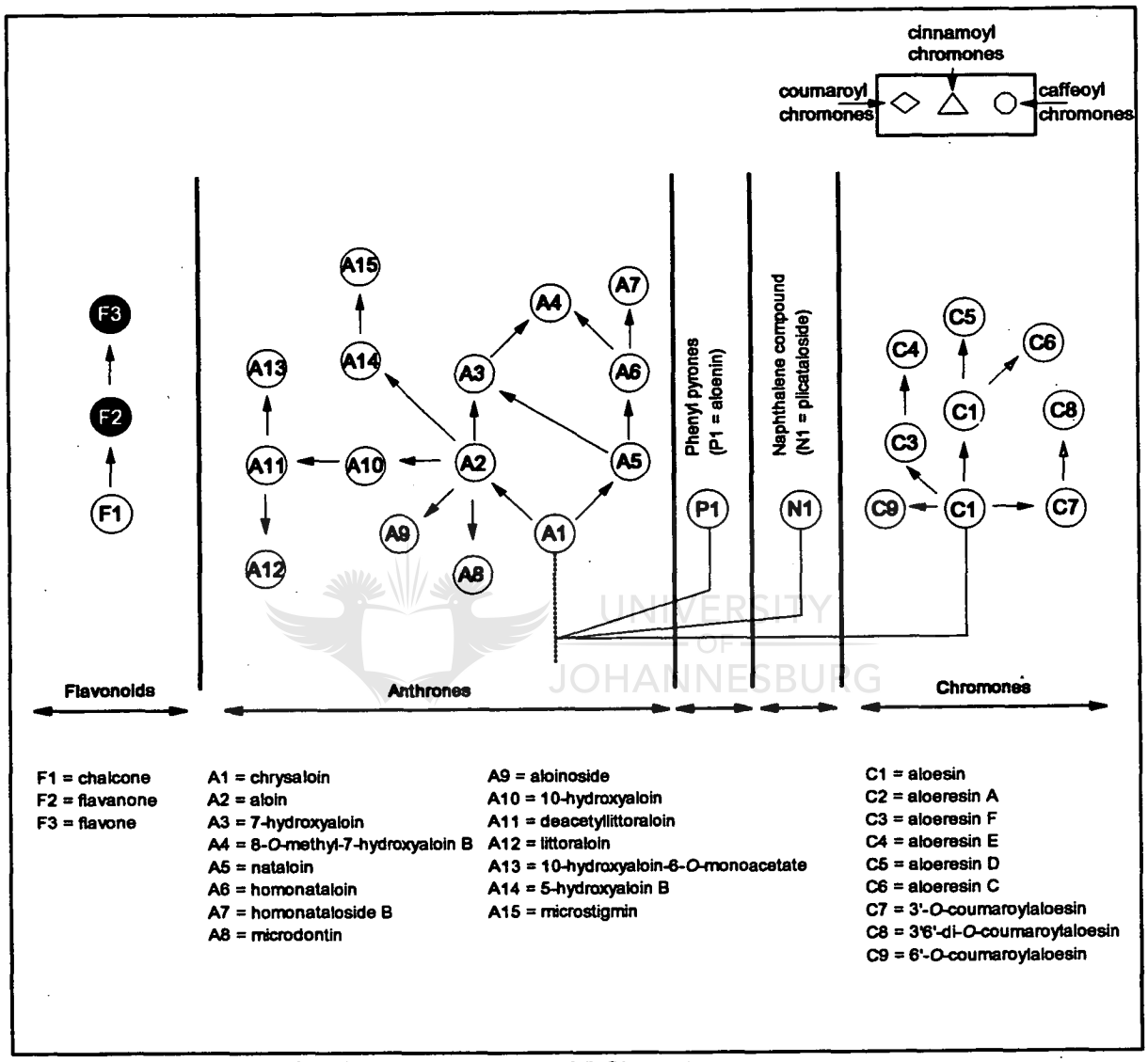
This chemotype also represents a transition from Chemotype A4 to Chemotype B. Only two species, both Malagasy endemics, produce flavanones together with anthrones and chromones (Figure 15.6). Only trace amounts of chromones were detected in both species.

Table 15.4: Species included in the A4 Chemotype.

Species	Position in Reynolds' classification
A. helenae	Madagascar Group 9
A. vaotsanda	Madagascar Group 9

CHEMOTYPE A5 (FLAVANONES & FLAVONES)

Only one species is included in this chemotype, *Aloe suzannae*, which occupies a position in Group 9 of the Malagasy endemics. The chemical anomaly of *Aloe suzannae* is also reflected in its unique morphological features and does not bear a chemical or morphological resemblance with any other species of *Aloe*. It is the only species of *Aloe* where flavones and flavanones co-occur (Figure 15.7).



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A14 = 5-hydroxyaloin B
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C3 = aloeresin F
C4 = aloeresin E
C5 = aloeresin D
C6 = aloeresin C
C7 = 3'-*O*-coumaroylaloesin
C8 = 3'6'-di-*O*-coumaroylaloesin
C9 = 6'-*O*-coumaroylaloesin

Figure 15.7: Presence of leaf compounds in the A5 Chemotype.

CHEMOTYPE B - ANTHRONES

The anthrone-accumulating aloes are divided into two subtypes:

Ba - the aloin producing species (or derivatives of aloin)

Bh - the homonataloin producing species

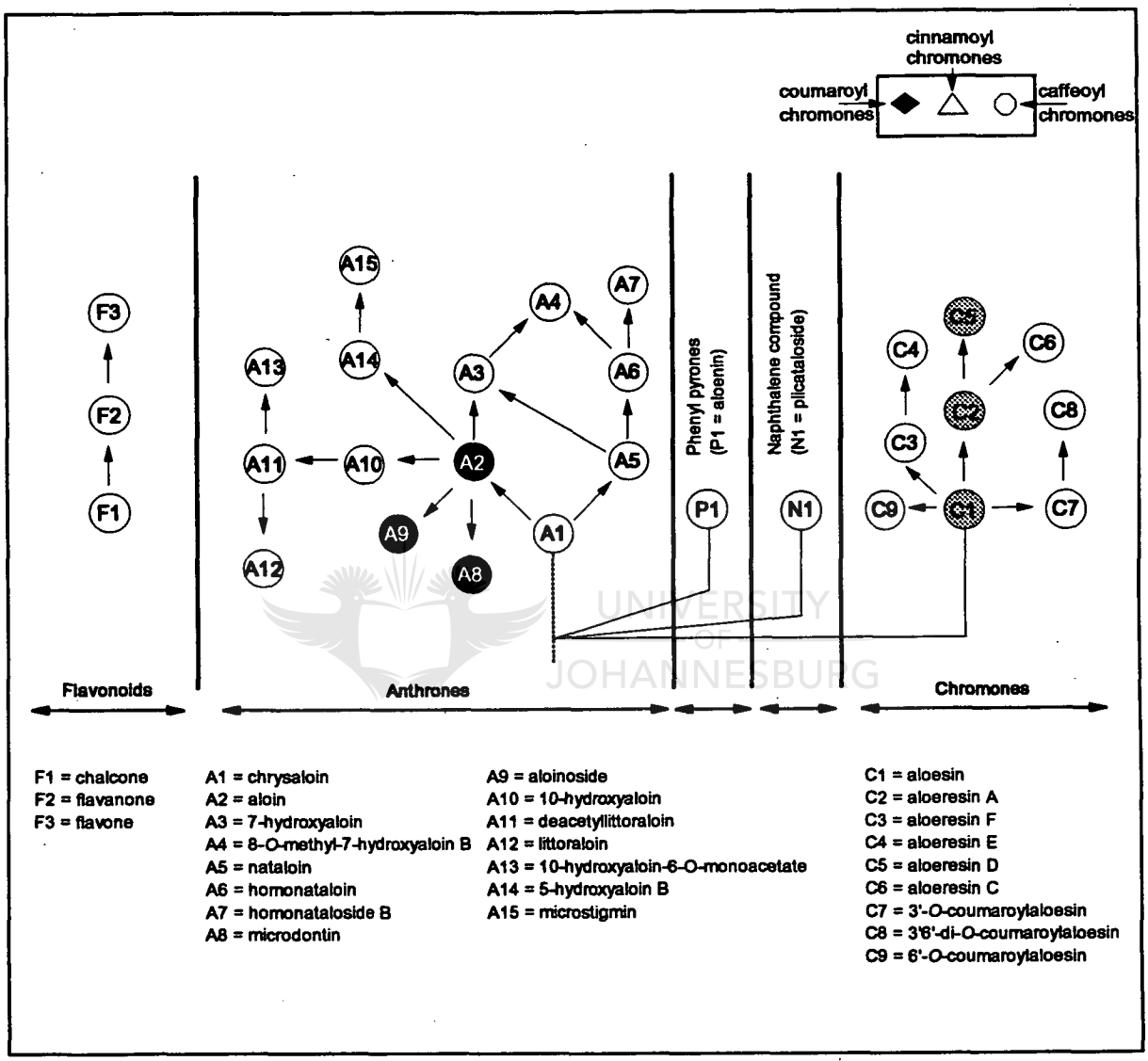
The justification of this division is summarised in Figure 15.2 and explained in Chapter 6. These two anthrones are found to be mutually exclusive with most aloes producing aloin. Fewer species accumulate homonataloin and only one derivative of homonataloin, homonataloside B, has been described thus far.

CHEMOTYPE Ba1 (ALOIN A & B, ALOINOSIDE A & B AND MICRODONTIN A & B)

This is the largest of all the chemotypes identified in this study and this group is characterised by three isomer pairs, thus six chemotaxonomic marker compounds (Figure 15.8). A great deal of variation has been detected in this vast group. Some species only produce the anthrones and no chromones while others produce only aloin and aloinoside. As microdontin is a further modification of the two anthrone isomers, aloin A and B, all species that have this pathway active have been included in this chemotype.

Table 15.5: Species included in the Ba1 Chemotype.

Species	Position in Reynolds' classification
A. aageodonta	Tropical Group 17
A. africana	section *Pachydendron*
A. boscawenii	Tropical Group 19
A. brunneostriata	Subsection *Orthlophae*
A. buchlohii	Madagascar Group 3
A. calidophila	Tropical Group 17
A. cameronii	Tropical Group 19
A. camperi	Tropical Group 13
A. canarina	Tropical Group 17
A. chrysostachys	series *Aethiopicae*
A. diolii	Tropical Group 4
A. elegans	Tropical Group 13 .../cont.



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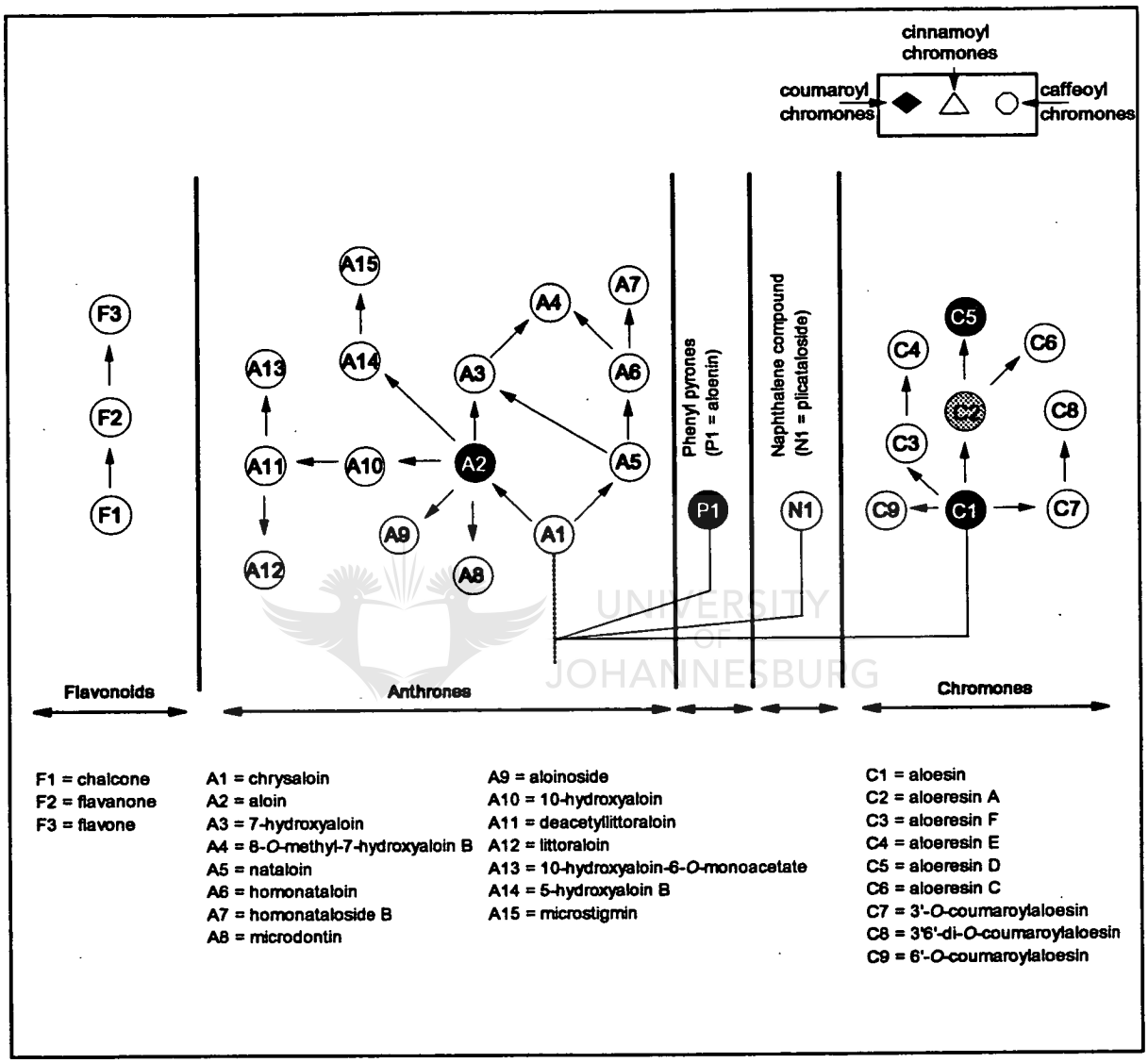
C8 = 3'6'-di-O-coumaroylaloesin
C9 = 6'-O-coumaroylaloesin

Figure 15.8: Presence of leaf compounds in the Ba1 Chemotype.

Species	Position in Reynolds' classification
A. ferox	section *Pachydendron*
A. fleurentiniorum	subsection *Ortholophae*
A. flexilifolia	Tropical Group 19
A. gilberti	Tropical Group 17
A. guillaumetii	Madagascar Group 5
A. harlana	Tropical Group 16
A. hemmingii	Tropical Group 4
A. lensayuensis	Tropical Group 17
A. mcloughlinii	Tropical Group 4
A. megalacantha	Tropical Group 17
A. microdonta	Tropical Group 17
A. ngongensis	Tropical Group 19
A. peckii	Tropical Group 4
A. penduliflora	Tropical Group 19
A. rabaiensis	Tropical Group 19
A. rivae	series *Aethiopicae*
A. scabrifolia	Subsection *Ortholophae*
A. schelpei	Tropical Group 17
A. scobinifolia	Tropical Group 13
A. sinkatana	Tropical Group 13
A. somaliensis	Tropical Group 4
A. steudneri	Tropical Group 16
A. tewoldei	Tropical Group 4
A. tweediae	Tropical Group 16

In stark contrast with the other groups mentioned above, this large chemical assemblage of species shows no correlation with the present taxonomic positions of most species. Most species are found in tropical Africa, and indeed it is this group of aloes which are taxonomically problematic.



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F2 = flavanone
F3 = flavone

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A2 = aloin
A3 = 7-hydroxyaloin
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A5 = nataloin
A6 = homonataloin
A7 = homonataloside B
A8 = microdontin
A9 = aloinoside
A10 = 10-hydroxyaloin
A11 = deacetylittoraloin
A12 = littoraloin
A13 = 10-hydroxyaloin-6-*O*-monoacetate
A14 = 5-hydroxyaloin B
A15 = microstigmin

C1 = aloesin
C2 = aloeresin A
C3 = aloeresin F
C4 = aloeresin E
C5 = aloeresin D
C6 = aloeresin C
C7 = 3'-*O*-coumaroylaloesin
C8 = 3'6'-di-*O*-coumaroylaloesin
C9 = 6'-*O*-coumaroylaloesin

Figure 15.9: Presence of leaf compounds in the Ba2 Chemotype.

CHEMOTYPE Ba2 (ALOIN A & B & ALOENIN)

The phenyl-pyrone, aloenin is always associated with aloin, except in the case of *A. kedongensis* where nataloin is the major anthrone. It has been debated in Chapter 6 that nataloin is formed when crossing aloin- and homonataloin-producing species. *Aloe kedongensis* is believed to be of hybrid origin between an aloenin (and aloin) and homonataloin containing species. The hypothesised biochemical pathways shows that aloenin is not associated with the anthrone pathway, yet this compound is always in co-occurrence with aloin (Figure 15.9). It is proposed that aloenin formed independently in an aloin-producing species and gave rise to a number of species with this characteristic combination of exudate compounds.

Table 15.6: Species representing the Ba2 Chemotype.

Species	Position in Reynolds' classification
A. arborescens	series *Arborescentes*
A. brandhamii	Subsection *Ortholophae*
A. leachii	Subsection *Ortholophae*
A. secundiflora	Subsection *Ortholophae*
A. bussei	Tropical Group 5
A. dorotheae	Tropical Group 5
A. leptosiphon	Tropical Group 5
A. brachystachys	Tropical Group 11
A. classenii	Tropical Group 16
A. monticola	Tropical Group 16
A. cheranganiensis	Tropical Group 19
A. dawei	Tropical Group 19
A. gossweileri	Tropical Group 19
A. kedongensis	Tropical Group 19
A. nyeriensis	Tropical Group 19
A. tororoana	Tropical Group 19

From Table 15.6 it can be seen that there is partial congruence with the present classification

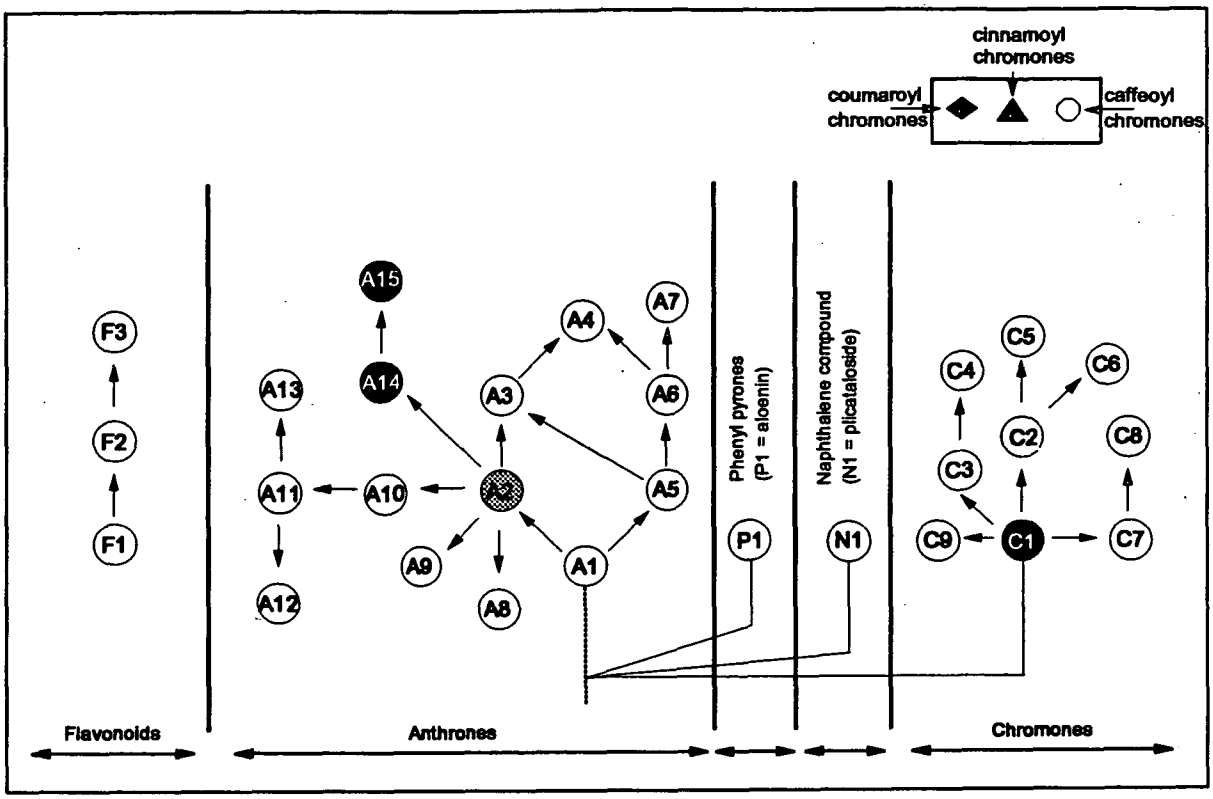


Figure 15.10: Presence of leaf compounds in the Ba3 Chemotype.

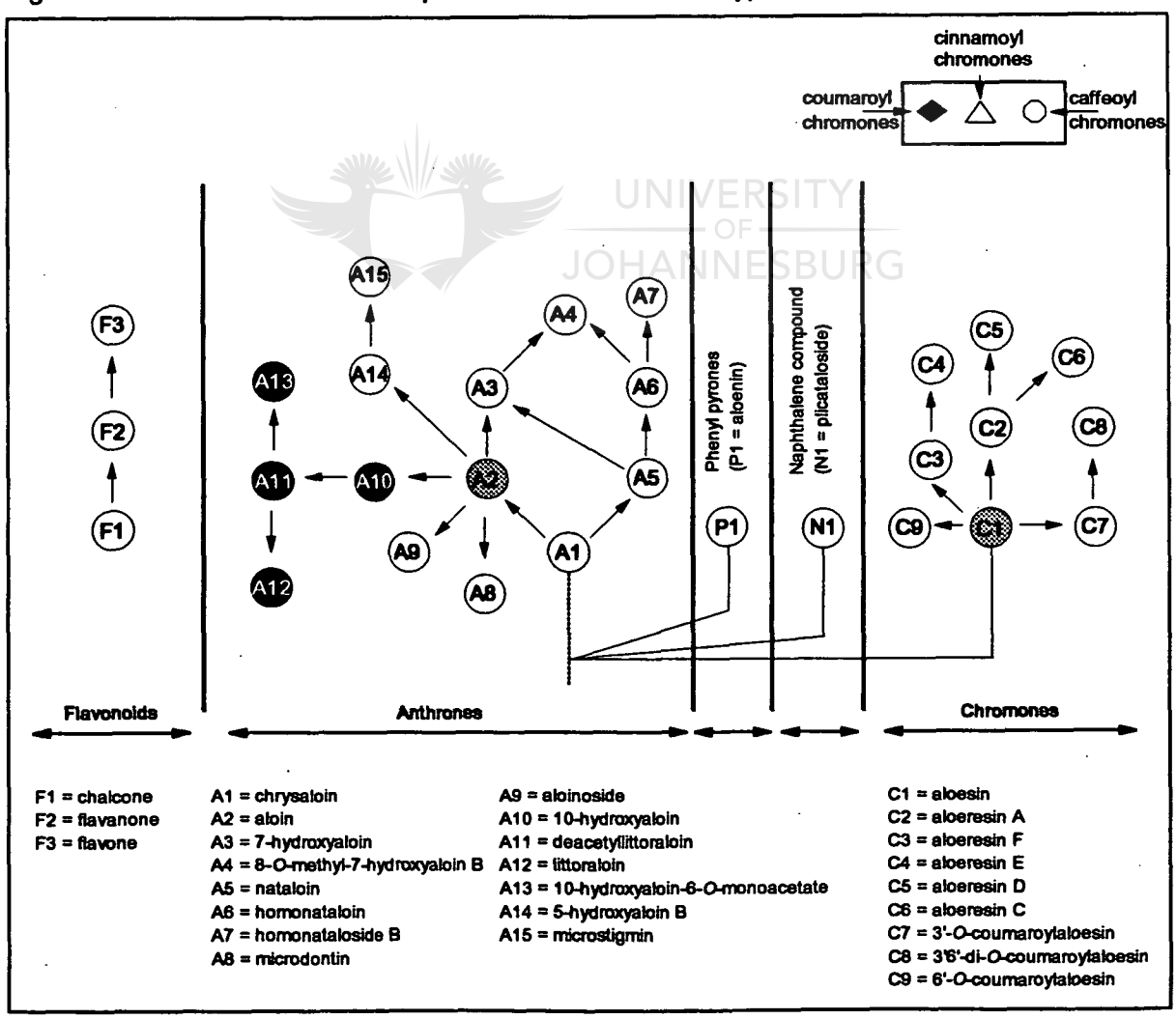


Figure 15.11: Presence of leaf compounds in the Ba4 Chemotype.

system. Six species in Group 19 contains this combination of compounds, three in Group 5 and three in subsection *Orthlophae*.

CHEMOTYPE Ba3 (MICROSTIGMIN)

Microstigmin, a derivative of aloin is a chemotaxonomic marker for six species of which some have not previously been associated. In the case of *A. broomii* and *A. chlorantha*, aloin is in co-occurrence with microstigmin (Figure 15.10).

Table 15.7: Representatives of the Ba3 Chemotype.

Species	Position in Reynolds' classification
A. framesii	series *Purpurascentes*
A. khamiesensis	series *Purpurascentes*
A. microstigma	series *Purpurascentes*
A. pictifolia	allied to *A. microstigma*
A. broomii	series *Longistylae*
A. chlorantha	allied to *A. broomii*

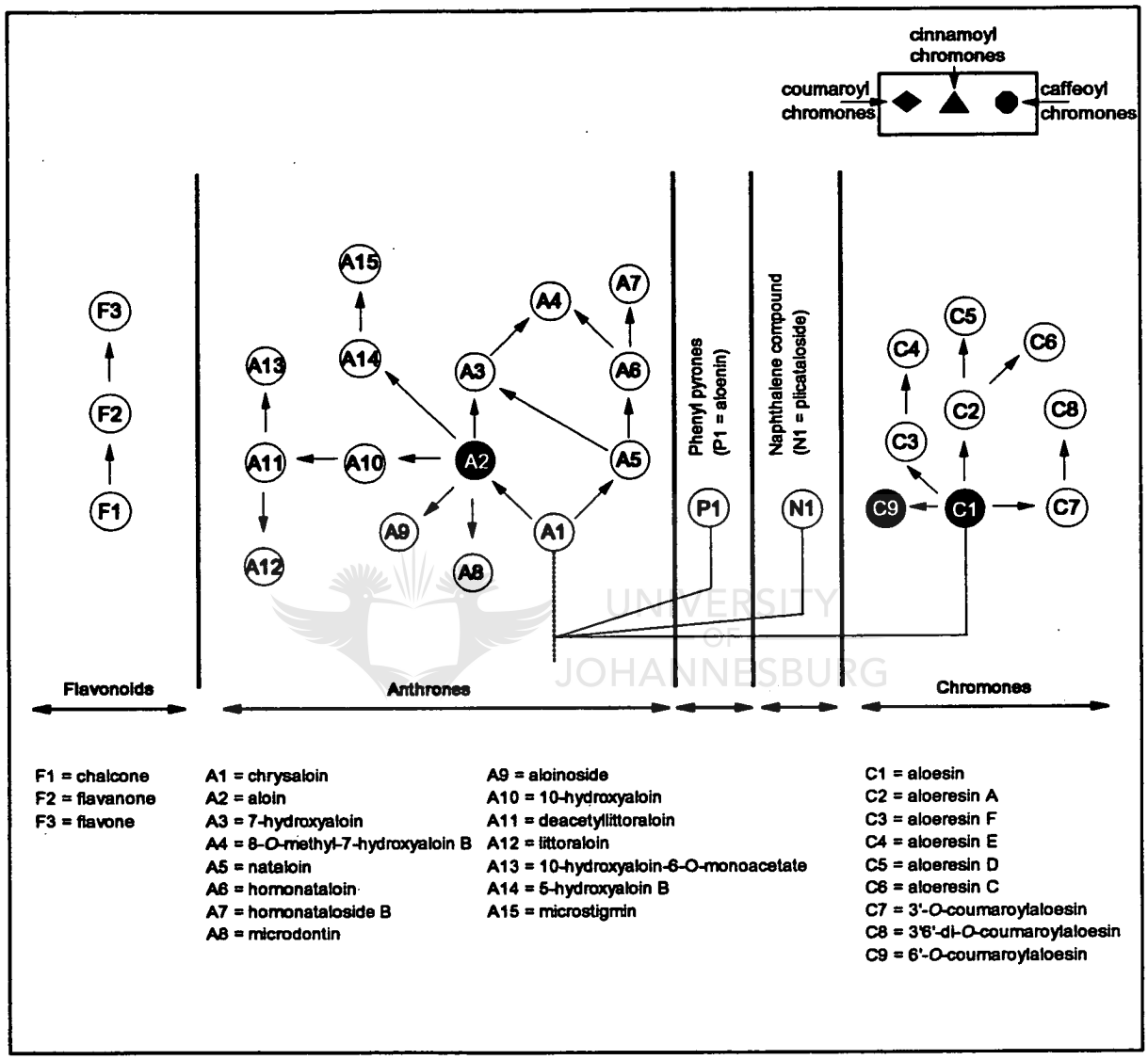
CHEMOTYPE Ba4 (10-HYDROXYALOIN AND DERIVATIVES THEREOF)

Another example where the infrageneric taxonomy is fully congruent with the chemotaxonomic data is shown by Chemotype Ba4. The only exception is the taxonomically problematic *A. littoralis* which shows an exudate profile identical to its *Asperifoliae sensu stricto* counterparts. In most species aloin is absent with 10-hydroxyaloin and derivatives thereof present (Figure 15.11).

Table 15.8: Species representing the Ba4 Chemotype.

Species	Position in Reynolds' classification
A. argenticauda	series *Asperifoliae*
A. asperifolia	series *Asperifoliae*
A. claviflora	series *Asperifoliae*
A. corallina	series *Asperifoliae*
A. dewinteri	series *Asperifoliae*
A. esculenta	allied to *A. littoralis*

.../cont.



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F2 = flavanone
F3 = flavone

A1 = chrysaloin
A2 = aloin
A3 = 7-hydroxyaloin
A4 = 8-*O*-methyl-7-hydroxyaloin B
A5 = nataloin
A6 = homonataloin
A7 = homonataloside B
A8 = microdontin
A9 = aloinoside
A10 = 10-hydroxyaloin
A11 = deacetyllittoraloin
A12 = littoraloin
A13 = 10-hydroxyaloin-6-*O*-monoacetate
A14 = 5-hydroxyaloin B
A15 = microstigmin

C1 = aloesin
C2 = aloeresin A
C3 = aloeresin F
C4 = aloeresin E
C5 = aloeresin D
C6 = aloeresin C
C7 = 3'-*O*-coumaroylaloesin
C8 = 3'6'-di-*O*-coumaroylaloesin
C9 = 6'-*O*-coumaroylaloesin

Figure 15.12: Presence of leaf compounds in the Ba5 Chemotype.

Species	Position in Reynolds' classification
A. falcata	series *Asperifoliae*
A. littoralis	Series *Percrassa*
A. namibensis	series *Asperifoliae*
A. pachygaster	series *Asperifoliae*

CHEMOTYPE Ba5 (ALOIN A & B10 AND 6'-*O*-COUMAROYLALOESIN)

It is only in two groups that chromones were found to be of additional chemotaxonomic value at the infrageneric level, in Chemotype Ba5 and Bh2. The species in Table 15.9 all contain the aloin isomers together with a series of chromones of which 6'-*O*-coumaroylaloesin was always present (Figure 15.12). This is another example where chemotaxonomic data is in full agreement with the infrageneric taxonomy.

Table 15.9: Species in the Ba5 Chemotype.

Species	Position in Reynolds' classification
A. alooides	section *Anguialoe*
A. castanea	section *Anguialoe*
A. dolomitica	section *Anguialoe*
A. spicata	section *Anguialoe*
A. vryheidensis	section *Anguialoe*
A. tauri	section *Anguialoe*

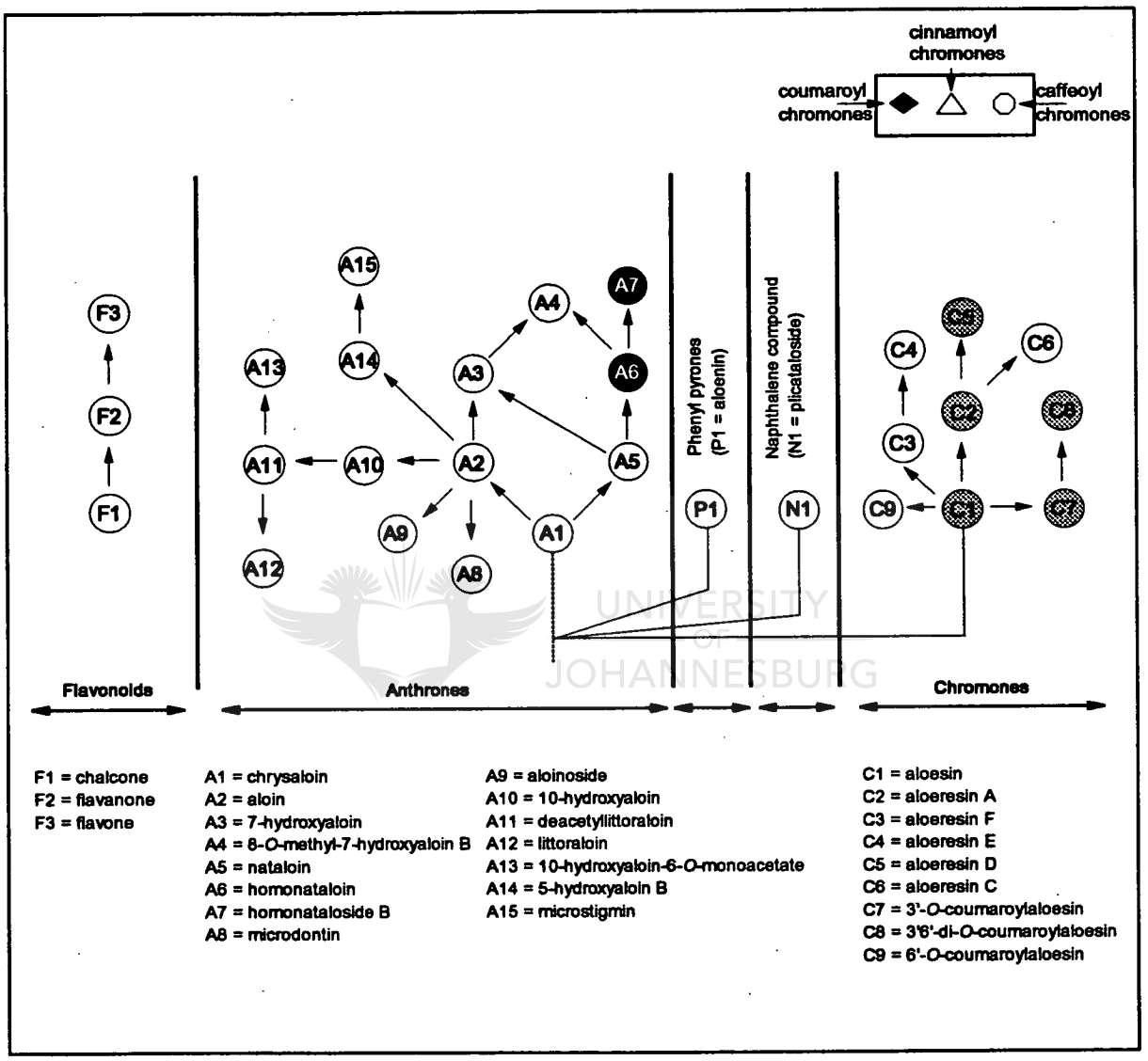
CHEMOTYPE B - ANTHRONES

Homonataloin

The distribution of homonataloin in the genus *Aloe* has been discussed in Chapter 14, hence it would suffice to briefly mention the chemotypes.

CHEMOTYPE Bh1 (HOMONATALOIN A & B AND HOMONATALOSIDE B)

Discussion of the aloin chemotypes above has illustrated the ability of aloes to produce several derivatives of aloin. Only a single derivative of the other major anthrone found in *Aloe*, homonataloin, has been recorded, homonataloside B. This anthrone diglucoside is always associated with homonataloin (Figure 15.13) except in *A. molederana* which produces aloin.



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F2 = flavanone
F3 = flavone

A1 = chrysaloin
A2 = aloin
A3 = 7-hydroxyaloin
A4 = 8-*O*-methyl-7-hydroxyaloin B
A5 = nataloin
A6 = homonataloin
A7 = homonataloside B
A8 = microdontin

A9 = aloinoside
A10 = 10-hydroxyaloin
A11 = deacetylittoraloin
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A14 = 5-hydroxyaloin B
A15 = microstigmin

C1 = aloesin
C2 = aloeresin A
C3 = aloeresin F
C4 = aloeresin E
C5 = aloeresin D
C6 = aloeresin C
C7 = 3'-*O*-coumaroylaloesin
C8 = 3'6'-di-*O*-coumaroylaloesin
C9 = 6'-*O*-coumaroylaloesin

Figure 15.13: Presence of leaf compounds in the Bh1 Chemotype.

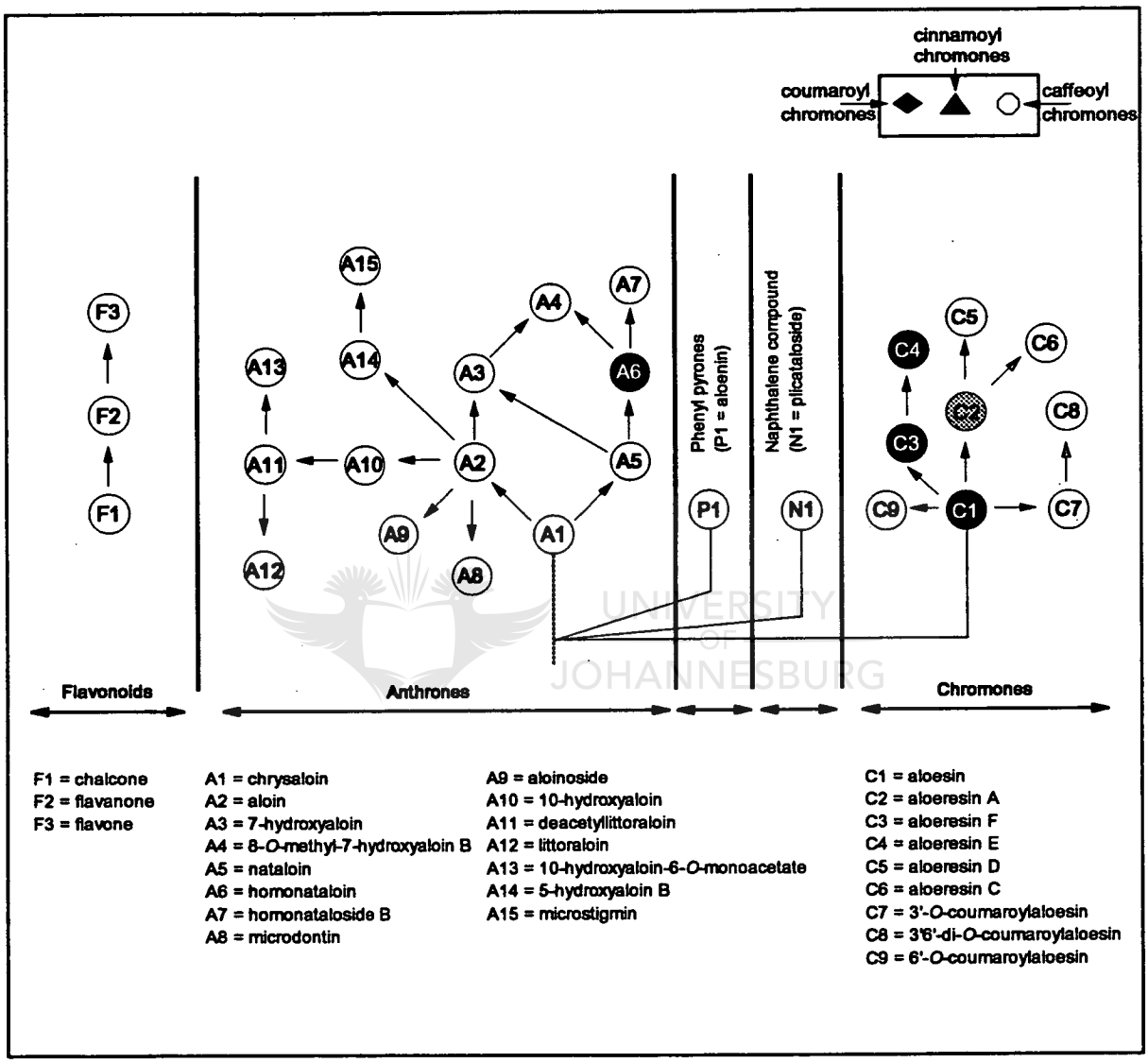
This chemotype shows very little congruence with the present taxonomic position of the individual species.

Table 15.10: Species representing the Bh1 Chemotype.

Species	Position in Reynolds' classification
A. lutescens	series *Latebracteatae*
A. wickensii	series *Latebracteatae*
A. cryptopoda	series *Latebracteatae*
A. erensii	Tropical Group 4
A. bargalensis	unknown
A. citrina	unknown
A. abyssicola	Tropical Group 10
A. mendesii	Tropical Group 10
A. breviscapa	Tropical Group 16
A. dhufarensis	Tropical Group 16
A. amicorum	Subsection *Ortholophae*
A. krapohliana	series *Echinatae*
A. tomentosa	Tropical Group 9
A. molederana	Tropical Group 9

CHEMOTYPE Bh2 (HOMONATALOIN A & B AND ALOERESIN E & F)

The combination of homonataloin A and B with the two cinnamoyl chromones (Figure 14.15) unites the species of *Aloe* series *Mitriformes* with other species not previous associated with this infrageneric group. The taxonomic relationships and a phylogeny for the group is presented in Chapter 11. This chemotype correlates well to the present taxonomic understanding of this group (e.g. series *Mitriformes*) yet, many species of which the taxonomic affinities are obscure are included in this chemotype (e.g. *A. melanacantha*).



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A4 = 8-*O*-methyl-7-hydroxyaloin B
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A6 = homonataloin
A7 = homonataloside B
A8 = microdontin

A9 = aloinoside
A10 = 10-hydroxyaloin
A11 = deacetylittoraloin
A12 = littoraloin
A13 = 10-hydroxyaloin-6-*O*-monoacetate
A14 = 5-hydroxyaloin B
A15 = microstigmin

C1 = aloesin
C2 = aloeresin A
C3 = aloeresin F
C4 = aloeresin E
C5 = aloeresin D
C6 = aloeresin C
C7 = 3'-*O*-coumaroylaloesin
C8 = 3'6'-di-*O*-coumaroylaloesin
C9 = 6'-*O*-coumaroylaloesin

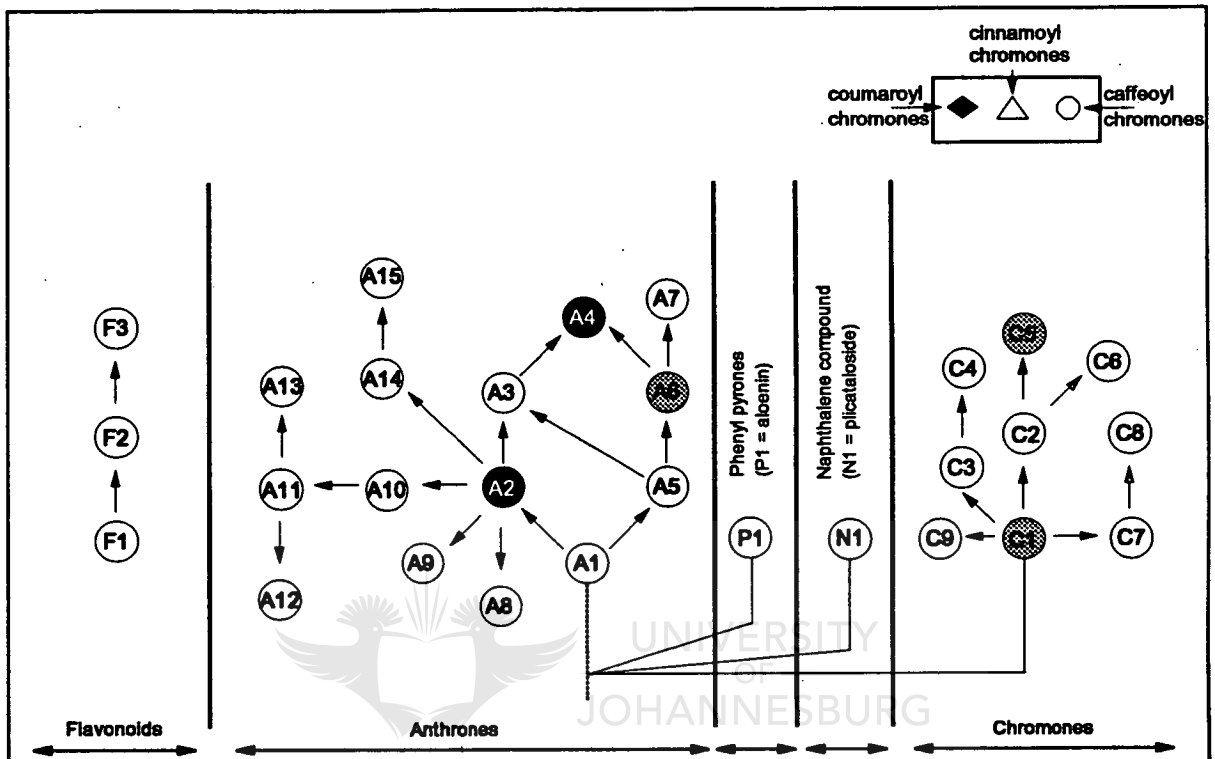
Figure 15.14: Presence of leaf compounds in the Bh2 Chemotype.

Table 15.11: Species representing the Bh1 Chemotype.

Species	Position Reynolds' classification
A. arenicola	series *Mitriformes*
A. comptonii	series *Mitriformes*
A. dabenorisana	series *Mitriformes*
A. distans	series *Mitriformes*
A. mitriformis	series *Mitriformes*
A. meyeri	series *Mitriformes*
A. pearsonii	series *Macrifoliae*
A. peglerae	series *Longistylae*
A. melanacantha	series *Echinatae*
A. erinacea	series *Echinatae*
A. angelica	section *Pachydendron*
A. yavellana	Tropical Group 19

CHEMOTYPE Bah (8-*O*-METHYL-7-HYDROXYALOIN IN THE PRESENCE OF HOMONATALOIN A & B AND / OR ALOIN A & B)

The last chemotype included in the anthrone category is the Bah chemotype. It has been shown in Chapter 6 that when hybridizing an aloin and homonataloin producing species, 8-*O*-methyl-7-hydroxyaloin is formed. The species included in this chemotype are not necessarily related, but their positions within the taxonomic hierarchy become questionable and doubtful if they are of possible hybrid origin. As they do not fit comfortably in any other group, they are housed here within the Chemotype Bah as their positions may become clear as new data becomes available. These species may contain aloin or homonataloin or both aloin and homonataloin. Both aloin and homonataloin could lead to the synthesis of 8-*O*-methyl-7-hydroxyaloin as illustrated in Figure 15.15.



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C1 = aloesin
C2 = aloeresin A
C3 = aloeresin F
C4 = aloeresin E
C5 = aloeresin D
C6 = aloeresin C
C7 = 3'-*O*-coumaroylaloesin
C8 = 3'6'-di-*O*-coumaroylaloesin
C9 = 6'-*O*-coumaroylaloesin

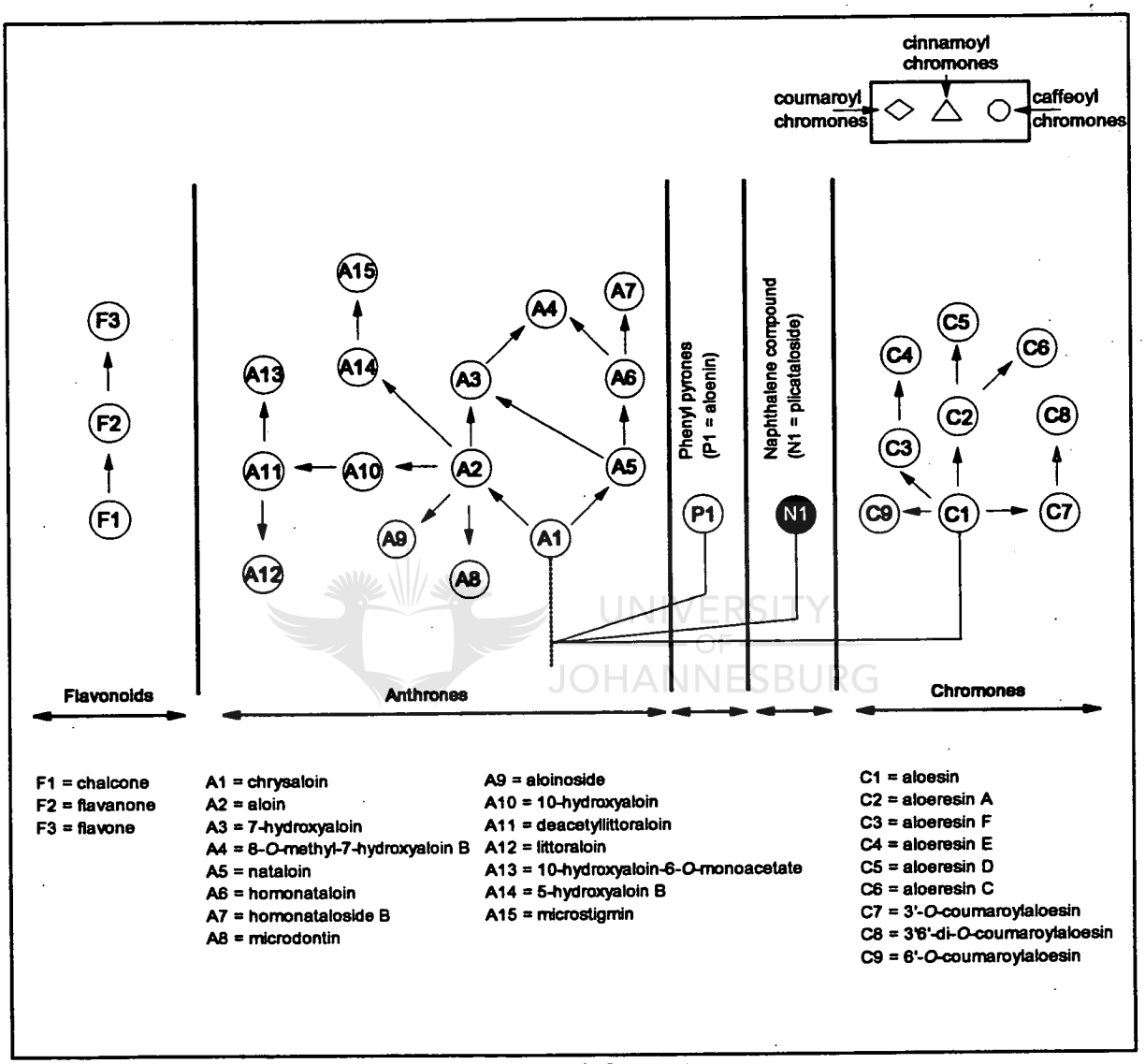
Figure 15.15: Presence of leaf compounds in the Bah Chemotype.

Table 15.12: Species included in the Bah Chemotype.

Species	Position in Reynolds' classification
A. antandroi	Madagascar Group 8
A. christianii	series *Superpositae*
A. hemmingii	Tropical Group 4
A. isaloensis	Madagascar Group 8
A. menachensis	Tropical Group 9
A. millottii	Madagascar Group 8
A. mutabilis	series *Arborescentes*
A. niebuhriana	Tropical Group 9
A. officinalis	Tropical Group 9
A. pubescens	Tropical Group 9
A. retrospiciens	Tropical Group 19
A. schelpei	Tropical Group 17
A. sinana	Tropical Group 13
A. sinkatana	Tropical Group 13
A. turkanensis	Tropical Group 14
A. vaombe	Madagascar Group 9
A. steudneri	Tropical Group 18

CHEMOTYPE C - PLICATALOSIDE

This naphthalene compound assembles all the plicataloside producing species in Chemotype C. What the 'relation' of this chemotype is with the other chemotypes in Figure 15.16 is uncertain. Most species in this chemotype produce plicataloside as the only exudate compound with anthrones and chromones being absent. Although some of the plicataloside species are thought to be taxonomically related many of the taxa included in this chemotype have not been taxonomically associated with other plicataloside-bearing equivalents.



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C3 = aloeresin F
C4 = aloeresin E
C5 = aloeresin D
C6 = aloeresin C
C7 = 3'-*O*-coumaroylaloesin
C8 = 3'6'-di-*O*-coumaroylaloesin
C9 = 6'-*O*-coumaroylaloesin

Figure 15.16: Presence of leaf compounds in the C Chemotype.

Table 15.13: Species defining Chemotype C.

Species	Position in Reynolds' classification
A. archeri	allied to *A. tugenensis*
A. babatiensis	Tropical Group 19
A. chabaudii	Series *Aethiopicae*
A. deserti	Tropical Group 19
A. elgonica	Tropical Group 19
A. fibrosa	Tropical Group 19
A. francombei	allied to *A. pustuligemma*
A. labworana	allied to *A. schweinfurthii*
A. monjensis	allied to *A. fibrosa* and *A. babatiensis*
A. multicolor	allied to *A. gilberti*
A. munna	allied to *A. guerrae*
A. otallensis	Tropical Group 9
A. palmiformis	Tropical Group 19
A. parvidens	Tropical Group 4
A. plicatilis	section *Kumara*
A. pustuligemma	allied to *A. francombei*
A. rugosifolia	Tropical Group 4
A. schweinfurthii	Tropical Group 17
A. tugenensis	Tropical Group 11
A. ukambensis	Tropical Group 16

A summary of the species in their respective chemotypes have been shown above. Three aspects require further elaboration:

1. The chemotaxonomy of the species which have not been discussed in Chapters 5 to 14 and which are thus not included in the chemotypes summarised above.
2. The position of the species which are devoid of anthrones, chromones and other phenolics (i.e. those species not showing any peaks under the analysing parameters used in this study).
3. The status of the species which have not been analysed in this study.

Firstly, the species which have not allowed themselves to be associated with any of the chemotypes defined above will be discussed alphabetically. A summary table will be presented at the end of the discussion in which each species will be assigned to a chemotype according to Figure 15.1.

Aloe aculeata is placed in section *Pachydendron* where it is suggested to be closely related to *A. gerstneri*, *A. petricola* and *A. reitzii*. Indeed, the leaf exudate composition of these four species are very similar. They all produce the aloin isomers and coumaroyl chromones. In all the species very low concentrations of the aloinosides were detected but this needs confirmation. The presence of these compounds would place all four of them in Chemotype Ba1.

Aloe acutissima, this Malagasy endemic accumulates a series of coumaroyl chromones but produces no anthrones. The chemical and taxonomic affinities of this species is uncertain.

Aloe barberae (syn. *A. bainesii*), like all the other tree-like aloes, this species produces a unique exudate profile. A series of anthrones, all with UV spectra resembling that of aloin was detected in low concentration. No chromones were detected in the leaf exudate.

Aloe bella from northern Somalia contains aloin and a series of chromones. Lavranos (1973) speculates that this species might be related to *A. sinkatana* or *A. elegans*. Both these species are placed in Chemotype Ba1 as they too contain aloin but in the presence of aloinoside and or microdontin.

Aloe brevifolia, a poor producer of exudate, contains a single chromone and a series of anthrones with a UV spectrum similar to that of 5-hydroxyaloin. As similar exudate profile was recorded for *A. longistyla*. *A. brevifolia* is placed in the monotypic series *Proliferae*.

Aloe buchlohii from the southern parts of Madagascar has a characteristic chemical profile consisting of a series of unidentified compounds in co-occurrence with aloin. Microdontin A and B was also positively identified but this needs confirmation as no other Malagasy species was found to contain microdontin.

Aloe bukobana produces homonataloin together with cinnamoyl chromones. This is the only species in series *Aethiopicae* which has this combination of exudate compounds. Its position within the homonataloin Chemotype (Bh) is uncertain.

Aloe bulbillifera, like most Malagasy species, produce very little exudate. Two unidentified anthrones were recorded in this species.

Aloe capitata, in addition to aloin, accumulates a series of unidentified aloin derivatives not detected in any other species of *Aloe*.

Aloe catengiana, a shrubby species from Angola shows the presence of homonataloin and chromones. Only three other species in Group 19 produce homonataloin; *A. retrospiciens*, *A. yavellana* and *A. squarrosa*.

Aloe comosa, a morphologically distinct species produces homonataloin and chromones. Chapter 14 (Figure 14:15) indicates a possible taxonomic affinity with *A. gariepensis*, the latter species also accumulates homonataloin.

Aloe confusa contains three exudate compounds; aloeresin D and nataloin A & B. The latter isomers have been shown to form during hybridization of aloin and homonataloin containing species (Chapter 6) making the taxonomic position of this species dubious.

Aloe congdonii, like its close relative (*A. mzimbana*) contains homonataloin of which the affinities have been shown in Figure 14:15.

Aloe conifera also contains homonataloin but the identity of the chromone compounds in this Malagasy species could not be confirmed.

Aloe cremnophila is placed with all the pendent species in Group 10 of the tropical species. Only two species in this group produce homonataloin. The other species, *A. abyssicola* contains homonataloside placing it in Chemotype Bh1.

Aloe descoingsii located in the southern parts of Madagascar, shows an HPLC profile not repeated in any other species in this survey. It is placed with all the dwarf aloes in Group 1.

Aloe dichotoma, like *A. barberae*, shows the presence of unidentified compounds. The two anthrones detected in this species shows the same UV spectrum as 5-hydroxyaloin.

Aloe debrana (syn. *A. berhana*), the highly localised Ethiopian endemic contains the anthrones aloin in conjunction with a series of cinnamoyl chromones. Reynolds (1966) mentions that this species is related to *A. percrassa* which also produces the same cinnamoyl chromones. *Aloe percrassa* also contains 7-hydroxyaloin, a 'hybrid compound' which obscures its taxonomic position as reflected in the exudate profile as a whole.

Aloe decurva, a morphologically distinctive species from Mozambique accumulates the anthrone aloin in the presence of a series of coumaroyl chromones. Reynolds (1966)

relates this species to *A. ortholopha* which is devoid of any anthrones but contains a series of unidentified coumaroyl chromones. These two species are very similar in flower characters.

Aloe divaricata from the southern parts of Madagascar, shows distinctive chemical features, an anomaly also reflected macromorphologically. Although this species contains the aloin isomers it produces many unidentified anthrones with the same UV spectrum as that of aloin.

Aloe eminens with its peculiar morphological features also produces a characteristic exudate profile. This species contains aloin and unidentified compounds. The other tree-like aloes also produce aloin or derivatives thereof.

Aloe excelsa, another producer of aloin, contains a series coumaroyl chromones. Reynolds (1966) suggests that this species is related to *A. rupestris*. The latter species does not contain any anthrones (probably a secondary loss) but in addition produces a range of coumaroyl and caffeoyl chromones.

Aloe forbesii produces very low levels of exudate phenolics which include aloin and coumaroyl chromones. Together with its closely allied species, *A. perryi*, Reynolds (1966) places these species in Group 13, which contains all species with clavate perianths. No anthrones or chromones were detected in *A. perryi*.

Aloe fragilis, distributed in the northern parts of Madagascar, contains a series of unidentified compounds. This species contains cinnamoyl chromones, a chemical rarity in the Malagasy species. It also produced an unidentified compound which has been seen in species of the *Purpurascentes*. In his species description Lavranos (1994) suggest this species to be related to *A. rauhii* and *A. guillaumettii*. The latter species has been placed in Chemotype Ba1 while no leaf exudate compounds were detected *A. rauhii*. The chemical similarity with the *Purpurascentes* could be a case of convergence although the spotted leaves is reminiscent of *A. pictifolia* and other species in the group of aloes with 'speckled leaves'.

Aloe gariepensis occupies a taxonomic position in series *Purpurascentes*. The leaf exudate of this species is however very different from the other members in the *Purpurascentes* group (See chapter 8). In Chapter 14 (Figure 14.15) it has been speculated that *A. gariepensis* could be related to another homonataloin species, *A. comosa* with which it shares morphological features (e.g. large bracts). See *A. comosa* above.

Aloe gerstneri, see *A. aculeata* above.

Aloe globuligemma, with its oblique inflorescences is suggested to be superficially related to *A. marlothii*. *A. globuligemma* does not accumulate any anthrones for which it seems to compensate by producing a complex series of unidentified chromones. The leaf exudate composition of this species does not match that of any other species in this study.

Aloe hardyi is suggested by Glen (1987) to have a taxonomic affinity with *A. mutabilis*. The latter species is suggested in Chapter 6 to be of hybrid origin. This species too contains homonataloin as in the case of *A. hardyi*. Chapter 14 has hinted at a possible relationship between *A. hardyi*, *A. mutabilis* and *A. suprafoliata*.

Aloe hereroensis, in addition to the homonataloside isomers contains a number of unique and unidentified compounds. Chapter 14 has shown a possible taxonomic alignment with *A. viridiflora* / *A. congdonii* and *A. mzimbana*.

Aloe hildebrandtii has a complex leaf exudate profile which is very different from any other species of *Aloe* studied. Reynolds (1966) places this species in a large group which houses all species with a shrubby habit. In some aspects the profile resembles some of the peaks recorded for *A. jacksonii*.

Aloe inermis, one of the earliest species of *Aloe* to be recorded, has an unique profile representing a series of unidentified peaks not found in other species. Lavranos (1992) regards this species, *A. brunneostriata* and *A. luntii* to be closely related. *Aloe brunneostriata* is placed in Chemotype Ba1 while no chromones and anthrones were detected in *A. luntii*. *Aloe inermis* contains various unidentified compounds of which the UV spectrum of one was similar to that recorded for microdontin.

Aloe jacksonii, shows a series of unidentified chromones and anthrones. Although the exudate compounds have been studied extensively by Conner *et al.* (1987 & 1989) no standards could be obtained to identify the peaks. The anthrones are all derivatives of homonataloin.

Aloe jucunda, is placed with all the other species which have a striped perianth in Group 4. Two unidentified compounds co-occur with the aloin isomers. The leaf exudate chemistry of this group is diverse with no two species producing the same major exudate compounds.

Aloe kulalensis, a pendulous species from Kenya, produces aloin and coumaroyl chromones. This species is placed in Group 10 of the tropical aloes (Newton & Beentjie 1990) with comments of a possible relationship with *A. confusa*. The leaf exudate of all pendulous

species are very different and that of *A. confusa* has been discussed above.

Aloe longistyla - see *A. brevifolia.*

Aloe macroclada - The HPLC profile of the widespread Malagasy endemic indicates the presence of aloin isomers and a series coumaroyl chromones.

Aloe macrosiphon is placed in Group 11 (Reynolds 1966). Judged by bract characters this species resembles *A. deserti* and species of series *Latebracteatae*. Species in the latter infrageneric group all produce homonataloin while *A. deserti* with its white, brittle bracts accumulates plicataloside.

Aloe marlothii is chemically the most variable species analysed in this study. Some individuals produce homonataloin while others accumulate aloin. In both chemotypes a series of coumaroyl chromones are also produced. It is speculated that the homonataloin of this species is not homologous with the homonataloin produced by other species.

Aloe massawana is placed with a large group of other species in Group 9 of Reynolds (1966) who also suggests that morphologically this species resembles *A. vera* and *A. trichosantha*. Both these species, like *A. massawana*, contain aloin and coumaroyl chromones.

Aloe mawii is shown in Chapter 14 to accumulate homonataloin and a series of cinnamoyl chromones, very much the same pattern as recorded for series *Mitriformes* and other species in Chapter 11. The resemblance in perianth characters as illustrated in Figure 14.16 further suggests a possible support for this hypothesis.

Aloe mayottensis from the isolated Mayotte Island north of Madagascar accumulates homonataloin. The occurrence of homonataloin-producing species in Madagascar is restricted to a small number of species of which *A. isaloensis*, in the same group as *A. mayottensis* is one such a species.

Aloe munchii is placed in Group 18 of the tropical aloes (*Pachydendron pro parte*). In macromorphological features is bears a striking resemblance with *A. angelica*. Both species produce the homonataloin anthrones. It has been suggested in Chapter 14 that *A. munchii* could be distantly related to other species in series *Mitriformes* discussed in Chapter 11 (e.g. *A angelica* and *A. yavellana*).

Aloe mzimbana has been suggested above and in Chapter 14 to possibly be related to the *A. hereroensis / A. congdonii / A. viridiflora* alliance. All these species produce homonataloin and are characterised by their capitate racemes.

Aloe ortholopha - see *A. decurva*.

Aloe percrassa - see *A. debrana*.

Aloe petricola - see *A. aculeata*.

Aloe polyphylla - as mentioned several times in this discussion, it is frequent that the anomalous morphology of a species is also reflected in the unique exudate chemistry. This is the case in the 'spiral aloe' of which the taxonomic affinities are obscure. This species produces a range of nataloin / 7-hydroxyaloin related compounds which have been shown in Chapter 6 to be products of hybridization events.

Aloe pulcherrima, like *A. polyphylla*, accumulates nataloin and 7-hydroxyaloin derivatives making arguments mentioned under *A. polyphylla* relevant. Gilbert and Sebsebe (1997) suggests that this species could be related to *A. steudneri*. The latter species has a very different leaf exudate composition which has placed it in Chemotype Ba1.

Aloe ramosissima, like all the other tree aloes, has an unique exudate profile. No class of compound could be ascribed to the unidentified phenolics in this species.

Aloe reitzii, see *A. aculeata*.

Aloe rigens, like all other species with a pubescent perianth is placed in Group 9 of the tropical aloes. Some species in this group contain aloin while others contain homonataloin. Some also contain the 'hybrid chemicals' discussed in Chapter 6 indicating that this group has possibly been involved in hybridization events.

Aloe rubroviolacea - see comments under *A. polyphylla* as this species too contains derivatives of 7-hydroxyaloin and nataloin.

Aloe rupestris produces a series of unidentified chromones and shows the complete absence of anthrones. The chromone composition of this species is identical to that of *A. thraskii*, with the exception that *A. thraskii* shows trace amounts of homonataloin (see Chapter 16). It is here suggested that these two species are closely related and that the absence of homonataloin in *A. rupestris* represents a secondary loss of this pathway.

Aloe speciosa, placed in the monotypic series *Principales*, accumulates homonataloin. It has been discussed in Chapter 14 that this species could possibly be related to *A. mawii* with which it shares chemical and floral characters.

Aloe splendens, isolated on the Arabian peninsula, produces homonataloin and a series of coumaroyl chromones. In his description of this species Lavranos (1965) states this species is distinct but could possibly be related to *A. megalacantha*. The latter species

has a very different anthrone composition which has placed it in Chemotype Ba1.

Aloe succotrina - see comments under *A. polyphylla*. This species is presently placed in *Aloe* series *Purpurascentes* but it lacks the characteristic profile of the other members of this group.

Aloe suffulta has a distinctive inflorescence character not found in any other species of *Aloe*. It also has an exudate profile unique to this species. On the basis of perianth characters Reynolds (1966) places this species in series *Aethiopicae*, a group diverse in leaf exudate composition. This morphologically anomalous species yields homonataloin and various chromones.

Aloe suprafoliata is placed in series *Superpositae* together with flavanone accumulating species here placed in Chemotype A3. *A. suprafoliata*, however, accumulates homonataloin. Chapter 14 has suggested a distant taxonomic relationship between this species and *A. mutabilis* / *A. hardyi* / and various species in Group 9 of the tropical aloes (see Figure 14.15)

Aloe thraskii - see *A. rupestris*.

Aloe trichosantha, a species with a pubescent perianth, accumulates aloin. See comments under *A. rigens*.

Aloe vacillans, like many species in this discussion of taxa which do not fall into any of the chemotypes, *A. vacillans* produces leaf compounds not found in any other species analysed. This species is devoid of any anthrones. At present, it is placed in Group 9 of the tropical aloes.

Aloe vanbalenii, like *A. vacillans*, contains exudate compounds unique to this species. *A. vanbalenii* does however contain the anthrones, aloin A and B. This species is placed in series *Arborescentes*, an infrageneric group of which the species show no chemical coherence.

Aloe vera shows an exudate profile as enigmatic as its history. This species, never collected in its natural habitat, contains aloin and 7-hydroxyaloin. The latter compound is one of the 'hybrid chemicals' discussed in Chapter 6. In addition to these compounds it contains a series of unidentified chromones not found in any other species.

Aloe veseyi, a pendent species from Zambia, accumulates the 'hybrid compound' nataloin. Reynolds (1966) suggests the closest relative of this species to be *A. confusa* which too produce nataloin. It could be that these two species have originated from two independent hybridization events, or that initial hybridization was followed by divergent

speciation of one of the hybrid off-spring.

Aloe viridiflora, a homonataloin containing species, has been implicated under *A. hereroensis* and *A. mzimbana*.

Aloe volkensii shows an HPLC profile containing homonataloin. In Chapter 14 it has been suggested that this species could possibly be related to the other homonataloin-producing species presently placed in section *Pachydendron*.

Aloe wilsonii accumulates large volumes of homonataloin in conjunction with cinnamoyl chromones. Although it lacks aloeresin E and F, the defining cinnamoyl chromones of Chemotype Bh2, the presence of the same class of chromones suggests a possible alliance with the *Mitriformes* group discussed in Chapter 11.

The foregoing alphabetical discussion of each of the species which do produce exudate but do not fit in the chemotype categories created in Figure 15.1 illustrates the limitation of any taxonomic character, in this case chemical characters. Many species might be related to one of the species placed in a chemotype but they lack the diagnostic compound or profile due to a secondary loss or possible incorrect identification of material sampled, or chemical variation of the species not detected in this study. In Table 15.14 below these species are assigned to various chemotypes where possible. This placement could be 'taxonomically peripheral' within the group and will be indicated by *. In most cases it is impossible to assign the species to an 'exact category' and for these species they will be placed provisionally in the broader category ie. Ba if it accumulates aloin and Bh is the species contains homonataloin.

Table 15.14. Species which do not fit into any of the chemotypes summarised above. An attempt has been made to show the most likely chemotaxonomic relationships.

Species	Chemotype
A. aculeata	Ba1*
A. acutissima	?
A. barberae	Ba
A. bella	Ba
A. brevifolia	Ba
A. buchlohii	Ba1 (?)

Species	Chemotype
A. longistyla	?
A. macroclada	Ba
A. macrosiphon	Bh
A. marlothii	Ba & Bh (?)
A. massawana	Ba
A. mawii	(Bh2?)

Species	Chemotype
A. bukobana	Bh (Bh2?)
A. bulbillifera	?
A. capitata	Ba
A. catengiana	Bh
A. comosa	Bh
A. confusa	?
A. congdonii	Bh
A. conifera	Bh
A. cremnophila	Bh
A. descongsii	?
A. dichotoma	Ba
A. debrana	Ba
A. decurva	Ba
A. divaricata	Ba
A. eminens	Ba
A. excelsa	Ba
A. forbesii	Ba
A. fragilis	Ba3 (?)
A. garlepensis	Bh
A. gerstneri	Ba1*
A. globuligemma	?
A. hardyi	Bh
A. hereroensis	Bh
A. hildebrandtii	?
A. inermis	Ba1 (?)
A. jacksonii	Bh (?)
A. jucunda	Ba
A. kulalensis	Ba

Species	Chemotype
A. mayottensis	Bh
A. munchii	Bh2 (?)
A. mzimbana	BH
A. ortholopha	?
A. percrassa	Ba (?)
A. petricola	Ba1*
A. polyphylla	?
A. pulcherrima	?
A. ramosissima	Ba (?)
A. reitzii	Ba1*
A. rigens	?
A. rubroviolacea	?
A. rupestris	Bh (?)
A. speciosa	Bh
A. splendens	Bh
A. succotrina	?
A. suffulta	Bh (?)
A. suprafoliata	Bh
A. thraskii	Bh
A. trichosantha	Ba
A. vacillans	?
A. vanbalenii	Ba
A. vera	Ba
A. veseyi	?
A. viridiflora	Bh
A. volkensii	Bh
A. wilsonii	Bh2(?)

TRANSFORMING CHEMICAL DATA INTO TAXONOMIC INFORMATION

Chapter 1 has indicated the present taxonomic status for the genus *Aloe*. The basis of the classification is that of Berger (1908). This treatment was adopted by Reynolds (1950 & 1960) with slight modifications. The treatment of Berger only dealt with the *ca.* 180 taxa that were described at that time. The number of taxa since this monumental work has more than doubled bringing the number of species to *ca.* 420. The greatest challenge facing Reynolds was to organise his new species according to the system of Berger. This proved problematic especially in his seconds publication (1966) on the tropical species. The present classification system has provided an excellent 'handle' for anyone interested in *Aloe* to obtain a firm grip on the large number or species with their range of perplexing morphological characters. It has also had its disadvantages in that all post-Reynolds species are forced into this hierarchy even though the authors are not convinced that the suggested taxonomic affiliation is correct. Slotting species into this framework has caused a total distortion of taxonomic relationships. The present system is also often based on a single character, macromorphology . Some of the groups are ill-defined and taxonomically ambiguous e.g.

> Group 6: "Plants of medium size, acaulescent or with a short stem, solitary or in groups, spotted on one or both sides, margins mostly sinuate-dentate .....inflorescence mostly a branched panicle...." (Reynolds 1966).

It is clear that although Reynolds 'felt' that certain species were related he could not define the group by a set of correlated morphological characters. Some of the groups are defined by a single character e.g. Group 5 - plants with a striped perianth, Group 9 - plants with a pendent habit, Group 13 - plants with clavate perianths. Although all species in group 13 might have plants with clavate perianths they are diverse when comparing other character states.

The foregoing Chapters (5 to 13) have discussed various chemotaxonomic compounds where the occurrence of a chemical marker compound in various species were superimposed on the present taxonomic arrangement of the species. A diagrammatic summary of possible taxonomic relationships within this group was presented and dendrograms showed the clustering of species which are chemically identical. In Chapter 14 the classes of chemical compounds (e.g. chromones and anthrones) were broadly discussed showing possible chemical congruence between the data for various chemical groups in Chapter 5 - 13. For example, Chapter 11 discussed the chemotaxonomic value of two cinnamoyl chromones aloeresin E and F in the *Mitriformes* group and related species. Chapter 14 demonstrated that

the distribution of homonataloin and the cinnamoyl group in a broader sense also draws in 'peripheral species' (e.g. *A. retrospiciens* and *A. hereroensis*) into this group. In a chemotaxonomic study (as is the case when using any other taxonomic character) many species will not allow themselves to be 'boxed' into chemical groups and they become outliers of this study group.

It is often found in chemotaxonomic studies that authors report total congruence between the chemical data and the present classification system for the taxa under investigation, this is considered to be 'good data', but purely conformational. On the other hand, when there is total conflict between the two data sets it is considered 'bad data'. Confirmation is valuable because it supports the existing hypothesis and is an independent test of the presumed relationships. Conflict on the other hand, may show weaknesses in the existing hypothesis and may point to new groups and associations which may lead to new discoveries of relationships which may previously have been overlooked. The greatest contribution of any chemotaxonomic exercise would be to transform the chemical data into taxonomically useful information. Figure 15.17 illustrates the chemotypes of *Aloe* superimposed on the present classification system for the genus. In many instances the data is in full agreement e.g. aloeresin E and F in series *Mitriformes*, 6-*O*-coumaroylaloesin in section *Anguialoe*, 10-hydroxyaloin B in series *Asperifoliae* and microstigmin in the *Purpurascentes*. These groups are taxonomically well defined and no problem is encountered with the infrageneric position of these species. Visual assessment of Figure 15.7 of the tropical aloes however, shows a very different and erratic distribution of exudate compounds. One is inclined to at least expect some degree of coherence between the aloinoside species and a measure of taxonomic unity within the plicataloside containing species.

To suggest that chemical characters should enjoy preference above any other character would be both premature and naive but this study has indicated that chemical characters in *Aloe* are one of the most conservative classes of characters, with obvious taxonomic value. The question is often asked: 'is a chemical profile a more reliable character than any others?' or 'does chemical similarity necessarily indicate taxonomic alliance?' It has to be stated that all the problems encountered with morphological characters (e.g. convergence) are also true for chemical characters. Chemical characters should be viewed as additional data which should firstly be used as an independent test of the morphological pattern and secondly be integrated

with existing data sets in an attempt to reach a consensus. It is interesting that the chemical similarity between species often forces one to scrutinise the taxa under investigation in an attempt at finding supporting morphological evidence. Leaf exudate composition in itself is not a taxonomically unifying character but when considered in concordance with other forms of taxonomic evidence it could lead to more convincing hypotheses on the taxonomic alignment of taxa. Various studies have been undertaken to assess chromatographic patterns in the genus *Aloe* (Cutler 1980 & Reynolds, 1985,1986 & 1990) but the chemotaxonomic utility of chemical characters at the infrageneric level has not been fully explored. It is encouraging that there are many examples of congruence between the chemotaxonomic data and the alpha taxonomic treatment for *Aloe*. It would be wrong to apply chemotaxonomic data 'inconsistently' and consider this character only valuable where there is total congruence between the formal taxonomy and chemical data.

The core of the taxonomic problem in *Aloe* starts at the various hierarchical levels as there are simply to many divisions or species categories. This study has suggested that *Aloe* should rather be seen as one mega species complex where hybridization has succeeded in obscuring taxonomic relationships. Taxonomically this implies that it would be more realistic to have a 'more lose' taxonomic system as apposed to a system consisting of many strongly demarcated infrageneric groups. In order to achieve a more natural arrangement of the species the entire hierarchal structure needs to be evaluated. At the sectional level the following changes are proposed (see Figure 15.18):

Sections *Graminialoe* and *Leptoaloe* should be amalgamated in a single section *Aloe* section *Leptoaloe*, to house all the grass-like aloes. The distinction between the *Graminialoe* and *Leptoaloe* is vague with no single character for any one of the two groups. *Aloe haemanthifolia*, presently in a monotypic series *Haemanthifoliae*, should also be included in this group. The section *Bulbiformes* becomes a subsection of section *Leptoaloe*. The four species in subsection *Bulbiformes* are characterised by an underground 'bulb-like' structure. Two species were investigated chemically and were also free of chromones and anthrones. *Aloe* series *Macrifoliae* is elevated to sectional level. The five species in this group resemble the members of the *Leptoaloe* in leaf characters (lower leaf succulency, soft cartilaginous teeth). The inflorescence is mostly simple, cylindrical and laxly flowered. The flavones found in the *Leptoaloe* are also present in the *Macrifoliae* with the difference that high quantities of aloin are produced. The members of this group are characterised by sheathing leaves

arranged on long slender stems, forming internodes. It is suggested through chemical evidence that this group represents a transition from the grass-like aloes to the 'true aloes' in section *Eualoe.*

Recently Rowley (1996) suggested the inclusion of *Lomatophyllum* in *Aloe* for which he created the section *Lomatophyllum.* Rowley suggests that *Lomatophyllum* could be paraphyletic but for purpose of identification he unites all 'berried aloes' in section *Lomatophyllum.* This was criticised by Newton (1998) who suggested that the infrageneric classification is obscure and that *Aloe* has to be revised to ascertain the position of *Lomatophyllum.* He further speculates that *Lomatophyllum* might not be a natural group hinting on the paraphyletic origin as suggested by Rowley. It could indeed be that the species of the section *Lomatophyllum* are not necessarily taxonomically coherent, but the five species (of the 20 species) studied indicated that *Lomatophyllum* is chemically related to the grass-like aloes and the *Macrifoliae* hence it also belongs to a basal position in *Aloe.* The distinct apomorphy for section *Lomatophyllum* is the fruit which is a berry.

Aloe section *Eualoe,* the 'true aloes' is the largest section in the genus and it is a complex assemblage of species of which the morphological and chemical distinction is obscure. This section will be discussed later.

It is suggested that series *Saponariae* should be raised to sectional level and should include series *Paniculatae* as subsection *Paniculatae. Aloe* section *Saponariae* is an obvious monophyletic group with distinct floral characters. The *Saponariae* (and *Paniculatae*) do not accumulate anthrones and chromones in the leaves and the presence of the root compound, isoelutherol is a convincing chemical apomorphy for the *Saponariae. Aloe* sections *Anguialoe* and *Pachydendron* as well as subsection *Ortholophae* should all be transferred to section *Eualoe.*

It is here proposed that all the 'tree-like' aloes should be united in a single section, *Aloidendron* to include *A. dichotoma*, *A. ramosissima*, *A. pillansii*, *A. barberae*, *A. eminens* and *A. sabaea.* All species are characterised by an arborescent habit, usually with a 'trunk' and the dry leaves are not persistent. The 'tree-like' aloes do not produce the leaf exudate compounds characteristic of the other members of the genus. Section *Kumara* should be included in section *Eualoe.* The sections defined above provides a rigorous taxonomic framework for the genus *Aloe.*

The taxonomic arrangement of taxa which strongly reflects chemotaxonomic data is presented in Figures 15.18 and 15.19. Figure 15.20, like Figure 15.17, shows the chemotypes defined

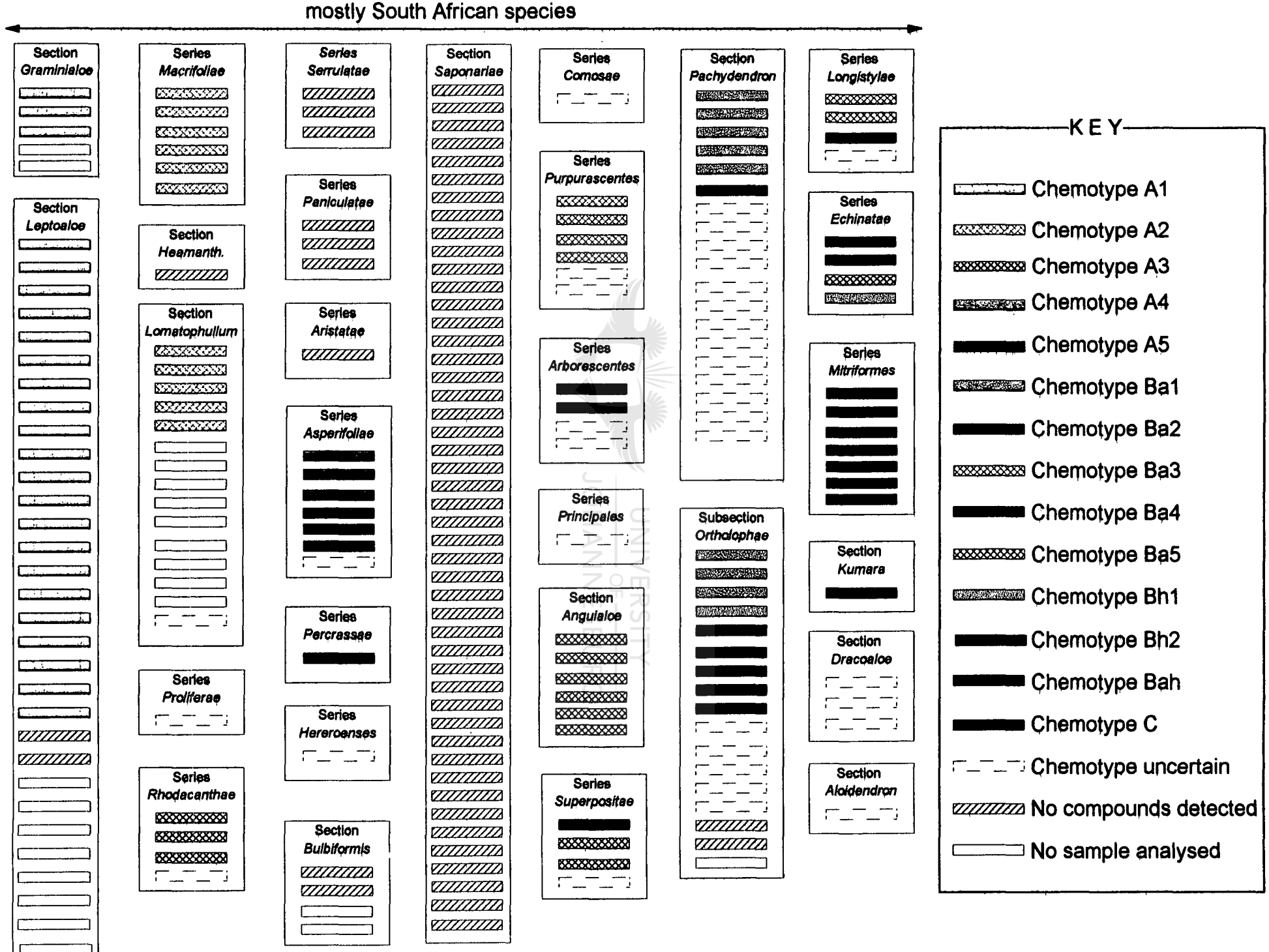


Figure 15.17: Chemotypes (Figure 15.1) superimposed over the present classification system (Reynolds 1950 & 1966).

Figure 15.17 cont.

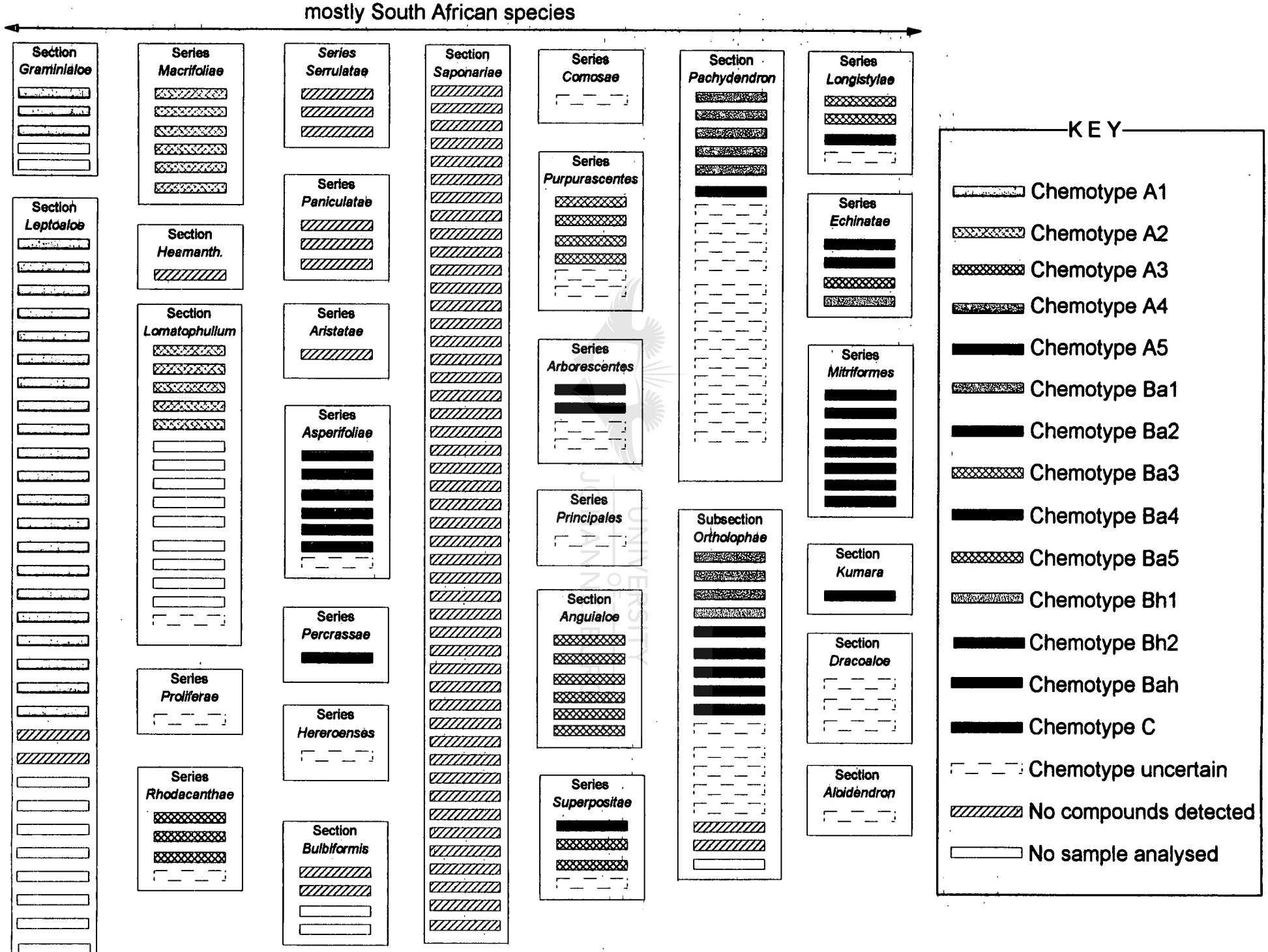


Figure 15.17: Chemotypes (Figure 15.1) superimposed over the present classification system (Reynolds 1950 & 1966).

Figure 15.17 cont.

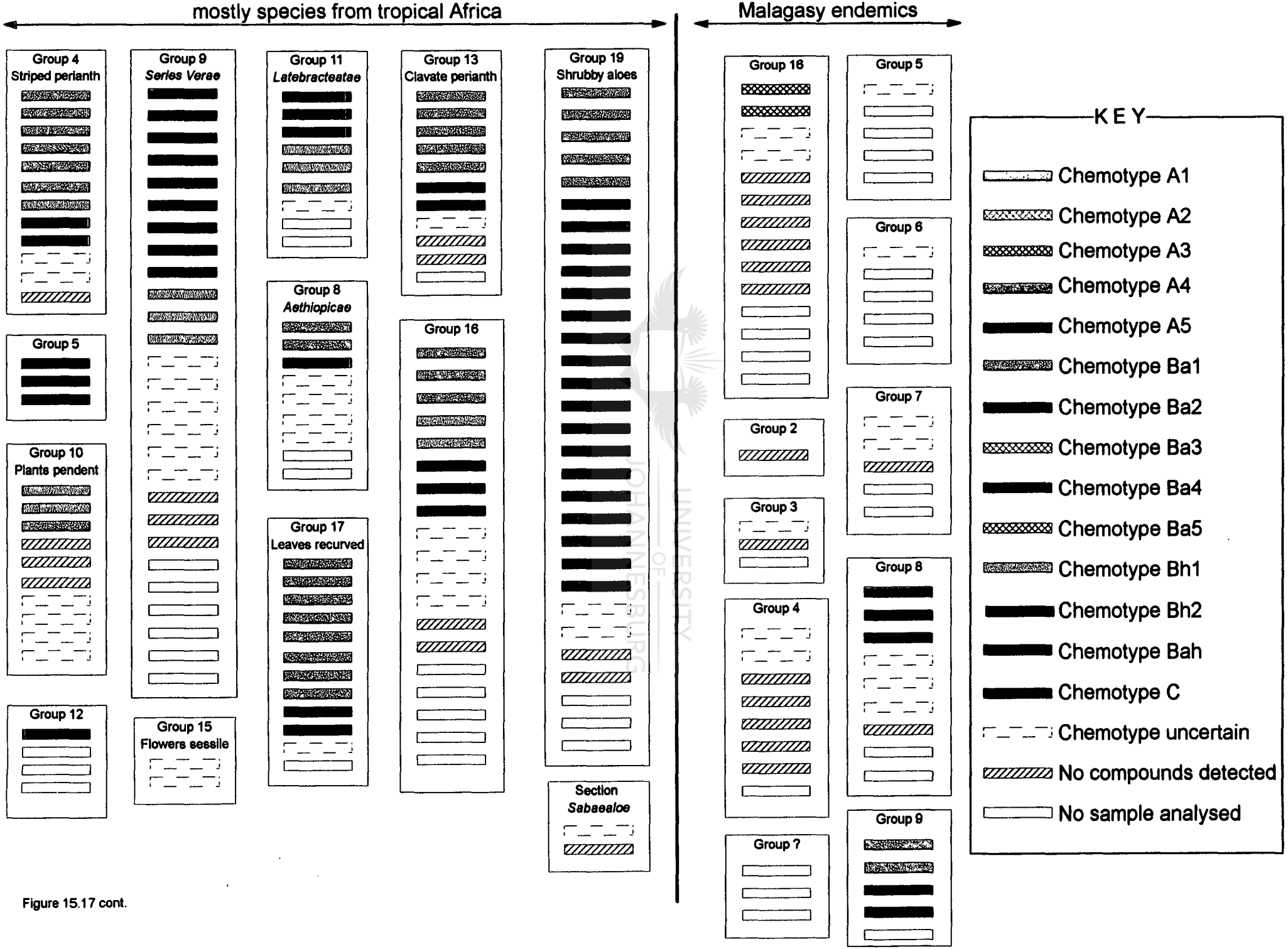


Figure 15.17 cont.

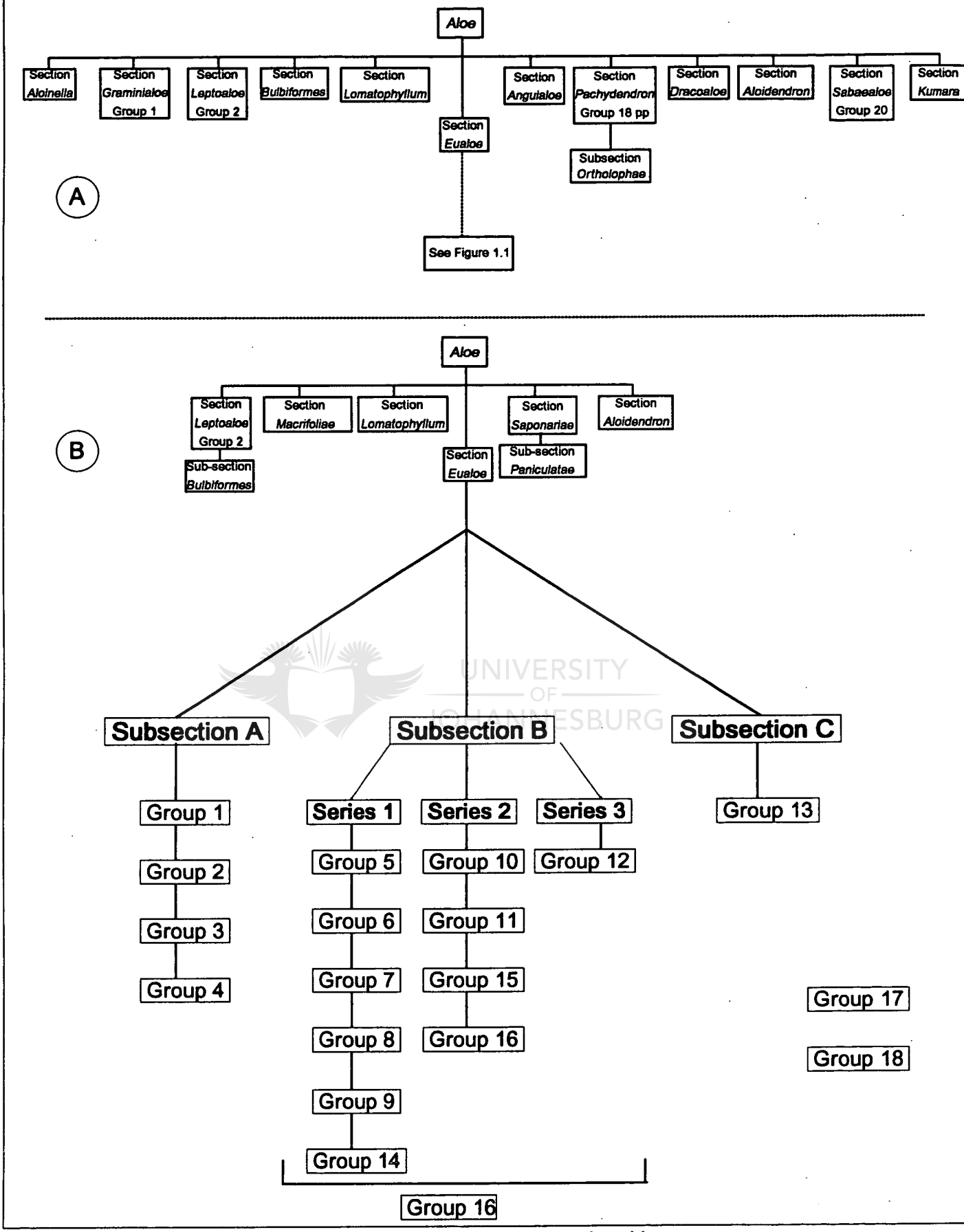


Figure 15.18: Taxonomic arrangement of taxa using chemotaxonomic evidence.
A = Reynolds (1950 & 1966), B = Viljoen & Van Wyk (in prep.).

in this study superimposed on the new taxonomic arrangement of species as suggested in Figure 15.18.

Groups defined in *Aloe* section *Eualoe*:

Subsection A (Chemotype A3, flavanone-containing species)

Group 1: *A. glauca*, *A. lineata*, *A. pretoriensis* & *A. thorncroftii*

Group 2: *A. humilis*, *A. pratensis*, *A. bakeri*, *A. bellatula*

Group 3: *A. helenae* & *A. vaotsanda*

Group 4: *A. suzannae*

Subsection B (Chemotype B, anthrone-containing species)

Series 1 (aloin-containing species)

Group 5: All species included in Table 15.5 (Chemotype Ba1, aloin, aloinoside, microdontin)

Group 6: All species included in Table 15.6 (Chemotype Ba2, aloin and aloenin)

Group 7: All species included in Table 15.7 (Chemotype Ba3, microstigmin)

Group 8: All species included in Table 15.8 (Chemotype Ba4, 10-hydroxyaloin derivatives)

Group 9: All species included in Table 15.9 (Chemotype Ba5, aloin and 6'-*O*-coumaroylaloesin)

Group 14.

Series 2 (homonataloin-containing species)

Group 10: All species included in Table 15.10 (Chemotype Bh1, homonataloside)

Group 11: All species included in Table 15.11 (Chemotype Bh2, aloeresin E and F)

Group 16.

Series 3 (8-*O*-methyl-7-hydroxyaloin-containing species)

Group 12: All species included in Table 15.12 (Chemotype Bah)

Subsection C

Group 13: All species included in Table 15.13 (Chemotype C, plicataloside)

As mentioned previously, chemical data is not superior to any other taxonomic characters and I have been faced with much the same problem as encountered by Reynolds and aloe

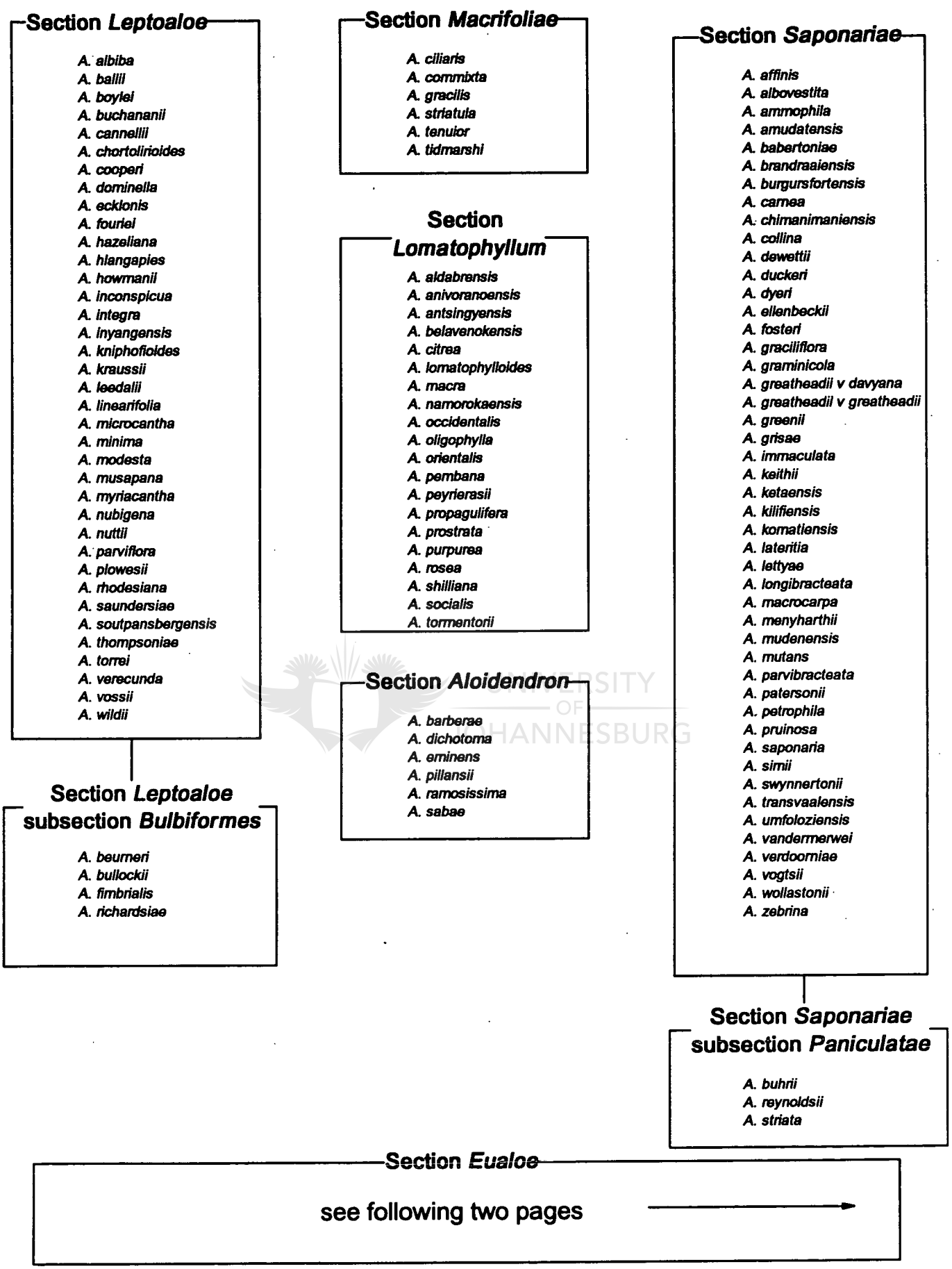


Figure 15.19. Diagrammatic representation of taxonomic groups as shown in Figure 15.18.

Section *Eualoe*

Subsection A

Group 1
A. glauca
A. lineata
A. pretoriensis
A. thorncroftii

Group 2
A. humilis
A. pratensis
A. bakeri
A. bellatula

Group 3
A. helenae
A. vaotsanda

Group 4
A. suzannae

Subsection B

Series 1

Group 5
A. aageodonta
A. africana
A. boscawenii
A. brunneostriata
A. buchlohii
A. calidophila
A. cameronii
A. canarina
A. chrysostachys
A. diolii
A. elegans
A. ferox
A. fleurentiniorum
A. flexilifolia
A. gilberti
A. guillaumetii
A. harlana
A. hemmingii
A. lensayuensis
A. mcloughlinii
A. megalacantha
A. microdonta
A. ngongensis
A. peckii
A. penduliflora
A. rabaiensis
A. rivae
A. scabrifolia
A. schelpei
A. scobinifolia
A. sinkatana
A. somaliensis
A. steudneri
A. tewoldei
A. tweediae

?

A.aculeata
A. bella
A. gerstneri
A. petricola
A. reitzii

Group 6
A. arborescens
A. brachystachys
A. brandhamii
A. bussei
A. cheranganiensis
A. classenii
A. dawei
A. dorotheae
A. gossweileri
A. kedongensis
A. leachii
A. leptosiphon
A. monticola
A. nyeriensis
A. secundiflora
A. tororoana

Group 7
A. broomii
A. chlorantha
A. framesii
A. khamiesensis
A. microstigma
A. pictifolia

Group 8
A. argenticauda
A. asperifolia
A. claviflora
A. corallina
A. dewinteri
A. esculenta
A. falcata
A. littoralis
A. namibensis
A. pachygaster

Group 9
A. alooides
A. castanea
A. dolomitica
A. spicata
A. vryheidensis
A. tauri

Group 13
Position within series 1 uncertain

A. brevifolia
A. capitata
A. debrana
A. decurva
A. divaricata
A. excelsa
A. forbesii
A. fragilis
A. hildebrandtii
A. jucunda
A. kulalensis
A. longistyla
A. macroclada
A. macrosiphon
A. massawana
A. percrassa
A. scorpioides
A. trichosantha
A. vera

Section *Eualoe*

Subsection B

Series 2

Group 10

A. abyssicola
A. amicorum
A. bargalensis
A. breviscapa
A. citrina
A. cryptopoda
A. dhufarensis
A. erensii
A. krapohliana
A. lutescens
A. mendesii
A. molederana
A. tomentosa
A. wickensii

Group 11

A. angelica
A. arenicola
A. comptonii
A. dabenorisana
A. distans
A. erinacea
A. melanacantha
A. meyeri
A. mitriformis
A. pearsonii
A. peglerae
A. yavellana

?

A. bukobana
A. congdonii
A. conifera
A. hereroensis
A. viridiflora
A. mzimbana
A. mawii
A. munchii
A. speciosa
A. wilsonii

Group 15
Position within series 2 uncertain

A. catengiana
A. comosa
A. cremnophila
A. gariepensis
A. hardyi
A. jacksonii
A. mayottensis
A. rigens
A. rupestris
A. splendens
A. suffulta
A. suprafoliata
A. thraskii
A. volkensii

Series 3

Group 12

A. antandroi
A. christianii
A. hemmingii
A. isaloensis
A. menachensis
A. millottii
A. mutabilis
A. niebuhriana
A. officinalis
A. pubescens
A. retrospiciens
A. schelpei
A. sinana
A. sinkatana
A. turkanensis
A. vaombe
A. steudneri

Subsection C

Group 13

A. archeri
A. babatiensis
A. chabaudii
A. deserti
A. elgonica
A. fibrosa
A. francombei
A. labworana
A. morijensis
A. multicolor
A. murina
A. otallensis
A. palmiformis
A. parvidens
A. plicatilis
A. pustuligemma
A. rugosifolia
A. schweinfurthii
A. tugenensis
A. ukambensis
A. wrefordii

Group 16
Position within section *Eualoe* uncertain

A. acutissima
A. confusa
A. descongsii
A. globuligemma
A. hildebrandtii
A. inermis
A. marlothii
A. ortholophae
A. polyphylla
A. pulcherrima
A. rubroviolacea
A. succotrina
A. vacillans
A. vanbalenii
A. veseyi

Group 17
Position within *Aloe*
uncertain - no leaf phenolics

A. adigratana
A. ambigens
A. andongensis
A. aristata
A. betsileensis
A. boiteaui
A. bowiea
A. buettneri
A. castellorum
A. collenetteae
A. compressa
A. deltoideodonta
A. dinteri
A. elata
A. enotata
A. erythrophylla
A. fievetii
A. gillettii
A. gracilicaulis
A. haemanthifolia
A. haworthioides
A. heliderana
A. ibityensis
A. imalotensis
A. inamara
A. juvenna
A. luntii
A. madecassa
A. medishiana
A. metallica
A. monotropa
A. parallelifolia
A. parvula
A. pendens
A. perryi
A. pirottae
A. pluridens
A. rauhii
A. rivierei
A. rupicola
A. ruspoliana
A. schorneri
A. sladeniana
A. trachyticola
A. variegata
A. versicolor
A. viguieri
A. vituensis
A. whitcombei
A. yemenica

Group 18
Position within *Aloe* uncertain
no leaf samples

A. acutissima
A. albiflora
A. alfredii
A. andringitrensis
A. angolensis
A. ankoberensis
A. ballyi
A. berevoana
A. bicornitum
A. bulbicaulis
A. bulbillifera
A. burgersfortensis
A. calcairophila
A. camperi
A. crassipes
A. cremersii
A. cryptoflora
A. cyrtophylla
A. decorsei
A. delphinensis
A. doei
A. eremophila
A. ericetorum
A. fulleri
A. glabrescens
A. grata
A. guerrae
A. hendricksii
A. humbertii
A. medishiana
A. itremensis
A. xkeayi
A. ketabrowniorum
A. laeta
A. lavranosii
A. leandrii
A. lindenii
A. luapulana
A. lucile-allorgeae
A. macleayi
A. megalocarpa
A. micracantha
A. milne-redheadii
A. mubendiensis
A. paedogona
A. perrieri
A. powysiorum
A. procera
A. shilliana
A. schoelleri
A. seretii
A. serriyensis
A. sheilae
A. silicicola
A. squarrosa
A. subacutissima
A. trigonantha
A. vallaris

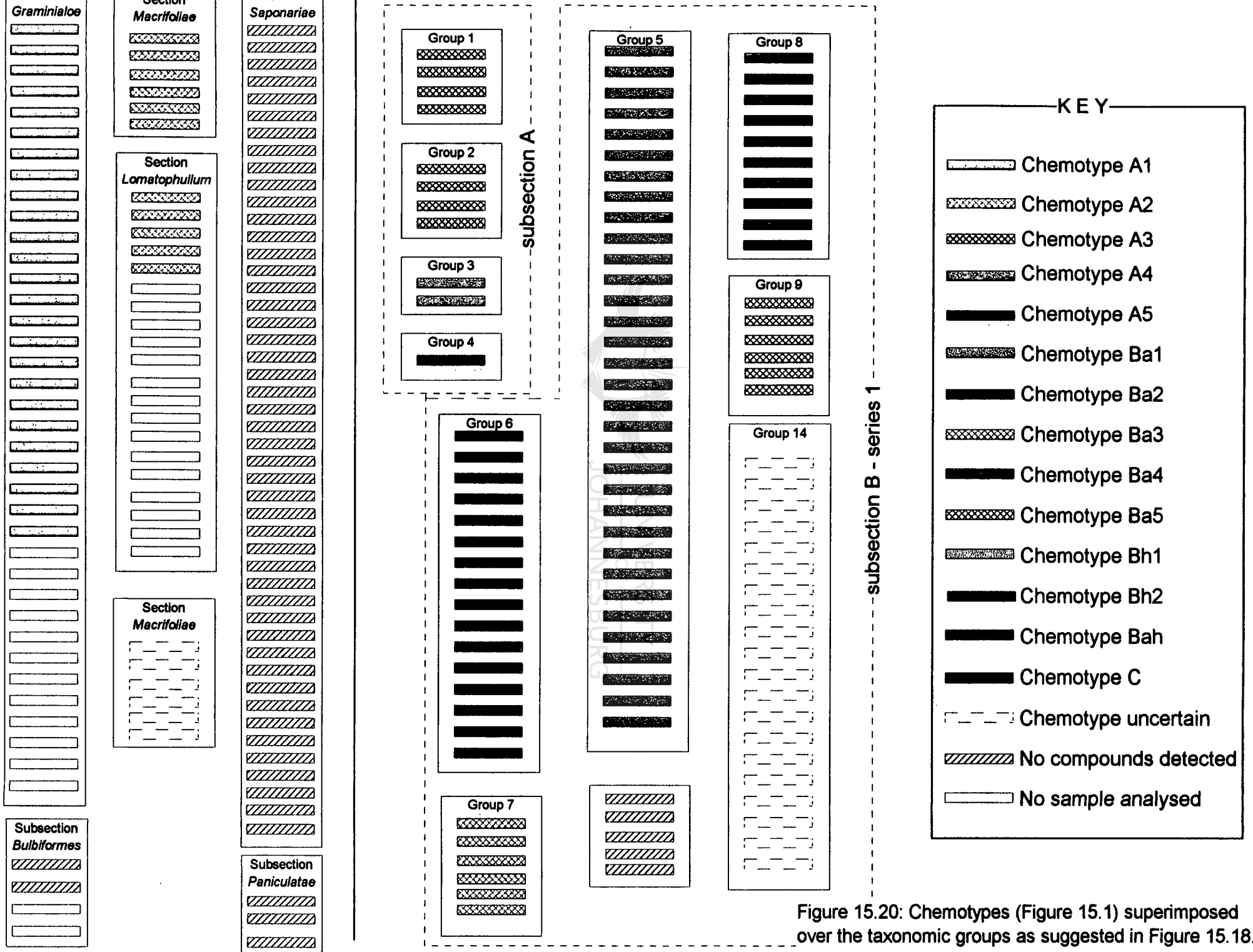


Figure 15.20: Chemotypes (Figure 15.1) superimposed over the taxonomic groups as suggested in Figure 15.18.

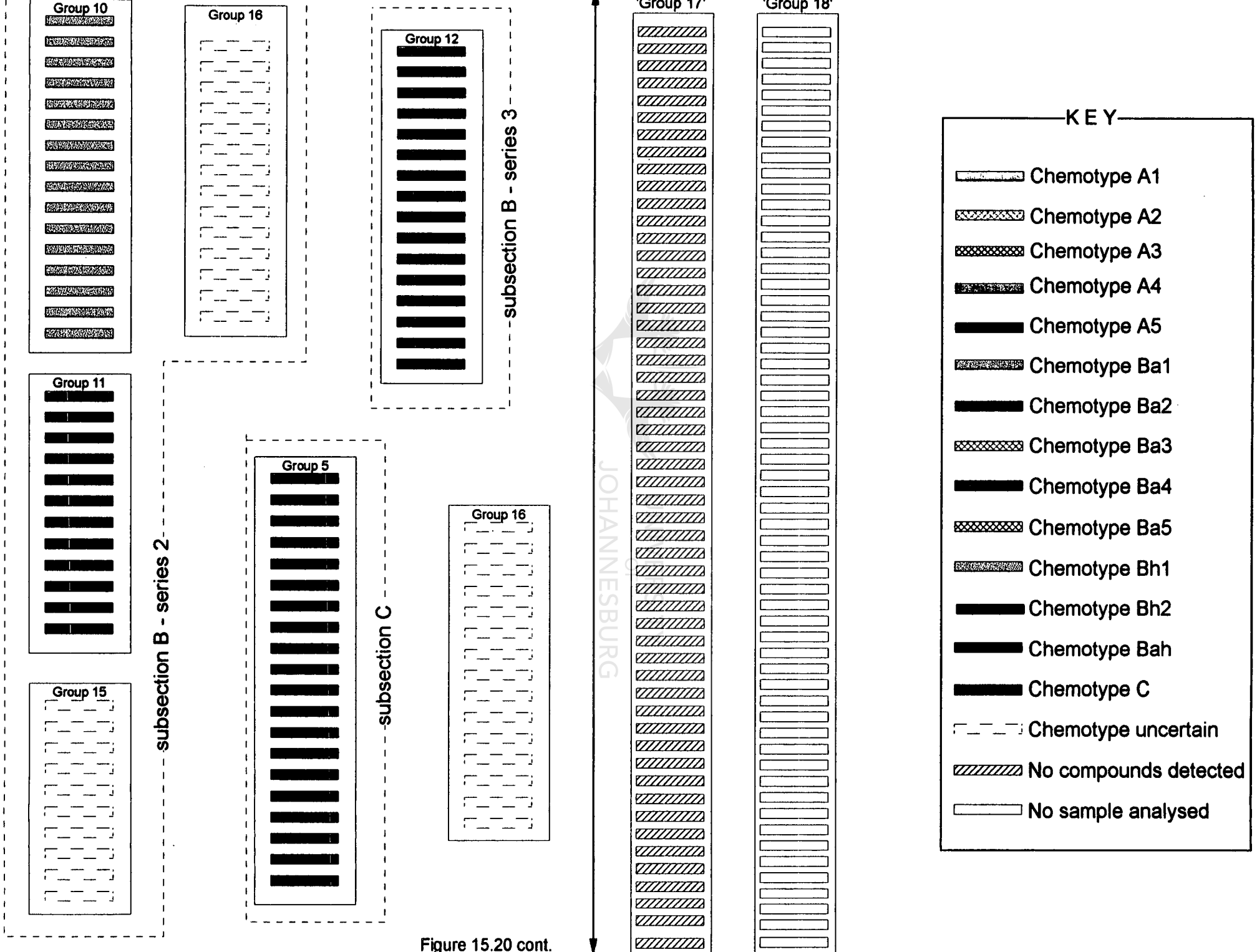


Figure 15.20 cont.

taxonomists after Reynolds. For many species the taxonomic relationships, as reflected by chemotaxonomic evidence will remain vague. Species in Group 14 all contain aloin, the defining chemical character for series 1. The option exists to align these species close to species with which the author in the species description suggested a taxonomic affinity. For many reasons this is problematic. Many of these chemically anomalous species were merely assigned to groups in Reynolds (1966). These groups have been totally dismantled in Figure 15.18 with the species originally included in a single group now occupying diverse positions in the new arrangement as shown in Figure 15.18. In many cases the closest suggested ally of a species will be placed in a different series, group or even subsection. Again, it would be inconsistent to apply the chemical data selectively and it would be 'taxonomically correct' to leave these species ungrouped until new taxonomic evidence allows for a more convincing taxonomic position of the anomalous species. Group 15 contains a number of species which contain homonataloin and cinnamoyl chromones. Although they lack the defining character of Group 11 (aloeresins E and F, which are also cinnamoyl chromones), they show a chromatographic similarity with this group of species.

Group 12 is an assemblage of species which are probably not related as Chapter 6 has illustrated that all these species are of possible hybrid origin of which the taxonomic affinities are not clear. Group 16 includes the species of which chromone and anthrone composition is very different from all the other members in section *Eualoe*. Group 17 constitutes a large number of species which have been analysed but are devoid of any leaf phenolics, the taxonomic characters used in this study. Group 18 is a large number of species of which leaf samples could not be obtained. These last two groups reflect the restrictions of the study and the relationships of these species will only become clear when additional data becomes available.

No attempt will be made here to suggest a new formal taxonomy for species included in *Aloe* section *Eualoe*. The groupings discussed here, as well as the new proposed sections in Figure 15.18 is not meant to replace the present system but rather to produce an alternative system based on chemical evidence. It is only through a complete integration of all data sets; morphology, anatomy, chemistry and hopefully soon, DNA data, that one could present a new convincing hypothesis of natural relationships in *Aloe*. The aim of this contribution is to document one of the classes of evidence (chemotaxonomic evidence) which will be instrumental in unravelling taxonomic relationships in an eventual multidisciplinary revision.

Chapter 16

Chemical variation in *Aloe*

CHAPTER 16

CHEMICAL VARIATION IN *ALOE*

For a study of this nature it is imperative to establish what the variation of the characters are under investigation. In this chapter the variation in leaf exudate composition (quantitatively and qualitatively) will be examined. Various examples of population studies will be presented to determine the variation between populations and within a single population for various taxa. In the first example the commercially important *Aloe ferox* is shown to be almost invariable in terms of leaf exudate composition. The leaf exudate of a closely related taxon *A. candelabrum* shows the same leaf exudate composition as that recorded for *A. ferox* throughout its distribution range. Chemical data, together with morphological and genetic evidence supported the notion that *A. candelabrum* is merely a geographical form of the variable and widespread *A. ferox*. The chemical invariability of *A. ferox* is contrasted with the second example, *A. marlothii*. An extensive study of the leaf exudate of this species shows high levels of variation both within and between populations. The leaf exudate composition of various other species; *A. arborescens*, *A. thraskii*, *A. rupestris* and *A. nyeriensis* also illustrates that the exudate composition is a reliable chemotaxonomic character and for most species it is invariable although it is advisable to study the leaf exudate from more than one individual in a population and also to investigate various populations.

A CHEMOTAXONOMIC AND BIOCHEMICAL EVALUATION OF *A. FEROX* AND *A. CANDELABRUM*

> *In situ* morphological analysis of plants from the entire distribution areas support the assumption that *Aloe candelabrum*, by its reproductive and vegetative characters, falls well within the taxonomic concept of *A. ferox*. The identical chemical composition of leaf exudate with regard to secondary compounds (chromone and anthrone derivatives) supports this conclusion. Gene products at 23 enzyme-coding loci, analysed by horizontal starch gel-electrophoresis, revealed no fixed allele differences between *A. candelabrum* and *A. ferox*. The differences on which the two species were previously separated can be explained as local variation within a single and widespread taxon. It is therefore proposed that *A. candelabrum* should be subsumed under *A. ferox*.

Aloe candelabrum is described by Reynolds (1950) as a striking and stately species of *Aloe* section *Pachydendron*. Its similarity with *A. ferox* has, however, been a topic of dispute and source of confusion. Reynolds (1950), Jeppe (1969) and Bornman & Hardy (1971) have invoked certain diagnostic characters in their attempts at making the two taxa mutually

Aloe marlothii, a species characterised by extreme chemical variation (Photo: Ben-Erik van Wyk).

Table 16.1. Mean values of major leaf exudate compounds in *Aloe ferox* and in 15 populations of *A. candelabrum* (expressed as percentage of total yield as estimated from HPLC results). The lowest and highest population means for all 26 populations of *A. ferox* (see Van Wyk *et al.*; 1995), and the means for individual populations of *A. candelabrum* are given. Compounds: 1 = aloesin, 2 = aloeresin C, 3 = aloeresin A, 4 = 5-hydroxyaloin B, 5 = aloin B, 6 = aloin A, 7 = aloinoside B, 8 = aloinoside A.

Population Number	Locality	Sample Number	Major compounds						
			1	2	3	4	5	6	7 & 8
A. ferox									
1 to 26	range over entire distribution	76	25.8 - 32.4	2.2 - 8.4	34.9 - 52.3	2.8 - 7.7	5.2 - 15.4	4.8 - 16.2	0.0 - 3.4
A. candelabrum									
27	Umtamvuna River valley	3	24.0	0.0	45.0	5.9	5.4	6.5	0.0
28a	Oribi Gorge	3	30.5	0.6	41.9	3.9	4.2	5.0	0.0
28b	15 km on road to Oribi Flats	3	30.1	0.0	45.0	6.3	3.7	4.7	0.0
28c	7 km on road to Oribi Flats	3	32.0	0.0	42.1	5.1	3.7	4.4	0.0
29a	11 km northwest of iZingolweni	3	29.0	0.0	44.0	4.9	3.9	4.3	0.0
29b	17 km northwest of iZingolweni	3	24.9	0.0	33.2	8.2	8.9	10.6	0.0
29c	31 km northwest of iZingolweni	3	23.2	0.0	42.2	5.1	7.0	8.5	0.0
30	11 km north of uMzimkhulu	3	20.3	1.2	31.4	5.9	12.3	14.9	0.0
31a	21 km north of Ixopo	3	26.4	1.1	35.0	6.2	6.0	7.1	0.0
31b	28 km north of Ixopo	3	25.6	0.6	29.5	4.8	4.2	5.3	0.0
31c	33 km north of Ixopo	3	18.6	1.7	28.5	4.9	7.2	8.7	0.0
32	Otto's Bluff	3	17.8	1.0	35.4	1.6	10.8	14.6	0.0
33a	Ashburton	3	21.6	0.6	37.8	4.7	6.9	8.9	0.0
33b	Inchanga	3	26.8	1.5	36.1	5.0	4.9	5.8	0.0
33c	40 km east of Pietermaritzburg	3	25.4	0.0	38.7	7.3	5.7	6.4	0.0

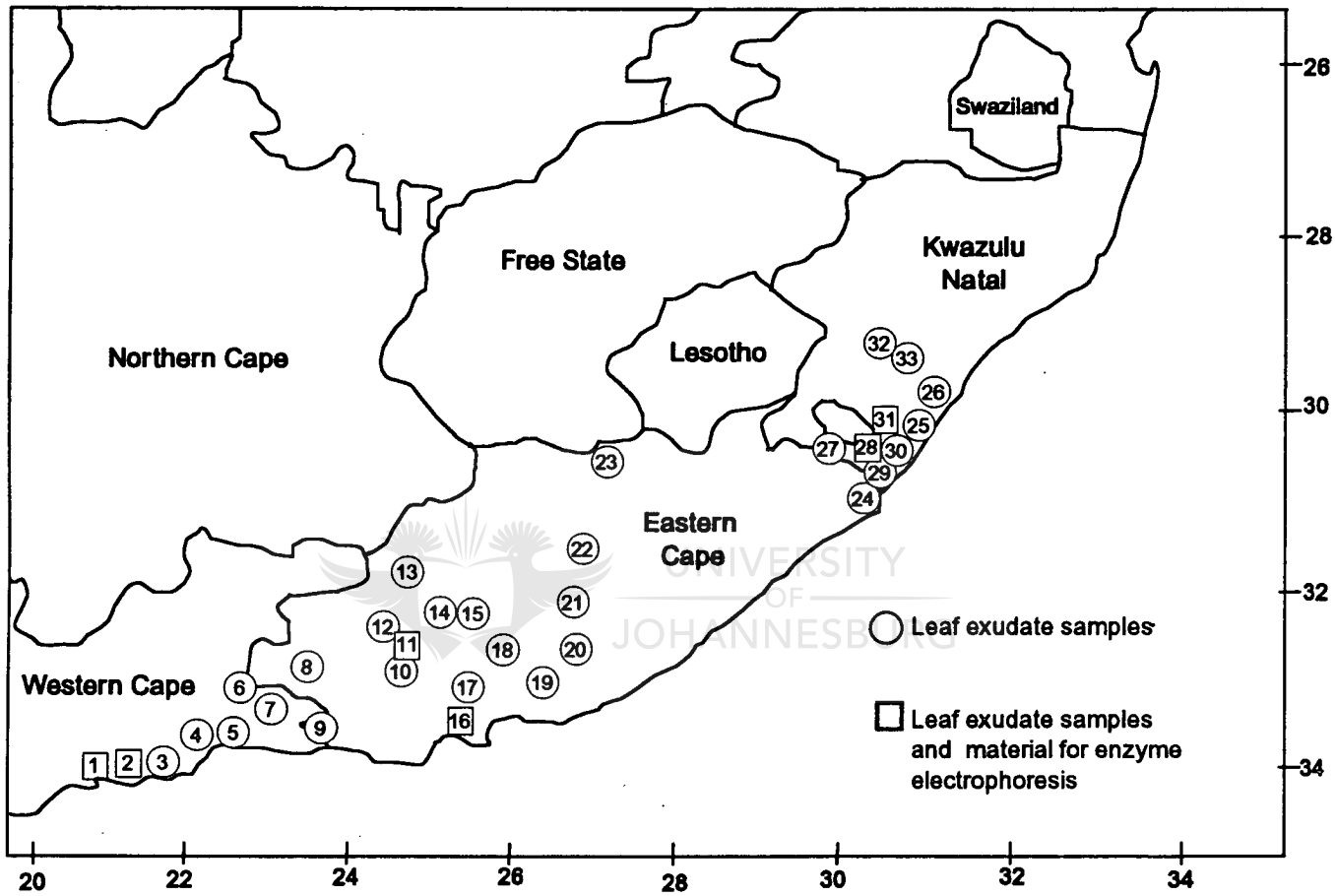


Figure 16.1: The geographical distribution of *A. ferox* and *A. candelabrum* combined, with circles denoting the sampled populations (*A. ferox*: 1 - 26; *A. candelabrum*: 27 - 33), and squares denoting the source of enzyme samples (*A. ferox*: 1, 2, 11 & 16; *A. candelabrum*: 28, 31). Locality details are given in Table 16.1 and 16.3.

exclusive. Results of a comparison of the morphology, leaf exudate chemistry and allozyme variation throughout the natural distribution areas are reported below. The aim is a critical evaluation of the currently accepted hypothesis that *A. candelabrum* and *A. ferox* are two geographically vicarious species.

Morphology

Morphological variation in populations of *A. ferox* and *A. candelabrum* was compared in their wild habitat during two successive flowering seasons (southern hemisphere winters of 1993 and 1994). Together the field trips covered almost the entire geographical distribution range of the two taxa (Figure 16.1). During these surveys particular attention was paid to the diagnostic characters used by Reynolds (1950). Reynolds (1950: 465, 470) discussed the supposed reproductive and vegetative morphological differences between *A. ferox* and *A. candelabrum* in his bench mark publication on *Aloe*, as listed in Table 16.2.

Table 16.2. Summary of the main morphological distinctions between *Aloe ferox* and *A. candelabrum* as given by Reynolds (1950: 463, 468 & 469).

	Rosette	Leaf disposition and length	Upper leaf surface	Terminal raceme	Inner perianth segment apices
A. ferox	smaller than in *A. candelabrum*	densely crowded, shorter than in *A. candelabrum*	flat near base, canaliculate upwards; smooth and spiny	as long as the lateral ones	brown to deep brown
A. candelabrum	larger than in *A. ferox*	spreading to recurved, longer than in *A. ferox*	rather densely channelled, smooth	longer than the lateral ones	clear white

Unfortunately some of these differences are weak and not fully diagnostic, e.g. leaf length. Also, our own observations are often at variance with that of Reynolds. For example, plants growing close to the Umtamvuna River at the eastern border of the Eastern Cape Province (population 27), have the apex of the inner perigone segments distinctly white, even though the plants that occur in this area fall into Reynolds' concept of *A. ferox*, in which the apex of the inner perigone segments is supposed to be brown to deep brown (Table 16.2). In the Umtamvuna region, as in several other localities, the terminal racemes are sporadically taller than the lateral ones, a character state supposedly diagnostic for *A. candelabrum*. In all characters listed in Table 16.2, *A. ferox* is an extremely variable species across its entire distributional range, which stretches over more than 1000 km (Figure 16.1). The differences between *A. ferox* and *A. candelabrum* as enumerated by Reynolds (1950) are merely of

degree, indicating that upholding both as separate species is not justified.

Leaf exudate chemistry

Leaf exudate samples were collected from three to seven individuals in each of 41 populations, resulting in a total of 169 samples (Figure 16.1, Table 16.1). As all samples were collected in July, seasonal variation is eliminated as a possible distorting factor. The fresh exudate was air-dried and investigated by thin layer chromatography (TLC) and high pressure liquid chromatography (HPLC). The geographical variation of *A. ferox* leaf exudate chemistry is detailed in Van Wyk *et al.* (1995). The composition of major chromone and anthrone derivatives was found to vary remarkably little. The main components characteristic of *A. ferox* (the fresh leaf exudate as well as the commercial dry product known as Cape Aloes) are aloesin, aloeresin A, aloeresin C, 5-hydroxyaloin A, and two isomers each of aloin and its rhamnosides (Hörhammer *et al.*, 1963 & 1965; Van Rheede van Oudtshoorn & Gerritsma, 1964; Gramatica *et al.*, 1982; Speranza *et al.*, 1985; Rauwald & Beil, 1993a). Aloesin, aloin A, aloin B and 5-hydroxyaloin A have been reported from *A. candelabrum* (McCarthy, 1969; Rauwald & Beil, 1993b). The characteristic chemical profile of *A. ferox* is repeated in *A. candelabrum* in all populations investigated (Table 16.1). Figure 16.2 and Table 16.1 allow for a visual assessment of the quantitative similarity in the composition of compounds. The range of variation in each of the major constituents is remarkably similar. The apparent difference in mean aloin concentrations does not reflect the close agreement of the eastern populations of *A. ferox* with *A. candelabrum*. Although chemical similarity is in itself not evidence for combining taxa, the important point here is that *A. ferox* and *A. candelabrum* are the only two species of *Aloe* section *Pachydendron* which are chemically identical. Furthermore, none of the other species of the section has the characteristic composition of chromone and anthrone derivatives as shown in Figure 16.2.

Allozymes

This part of the study was done in collaboration with Prof F.H van der Bank, Dept. of Zoology, and Mrs M. van der Bank, Dept. of Botany, both at the Rand Afrikaans University.

For electrophoretical analysis, leaf samples from six distant populations were collected (Table 16.3; Figure 16.1) . The populations were chosen because they are geographically isolated from each other so that there is no possibility of hybridisation or introgression and also because they represent the full range of morphological and chemical variation within the species. *Aloe candelabrum* populations from Ixopo (population 31) and the Umtamvuna Valley (population 28) were selected since they display the highest levels of terrain and morphological

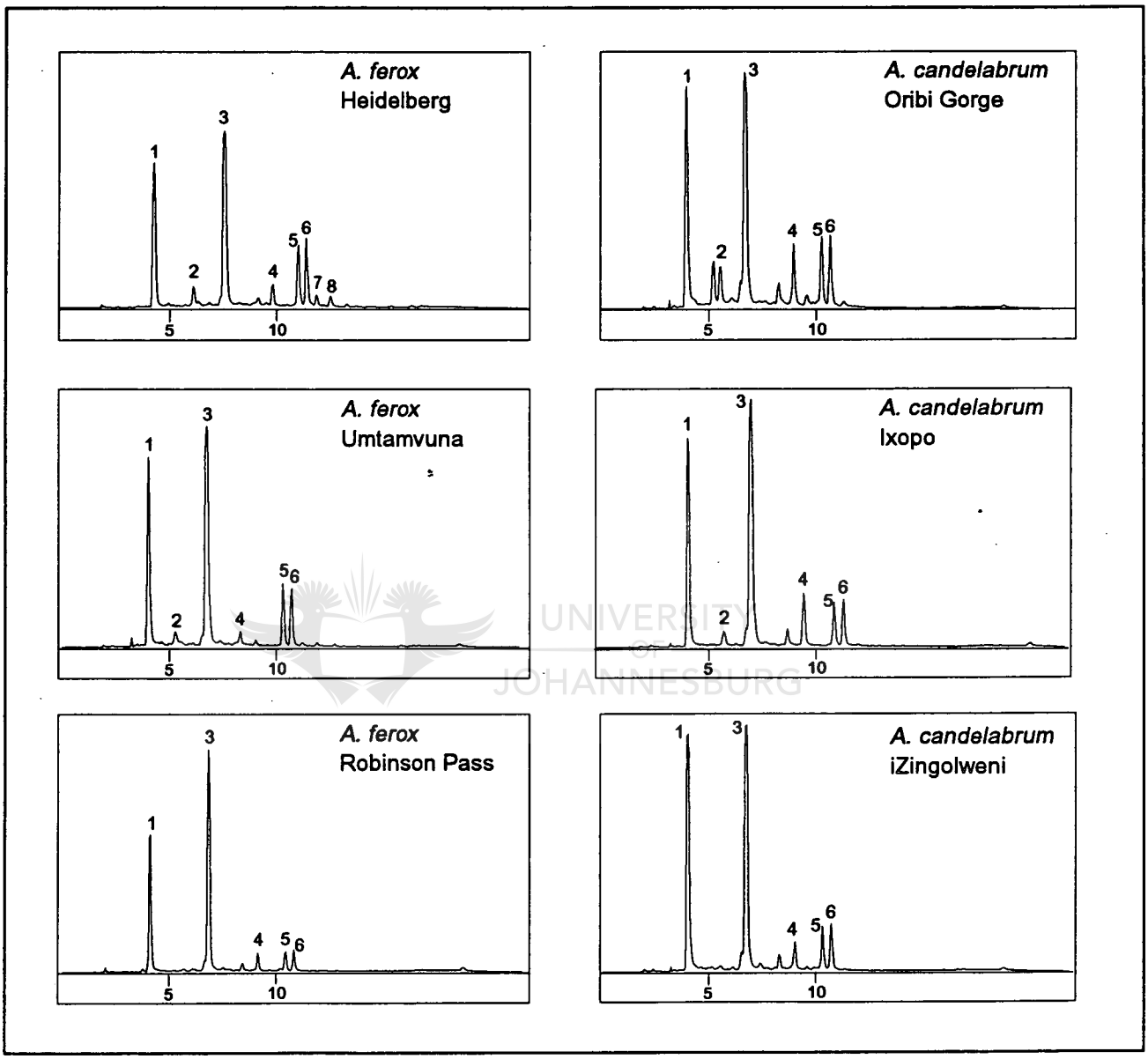


Figure 16.2: HPLC chromatograms of *Aloe ferox* (left) and *A. candelabrum* (right). Peak numbers correspond to compound names in Table 16.1.

diversity. This area represents an assemblage of reproductive and vegetative characters suggested to be diagnostic for both *A. candelabrum* (i.e. white-lipped petals) and *A. ferox* (i.e. erect leaves).

Table 16.3. Localities and sample size of *Aloe* populations and species used for enzyme electrophoresis.

Species	Locality	n	Population
A. candelabrum:	Ixopo	25	31
	Oribi Flats	25	28
A. ferox:	Stormvleikloof	55	1
	Riversdale	25	2
	Jansenville	25	11
	Perseverance	25	16

The approximate distances between these populations, and the *A. ferox* populations are: Stormvleikloof to Riversdale *ca.* 107 km, Riversdale to Perseverance *ca.* 388 km, Perseverance to Jansenville *ca.* 142 km, Jansenville to Oribi Flats *ca.* 550 km, and Oribi Flats to Ixopo *ca.* 60 km. Collection, tissue preparation, extraction buffers, electrophoresis, staining of gels, interpretation of results, locus nomenclature and statistical analysis follow Van der Bank & al. (1995b). Gel and electrode buffers (Table 16.4) are described by Kephart (1990). Wright's (1978) fixation index of individuals relative to the total population, F_{IS}, for the total population and its subpopulations (F_{IT}) and F_{ST} (for the amount of differentiation among subpopulations relative to the limiting amount under complete fixation) were also calculated. Twenty-three protein coding loci provided interpretable results in all *Aloe* populations analysed, and this data could be used for comparative studies and to calculate the extent of differentiation between populations. Fifteen of the loci (65.2%) displayed monomorphic gel banding patterns (Table 16.4) in all populations, and allozyme variation occurred at eight loci (Table 16.5). Fixed allele differences were not found in any of the populations studied, and the *A. ferox* populations (1, 2, 11 and 16) displayed the dominant alleles found in the *A. candelabrum* populations. Average heterozygosity (*H*) values, mean number of alleles per locus (*A*) and percentage of loci polymorphic (*P*) are also listed in Table 16.5. The *H* values were zero in *A. ferox*, 0.12 in population 28 and as high as 0.148 (31) in *A. candelabrum*.

Other genetic variation parameters (*P* and *A*) showed a similar trend as for *H*, with an increase in variation from the south-western to north-eastern regions of the country (Table 16.5).

Table 16.4: Allozyme analysis performed on 6 populations (see Table 16.3) of *Aloe ferox* and *A. candelabrum*. Locus abbreviations, enzyme commission numbers (E.C. No.) and buffer systems used are listed after each enzyme. *: Monomorphic loci; **AA**: Tris-EDTA-Borate; **HC**: Histidine-Citrate; **MF**: Tris-EDTA-Borate; **PO**: Tris-Citrate

Enzyme (Loci)	E.C. No.	Buffer	pH
Aspartate aminotransferase (AAT-1,-2)	2.7.3.2	PO	8.7
Cytosol aminopeptidase (CAP)	3.4.11.1	AA	8.6
Dihydrolipoamide dehydrogenase *(DDH-1,-2)	1.8.1.4	HC	5.7
Esterase (EST-1,-2)	3.1.1.-	HC	5.7
Glucose-6-phosphate isomerase *(GPI-1,-2)	3.5.1.9	MF	8.6
Isocitrate dehydrogenase *(IDH-1,-2,-3)	1.1.1.42	HC	6.5
Malate dehydrogenase *(MDH-1,-2,-3)	1.1.1.37	HC	5.7
Menadione reductase *(MNR-1,-2)	1.6.99.-	AA	8.6
Phosphoglucomutase (PGM)	5.4.2.2	MF	8.6
		HC	5.7
6-Phosphogluconate dehydrogenase (PGD)	1.1.1.44	HC	6.5
Peroxidase *(PER-1,-2)	1.11.1.7	AA	8.6
Shikimate dehydrogenase (SKDH)	1.1.1.25	HC	6.5
Superoxide dismutase *(SOD)	1.15.1.1	MF	8.6

Deviations of allele frequencies from expected Hardy-Weinberg proportions occurred at none (1, 2, 11 and 16), four (28) and five (31) of the loci studied (Table 16.5). Since it was not observed at all of the loci, non-random mating, gene flow and genetic drift were probably not the factors to influence it, since these processes should affect all loci equally (Soltis & Soltis, 1988). Selection could probably have contributed to the above result. Nevertheless, it is evident that the western (1, 2, 11 and 16) populations of *A. ferox* are depauperate of genetic variation (Table 16.5) compared to that of the *A. candelabrum* populations (28 and 31). The latter population (31) has the highest amount of variation (*H*=14.8%), followed by population

28 (*H*=12%), and the *A. ferox* populations (*H*=0%). This, together with the latter populations (1, 2, 11 and 16) displaying only the dominant alleles (Table 16.5), indicate that a south-western invasion route was followed.

Table 16.5: Results of allozyme analysis performed on 6 populations (see Table 16.3) of *A. candelabrum* (28, 31) and *A. ferox* (1, 2, 11 & 16). Allele frequencies for polymorphic loci, fixation indices, average heterozygosity (*H*), mean number of alleles per locus (*A*), standard errors thereof, and percentage of loci polymorphic (*P*). * = Significant (P<0.05) deviations of allele frequencies from expected Hardy-Weinberg proportions.

		Population			Wright's (1978) *F*-statistics		
Locus	Allele	3	28	1,2,11 &16	F_{IS}	F_{IT}	F_{ST}
AAT-1	A	0.075*	0.063*	-	0.631	0.664	0.089
	B	0.825	0.708	1.000			
	C	0.100	0.229	-			
AAT-2	A	0.094	0.214	-	-0.028	0.058	0.083
	B	0.906	0.786	1.000			
CAP	A	0.262	0.083	-	0.250	0.338	0.117
	B	0.738	0.917	1.000			
EST-1	A	0.412	0.423	-	0.121	0.290	0.193
	B	0.588	0.577	1.000			
EST-2	A	0.568*	0.636*	1.000	0.571	0.650	0.184
	B	0.432	0.364	-			
PGM	A	0.182*	0.109	-	0.372	0.412	0.064
	B	0.818	0.891	1.000			
PGD	A	0.375		-	0.758	0.856	0.407
	B	0.375	0.250*	1.000			
	C	0.250	0.750	-			
SKDH	A	0.348*	0.114	-	0.798	0.830	0.116
	B	0.652	0.886	1.000			
H (SE)		0.148 ± 0.048	0.120 ± 0.039	0.00 ± 0.000			
A (SE)		1.43 ± 0.14	1.39 ± 0.12	1.00 ± 0.00			
P		34.78	34.78	0.00			

Wright's (1978) fixation index measures differentiation between populations. The mean F_{ST} value (0.203) for polymorphic loci (Table 16.5) in the aloes studied is an indication of little genetic differentiation between the populations resulting from genetic drift. The extent of allelic fixation of individuals relative to its subpopulations (F_{IS}=0.465) also reflects the above phenomenon. Values of F_{IS} are close to zero in most natural populations where random mating within subpopulations occur (Nei, 1986). The F_{IT} value of 0.574 (which quantify inbreeding due to population subdivision), is not indicative of effective barriers to gene flow between the populations studied. This is in agreement with geographical data (no allopatric species boundaries exists between the taxa studied).

Genetic distance (Nei 1978) values ranged from 0.01 between the conspecific *A. candelabrum* populations (28 and 31) to 0.04 between the congeneric species (*A. candelabrum* and *A. ferox*) studied. Nei's (1972) genetic distance values were 0.016 between populations 28 and 31, 0.040 between population 31 and *A. ferox*, and 0.046 between population 28 and *A. ferox*. Nei's (1972) measure was used by Thorpe (1982) to estimate genetic distance values between animal and plant taxa. Values of less than 0.3 for conspecific populations were predicted. We calculated a maximum genetic distance (Nei, 1972) between population 28 and the *A. ferox* populations of 0.046. This value is almost an order less than the lower range given by Thorpe (1982) for populations from the same species. However, Nei's (1978) genetic distance is better suited for small sample sizes. The values are similar for both of Nei's (1972, 1978) indices (indicating that the genetic differentiation between the species studied, is comparable to that predicted for conspecific populations).

No biochemical differences were found to distinguish *A. candelabrum* from *A. ferox*. The suggested conspecificity is also substantiated by distributional patterns (i.e. no barrier exist to separate these taxa from each other allopatrically) and with overlapping morphological characters. We also reported high amounts of genetic variation in populations 28 and 31 (Table 16.5). The average *H* value of 4.5% for all six populations studied is concordant with expected values for natural plant taxa (see Van der Bank *et al.*, 1995a). This contradicts the original hypothesis by Van der Bank *et al.* (1995b) to explain the low amount of genetic variation obtained in populations 1, 2, 11 and 16.

No single morphological, chemical or biochemical character, or a combination of characters could be found to support the division of *A. ferox* into more than one species: 1, The morphological distinction breaks down; 2, The leaf exudate chemistry is identical and

exceptionally uniform throughout the geographical distribution range; 3, There are no fixed allele differences between the two entities. In view of this lack of diagnostic characters, we are convinced that *A. candelabrum* is conspecific with *A. ferox*, the name that takes precedence. It is therefore proposed that *A. candelabrum* be included in the synonymy of *A. ferox*, as follows (for a complete list of synonyms, see Reynolds, 1950: 460-462):

Aloe ferox Mill., Gard. Dist., ed 8: *Aloe* No 22. 1768.

= *Aloe candelabrum* A. Berger, Notizbl. Königl. Bot. Gart. Mus. Berlin 4: 246-247. 1906.

The population study of *A. ferox* as detailed above is the most extensive example of research at the population level undertaken during this study. In following examples the research was restricted to the chemical variation within and between populations as manifested in the leaf exudate composition. Seasonal variation and chemical fluctuations within a plant have been shown by Beaumont *et al.* (1984) and Chauser-Volfson & Gutterman (1997) to be of minor importance and was not repeated in this study.

IS *ALOE MARLOTHII* DISTINCT FROM *A. SPECTABILIS*?

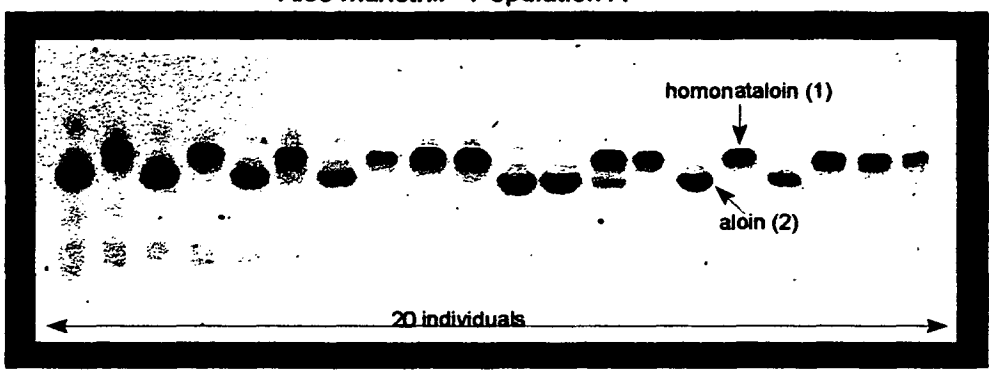
Aloe marlothii is one of the most abundant and widespread *Aloe* species in southern Africa. The common name *Bergaalwyn* indicates habitat preferences in the mountainous areas of north and eastern Transvaal and extends into KwaZulu-Natal, the northern Province and Mpumalanga. Leaf exudate of fifty individuals in each of 54 populations (Table 16.6) (amounting to 2 700 samples) were analysed on TLC for their chromone and anthrone derivatives.

Table 16.6. Locality details for the populations of *A. marlothii* (M) and *A. spectabilis* (S) studied. Fifty individuals were analysed from each of the 54 populations.

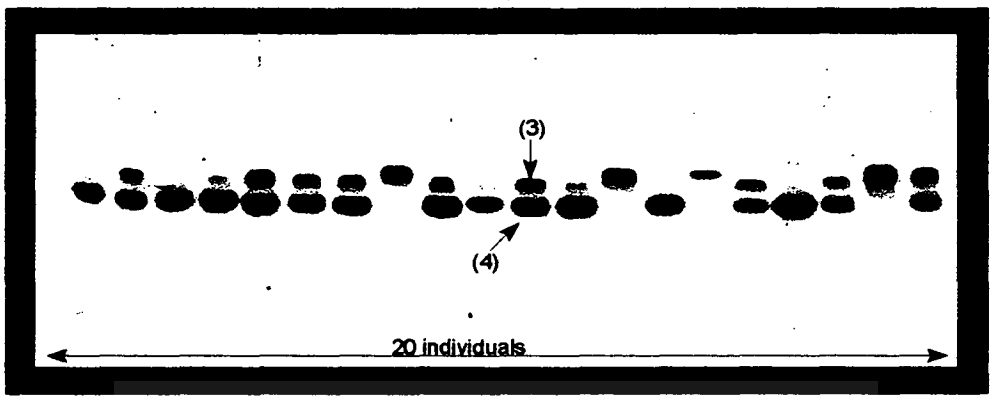
	Locality	Taxon
1a	On road from Louis Trichardt to Messina	M
1b	South of Verwoerd Tunnels - on road to Messina	M
1c	78 km N of Pietersburg to Louis Trichardt	M
2	10 km from Vivo to Louis Trichardt	M
3a	Smitsdrif, Boyne	M
3b	Moria, near Pietersburg	M
3c	16 km E of Pietersburg	M
4a	12 km N of Potgietersrus	M
4b	38 km N of Potgietersrus	M
4c	46 km N of Potgietersrus	M

4d	48 km N of Potgietersrus	M
5a	47 km N of Pietersburg (De Loskop)	M
5b	Kopermyn turn-off, 10 km S of Pietersburg	M
5c	26 km from Pietersburg on road to Chuniespoort	M
5d	Northern end of Chuniespoort	M
6	14 km S of Groblersdal	M
7a	46 km from Groblersdal on road to Elandslaagte	M
7b	58 km from Groblersdal on road to Elandslaagte	M
7c	48 km from Groblersdal on road to Stofberg	M
7d	34 km from Stofberg on road to Groblersdal	M
7e	15 km from Stofberg on road to Groblersdal	M
8a	43 km from Middelburg on road to Groblersdal	M
8b	40 km from Middelburg on road to Groblersdal	M
8c	39 km from Middelburg to Groblersdal - Diepkloof	M
9	80 km from Bronkhorstspruit on road from Groblersdal	M
10a	85 km N of Zeerust - Madique Game Reserve	M
10b	74 km N of Zeerust	M
10c	58 km N of Zeerust	M
10d	49 km N of Zeerust	M
11a	24 km N of Zeerust	M
11b	Groot Marico	M
12	Klipriviersberg	M
13	Suikerbosrand	M
14	Utrecht - Knights' Pass	M
15a	Golela	M
15b	Between Pongola en Magudu	M
16	Between Vryheid and Melmoth - Mahlabatini road	M
17	20 km S of Nongoma	M
18a	70 km N of Melmoth on road from Vryheid	M
18b	50 km N of Melmoth - 6 km S of Great Umfolozi	M
18c	Dingaanstat	M
19a	7 km on road to Blood River Monument	?
19b	2 km on road to Blood River Monument	?
20a	2 km S of Helpmekaar	S
20b	26 km S of Helpmekaar	S
21a	5 km from Dundee on road to Wasbank	S
21b	8 km from Dundee on road to Greytown	S
22a	4 km from Keate's Drift on road to Muden	S
22b	Mooi River Valley, 12 km from Muden	S
22c	14 km E of Muden on road from Greytown	S
23	Tugela Ferry	S
24a	16 km from Muden on road to Weenen	S
24b	4 km to Weenen on road from Muden	S
24c	14 km from Colenso on road from Weenen	S
25	Between Winterton and Bergville	S

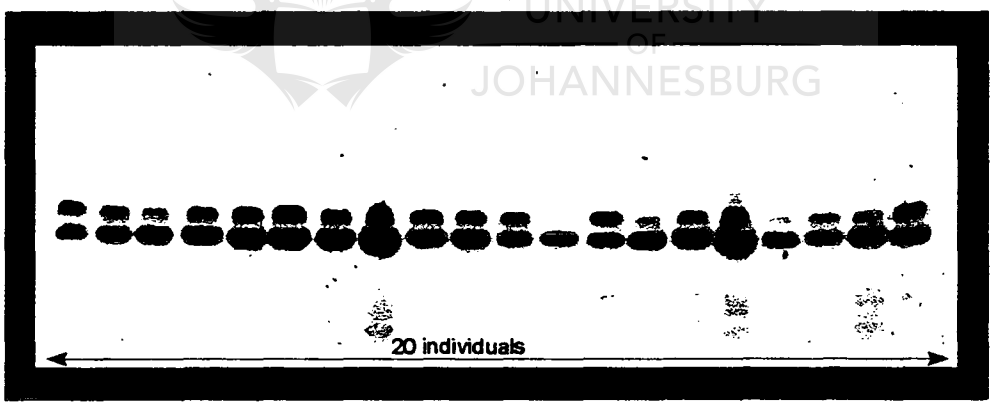
Aloe marlothii - Population A



Aloe marlothii - Population B



Aloe marlothii - Population C



Aloe spectabilis - Population A

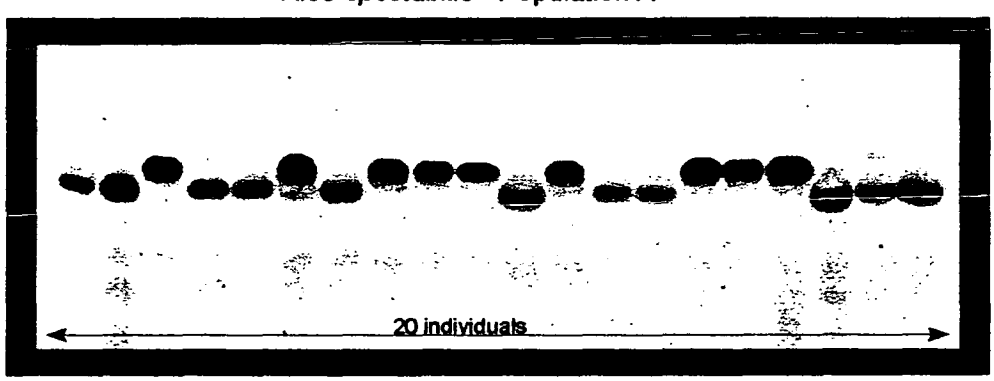
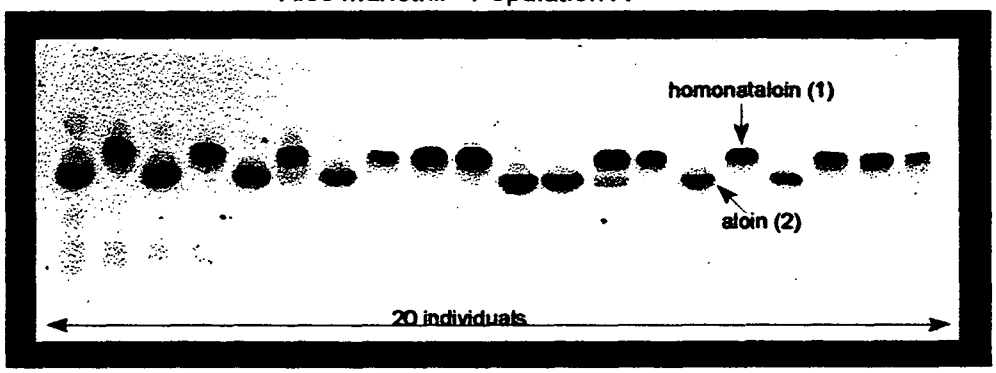
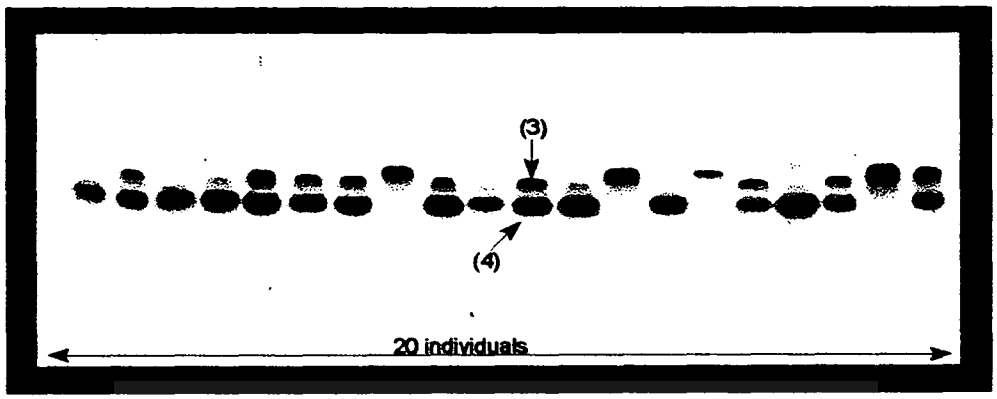


Figure 16.2: TLC results of three populations (A - C) for *A. marlothii* and one population of *A. spectabilis*.

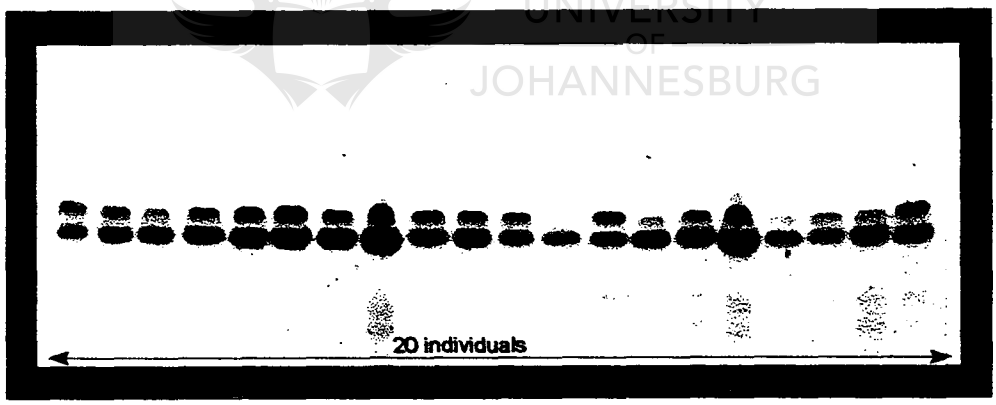
Aloe marlothii - Population A



Aloe marlothii - Population B



Aloe marlothii - Population C



Aloe spectabilis - Population A

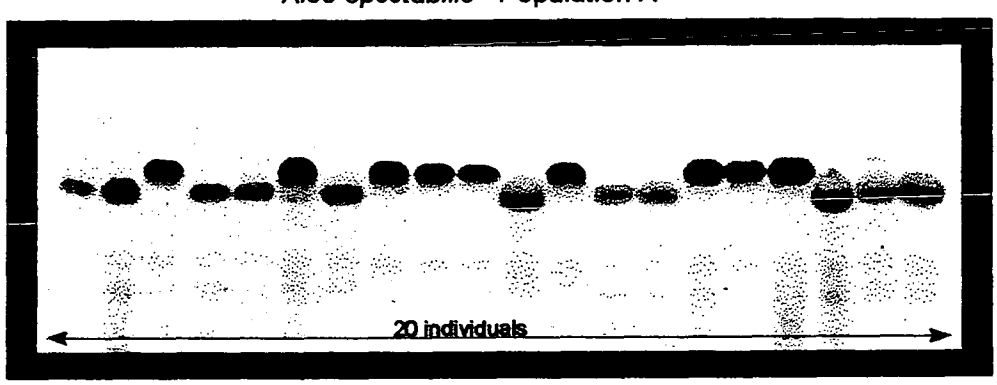


Figure 16.2: TLC results of three populations (A - C) for *A. marlothii* and one population of *A. spectabilis*.

A marlothii displays a mosaic variation in exudate composition, some populations, predominantly with homonataloin as major anthrone, while others produce aloin (or various derivatives of aloin) as the major anthrone. Figure 16.3 shows three TLC plates for *A. marlothii* from three different populations. Population A shows that 12 of the 20 individuals in this population produce homonataloin (higher R_f) while eight accumulate the aloin isomers (lower R_f) as major anthrone. The TLC plate for population B shows a pattern which could be misinterpreted as the co-occurrence of aloin and homonataloin. HPLC analysis confirmed spot 3 to be aloin while spot 4 is 5-hydroxyaloin. The third TLC plate shows a somewhat uniform anthrone pattern with most individuals containing aloin, 5-hydroxyaloin but in addition also produced a derivative of aloin (not distinguished on TLC). Figure 16.4 shows a selection of HPLC profiles for both *A. marlothii* and *A. spectabilis* and the chromatographic data is summarised in Table 16.7. The variation in leaf exudate compounds of these two taxa are erratic without any geographical correlations. This unique pattern (aloin and homonataloin individuals within a single population) is repeated in all populations of *A. spectabilis* sampled (Figures 16.3 & 16.4), indicating a chemical identity with *A. marlothii.*

Table 16.7: Absence and presence data for three populations of *A. marlothii* and one population of *A. spectabilis* (3 individuals per population). HPLC profiles are illustrated in Figure 16.4. **Compounds:** 1 = aloesin, 2 = 7-O-methylaloesin, 3 = coumaroyl chromone, 4 = aloeresin D, 5 = 5-hydroxyaloin B, 6 = aloin A & B, 7 = derivative of 5, 8 = homonataloin A & B.

Population	1	2	3	4	5	6	7	8
Vivo / plant 1	●	●	●	●		●		
Vivo / plant 2	●		●	●				●
Vivo / plant 3	●	●	●	●		●		
Groblersdal / plant 1	●	●	●	●	●	●		
Groblersdal / plant 2	●	●	●	●	●	●	●	
Groblersdal / plant 3	●	●	●	●	●	●	●	
Zeerust / plant 1	●	●	●	●	●	●	●	
Zeerust / plant 2	●	●	●	●		●		
Zeerust / plant 3	●	●	●	●		●		
Tugela Ferry / plant 1	●	●	●			●		
Tugela Ferry / plant 2	●	●				●		
Tugela Ferry / plant 3	●	●						●

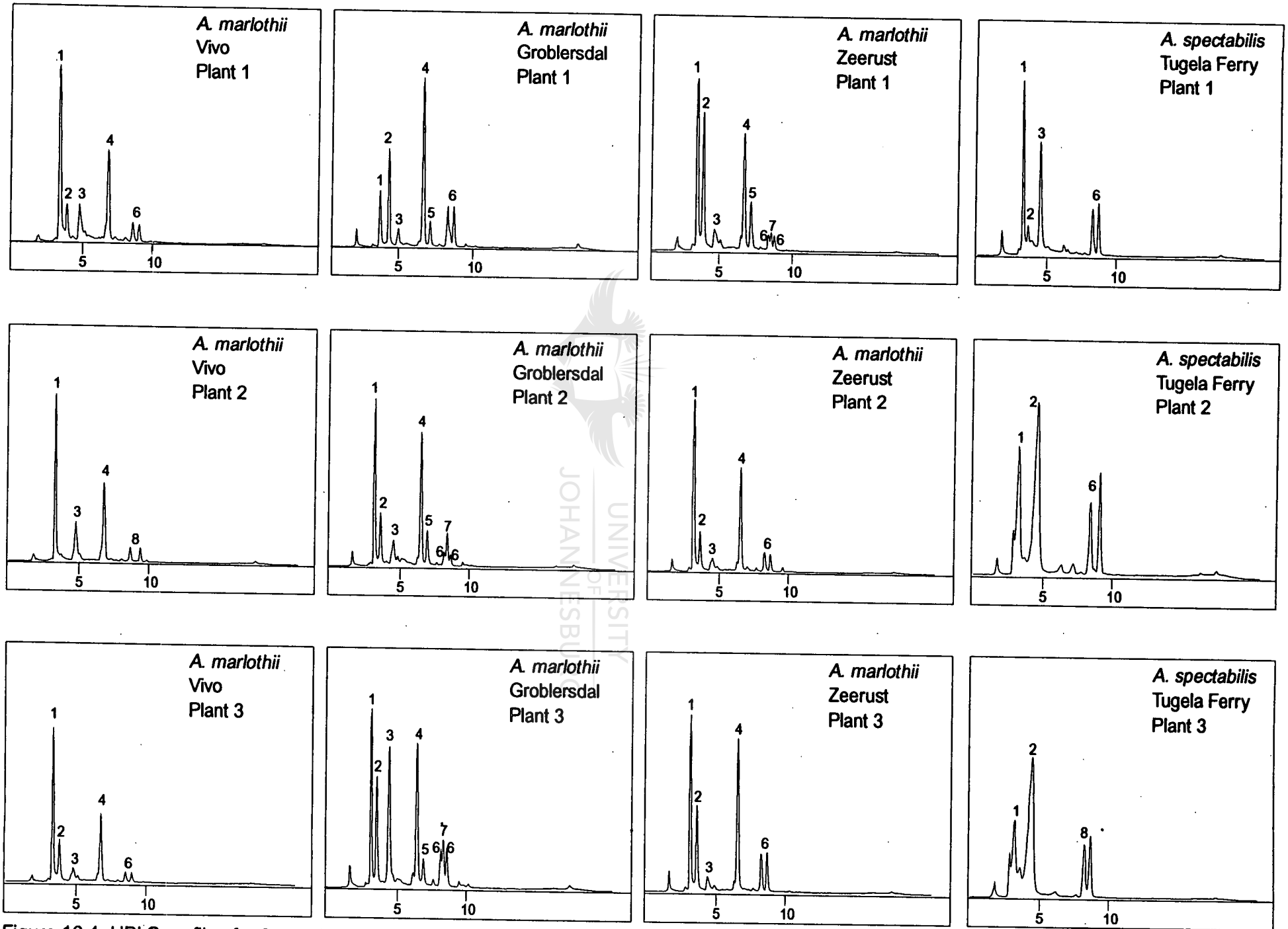


Figure 16.4: HPLC profiles for 3 populations of *A. marlothii* and 1 population (type locality) of *A. spectabilis*. Three individuals per population were analysed. Peak numbers correspond to compounds in Table 16.7.

The morphological characters used by Reynolds (1973) to distinguish *A. spectabilis* from *A. marlothii* were found to vary without any discontinuities despite the KwaZulu-Natal southern forms (Tugela catchment) having a rather distinct facies when compared to typical *A. marlothii.* As there are certain intermediate populations it would be preferable to interpret *A. spectabilis* as a geographic variant of the variable and widespread *A. marlothii.*

CHEMICAL VARIATION IN *ALOE ARBORESCENS*

Aloe arborescens is a widespread species common along the roadsides of South Africa. It has been planted by local inhabitants in and around their villages, both for beauty and 'fencing'. Numerous populations of *A. arborescens* have been collected and analysed during the course of this study (see Appendix 2). It was found that the leaf exudate was quantitatively invariable within a population. Quantitative and qualitative variation was documented between populations. A selection of HPLC profiles are shown in Figure 16.5 of which the results are tabulated below.

Table 16.8: Leaf exudate composition for 11 populations of *A. arborescens.* Due to the quantitative and qualitative invariability within a single population only one individual per population was analysed (see Storms River mouth population). **Compounds**: 1 = aloesin, 2 = aloenin, 3 = aloeresin D, 4 = aloin B, 5 = aloin A, 6 = cinnamoyl chromone

	Locality	1	2	3	4	5	6
1	Tradouws Pass	2	28	27	16	17	0
2	Swellendam	1	51	27	8	9	0
3	Gouritz River mouth	2	34	27	15	15	0
4	Stil Bay	tr	36	30	14	16	0
5.1	Storms River mouth / plant 1	2	39	27	14	15	0
5.2	Storms River mouth / plant 2	2	40	27	14	13	0
5.3	Storms River mouth / plant 3	2	41	28	12	13	0
6	Mossel Bay	1	29	34	15	16	0
7	Flagstaff	5	31	12	16	14	11
8	Malalotja	tr	35	5	15	17	20
9	Kaapsche Hoop	tr	39	4	14	15	16
10	Jozini Dam	2	32	8	17	18	20
11	Zimbabawe	3	42	0	10	11	24

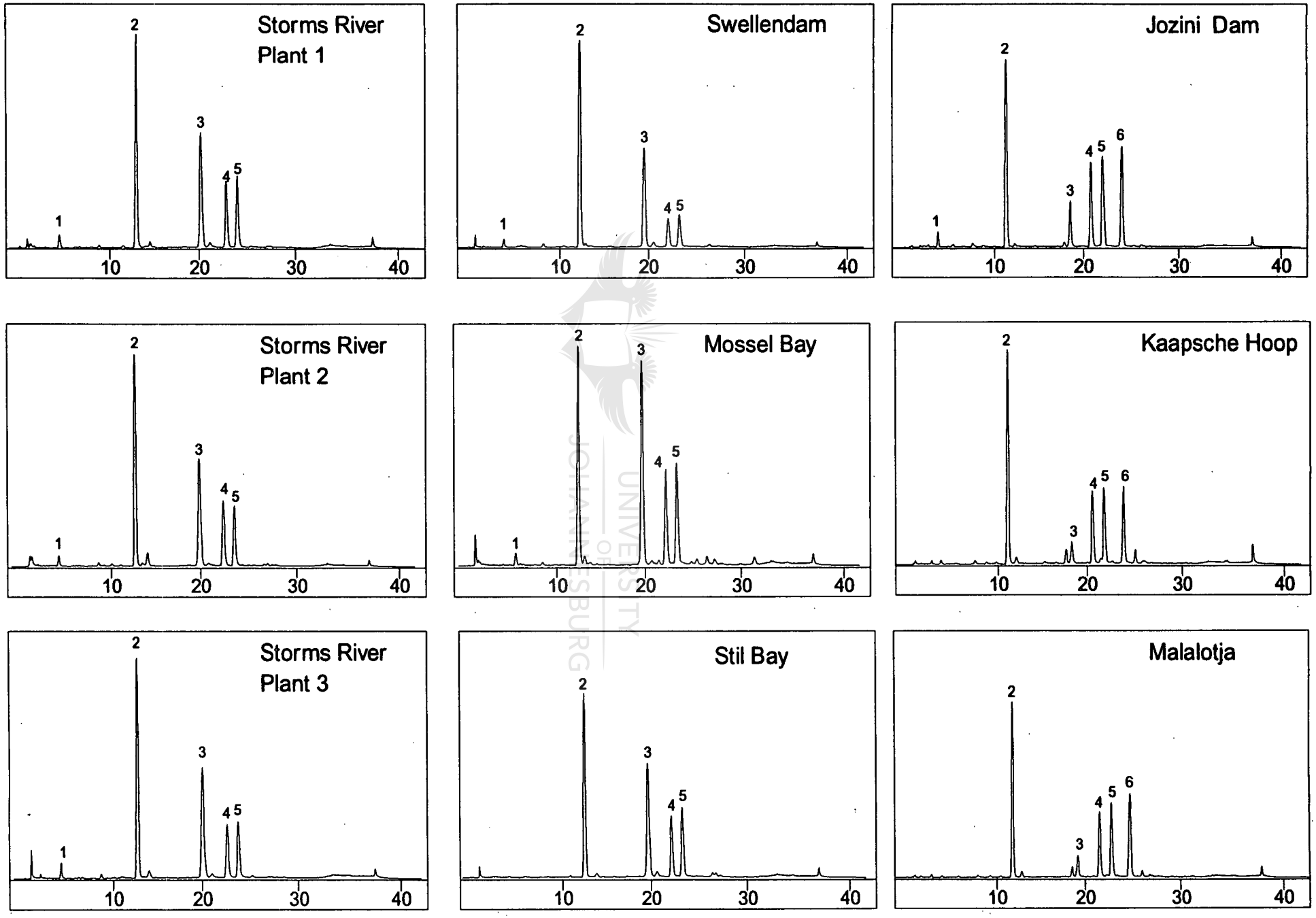


Figure 16.5: HPLC chromatograms for 7 populations of *Aloe arborescens*. Peak numbers correspond to compounds in Table 16.8.

The data in Table 16.8 and the HPLC profiles shown in Figure 16.5 indicates two chemotypes of *A. arborescens*. Chemotype 1 (populations 1 - 6) constitutes high yields of aloeresin D (compound 3) and lacks compound 6. Chemotype 2 (populations 7 - 11) shows low yields of aloeresin D but produces the cinnamoyl chromone (compound 6). It could be speculated that compound 6 is a cinnamoyl analogue of aloeresin D. These results are congruent with that of Reynolds (1991) indicating a northern and southern chemotype in *Aloe arborescens*. The populations in Table 16.8 are arranged from south to north (1 - 11) and the data clearly shows chemotype 1 to correspond to a southerly distribution while the populations in the northern part of the distribution range produce leaf exudate corresponding to chemotype 2. Population 7 seems to represent a transitional population between the two chemotypes.

POPULATION STUDIES OF *A. RUPESTRIS* AND *A. THRASKII*

A survey of the leaf exudate composition of species in *Aloe* section *Pachydendron* showed that both *A. rupestris* and *A. thraskii* have a very similar chromone pattern which is different from any other species in this section. *Aloe rupestris* is also thought to be a chemical deviant as this species did not contain any anthrones. As the chromone compliment of the two species were virtually identical, various populations of *A. thraskii* and *A. rupestris* were investigated to establish if some individuals of *A. thraskii* would show variation in the anthrone compliment and to determine if *A. rupestris* is always devoid of anthrones. Three individuals in three populations were investigated for both *A. thraskii* and *A. rupestris*. The HPLC profiles for *A. rupestris* are shown in Figure 16.6 and those for *A. thraskii* are illustrated in Figure 16.7. The HPLC data for both species are tabulated in Table 16.9.

Table 16.9: Summary of HPLC data recorded for *A. thraskii* and *A. rupestris* (see Figures 16.6 and 16.7). **Compounds**: 1 = aloesin, 2 = 7-*O*-methylaloesin, 3 = unidentified chromone 1, unidentified chromone 2, 5 = unidentified chromone 3, 6 = homonataloin A & B.

Locality	1	2	3	4	5	6
***Aloe rupestris*:**						
Coela / plant 1	●	●	●	●		
Coela / plant 2		●	●	●	●	
Coela / plant 3		●	●	●	●	
Dingaanstat / plant 1	●	●		●	●	
Dingaanstat / plant 2		●	●	●	●	
Dingaanstat / plant 3	●	●	●	●	●	
Muden / plant 1		●	●	●	●	

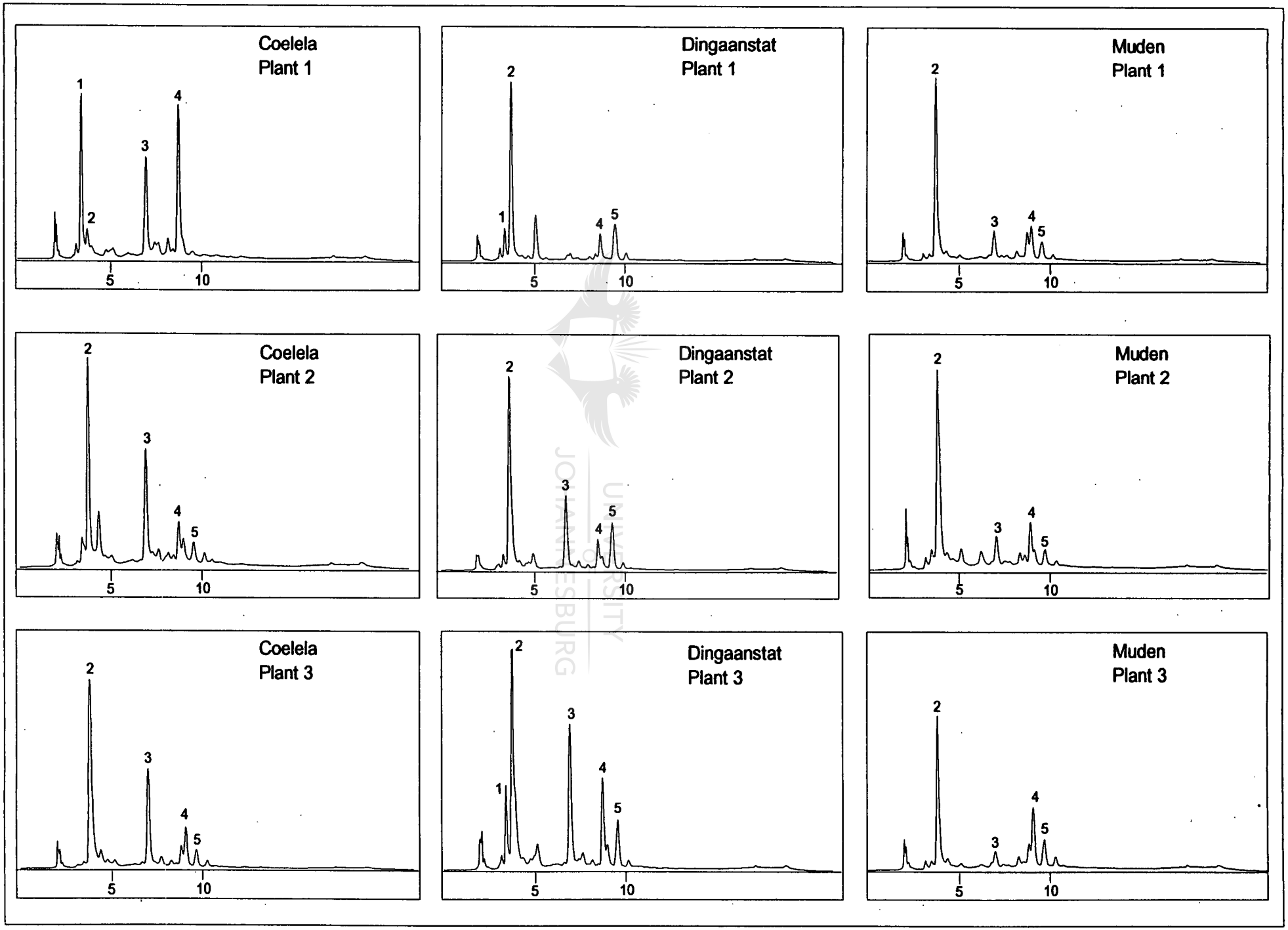


Figure 16.6 HPLC chromatograms of *Aloe rupestris*. Peak numbers correspond to compounds in Table 16.9.

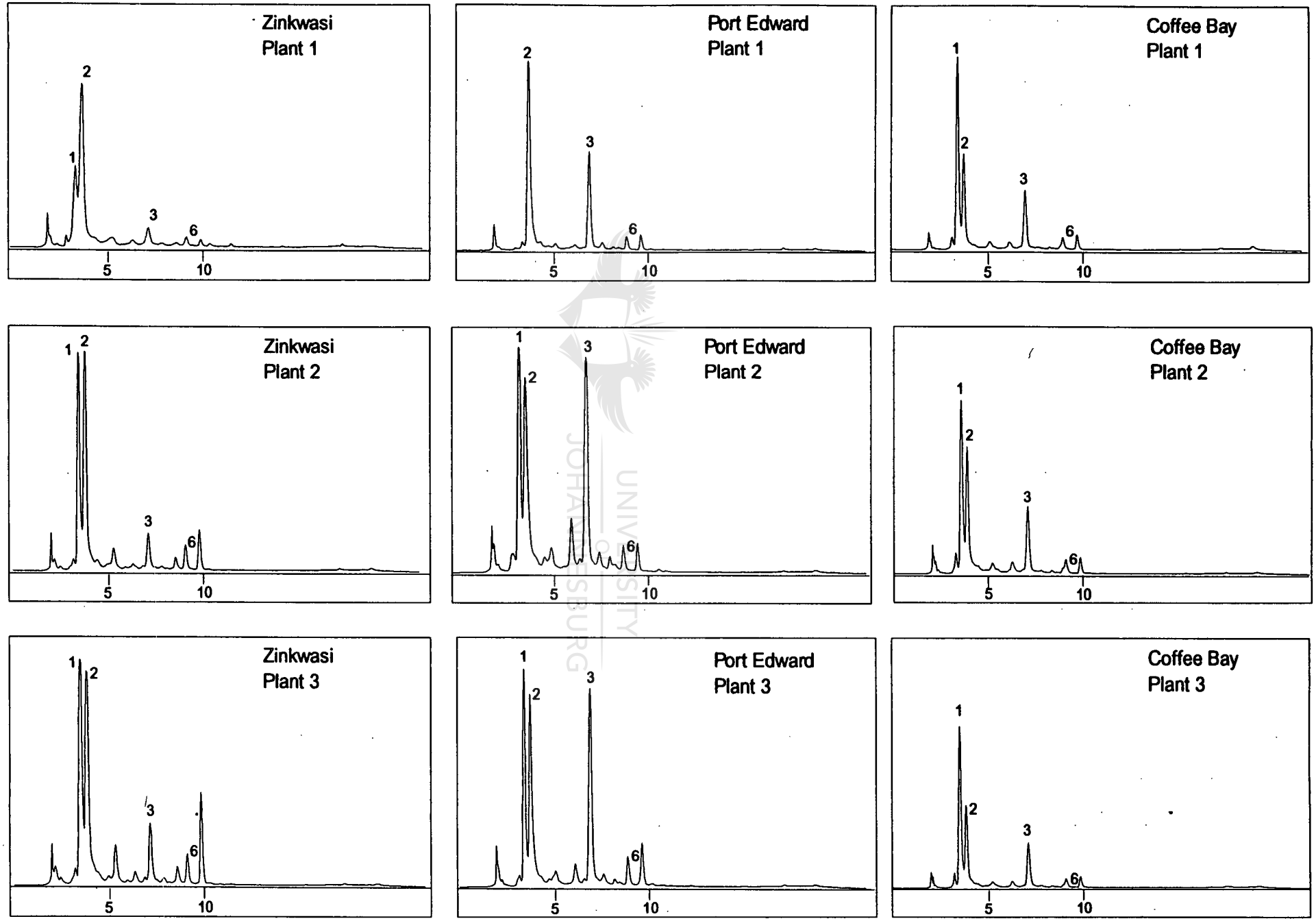


Figure 16.7: HPLC chromatograms for *Aloe thraskii*. Peak numbers correspond to compounds in Table 16.9.

Locality	1	2	3	4	5	6
Muden / plant 2		●	●	●	●	
Muden / plant 3		●	●	●	●	
***Aloe thraskii*:**						
Zinkwasi / plant 1	●	●	●			●
Zinkwasi / plant 2	●	●	●			●
Zinkwasi / plant 3	●	●	●			●
Port Edward / plant 1		●	●			●
Port Edward / plant 2	●	●	●			●
Port Edward / plant 3	●	●	●			●
Coffee Bay / plant 1	●	●	●			●
Coffee Bay / plant 2	●	●	●			●
Coffee Bay / plant 3	●	●	●			●

Table 16.9 and Figure 16.6 shows that although minor variation is recorded for the chromone complement of the leaf exudate, *A. rupestris* is invariably devoid of the anthrone homonataloin. *Aloe thraskii*, like *A. rupestris* always shows compounds 1 to 3 present, but in addition always has homonataloin present (although in very low concentrations).

CHEMICAL INVARIABILITY OF *A. NYERIENSIS*

The final example of study at the population level is that of *A. nyeriensis*. Good fortune allowed me to visit Kenya during which leaf exudate was collected from six individuals of two populations; 1. Gil-Gil and 2. Rumuruti. The results contained in Table 16.10 and Figure 16.8 show no qualitative variation. A measure of quantitative variation is visible in Figure 16.8. and is congruent with the results reported for this same species by Beaumont *et al.* (1984).

Table 16.10: Summary of qualitative HPLC data recorded for *A. nyeriensis* (see Figures 16.8).
Compounds: 1 = aloeresin A, 2 = aloeresin D, 3 = homonataloin B, homonataloin A

Locality	1	2	3	4
Gil-Gil / plant 1	●	●	●	●
Gil-Gil / plant 2	●	●	●	●
Gil-Gil / plant 3	●	●	●	●
Gil-Gil / plant 4	●	●	●	●
Rumuruti / plant 1	●	●	●	●
Rumuruti / plant 2	●	●	●	●
Rumuruti / plant 3	●	●	●	●
Rumuruti / plant 4	●	●	●	●

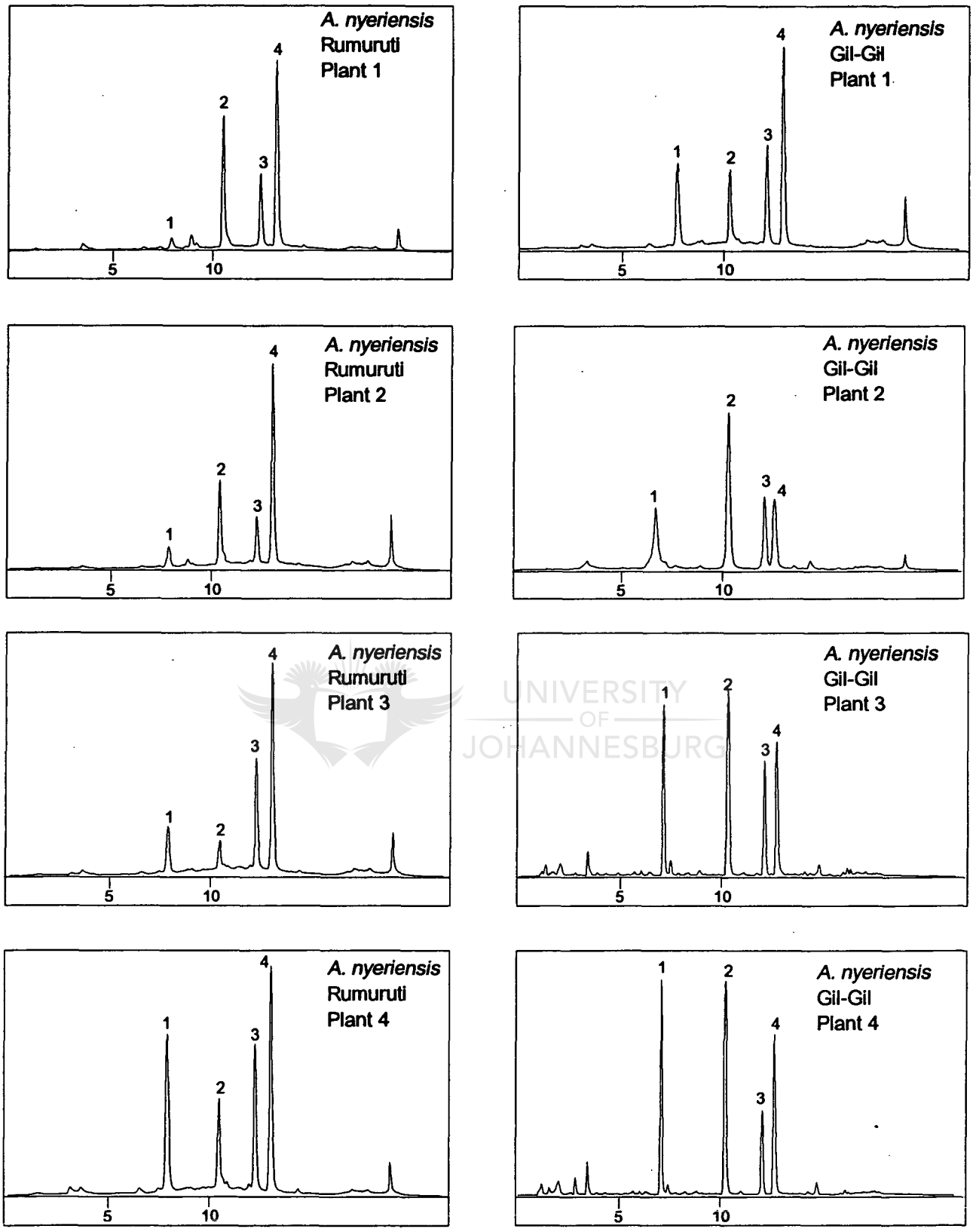


Figure 16.8: HPLC chromatograms of four individuals in two separate populations of *Aloe nyeriensis*. Peak numbers correspond to compound names in Table 16.10.

The examples depicted above emphasise the importance of variation studies and further confirms the consistency and invariability (both quantitatively and qualitatively) of aloe leaf exudate in most species. The subtle variations which have been detected are compensated for by including more than one population or individual in the study group (Table 3:3). The first example in this Chapter (*A. ferox* / *A. candelabrum*) illustrated that leaf exudate composition in concordance with additional data is a powerful taxonomic tool. Although the mosaic variation recorded for *A. marlothii* and *A. spectabilis* contrasts the invariability of *A. ferox*, this variation has assisted in questioning the species status of *A. marlothii* and *A. spectabilis*. These two species are viewed as chemically peculiar as no other species shows the immense variation recorded for these two taxa. *Aloe arborescens* displays variation in the chromone composition but always contains aloin and aloenin. The latter compound is shown to be of chemotaxonomic value in Chapter 7. The general pattern emerging from this study is that the chromones display high levels of variation while the anthrones are more 'stable'. This is encouraging as the chemotypes that have been created (Figure 15.1) have mostly relied on anthrone composition. Where the chromones have been used to circumscribe a chemotype, a series of these chromones in co-occurrence (e.g. aloeresin E & F in Chapter 11) defines the specific chemotype. These results serve as evidence that unlike morphological characters, leaf exudate chemistry is relatively invariable, implying chemotaxonomic data to be a reliable source of taxonomic information in *Aloe*.

Conclusions

CONCLUSIONS

The aim of this chapter is to summarise the main patterns that have emerged from the study and the new insights that have resulted from the chemotaxonomic survey.

1. The chemical complexity in *Aloe* has previously been under-estimated. The common occurrence and overall distribution of numerous compounds and classes of compounds (e.g. flavonoids) are shown for the whole genus for the first time. A large number of unidentified compounds remains to be isolated and identified.

2. The chemical pattern in *Aloe* is not random, but shows a high degree of correlation with existing albeit scanty evidence of relationships in the genus. The overall pattern is that some 'chemical groups' are well supported by morphological evidence (e.g. microstigmin in Chapter 8, 10-hydroxyaloin in Chapter 9 and aloeresin E and F in Chapter 11), while others are less convincing, with no morphological or other evidence in support of the supposed relationships (e.g. the plicataloside group in Chapter 13).

3. An exciting discovery was chemotaxonomic evidence for hybridization in *Aloe.* The discovery of 'hybrid compounds' formed by the combination of biochemical pathways (enzymes) in chemical dissimilar parents, thus leading to new combinations of functional groups (e.g. methoxy and hydroxy groups) is an important step forward in our understanding of evolutionary mechanisms in *Aloe.* It provides a means of detecting the non-homology of chemical characters even when the end products are identical.

4. The patterns of co-occurrence were shown to be more significant than the mere absence or presence. The 'profiles' or 'patterns' provide important clues about the presence or absence of whole biochemical pathways and thus add a new dimension to our understanding of relationships, chemical homology and hybridization events.

5. For reasons mentioned in 4 above, all profiles ('patterns') generated during the study are attached as an appendage. Future students of the chemistry of aloe may benefit from the recorded profiles firstly, by identifying the new / unknown chemical compounds indicated in the spectra and secondly, by studying the patterns of co-occurrence to discover new (previously undetected) non-homologies e.g. the possible presence of different ester groups - coumaroyl vs cinnamoyl, or the possible different placements of the sugar moieties as shown by van Heerden *et al.* (1997).

6. A clear evolutionary pattern that has emerged repeatedly in the study is drought adapted clades of tropical origin which appear to have diversified in the arid western parts of southern Africa, possibly in response to winter rainfall and summer aridity. Examples are the aloeresin E and F group in Chapter 11 and the microstigmin group discussed in Chapter 8. It has also been demonstrated that many species distributed in southern Africa have their closest relatives in tropical east Africa. These 'chemogeographical patterns' have allowed suggestions of evolutionary trends between many species of which the taxonomic relationships have hitherto been a mystery and provided general clues to the evolutionary history of the genus *Aloe* on the African continent and on Madagascar.

7. Perhaps the most profound new insight is the importance of reticulate evolution, which calls for a new analytical approach in the reconstruction of phylogenetic relationships. Characters are reasonably congruent in smaller groups which are certain to be monophyletic, but in larger groups (and in the genus as a whole), there are no obvious morphological or chemical patterns that would lead to a single simple taxonomic hierarchy. It seems that speciation in *Aloe* has followed a similar pattern to that found in large species complexes where morphological and genetic characters (as judged from enzyme electrophoretic data) evolve at different rates. It seems that chemical and morphological evolution in *Aloe* are similarly 'out of phase' and that selection pressures and breeding isolation may not have had sufficient impact to create the convenient discontinuities found in many other groups with divergent patterns of character state changes.

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Appendix 1

Abstracts of publications and conference contributions emanating from this study

This Appendix includes all abstracts of poster presentations, papers presented at conferences and the abstract of publications which have all emanated from this study. In most cases published papers have been integrated in various chapters and copies of these papers are not included in this appendix. Published papers of which the content has not been discussed in the thesis are included in Appendix 1.1 - 1.6.

POSTER PRESENTATIONS:

A chemotaxonomic comparison of *Aloe candelabrum* and *A. ferox* (Aloaceae)

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*National Botanical Institute, Pretoria.

The obvious similarity between *Aloe candelabrum* Berger and *A. ferox* Miller has been a topic of debate as to whether the two entities should be considered as separate species. The literature assigns certain diagnostic characters in attempts at making the species mutually exclusive. *In situ* investigation of 41 populations representative of the entire range of distribution of both species was carried out. The conspicuous similarity in morphological characters and the ambiguity of transitional populations (Umtamvuna Valley) confirmed that no morphological discontinuities exist between the two entities. The affinity is also repeated at the chemical level. Exudate samples of 172 individuals showed that chemically *A. candelabrum* is identical to *A. ferox*. We suggest that *A. candelabrum* is merely a geographical form of *A. ferox*.

Poster presentation: South African Association of Botanists, University of the Orange Free State, 1995
Partially incorporated in Chapter 16

Is *Aloe spectabilis* distinct from *A. marlothii*?

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*National Botanical Institute, Pretoria. **South African Druggists, Johannesburg

Aloe marlothii Berger, is one of the most abundant and widespread *Aloe* species in southern Africa. The common name *Bergaalwyn* indicates habitat preferences in the mountainous areas of north and eastern Transvaal and extending into KwaZulu and northern Natal. Leaf exudate of fifty individuals in each of 54 populations (2 700 samples) were analysed for their chromone and anthrone derivatives. *A marlothii* displays a mosaic variation in exudate composition, some populations, predominantly with homonataloin as major anthrone, while others produce aloin (or various derivatives of aloin) as the major anthrone. In some populations, mixtures of these chemical varieties can be found, but generally each population comprises only one major chemovar. This unique pattern is repeated in all populations of *A. spectabilis* sampled, indicating a chemical identity with *A. marlothii*. The morphological characters used by Reynolds (1973) to distinguish *A. spectabilis* from *A. marlothii* were found to vary without any discontinuities despite the Natal southern forms (Tugela catchment) having a rather distinct facies when compared to typical *A. marlothii*. As there are certain intermediate populations we prefer to interpret *A. spectabilis* as a geographic variant of the variable and widespread *A. marlothii*.

Poster presentation: South African Association of Botanists, University of the Orange Free State, 1995
Partially incorporated in Chapter 16

The taxonomic significance of 10-hydroxyaloin in the genus *Aloe*

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In his taxonomic treatment of the genus *Aloe*, Reynolds included five species in *Aloe* section *Asperifoliae*. Four new species have since been described which have an affinity with the species pertaining to *Aloe* series *Asperifoliae*. The species of this series are endemic to Namibia, north western Cape and the Karoo region of South Africa and are characterized by plants of which the leaf surface is asperous. A comprehensive taxonomic study of the genus *Aloe* indicated 10-hydroxyaloin to be restricted in distribution to species of the *Asperifoliae* and *A. littoralis*. Two novel nilic acid esters of 10-hydroxyaloin, littoraloin A and littoraloin B have been isolated and characterized from *A. littoralis*. A cladistic analysis of the chemotaxonomic and morphological characters has led to a new hypotheses of relationships with the series *Asperifoliae*. The conservative leaf exudate chemistry shows that the circumscription of the series should be modified to exclude *A. viridiflora* but to include *A. littoralis*, which is considered to be basal to the group. A rigorous comparison of the morphological and chemical evidence have resulted in a new and better understanding of affinities within the series *Asperifoliae* and related species.

Poster presentation: NAPRECA, Makerere University, Uganda, 1995. Partially incorporated in Chapter 9

The diagnostic value of leaf exudate in "fingerprinting" species of *Aloe*

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The historic and renewed interest in the medicinal, cosmetic and horticultural properties of *Aloe* has led to large scale collection and cultivation of various species. Due to the practical value of *Aloe*, it would be useful to correctly identify material of uncertain origin by a chemical fingerprint. Our chemotaxonomic survey of the genus *Aloe* has indicated that several compounds have been incorrectly detected in certain species. This may be due partly to the use of cultivated plants of uncertain origin and/or identity. The rigorous approach of our study has also shown that quantitative and qualitative information of the leaf exudate compounds can be used to distinguish among species of aloe. Members of the series *Pachydendron* are used to illustrate the application of the diagnostic value of leaf exudate composition. Species could firstly be separated on basis of the major anthrone produced, aloin or homonataloin. Each species could then be fingerprinted by the occurrence and combination of chromone compounds. Aloes are often used as ingredients in traditional medicines and when incorrectly used or applied could be hazardous. Anthraquinones are abortifacients and some species contain hemlock alkaloids. Providing each species with a distinct chemical fingerprint could assist in forensic studies. The ultimate aim is to provide a chemical key to identify each species on grounds of chemical composition. This would ensure that each laboratory involved in *Aloe* research could determine the authenticity of the materiel under investigation.

Poster presentation: South African Association of Botanists, University of Stellenbosch, 1996

Unusual chromone derivatives of *Aloe lutescens*

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The genus *Aloe* is exceptionally rich in species, many of which are morphologically poorly defined, so that chemosystematic information may add an important new dimension to our understanding of the species delimitations and infrageneric relationships. Problems with species delimitations are clearly exemplified by the series *Latebracteatae*, an exceptionally variable species complex. According to Reynolds (1950), the series comprises three species: *Aloe lutescens*, *A. wickensii* and *A. cryptopoda*. Although it is generally accepted that these species are differentiated on a regional basis, they are so closely related that they may eventually prove to be regional forms of the same *Aloe*. The obvious overall morphological similarity is also reflected in the chemical composition of the leaf exudate, which was found to be identical in the three species. In addition to the known chromone (aloesin) and anthrone (homonataloin A and B) derivatives, three unknown compounds ere detected by HPLC analysis. The structures of these three compounds were determined by NMR spectroscopy and it was found that these compounds were two novel, unusual chromone derivatives and a novel anthrone derivative. This poster discusses the structural determination of the three new compounds.

Poster presentation: South African Association of Botanists, University of Fort Hare, 1997.
Partially incorporated in Chapter 10.

Unravelling taxonomic relationships in a large genus - the taxonomic significance of chemical groups in *Aloe*

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A chemotaxonomic study on the leaf phenolics of virtually all species of *Aloe* has made it possible to define several chemical groups in the genus of 420 species. The chemical groups are either identified by a single marker compound or a series of unique compounds. The following groups have been identified and the chemotaxonomic value of each group will be shown with the aid of a dendrogram.

1. An aloin / aloinoside / microdontin group, comprising 36 species, mostly of tropical origin. This group includes species not previously associated with one another.
2. An 8-O-methyl-7-hydroxyaloin group. Here the co-occurrence of some leaf compounds suggests that 8-O-methyl-7-hydroxyaloin is not homologous in the 18 species where it has been detected.
3. An aloenin group, comprising 16 species which are believed to be a monophyletic group.
4. A microstigmin group, indicating a taxonomic alliance between series *Purpurascentes* and series *Anguialoe*, with *A. broomii* an intermediate between the two.
5. A 10-hydroxyaloin B group, represented by series *Asperifoliae* and related species, which appears to be a drought adapted clade of tropical origin.
6. A homonataloside group, comprising 14 species, suggesting a biochemical link between the aloes of north Africa and southern Africa.
7. An aloeresin E and F group, indicating a taxonomic alignment between series *Mitriformes* and five anomalous species.
8. A plicataloside group, with its single marker compound indicating a taxonomic relationship between 20 mostly tropical East African species.
9. A flavone group. The large number of species with flavones (Sections *Leptoaloe, Graminialoe, Lomatophyllum* and series *Macrifoliae*) are suggested to be basal in the genus.
10. A flavanone group. A few anomalous species produce flavanones but it is unlikely that they form a monophyletic group.

These chemical groups have lead to an improved understanding of natural relationships in a genus where no satisfactory infrageneric classification has hitherto been available.

Poster presentation: South African Society for Systematic Biology, University of Stellenbosch, 1998.

PAPER PRESENTATIONS:

A chemotaxonomic study of the genus *Aloe* (Aloaceae)

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The genus *Aloe* comprises close on to 400 species, with major areas of distribution being South Africa, East Tropical Africa and Madagascar. Leaf exudate of *Aloe* species contain complex mixtures of chromone, anthrone and flavonoid derivatives, the latter previously being underestimated as chemotaxonomic characters. The chemotaxonomic utility of the leaf compounds is evaluated at three different levels (an example of studies at each level of research will be discussed). 1. The population level. Populations of *A. ferox, A. candelabrum, A. marlothii and A. spectabilis* have been investigated throughout the known distributional range, both chemically and morphologically. The results unambiguously showed *A, candelabrum,* to be a geographical form of *A. ferox, A marlothii* displays a mosaic chemical pattern with populations containing both aloin- and homonataloin-producing individuals. This unique occurrence is repeated in *A. spectabilis* which, together with morphological information, leads to the conclusion that *A. spectabilis* is merely a localized form of *A. marlothii.* 2. The species level. Many species can be identified by their chemical profiles alone. This chemical "fingerprint" allows for the construction of a diagnostic key, which could be used to identify species in laboratories researching aloes and *Aloe*-derived products. Members of *Aloe* sect. *Pachydendron* will be discussed to illustrate such an application. 3. The infrageneric level. The root and leaf chemistry of *Aloe* species lead to the delineation of groups within the genus. Some groups form homogeneous subunits, while others are less conservative. The series *Mitriformes, Asperifoliae* and *Rhodacanthae* will be used to discuss research results at this level.

Paper presentation: South African Association of Botanists, University of the Orange Free State, 1995

Chemotaxonomic studies in African Aloaceae and Asphodelaceae

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Since the pioneering work of Hegnauer and Rheede van Oudtshoorn *Aloe* and related genera have been the subject of several chemotaxonomic and phytochemical investigations. Recent modifications to the circumscription of the Asphodelaceae *sensu lato* show the need for a more rigorous approach in comparative studies. Our paper gives an overview of recent chemotaxonomic work in African Asphodelaceae *sensu lato,* i.e. including the Aloaceae. The most important progress has come from root metabolites, notably the presence of a wide range or tetrahydroanthracenones, many of which are as yet unidentified. In contrast to the leaf compounds, the root metabolites are relatively conservative, and hence of value to determine relationships at the generic level. A preliminary hypotheses of generic relationships in both families is presented, based mainly on data from chemical characters, but also including leaf anatomy and various morphological characters.

Paper presentation: NAPRECA, Makerere University, Uganda, 1995

A chemotaxonomic study of the genus *Aloe* (Aloaceae)

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The genus *Aloe* comprises close on to 400 species of which 160 are endemic to South Africa. Aloes have been used for medicinal purposes since antiquity and in South Africa Cape aloes forms the basis of a large industry of traditional medicines. In addition to its purgative principles, the leaf exudate of aloes also has a traditional reputation for effective would healing and during the past few years there has been revived interest in aloe as cosmetic ingredient. Aloes are known to contain complex mixtures of anthraquinone and chromones in the leaf exudate and extract, but the chemotaxonomic potential of these compounds have however not been fully utilized in the past.

Research is being conducted at the following three levels:

Species level. An HPLC investigation of more than 300 species have shown the leaf exudate and extracts to be of diagnostic value as the chemical profiles can be used to "fingerprint" many *Aloe* species. A study of quantitative and qualitative variation in leaf exudate compounds allows for the construction of chemical identification keys, which can be used to readily distinguish between morphologically similar species. Species pertaining to *Aloe* section *Pachydendron* for example, can be distinguished by their major anthraquinones aloin or homonataloin), as well as the presence and combination of various chromones. *Aloes* have been reported to contain hemlock alkaloids and anthraquinone glycosides are known to contract intestinal muscle. Species with toxic principles (e.g. abortifacients) are often used indiscriminately in the preparation of traditional remedies as there is often no distinction between species in vernacular names. A practical application of research at this level is for the data to be made available to forensic laboratories, which would assist in identifying aloe ingredients in crude decoctions.

Populations level. A geographical variation study of the economically important *A. ferox* has shown little or no qualitative variation in the leaf exudate compounds. Qualitative variation in the anthrone C-glycoside aloin, the active component in Cape Aloes, allows for the selection of favourable chemotypes for improved commercial utilisation. Chemotaxonomic evidence unambiguously showed *A. candelabrum* to be merely a geographical form of the variable and widespread *A ferox*. In contrast to low levels of variation detected in *A. ferox, A. marlothii* is an extremely variable species. A total of 55 populations (*ca.* 3000 individuals) have been investigated to accurately document the unusually high degree of anthraquinone variation in and between populations predominantly with homonataloin as major anthrone, while others produce aloin or various derivatives of aloin. This unique chemical diversity is repeated al all populations of *A. spectabilis*, indicating a chemical identity with *A. marlothii*. The patterns of anthraquinone variation has allowed for A. *marlothii* and *A spectabilis* to be divided into chemotypes.

Infrageneric level. The genus *Aloe* displays many complex and variable morphological characters which are virtually impossible to interpret taxonomically and which inevitably leads to superficial taxonomic concepts. A study of the chemical compounds(mainly chromones and anthraquinones) provides an independent test of the morphological groups created by Reynolds and will result in a better understanding of the phylogeny of the genus *Aloe*. Certain groups are chemically uniform e.g. series *Mitriformes*, while others are chemically variable. *Aloe* series *Asperifoliae* is the only group where 10-hydroxyaloin and derivatives thereof are produced. Flavonoids have been a neglected chemotaxonomic character in the genus *Aloe*. The chemogeographical distribution of various leaf compounds, including flavonoids, provide valuable insight into biogeographical patterns. There is substantial chemical evidence, for example, to suggest a taxonomic alliance between the species of Madagascar and some counterparts of the African continent.

Hybridization has played a very important role in the evolution of the genus *Aloe* and it has probably complicated and masked many of the discreet chemical patterns which may have existed prior to the hybridization events. It can be concluded that extensive chemotaxonomic studies provides us with fundamental new knowledge to help resolve some of the taxonomic enigmas in the genus *Aloe*.

Paper presentation: NAPRECA, Makerere University, Uganda, 1995

Chemotaxonomic patterns in the genus *Aloe* – towards a new phylogeny.

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A rigorous comparison of chemical patterns based on leaf compounds in the genus *Aloe* is indicative of new hypotheses of taxonomic and biogeographic relationships within this genus of close to 400 species. Certain compounds are widely distributed throughout the genus (e.g. aloesin), while others are restricted and provide new ideas about natural relationships. These chemical patterns are often supported at the morphological level. An interesting example is *Aloe krapohliana* which has a chemical profile identical to the members pertaining to the series *Latebracteatae* (*A. lutescens, A. wickensii and A. cryptopoda).* The occurrence of the flavone isovitexin is surprising for two reasons: firstly, flavonoids have not previously been reported from *Aloe*; secondly, various glycosides of this aglycone are restricted to the sections *Leptoaloe* and *Graminialoe*, the series *Macrifoliae* and *Lomatophyllum*, the sister genus of *Aloe*. These groups have not previously been associated and may represent the most basal lineage. Two novel cinnamic acid esters of aloesin, aloeresin E and F, are characteristic of the series *Mitriformes* (including *A. pearsonii).* Likewise, the series *Purpurascentes* (including *A. chlorantha* and *A. pictifolia*) is characterised by novel derivatives of 5-hydroxyaloin. The geographical distributions of compounds such as naringenin (flavanone), dihydroisorhamnetin (dihydroflavonol) and 7-*O*-methyl aloin (anthraquinone) indicate an obvious alliance between the aloes of Madagascar and some of the aloeaceous counterparts on the African continent. In comparison with the chemical diversity in the aloes of South Africa, the aloes of Tropical East Africa are less variable in leaf exudate composition. For example, many of them have a distinct HPLC profile characteristic of the *Aloe aageodonta – A. ngongensis* complex. Furthermore, the novel naphthalene compound plicataloside is also restricted (with the exception of *A. plicatilis*) to about 17 tropical species.

Paper presentation: South African Association of Botanists, University of Stellenbosch, 1996

The evolution of aloes: new clues from their leaf chemistry

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Paper presentation: Succulenta, Johannesburg, 1996.

Aloe Chemotaxonomy – examples from A to Z.

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A chemotaxonomic survey is providing new and exciting insight into natural relationships in the genus *Aloe*. Chemical compounds (anthrones, chromones and flavonoids) contained in the leaves of aloes indicate taxonomic affinities amongst various taxa implicating biogeographical and evolutionary patterns. Evidence drawn from morphology, chemical data and anatomical studies are incorporated in a broad multi-disciplinary approach to develop, for the first time, a natural phylogeny for the genus. A selection of 20 species of aloes is discussed in alphabetical sequence to demonstrate the chemotaxonomic value of leaf chemistry at the species, population, and infrageneric levels.

Paper presentation: South African Association of Botanists, University of Fort Hare, 1997

Progress in the chemosystematics of *Aloe*

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A chemotaxonomic study of the genus *Aloe* has revealed distinct chemical groups at the infrageneric level. Some of these groups are congruent with the present classification system for *Aloe* that is largely artificial. The most interesting and challenging are the many examples where taxa not previously associated with one another have similar leaf exudate compositions. These groups will be discussed with reference to their morphology and chemistry. The evolutionary and biogeographical implications of these chemical indicators will be considered.

Paper presentation: South African Association of Botanists, University of Cape Town, 1998

Are chemical compounds reliable taxonomic signposts in the genus *Aloe*?

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See page 371

Paper presentation: The International Organisation for Succulent Plant Study, Kirstenbosch, 1998

Hybridization in *Aloe* and related genera

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The ability of aloes to hybridize is evidenced by the numerous garden varieties which are responsible for the horticultural value of this large genus of over 400 species. Reynolds (1950 & 1966) recorded all natural hybrids and gave comments on the dominance of certain morphological characters. A comprehensive study on the leaf exudate chemistry suggests that hybridization is one of the mechanisms of speciation in *Aloe*. The leaf exudate pattern of a hybrid aloe is usually a superimposition of the leaf chemistry of the parents but the parental patterns may not always be clearly visible. Hybridization at species level is best illustrated by evaluating the leaf chemistry and the morphology of *Aloe broomii* which is intermediate between section *Anguialoe* and series *Purpurascentes*. The leaf exudate of a putative hybrid between *Aloe claviflora* and *A. ferox* in Gamkapoort contains compounds characteristic of both putative parents. Barker *et al.* (1996) independently illustrated the hybrid origin of the Gamkapoort aloe using RAPD data. Identifying putative hybrids by their leaf exudate profiles and morphological intermediacy is relatively easy but how do we account for hybridization if one of the putative parents have become extinct or where hybridization defies any morphological and chemical detection?

The congruence of morphological and chemical characters in certain infrageneric groups and other genera of the *Asphodelaceae* questions the generic delineation of *Aloe*. Evidence from root chemistry suggests that *Aloe* series *Serrulatae* is the product of hybridization between *Aloe* and *Gasteria*. Likewise, *Aloe aristata* has the vegetative morphology and root compounds of the genus *Haworthia*. The ability of aloes, diverse in morphology, to hybridize readily between themselves and with members of other genera (e.g. *Gasteria* and *Haworthia*) complicates the infrageneric taxonomy and even the generic circumscription of *Aloe* within the *Asphodelaceae*.

Paper presentation: South African Association of Botanists, University of Stellenbosch, 1996.

PUBLICATIONS:

A chemotaxonomic comparison of *Aloe candelabrum* and *A. ferox* (Aloaceae)

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The obvious similarity between *Aloe candelabrum* Berger and *A. ferox* Miller has been a topic of debate as to whether the two entities should be considered as separate species. The literature assigns certain diagnostic characters in attempts at making the species mutually exclusive. *In situ* investigation of 41 populations representative of the entire range of distribution of both species was carried out. The conspicuous similarity in morphological characters and the am ambiguity of transitional populations (Umtamvuna Valley) confirmed that no morphological discontinuities exist between the two entities. The affinity is also repeated at the chemical level. Exudate samples of 172 individuals showed that chemically *A. candelabrum* is identical to *A. ferox*. We suggest that *A. candelabrum* is merely a geographical form of *A. ferox*.

Taxon 1996, 45: 1 - 11 Partially incorporated in Chapter 16

The taxonomy of *Aloinella, Guillauminia* and *Lemeea* (Aloaceae)

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The recent reinstatement of the genera *Guillauminia* and *Lemeea* (*Aloinella* Lemée non Cardot) in the *Aloaceae* is discussed. It is concluded that both should remain in the synonymy of *Aloe* L.

Taxon 1995, 44: 513 - 517 see page 376

Anthrones from *A. microstigma*

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5-Hydroxyaloin A and a new anthrone, names as microstigmin A, were isolated from the leaf exudate of *Aloe microstigma*. The structure of microstigmin A was determines by spectroscopic techniques as well as by conversion into 5-hydroxyaloin A.

Phytochemistry 1997, (44)7: 1271 - 1274 see page 381

10-hydroxyaloin-B 6'-O-Acetate, an oxanthrone from *Aloe claviflora*

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Analysis of the leaf exudate of *Aloe claviflora* resulted in the isolation of a new oxanthrone, 10-hydroxyaloin B 6'-O-acetate, whose structure was determined on the basis of spectral evidence as well as conversion to the known compound 10-hydroxyaloin B.

10-hydroxyaloin-B 6'-O-Acetate, an oxanthrone from *Aloe claviflora*

Journal of Natural Products 1998, (61)2: 256 - 257 see appendix 385

The taxonomic significance of 10-hydroxyaloin in the genus *Aloe*.

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In his taxonomic treatment of the genus *Aloe*, Reynolds included five species in *Aloe* series *Asperifoliae*. Four new species have since been described which have an affinity with the species pertaining to series *Asperifoliae*. The species of this series are endemic to Namibia, north west Cape and the Karoo region of South Africa and are characterized by plants of which the leaf surfaces are asperous. A comprehensive chemotaxonomic study of the genus *Aloe* indicated 10-hydroxyaloin to be restricted in distribution to species of the *Asperifoliae* and *A. littoralis*. Two novel niiic acid esters of 10-hydroxyaloin, littoraloin A and littoraloin B have been isolated and characterised from *A. littoralis*. A cladistic analysis of chemotaxonomic and morphological characters has led to a new hypotheses on relationships within the series *Asperifoliae*. The conservative leaf exudate chemistry shows that the circumscription of the series would be modified to exclude *A. viridiflora* but to include *A. littoralis*, which is considered to be basal to the group.

Kew Bulletin 1996, 51(4): 159 - 168 Partially incorporated in Chapter 9

Distribution and chemotaxonomic significance of flavonoids in *Aloe* (Asphodelaceae)

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A chemotaxonomic study of practically all the species of the genus *Aloe* showed that flavonoids occur as major compounds in 31 out of a total of 380 species investigated. Flavanones and dihydroflavonols are present in the exudate of species in *Aloe* ser. *Rhodacanthae* and *Superpositae* and also in a number of the endemic species from Madagascar. Flavones occur as the only major compound in the leaf extracts of the sects. *Leptoaloe* and *Graminialoe*, ser. *Macrifoliae* and in *Lomatophyllum*, the sister genus of *Aloe*, isovitexin co-occurred with the *C*-glucosylanthrone aloin. The chemotaxonomic implication of these results are discussed together with the significance of the taxonomic and chemogeographical distribution of flavonoids in *Aloe*. With a few rare exceptions, the leaf compounds from two different biogenetic pathways (polyketide pathway and flavonoid pathway) are mutually exclusive. Since flavonoids are restricted to the basal groups in *Aloe*, we conclude that flavonoids are plesiomorphic characters in *Aloe* reflecting ancient phylogenetic and biogeographic links.

Plant Systematics and Evolution 1998, 211: 31 - 42 Partially incorporated in er 12

Aloeresin E and F, two chromone derivatives from *Aloe peglerae*

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The structures of two new aloesin derivatives isolated from *Aloe peglerae, viz.*, 2-acetonyl-8-(2 cinnamoyl-B-D-glucopyranosyloxy-5-methylchromone (aloeresin E) and 2-acetonyl-8-(2cinnamoyl-B-D-glucopyranosyl)-7-hydroxy-5-methylchromone (aloeresin F) were determined by spectroscopic methods.

Phytochemistry 1996, 43(4): 867 - 869 Partially incorporated in Chapter 11 / see page 387

Plicataloside in *Aloe* - a chemotaxonomic appraisal

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In a chemotaxonomic survey of 380 taxa of *Aloe*, 20 species were found to contain the naphthalene derivative plicataloside as the major phenolic in the leaf exudate. Most of the species are restricted to East Africa (Kenya, Ugandan and Tanzania). Only three species (*A. chabaudii A. palmiformis, A. plicatilis)* in southern Africa contained this compound while the Malagasy endemics studied were found to be devoid of plicataloside. Macromorphology of the species was examined to search for other characters common to the species, and taxonomic affinities are assessed. Previous studies have suggested some of the taxa defined by this unique chemical compound to be taxonomically related, while many of the taxa have not previously been associated together.

Biochemical Systematics and Ecology 1998, 27(4): 507 - 517 Partially incorporated in Chapter 13

The evolution of aloes: new clues from their leaf chemistry

AM Viljoen and B-E van Wyk

"Red flower of endurance! Up from the dusty ways
Where tired feet are tramping, our wistful eyes we raise
And lo! thro' clouds, thro' shining, thro' every storm that blows
Fair Hope smiles ever o'er us, here where the Aloe *grows"*

Beatrice M. Bromley
(taken from "Where the *Aloe* grows and other songs of Africa," 1912)

Morphology alone can be misleading

The work of G.W. Reynolds (1950, 1966) has provided a firm foundation for any future contribution in the field of *Aloe* taxonomy. The approach followed by Reynolds was in many ways a utilitarian approach in which species were grouped together using morphological characters and, to a limited extent, geographical distribution as the only criteria. This becomes more obvious in his treatment of the aloes of tropical Africa and Madagascar, where one or two (variable) morphological character(s) were used to delimit infrageneric groups. This approach was by no means an ignorant one, and executed not out of choice but due to the paucity of morphological characters. It would seem virtually impossible to delimit neat, morphological groups reflecting true phylogenetic relationships within the genus *Aloe*.

The potential value of chemical characters

The chemical compounds in *Aloe* leaves have the potential to answer many of the uncertainties about relationships. There is an amazing range of different chemical compounds and one would expect related species to have the same or similar chemical constituents. Virtually all species of *Aloe* produce a yellow, bitter tasting leaf exudate. The many suggested medicinal properties of the exudate are often stressed, but not the wonderful taxonomic information which is contained in this honey-coloured syrup which freely oozes from the incised leaves of aloes.

Since the taxonomic work of Reynolds it has become the norm to incorporate as many characters or sub-disciplines in what is called a multidisciplinary taxonomic approach. In brief, this means using chemical, morphological, anatomical, genetic characters etc. in a comprehensive attempt to understand the taxonomic relationships. Another Reynolds,

Figure 1. *Aloe falcata.*

(T. Reynolds), based at the Jodrell Laboratory in Kew Gardens assessed and reviewed the chemical patterns in *Aloe* (Reynolds, 1985, 1986, 1990). Since the work of both Reynoldses, many powerful techniques have evolved which facilitate an accurate analysis of the leaf exudate using high pressure liquid chromatography. This technique could be explained as the separation of the complex mixture of compounds in the exudate (as it occurs in the plants) into several components or chemical compounds. It is the quantitative and qualitative presence of these compounds which are providing us with new and exciting information to gain insight into possible natural relationships within the genus *Aloe*. A drop of the exudate is injected into the apparatus which separates the compounds (the chromatograph). The output of this device is called a chromatogram, an example of which is shown in Figure 2. The individual compounds are represented as peaks, with the "height" or "area" an indication of the quantity of that particular compound in the leaf exudate. In the example depicted in Figure 2 it can be seen that the exudate contains five major compounds, each with its own chemical structure and name. We can further see that compound 2 (called aloeresin A) is the major component in the leaf exudate and accounts for about 45% of the total composition of the leaf exudate.

The use of chemical information to assist in pattern recognition to understand taxonomic relationships is called chemotaxonomy. The taxonomic value of the leaf exudate is best illustrated by referring to some of the results which have been generated in our laboratory.

Aloe ferox and *A. candelabrum*

Consider two morphologically similar species *Aloe candelabrum* and *Aloe ferox*. The topic has been debated as to whether or not these two entities are separate species. In view of the medicinal and economical importance of *Aloe ferox* we studied both species throughout their entire distributional range, collecting both morphological data and leaf exudate samples. If both species at the limits of their range are compared, *Aloe candelabrum* from Otto's Bluff and *Aloe ferox* from Stormsvleikloof, then certain subtle dif-

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ferences could be tabulated. Yet, while travelling through the entire distribution area it became glaringly obvious that the characters suggested to be diagnostic for *Aloe candelabrum* and *Aloe ferox* are weak and not fully diagnostic. Furthermore, the leaf exudate compositions of both species are identical. Although chemical similarity is in itself not evidence for combining taxa, the important point is that *Aloe candelabrum* and *Aloe ferox* are the only two species in *Aloe* section *Pachydendron* which are chemically identical. It has therefore been proposed that *Aloe candelabrum* should be subsumed under *Aloe ferox* (Viljoen *et al.* in press).

Aloe marlothii and *A. spectabilis*

Aloe ferox is an example of a species which displays little or no variation in leaf exudate composition throughout its entire range of distribution. In stark contrast, *Aloe marlothii* is an example of a species which displays an unusually high degree of variation in leaf exudate composition. Two adjacent plants in the same population could produce different major compounds in the leaf exudate. This variation seems to be random with no geographical correlation. The interesting observation, however, is that *Aloe spectabilis* is the only other species which displays this mosaic pattern of variation. Once again, if a representative of each species is taken from its type locality then one could reason that the oblique racemes of *Aloe marlothii* are obviously different from the erect racemes of *Aloe spectabilis* (Figure 3). As in the case of *Aloe ferox*, if one travels throughout the entire range of distribution you encounter populations where it becomes impossible to decide whether you are dealing with *Aloe spectabilis* or *Aloe marlothii*, as the racemes are at various inclinations with some plants resembling *Aloe marlothii* in inflorescence architecture while others correlate well with *Aloe spectabilis*. All the other species in *Aloe* section *Pachydendron* have a diagnostic chemical fingerprint (Viljoen *et al.* 1996), with *Aloe marlothii* and *Aloe spectabilis* producing various chemotypes. Considering the morphological evidence in conjunction with the chemical evidence it would, in our opinion, not be premature to suggest that *Aloe spectabilis* is a geographical form of the variable and widespread *Aloe marlothii* (Viljoen *et al*, 1995).

The *Asperifoliae* and *A. littoralis*

The series *Asperifoliae* is limited to the north-west Cape and Namib Desert. After obtaining leaf exudate samples of all the representatives (e.g. *Aloe claviflora*) we noticed that the chemical profiles of all the members in this group were, if not identical, very similar. The chemical marker has been isolated and the structure determined as 10-hydroxyaloin B (Dagne, *et al.* 1996). The three recently described species, *Aloe dewinteri*, *A. corallina* and *A. namibensis* also fit into this pattern. The interesting discovery though is that *Aloe littoralis* contains this unique compound in the leaf exudate. Do we now dismiss this as a chemical coincidence or do we try to account for the "unexpected appearance" of this compound in *A. littoralis*? Yes, surely if one compares *Aloe claviflora* to *Aloe littoralis* you may seriously question our sanity if we dare suggest a morphological correlation between the two species. However, if we place a juvenile plant of *Aloe littoralis* next to *Aloe falcata* (Figure 1) then there seems to be reason to reconsider. Both have a branched panicle with simple, undifferentiated tubular flowers, and, in addition, they are chemical fingerprints of one another. We have to emphasise that our approach is not to replace the present morphological classification of *Aloe* with a chemical one. The challenge is to superimpose the well documented morphological information onto the chemical discoveries. Namibia's rare endemic aloe, *Aloe viridiflora*, was included in this group, the *Asperifoliae*. *Aloe viridiflora* is closely allied to *Aloe hereroensis* with which it shares many morphological and chemical characters (Bruyns, 1988 and Van Jaarsveld, 1989). A rigorous comparison of the morphology and conservative leaf exudate chemistry suggests that the circumscription of the series *Asperifoliae* should be modified to exclude *Aloe viridiflora* but to include *Aloe littoralis*. This would result in a chemically uniform group representing a southern, drought adapted lineage of tropical origin, with *Aloe littoralis* as the basal species (Viljoen *et al.*, 1996).

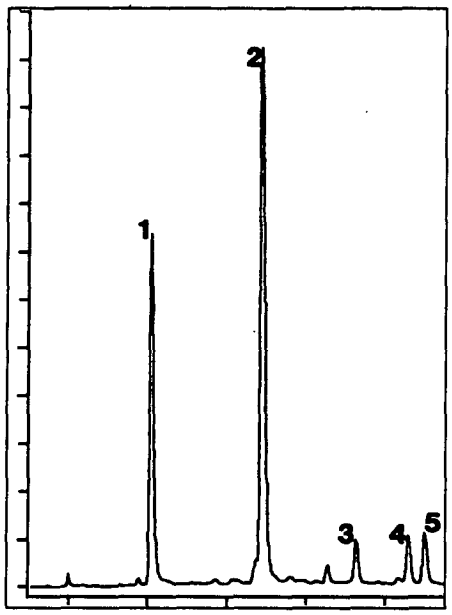

Figure 2. A typical chromatogram (HPLC profile) of *Aloe ferox* showing the five main components in the leaf exudate; 1 = aloesin (25%); 2 = aloeresin A (45%); 3 = 5-hydroxyaloin (2.1%); 4 = aloin B (8%) and 5 = aloin A (8%). The latter two compounds are the active ingedients often used as laxative in traditional medicines.

The grass aloes, the scandent aloes and *Lomatophyllum*

The grass-like aloes have proved to be a challenge in this investigation. Due to their inconspicuous nature, we had (initial) difficulty obtaining samples of these species. With the assistance of Charles Craib, Anthon Ellert, John Lavranos and Dave Hardy we managed to gain small pieces of leaf material of most of the grass-like aloes. As grass aloes produce little or no exudate, the leaf material was dried and pulverised after which it was extracted with a solvent and analysed. These aloes have very special compounds (flavonoids) in the leaf exudate, completely different from those discussed in the examples above. One of these flavonoids, called isovitexin, was detected in all the extracts of the grass aloes. The sampling was broadened to include members of the *Macrifoliae* (*Aloe ciliaris* group). Here too, this compound isovitexin occurred in the leaf extracts. *Lomatophyllum*, considered to be the sister-genus of *Aloe*, was investigated and also contained high levels of isovitexin. It is remarkable that in a survey of close onto 400 species, only representatives of these three groups contained this compound; surely there is some meaning to all of this? This discovery has led us to the conclusion that these chemical compounds have originated early in the evolution of the genus *Aloe*, implying that the grass-like aloes, the *Aloe ciliaris-A. gracilis* complex and *Lomatophyllum* represent some of the basal lineages in the genus *Aloe* (Viljoen *et al.*, submitted).

The Madagascar-Africa connection

A congruence in chemical characters has been discovered between various species of the African continent and Madagascar. *Aloe glauca* and *A. lineata* share a unique compound, naringenin (another flavonoid) which is limited in distribution and occurs in only ten *Aloe* species. This same compound has been discovered in the Malagasy endemics, *Aloe vaotsanda* and *A. suzannae*, with *A. pretoriensis* and *A. thorncroftii* forming part of this alliance. This interesting result firstly establishes a clear biogeographical link between southern Africa and Madagascar, and secondly it implies that these species appear to be ancient relicts from an era when these com-

pounds (flavonoids) were more widely distributed in the genus *Aloe*, having been gradually replaced by the more commonly encountered chomone and anthrone derivatives.

Tropical aloes

The information presented here has focused mainly on the aloes of South Africa. The greatest challenge, however, is to contribute to the taxonomy of the aloes of tropical east Africa. In the broader sense, the chemical patterns in the east African aloes seem less complex when compared to the aloes of South Africa. Once again, biogeographical links are drawn between various species in the tropics and South Africa. A unique compound, plicataloside, has recently been isolated from *Aloe plicatilis* (Wessels *et al.*, 1996). As implied by the name, the compound was isolated from the Fynbos-endemic *Aloe plicatilis* (back cover). The interesting fact is that it lacks the "normal" compounds usually found in the leaf exudate (chromones and anthraquinones), and only produces a naphthalene derivative, plicataloside. The compound has since been detected in various species in east Africa (e.g. *A. archeri*, *A. francombei*, *A. multicolor* and *A. pustuligemma*).

Another characteristic leaf exudate pattern containing microdontin A and B occurs in 18 species in east Africa (e.g. *Aloe aageodonta* and *A. ngongensis*). There is also a clear geographical discontinuity in the chemical distribution of this compound (microdontin) as it has only been detected in species of *Aloe* growing in east Africa and it is totally absent in South African and Malagasy aloes.

Conclusions

Although we sometimes tend to group species together with an emphasis on morphological similarities, one should bear in mind that a chemical pattern could be preserved over time while morphological adaptation and radiation could continue. This would result in two morphologically diverged species, yet in this hypothetical case, the leaf exudate chemistry would be a more accurate reflection of the ancestry of these two species. To draw a correlation between *Aloe plicatilis* in the western Cape and other plicataloside-containing species in east Africa for example, is in many ways a tall order. We have to remember that we cannot account for possible extinctions which have taken place along this line of evolution but, more importantly, we should not try to forge reasons for various occurrences if there does not exist a logical explanation within our framework of scientific reference.

Morphological resemblance does not necessarily imply common ancestry, nor does chemical identity suggest relationships. The challenge is to marry the morphological patterns with as many other characters as possible which would inevitably lead to a better and more comprehensive understanding of natural relationships within this interesting and enigmatic genus!

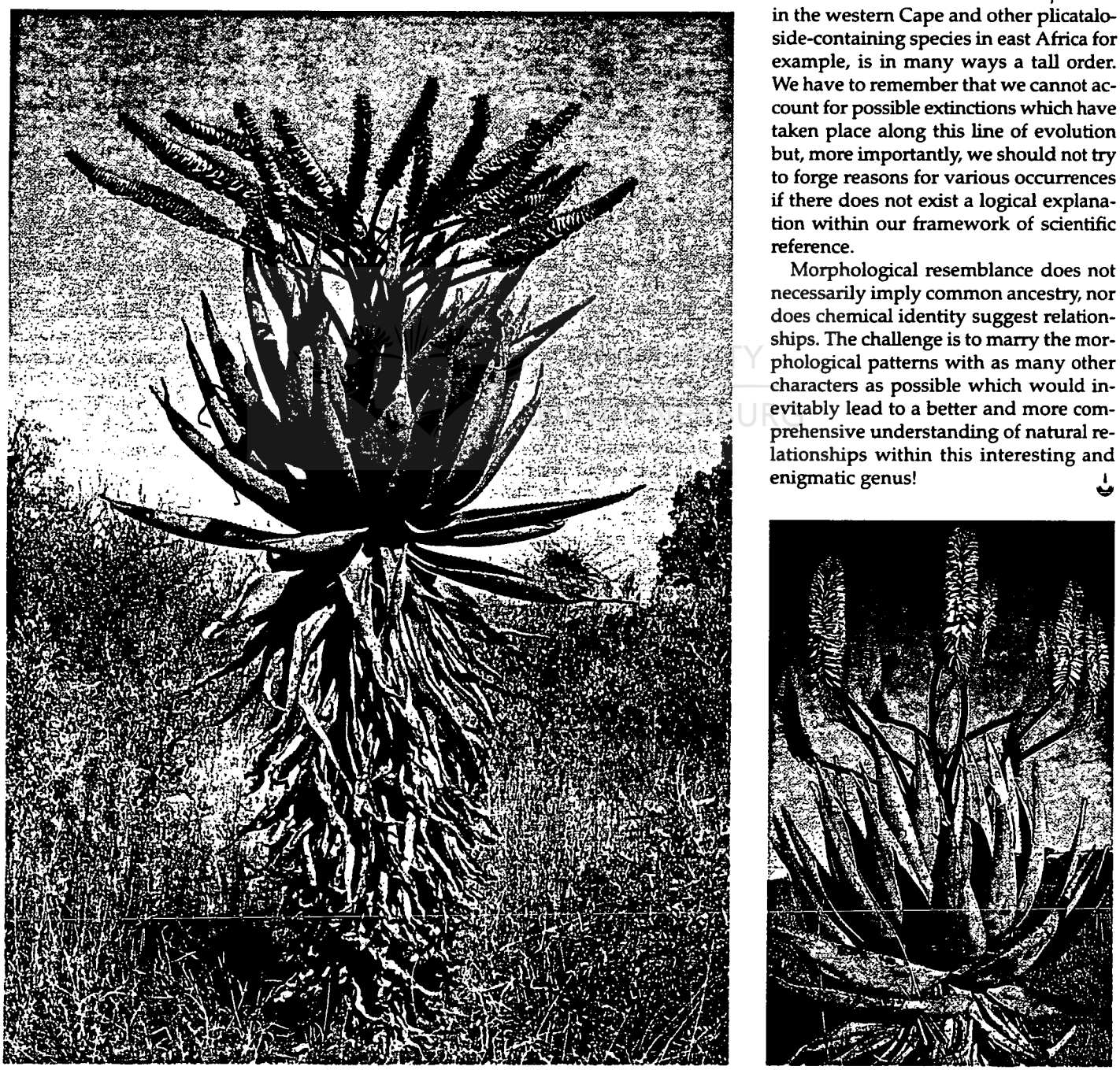

Figure 3. *Aloe marlothii* (left) and *Aloe spectabilis* (right)

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..."The crimson glow of thy blossoms upon the lonely height,
Telling of hope still living in nature's grimmest night.
Down at those far green pastures the children would pass thee by
For fairer and sweeter flowers that in their pathways lie;
These are little ones in thy kingdom whose hands would empty be
Of childhoods fairest heritage, O aloe, but for thee!"

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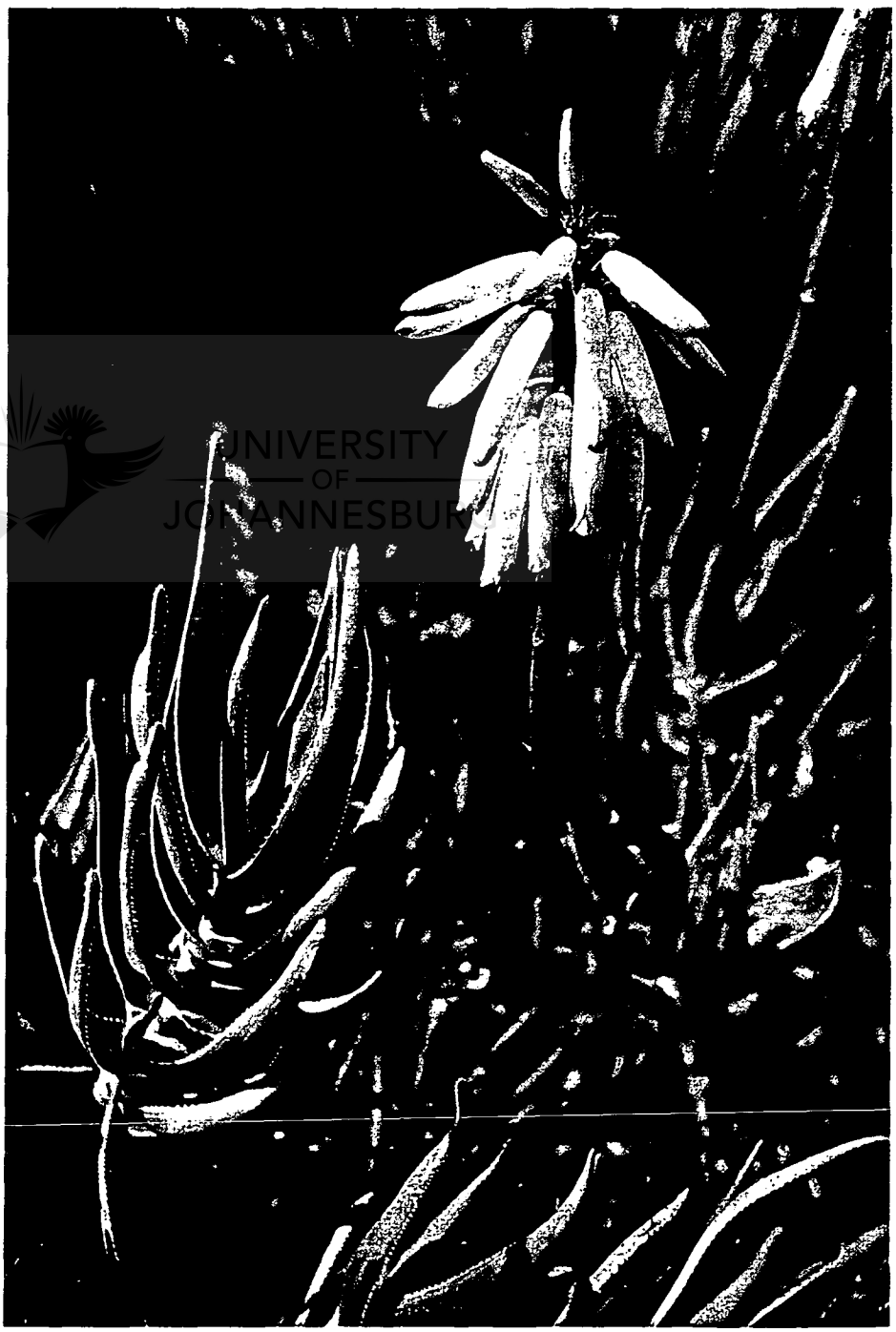

Figure 4. *Aloe commixta*. See also *Aloe krausii* on the front cover.

Are chemical compounds reliable taxonomic signposts in the genus *Aloe*?

Two case studies from series *Mitriformes* and section *Kumara*

Alvaro Viljoen and Ben-Erik van Wyk

"There seems to be no constancy of species, no fixation of characters, no relative stability, and nature refuses to be forced into the fetters of a man-made precise system." (Reynolds, 1950).

"The relationships within the genus ***Aloe*** *are often obscure and I have frequently experienced much difficulty in deciding upon the true affinities of certain species ..."* (Lavranos, 1973).

"Attempting to assess the relationships of the last two species demonstrates the problem of trying to find combinations of characters to define infra-generic groups." (Newton, 1994).

"It has proved virtually impossible to arrange the species of the Flora in a sensible phylogenetic sequence. There are no characters, ..."
(Susan Carter, 1994).

"Firstly the existing infra-generic classification of the genus ***Aloe*** *is far from satisfactory, and it is in need of revision. There are several species whose affinities within the genus are obscure ..."*
(Newton, 1998).

Figure 1. *Aloe cryptopoda* showing the distinct transverse bands on the leaves.

These quotations from the work of some of the veteran aloe specialists are indicative of the need to explore additional characters to assess relationships within this enigmatic, topical and challenging genus. Most studies on *Aloe* have accentuated the morphological similarities between taxa as indicators of taxonomic relationships. However, this does not seem sufficient to unravel affinities between taxa. The examples discussed below are drawn from a rigorous all-encompassing chemotaxonomic study. To suggest that chemical characters should enjoy preference above any other character would be both premature and naive but this study has indicated that chemical characters in *Aloe* are one of the most conservative classes of characters, with obvious taxonomic value. (The experimental methods that have been used in this study have been detailed in Viljoen & Van Wyk, 1996 and will not be repeated here.)

The question is often asked: "Is a chemical profile a more reliable character than any other? Or does chemical similarity necessarily indicate taxonomic alliance?" It has to be stated that all the problems encountered with morphological characters (e.g. convergence) are also true for chemical characters. Chemical characters should be viewed as additional data which should firstly be used as an independent test of the morphological pattern and secondly be integrated with existing data sets in an attempt to reach a consensus. It is interesting that the chemical similarity between species often forces one to scrutinise the taxa under investigation in an attempt to find supporting morphological evidence. This is evident from our work on *Aloe* series *Latebracteatae* which includes the three closely related taxa *A. cryptopoda*, *A. lutescens* and *A. wickensii*. To suggest that *A. krapohliana* is allied to this group would not be kindly accepted by many of the aloe enthusiasts, but allow for the motivation. The leaf exudate of these taxa all contain a very charac-

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teristic profile consisting of homonataloside B, *3'-O-coumaroylaloesin ans 3',6'-di-O-coumaroylaloesin* (Van Heerden *et al.*, 1997). This combination of exudate compounds is not widely distributed in *Aloe* and is restricted to 13 species, one of these being *A. krapohliana* which has an identity crisis, taxonomically speaking. The most outstanding feature of this species is the transverse bands which appear on the leaves. Closer inspection of *Aloe cryptopoda* has also shown the sporadic presence of these bands (Figure 1). Does this congruence in data not show us that these species are related?

Leaf exudate composition in itself is not a taxonomically unifying character but when considered in conjunction with other forms of taxonomic evidence it could lead to more convincing hypotheses on the taxonomic alignment of taxa. Various studies have been undertaken to assess chromatographic patterns in the genus *Aloe* (Cutler, 1980 and Reynolds, 1985, 1986 & 1990) but the chemotaxonomic utility of chemical characters at the infrageneric level has not been fully explored. A chemotaxonomic study of the genus *Aloe* has shown various chemical groups at the infrageneric level (Viljoen *et al.*, 1995 & 1998). For the purpose of this paper two examples have been selected to illustrate the chemotaxonomic value of the leaf exudate.

Example 1

In 1996 a unique naphthalene-like compound, plicataloside (Wessels *et al.*, 1996) was isolated from *A. plicatilis*. Initially it was thought that plicataloside was restricted to this morphologically anomalous species (Figure 4) which is suggested by its monotypic status as section *Kumara*. After a survey of 380 species of *Aloe*, plicataloside was detected in 20 species, mostly in tropical East Africa. From a chromatographic point of view it was interesting that plicataloside occurs in the absence of the chromones and anthrones which are usually present in *Aloe* (Figure 2). The 'affinity diagram' (Figure 7) shows all species which accumulate this unique chemical compound in the leaves. At first glance it is noted that a large number of the taxa have previously been taxonomically associated while a large number of species have not been suggested to be allied. Although the species in the *Flora of Tropical East Africa* treatment (Carter, 1994) are not arranged in a phylogenetic sequence, the author grouped species together which she thought were closely related. The species shown in Block A and Block B were suggested by the author to be related. Within this group (Block A) various authors have suggested taxonomic relationships e.g. Newton (1994) amplifies the similarity between *A. archeri*, *A. tugenensis* and *A. pustuligemma*. Morphologically *A. pustuligemma*, *A. francombei* and *A. otallensis* share the character of a pustulate perianth. *Aloe rugosifolia*, with its rough leaves, is included in this group. Rough leaves are also prominent in *A. archeri*, *A. deserti*, *A. francombei*, *A. murina* and *A. tugenensis*. *Aloe rugosifolia* and *A. deserti* both produce whitish deflexed bracts.

Block C represents four species placed in Group 19 (Reynolds, 1966) which is an assemblage of plants all with shrubby growth form. *Aloe morijensis* and *A. fribosa* have been suggested to be related to *A. palmiformis*. In a broader multi-disciplinary study, Cutler *et al.* (1980) suggests an affinity between *A. fibrosa*, *A. morijensis* and *A. babatiensis*. It is encouraging that previous authors who have studied the species in question have suggested taxonomic relationships which are here supported on the chemical level. More interesting, however, is the large number of species which have not previously been associated with one another. The three groups of species (as delineated in Blocks A, B and C) have not previously been suggested to be related, yet their leaf exudate compositions are identical. The position of the five peripheral species not associated with any other plicataloside-containing species remains a challenge. Of these, the most fascinating is *Aloe plicatilis* which is endemic to the south-western Cape. Is it possible that this species has its closest relatives in East Africa, or do we dismiss plicataloside as a chemotaxonomic coincidence?

Example 2

The observation that the species in *Aloe* series *Mitriformes* produce a remarkably similar leaf exudate profile should come as no surprise as the question has been debated as to whether all taxa in this group are not merely regional forms of a single species (e.g. Marais, 1980). In our survey of 380 species, only 12 species accumulated the coumaroyl chromones, aloeresin E and F (Van Heerden *et al.*, 1996), usually in the presence of homonataloin A and B (Figure 3). The present taxonomic arrangement

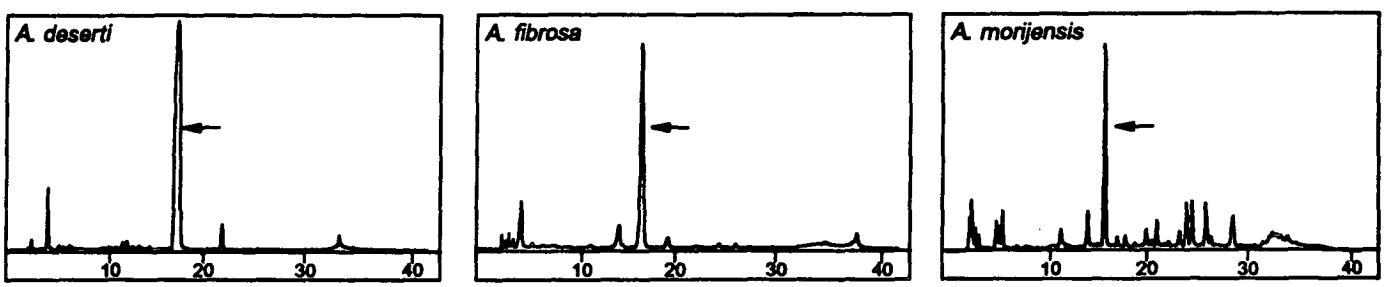

Figure 2. HPLC profiles of three plicataloside-containing species. Plicataloside is indicated by an arrow.

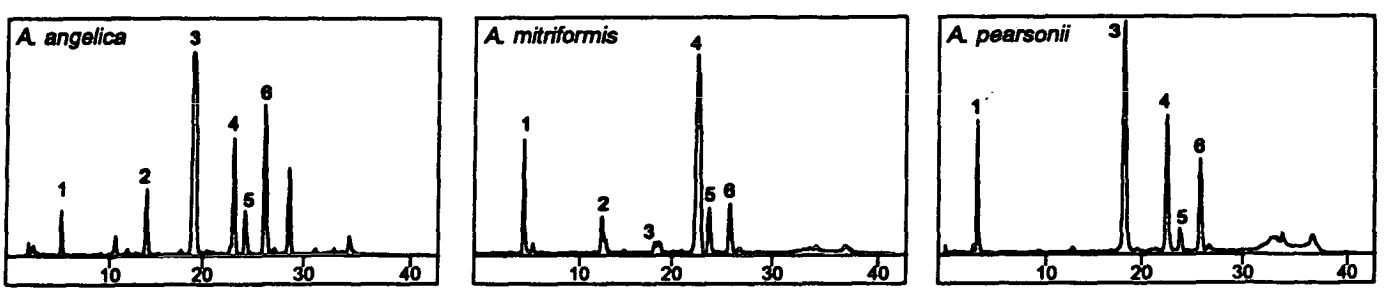

Figure 3. HPLC profiles of three aloeresin E & F-containing species. 1 = aloesin, 2 = aloeresin A, 3 = aloeresin E, 4 = aloeresin F, 5 = homonataloin B, 6 = homonataloin A.

Figure 4. *Aloe plicatalis*, the source from which plicataloside was isolated.

Figure 5. *Aloe comptonii*, a member of the Mitriformes.

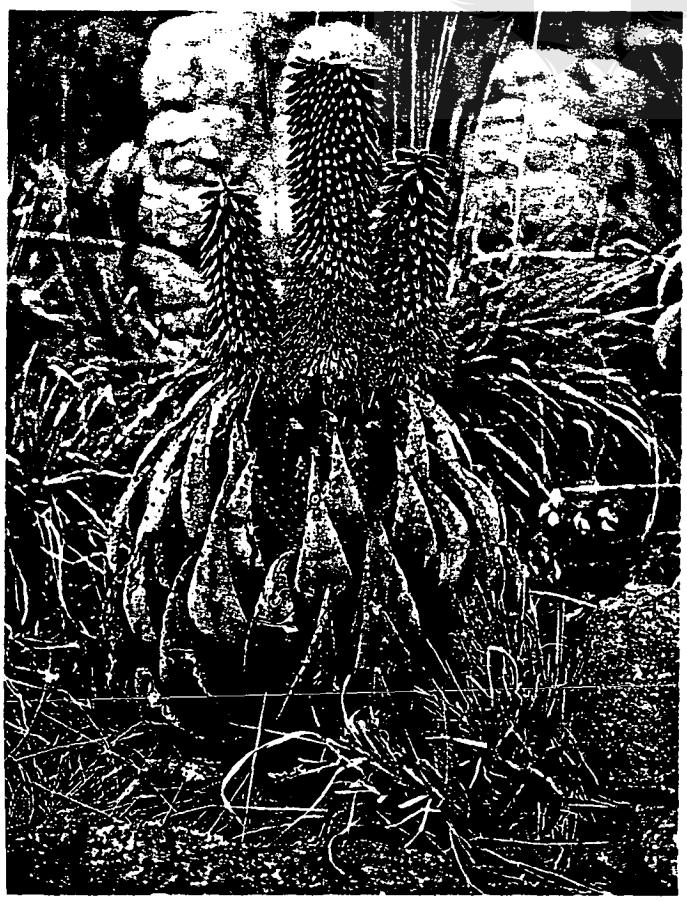

Figure 6. The coveted Magaliesberg endemic, *Aloe peglerae*.

of these taxa is represented diagrammatically in Figure 8. Reynolds (1950) delineated the series *Mitriformes* to include *A. mitriformis, A. arenicola, A. comptonii* (Figure 5) and *A. distans*. Since the work of Reynolds two additions have been made: *A. meyeri* (Van Jaarsveld, 1981) and *A. dabenorisana* (Van Jaarsveld, 1982).

Aloe pearsonii, erroneously placed in the series *Macrifoliae*, bears deflexed leaves which are obscurely lineate. *Aloe dabenorisana* is the only other species in which the leaves are deflexed. Although not explicitly stated, it can be assumed that Reynolds thought the *Macrifoliae* to be phylogenetically allied to the series *Mitriformes*, which is suggested in his taxonomic placement of *A. pearsonii*. Although *A. pearsonii* shares morphological characters with the rest of the series *Macrifoliae* (slender erect stems and conical racemes), the morphological characters conflicting with the status quo in the *Mitriformes* group does not necessarily warrant its omission from this group. The chemical evidence presented here gives convincing support for transferring *A. pearsonii* to the series *Mitriformes* as suggested by Venter and Beukes (1982).

Our studies unambiguously show that species belonging to *Aloe* series *Macrifoliae* have a different leaf chemistry. Firstly, the members of the *Macrifoliae* produce little or no exudate and the leaf extracts contain the flavonoid isovitexin as the major compound (Viljoen *et al.*, 1998). More interesting, however, are the six species which have not previously been associated with the taxa discussed above. *Aloe peglerae* (Figure 6), is placed in *Aloe* series *Longistylae* together with *A. longistyla* and *A. broomii*. The latter two aside, as we rather wish to emphasise the chemical similarity between the coveted Magaliesberg endemic, *A. peglerae* with other members included in this group, *A. erinacea* and *A.*

ıelanacantha . The latter species are placed in series *Echinatae* to-ether with *A. krapohliana* and *A. humilis*. *Aloe krapohliana* is hemically more closely related to *Aloe* series *Latebracteatae* vhile *A. humilis* is a flavonoid-producing species (Viljoen *et al.*, 998). *Aloe erinacea* was described by Hardy (1971) with com-ıents suggesting a relationship with *A. melanacantha*. Rowley 1980) believed that *A. erinacea* is merely a geographical form of *A. melancantha* while Rossouw (1980) demonstrated that the istinction in floral characters between the two species warrants pecific status for these two taxa. Within this group, *A. peglerae* s the closest morphological relative, as all three taxa have dark ungent thorns on the leaf margin and keel, they have a single nflorescence, larger bracts and the species are acaulescent to very hortly caulescent.

Aloe angelica is placed in *Aloe* section *Pachydendron* (Reynolds, 1950) with the following comments by the author: "*A. angelica* does not fit well into any series or section. It is a very distinctive species with its much branched inflorescence of bicoloured capitate racemes." The branched panicle and capitate racemes are shared with members of the *Mitriformes* (e.g. *A mitriformis*). The habitat preference of this species for the dense bushveld of the Soutpansberg leads to speculation as to whether the development of a stem could not be explained as a survival strategy to project above this dense bush.

Aloe yavellana represents an equally interesting situation. This species occupies a taxonomic position in Group 19 (Reynolds, 1966). In his description of *Aloe yavellana* Reynolds states: "Another peculiarity of *A. yavellana* is that it forms fairly compact

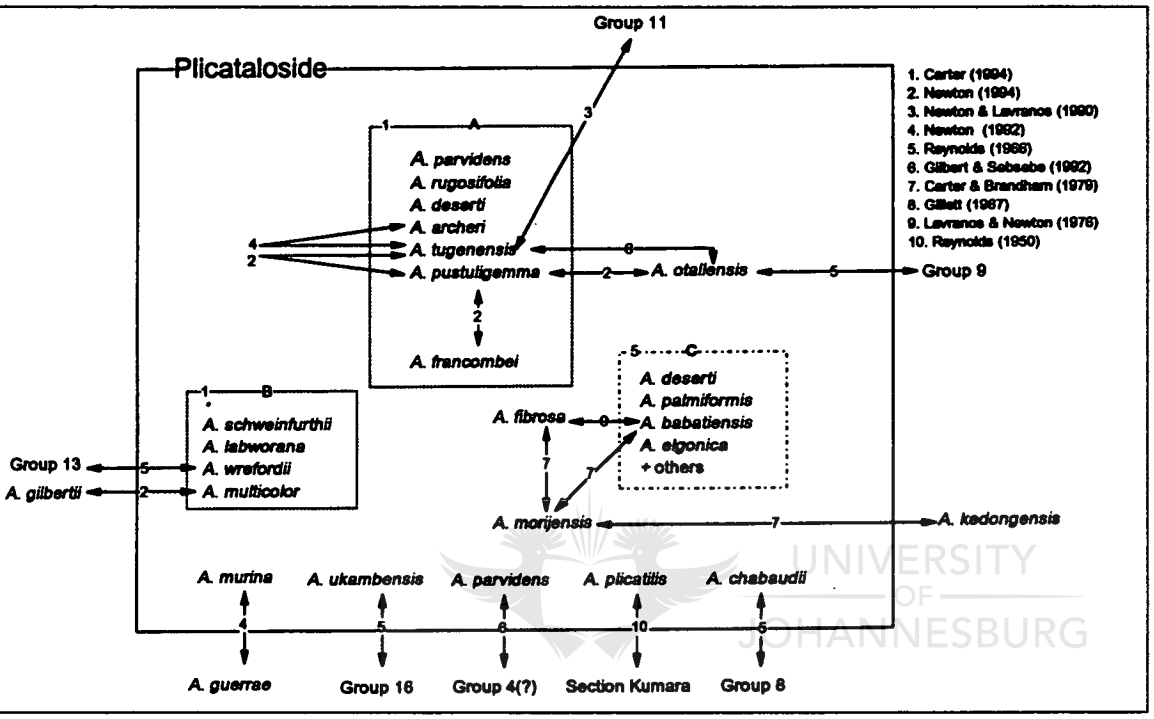

Figure 7. Taxonomic arrangement and affinities between species containing plicataloside.

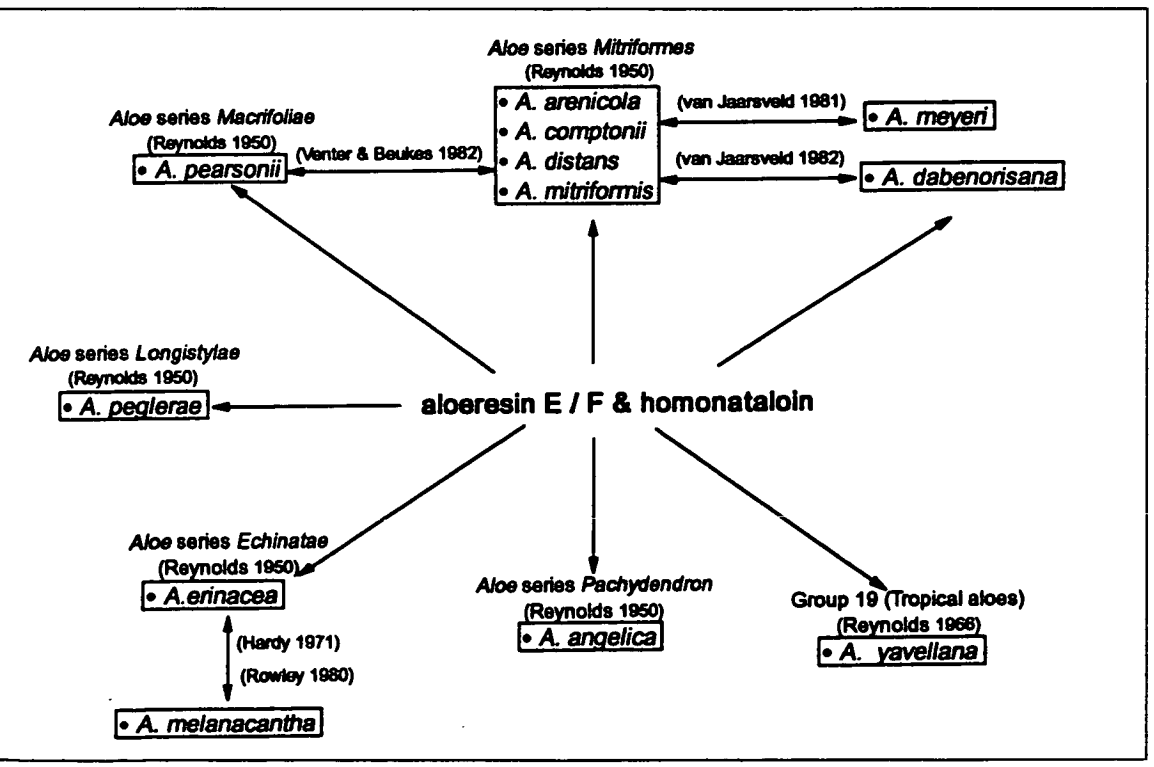

Figure 8. Taxonomic arrangement and affinities between species containing aloeresin E and F (usually in the presence of homonataloin A and B).

shrubs when stems are erect and not exceeding 1 m in length, but with development stems topple over and form sprawling shrubs with stems 2 – 3 m long, especially on steep slopes, with the foliate portion ascending." This description is identical to that of many of the species in *Aloe* series *Mitriformes*, and together with the resemblances in the inflorescence structure suggests a natural position in the *Mitriformes* group. Our chemotaxonomic survey of the genus *Aloe* has shown many examples of a 'chemical relationship' between species in South Africa and East Africa which has previously been reported by De Winter (1971) and Newton (1980) in broader floristic analyses. Similarly we have also shown sister group relationships in southern Africa between tropical species and extreme xerophytic species in the arid south-western regions. Examples are series *Asperifoliae* (Viljoen *et al.*, 1995) and also the *A. cryptopoda* group as mentioned above.

The two examples above are only a segment of the interesting discoveries which have been made by studying the chemical composition of the leaf exudate. General patterns are arising e.g. the taxonomic connection between the northern and southern species, drought-adapted clades of tropical origin and the observation that morphological characters alone provide a somewhat mosaic picture of taxonomic affinities. It is also clear that hybridisation has probably been a driving force in the evolution of *Aloe* and that morphological characters, viewed in isolation, could obscure patterns where species are obviously related. To answer the question posed in the title is not easy but it is evident that chemical patterns are paving the way to a better understanding of true phylogenetic relationships in the genus *Aloe*.

Acknowledgements

It would have been impossible to generate the data presented here without the cooperation of the following people who kindly supplied leaf exudate samples: S. Carter, Charles Craib, Ermias Dagne, Sebsebe Demissew, Anthon Ellert, Phillip Favell, Dave Hardy, Brian Kemble, John Lavranos, Len Newton, Gideon Smith, Ernst van Jaarsveld and Bosch van Oudtshoorn. Help from staff at the National Botanical Institute, Johannesburg Botanical Gardens and Royal Botanical Gardens (Kew) is gratefully acknowledged. A special word of thanks to Len Newton and John Lavranos for their dedicated interest and valuable discussions during the completion of this study.

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The taxonomy of *Aloinella, Guillauminia* and *Lemeea (Aloaceae)*

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Summary

Smith, G. F., Wyk, B. E. van, Mössmer, M. & Viljoen, A.: The taxonomy of *Aloinella, Guillauminia* and *Lemeea (Aloaceae)*. – Taxon 44: 513-517. 1995. – ISSN 0040-0262.

The recent reinstatement of the genera *Guillauminia* and *Lemeea* (*Aloinella* Lemée non Cardot) in the *Aloaceae* is discussed. It is concluded that both should remain in the synonymy of *Aloe* L.

Introduction

The *Aloaceae,* with seven genera and about 450 species, are a fairly small family of rosulate leaf succulent plants, centred in southern Africa. The names of genera belonging here are cited in the *Index nominum genericorum* (Farr & al., 1979), with some omissions recently pointed out by Smith & al. (1994). Generic delimitation and species concepts in the *Aloaceae* have been the subject of much discussion (Rowley, 1976a, b, c; Smith & Wyk, 1991). Many genera display unusual patterns of variation. Intergradations among populations may further complicate the assessment of the significance of reproductive and vegetative character variation for the alpha-taxonomy of the group.

Aloe L. is the largest genus in the family, and has the most diverse morphology. Fourteen generic names are currently included in the synonymy of *Aloe*. Two of these names were established for species from Madagascar: *Aloinella* (A. Berger) Lemée (1939) non Cardot (1909) for *Aloe haworthioides* Baker, and *Guillauminia* A. Bertrand (1956) for *A. albiflora* Guillaumin. Neither name has been widely accepted and both were included in the synonymy of *Aloe* by Reynolds (1958, 1966), who revised the genus on a global scale.

Recently, without a supporting argument, Heath (1993, 1994) reinstated both of these monotypic Madagascan genera. *Aloinella,* being a later homonym, was named *Lemeea* P. V. Heath. In addition to *Aloe haworthioides, A. boiteaui* Guillaumin and *A. parvula* A. Berger were also transferred to *Lemeea. A. bakeri* Scott-Elliot, *A. bellatula* Reynolds, *A. calcairophylla* Reynolds, *A. descoingsii* Reynolds, and *A. rauhii* Reynolds were transferred to *Guillauminia.*

Discussion

There is no single criterion which by itself can be regarded as unfailing for recognizing a genus. For practical purposes the genus should be regarded as an inclusive category whose species have more characteristics in common with each other than with species of other genera within the same family. There should be a clear morpho-

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Table 1. Morphological features used by Lemée (1939) to establish the genus *Lemeea* (as *Aloinella*) and shared with taxa of *Aloe*.

Diagnostic features	Selected taxa of *Aloe* sharing the features
Rosette small, dense	*A. aristata* Haw., *A. humilis* (L.) Mill.
Leaves narrowly linear	*A.* sect. *Graminialoe* Reynolds
Pedicels negligible	*A. insonspicua* Plowes, *A. bowiea* Schult. & J. H. Schult.
Outer perianth segments free	*A. broomii* Schönl., *A. saundersiae* (Reynolds) Reynolds
Filaments broad	–
Anthers exserted	*A. bowiea*, *A.* sect. *Anguialoe* Reynolds
small	–
bright orange	*A. ferox* Mill.
"Ovary acute" (erroneous)	–

logical break between the members of a particular genus and the members of other related genera. Past and current practice are also important, since a major change in classification and naming can create communication problems and result in loss of information (Jeffrey, 1968).

Our investigation has shown that *Aloe* is polymorphic in most of the characters used by Lemée (1939) and Bertrand (1956) to segregate *Lemeea* and *Guillauminia*, and that these supposedly diagnostic features are found elsewhere in *Aloe* (Table 1-2).

The only characters that separate *Lemeea* from similar miniature *Aloe* species are its small anthers and the broad, bright orange filaments which form a "tube" at anthesis (Fig. 3, Table 1). Anther size varies widely in *Aloe* and can hardly be used as a diagnostic character at generic level. Lemée's (1939) description of the ovary as acute is erroneous: each flower we examined had a rounded ovary.

The genus *Guillauminia* has been distinguished by its campanulate flowers and apparent lack of nectar production. Somewhat less distinctly campanulate flowers are also found in *Aloe* sect. *Anguialoe* (Table 2).

Table 2. Morphological features used by Bertrand (1956) to establish the genus *Guillauminia* and shared with taxa of *Aloe*.

Diagnostic features	Selected taxa of *Aloe* sharing the features
Inflorescence lax	*A. bowiea*, *A. gracilis* Haw.
Peduncle slender	*A. bowiea*, *A. tenuior* Haw.
Perianth segments free	*A. myriacantha* (Haw.) Schult. & J. H. Schult.
white	*A. albida* (Stapf) Reynolds
campanulate	*A.* sect. *Anguialoe*
Anthers exserted	*A. bowiea*, *A.* sect. *Anguialoe*

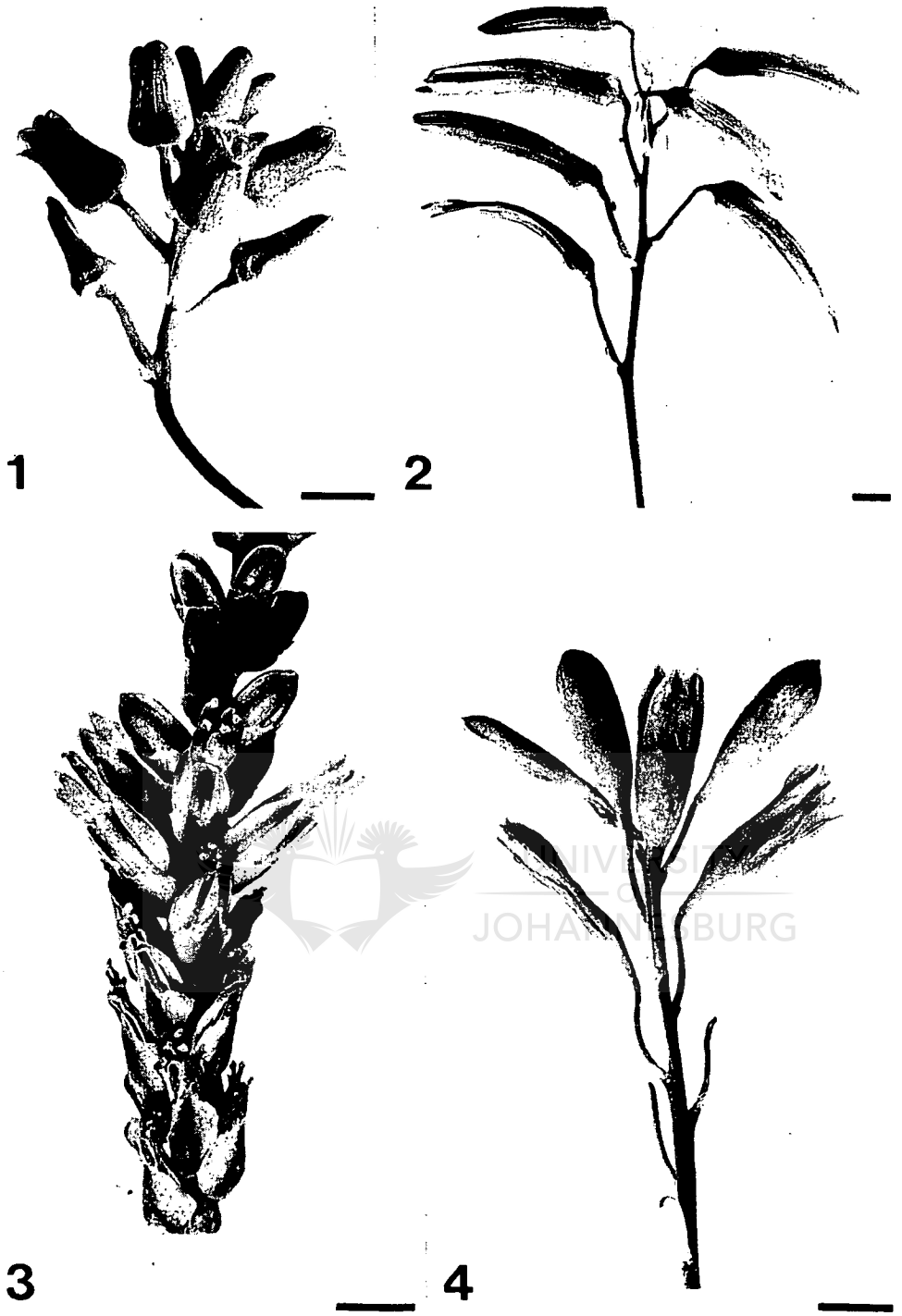

Fig 1-4. Inflorescences of selected Madagascan species of *Aloe* recently transferred to *Lemeea* (3) and *Guillauminia* (1, 2, 4). *1, A. descoingsii; 2, A. rauhii; 3, A. haworthioides; 4, A. bellatula.* The morphology of the flowers and inflorescences varies widely and inconsistently. *A. rauhii* stands out by its pendulous flowers. – Scale bar = 5 mm.

Table 3. The presence (+) or absence (–), in the species assigned by Heath (1993, 1994) to *Lemeea*, of the purportedly diagnostic features of that genus.

	A. haworthioides	*A. parvula*	*A. boiteaui*
Rosette small, dense	+	+	–
Leaves narrowly linear	+	+	+
Pedicels negligible	+	–	–
Outer perianth segments free	+	–	–
Filaments broad	+	–	–
Anthers exserted	+	–	+
small	+	–	–
bright orange	+	–	–
Ovary acute	–	–	?

The species transferred by Heath (1993, 1994) to either genus do not have any features that might even remotely warrant their segregation from *Aloe* (Fig. 1, 2, 4). Most do not show the diagnostic features of the genus to which they were transferred (Table 3-4).

We must conclude that neither segregate genus deserves recognition. Should Heath's views be followed, many more *Aloe* segregates would have to be reinstated or created for the sake of consistency. This would be detrimental to stability in the taxonomy and nomenclature of the *Aloaceae*. We conclude that both *Lemeea* and *Guillauminia* are best regarded as synonyms of *Aloe*.

Table 4. The presence (+) or absence (–), in the species assigned by Heath (1994) to *Guillauminia*, of the purportedly diagnostic features of that genus.

	A. albiflora	*A. bakeri*	*A. bellatula*	*A. calcairophylla*	*A. descoingsii*	*A. rauhii*
Inflorescence lax	+	+	+	+	+	+
Peduncle slender	+	+	+	+	+	+
Perianth segments free	+	+	–	–	–	+
white	+	–	–	+	–	–
campanulate	+	–	–	–	–	–
Anthers exserted	+	+	+	–	–	+

The nomenclature of *Aloe* species assigned by Heath to either *Lemeea* or *Guillauminia* resolves as follows:

Aloe albiflora Guillaumin in Bull. Mus. Hist. Nat. Paris, ser. 2, 12: 353. 1940 ≡ *Guillauminia albiflora* (Guillaumin) A. Bertrand in Cactus (Paris) 49: 41. 1956.

Aloe bakeri Scott-Elliot in J. Linn. Soc., Bot. 29: 60. 1891 ≡ *Guillauminia bakeri* (Scott-Elliot) P. V. Heath in Calyx 4: 147. 1994.

Aloe bellatula Reynolds in J. S. African Bot. 22: 132. 1956 ≡ *Guillauminia bellatula* (Reynolds) P. V. Heath in Calyx 4: 147. 1994.

Aloe boiteaui Guillaumin in Bull. Mus. Hist. Nat. Paris, ser. 2, 14: 349. 1942 ≡ *Lemeea boiteaui* (Guillaumin) P. V. Heath in Calyx 4: 147. 1994.

Aloe calcairophylla Reynolds in J. S. African Bot. 27: 5. 1961 ≡ *Guillauminia calcairophylla* (Reynolds) P. V. Heath in Calyx 4: 147. 1994.

Aloe descoingsii Reynolds in J. S. African Bot. 24: 103. 1958 ≡ *Guillauminia descoingsii* (Reynolds) P. V. Heath in Calyx 4: 147. 1994.

Aloe haworthioides Baker in J. Linn. Soc., Bot. 22: 529. 1887 ≡ *Aloinella haworthioides* (Baker) Lemée, Dict. Gen. Pl. Phan. 7, Suppl.: 27. 1939 ≡ *Lemeea haworthioides* (Baker) P. V. Heath in Calyx 3: 153. 1993.

Aloe parvula A. Berger in Engler, Pflanzenr. 33: 172-173. 1908 ≡ *Lemeea parvula* (A. Berger) P. V. Heath in Calyx 4: 147. 1994.

Aloe rauhii Reynolds in J. S. African Bot. 29: 151. 1963 ≡ *Guillauminia rauhii* (Reynolds) P. V. Heath in Calyx 4: 147. 1994.

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ANTHRONES FROM *ALOE MICROSTIGMA*

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Key Word Index—*Aloe microstigma*; Aloaceae; *C*-glucoside anthrone; 5-hydroxyaloin A; microstigmin A; caffeate; chemotaxonomy.

Abstract—5-Hydroxyaloin A and a new anthrone, named as microstigmin A, were isolated from the leaf exudate of *Aloe microstigma*. The structure of microstigmin A was determined by spectroscopic techniques as well as by conversion into 5-hydroxyaloin A. Copyright © 1997 Elsevier Science Ltd

INTRODUCTION

As part of our continuing study of the chemistry of *Aloe* species of Africa [1–3], we have investigated the constituents of the leaf exudate of *A. microstigma* Salm-Dyck, a species endemic to South Africa. We now report the isolation and characterization of the rare anthrone 5-hydroxyaloin A (**1**) as well as of its new natural derivative, 6′-*O*-caffeoyl-5-hydroxyaloin A (**2**), for which the trivial name microstigmin A is suggested. Rauwald and Beil [4] have already demonstrated the presence of **1**, the so-called 'periodate-positive substance' [5], in the leaf exudate of *A. microstigma* by means of TLC and HPLC analysis. The new compound **2** is restricted in its taxonomic distribution to species placed by Reynolds [6] in the *Aloe* series *Purpurascentes* Salm-Dyck (excluding *A. gariepensis* Pillans and *A. succotrina* Lam., but including *A. broomii* Schonl., *A. chlorantha* Lavranos and *A. pictifolia* Hardy). Compound **2** is thus an important chemotaxonomic marker for the series *Purpurascentes* as redefined here. A detailed phylogenetic analysis of the morphology, based on chemical characteristics, is in progress.

RESULTS AND DISCUSSION

Our investigation of the methanol-soluble part of the leaf exudate of *A. microstigma* showed three main constituents on TLC, with R_f values of 0.3, 0.5 and 0.6 (silica gel chloroform–methanol, 4:1). Column chromatography over silica gel with ethyl acetate–methanol gradients followed by further purification by prep. TLC and by column chromatograph, on Sephadex LH-20, eluting with methanol, led to the isolation of the two less polar substances (**1** and **2**). Work on the most polar substance with R_f 0.3 is in progress.

Identification of 5-hydroxyaloin A (**1**)

The yellow amorphous compound **1** with R_f 0.5 could be identified as the known 5-hydroxyaloin A according to the ^1H and ^{13}C NMR data (Tables 1 and 2) including the NOESY spectra. The negative-ion FAB mass spectrum exhibited a $[M-H]^-$ ion peak at m/z 433, which is in agreement with $C_{21}H_{22}O_{10}$ for 5-hydroxyaloin A. This compound has been reported earlier to occur only in a few *Aloe* species and is also known as a minor constituent of *A. ferox* Mill., the major source of Cape aloe [7].

Microstigmin A (**2**)

The constituent **2** with R_f 0.6 was obtained as a yellow amorphous solid. Positive-ion FAB mass analysis showed a pseudomolecular ion peak at m/z 597 $[M+H]^+$ indicating a M_r of 596. The molecular formula was found to be $C_{30}H_{28}O_{13}$ by HR mass spectrometry (597.1602 for $[M+H]^+$). In addition, the base peak in the EI mass spectrum at m/z 272 was in agreement with an anthrone moiety. The fragmentation pattern with peaks at m/z 180 $[(HO)_2C_6H_3CH{=}CHCOO]^+$, 163 $[(HO)_2C_6H_3CH{=}CHCO]^+$, 136 $[(HO)_2C_6H_3CH{=}CH+1]^+$, 123 $[(HO)_2C_6H_3CH+1]^+$

Table 1. ^{1}H NMR spectral data for 5-hydroxyaloin A (1) (in acetone-d_6) and microstigmin A (2) (in methanol-d_4-dimethyl sulphoxide-d_6)

H	1	2
1-OH	11.87 *s*	11.50 *s*
8-OH	11.46 *s*	11.20 *s*
2	6.89 *br s*	6.84 *d*(1.0)
4	7.16 *br s*	7.05 *d*(1.0)
6	6.78 *d*(8.9)	6.77 *d*(8.9)
7	7.18 *d*(8.9)	7.12 *d*(8.9)
10	4.83 *d*(2.1)	4.85 *d*(1.9)
H_2-15	4.69 *s*	4.64 *s*
1′	3.55 *dd*(9.7, 2.1)	3.40 *dd*(9.5, 1.9)
2′	2.88 *dd*(9.7, 9.6)	3.02 *dd*(9.5, 9.4)
3′	3.30	3.34 *t*
4′	3.03	2.98 *t*
5′	3.01	3.14 *ddd*(9.5, 6.9, 1.9)
6′$_a$	3.45 *dd*	3.93 *dd*(11.8, 6.9)
6′$_b$	3.56 *dd*	4.34 *dd*(11.8, 1.9)
2″		7.14 *d*(1.9)
5″		6.87 *d*(8.2)
6″		7.04 *dd*(8.2, 1.9)
7″		7.45 *d*(15.9)
8″		6.20 *d*(15.9)

Coupling constants (J in Hz) in parentheses.

Table 2. ^{13}C NMR spectral data of 5-hydroxyaloin A (1) (in acetone-d_6) and microstigmin A (2) (in methanol-d_4)

C	1	2
1	162.8	162.8
2	113.6	114.2
3	152.7	152.0
4	117.6	117.5
5	147.0	147.3[a]
6	117.3	117.6
7	125.3	124.6
8	156.8	156.9
9	195.3	195.4
10	40.9	40.6
11	118.5	119.2
12	126.9	126.4
13	117.1	118.2
14	145.4	146.4
15	64.1	64.5
1′	84.4	85.8
2′	72.8	73.0
3′	78.9	78.6
4′	72.0	71.9
5′	81.0	79.0
6′	63.3	64.8
1″		127.9
2″		115.6
3″		146.7[a]
4″		149.5
5″		116.4
6″		123.0
7″		146.9
8″		115.0
9″		169.0

[a] Assignments may be interchanged in this column.
Signal assignments are based on ^{1}H–^{13}C COSY spectrum.

and 110 $[(HO)_2C_6H_3+1]^+$ suggested a caffeate unit as part of the molecule.

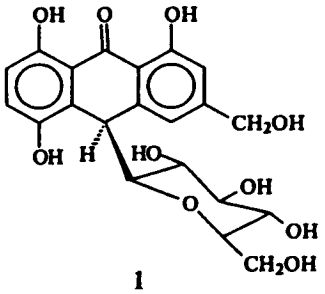
The IR spectrum of **2** exhibited absorptions consistent with a hydroxyl (3390 cm^{-1}), a conjugated ester carbonyl (1685 cm^{-1}) and a chelated carbonyl group (1637 cm^{-1}). The ^{13}C NMR and DEPT spectra showed signals for 30 different carbon atoms corresponding to two oxymethylenes, 15 methines and 13 quaternary carbon atoms including one chelated carbonyl (δ 195.4) and one ester carbonyl carbon (δ 169.0). Further evidence was obtained from the ^{1}H NMR spectrum of **2**, which showed signals comparable to those of **1**: oxymethylene protons H_2-15 (δ 4.64, *s*), a methine proton H-10 (δ 4.85, *d*, J = 1.9 Hz), two *meta*-coupled aromatic protons H-2 (δ 6.84, *d*, J = 1.0 Hz) and H-4 (δ 7.05, *d*, J = 1.0 Hz) as well as two *ortho*-coupled aromatic protons H-6 (δ 6.77, *d*, J = 8.9 Hz) and H-7 (δ 7.12, *d*, J = 8.9 Hz). The downfield shift of the signals corresponding to the C-6′-methylene protons in **2** (from δ 3.45 and 3.58 in **1** to δ 3.93 and 4.34 in **2**) is in agreement with the esterification of this hydroxyl group. Analysis of the signals for protons assignable to two *trans*-vinyl H-8″ (δ 6.20, *d*, J = 15.9 Hz) and H-7″ (δ 7.45, *d*, J = 15.9 Hz) and to three aromatic protons H-2″ (δ 7.14, *d*, J = 1.9 Hz), H-5″ (δ 6.87, *d*, J = 8.2 Hz) and H-6″ (δ 7.04, *dd*, J = 8.2 and 1.9 Hz) led to a *trans*-caffeoyl residue as carbonyl part.

Compound **2** was hydrolysed under acidic conditions to give **1**. Important observations from the NOESY and ^{1}H–^{1}H COSY can be summarized as follows (see also Fig. 1): (i) cross peaks between the methine proton H-10 (δ 4.85, *d*) with H-1′ (δ 3.40, *dd*) of the glucose moiety and with only one of the aromatic protons H-4 (δ 7.05, *d*); (ii) cross peaks of the oxymethylene protons H_2-15 (δ 4.64, *s*) with two aromatic protons H-2 (δ 6.84, *d*) and H-4 (δ 7.05, *d*); (iii) *ortho* coupling between the two aromatic protons H-6 (δ 6.77, *d*) and H-7 (δ 7.12, *d*).

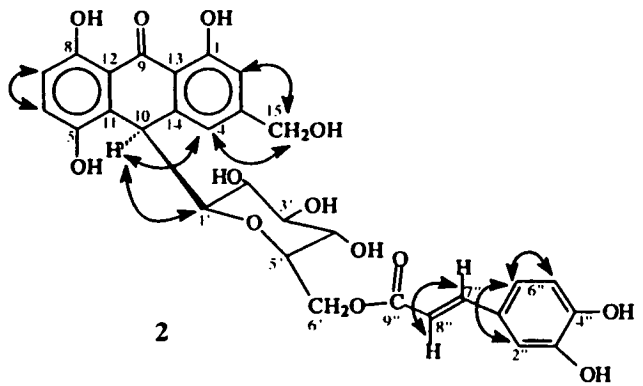
Rauwald and Beil have already demonstrated, that **1** naturally exists only in the more stable A form, in which the glucose moiety has a β-orientation at C-10 [4]. This is in contrast to aloin, which is found as a mixture of the A and the B form. Indeed, for **1** we do not observe signal doubling in the ^{1}H and ^{13}C NMR spectra or other characteristics (e.g. two spots on TLC) which are typical of aloe anthrones existing as diastereomeric pairs. Since the circular dichroic spectra (Fig. 2) of **1** and **2** are very similar, the β-orientation can be deduced also for the glucose moiety at C-10 in **2**. All of the above data are in agreement with structure **2** for the new compound: 6′-*O*-*trans*-caffeoyl-5-hydroxyaloin A, named as microstigmin A.

EXPERIMENTAL

General. Mps: uncorr. Optical rotation in MeOH; UV in MeOH; IR: KBr discs; ^{1}H and ^{13}C NMR



1



2

Fig. 1. NOESY and ^1H–^1H correlations of compound 2.

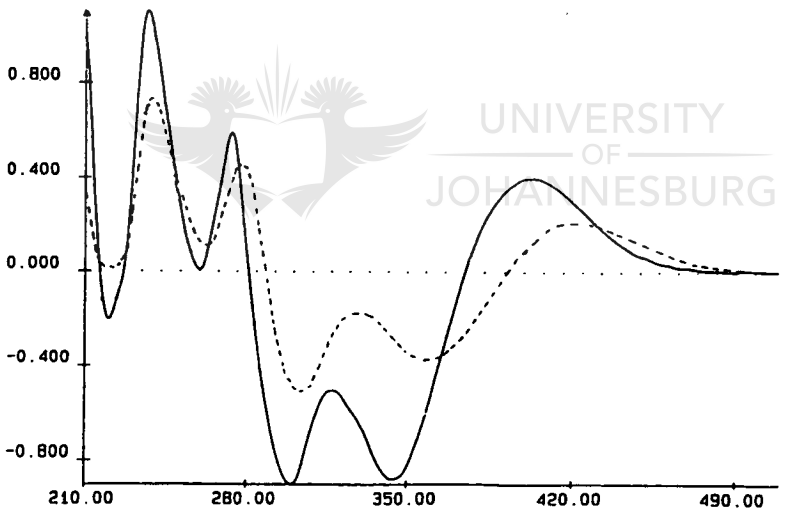


Fig. 2. CD spectra in methanol of microstigmin A (——) and 5-hydroxyaloin A (– – –).

(Bruker ARX 300, 300 and 75 MHZ, respectively) in Me_2CO-d_6 or MeOH-d_4 with the solvent as int. standard; FAB-MS (Finnigan MAT 90 or Finnigan MAT 95Q double focusing instrument with Cs gun): *m*-NBA-matrices; TLC solvent system on silica gel: I($CHCl_3$–MeOH, 4:1).

Plant material. A bulk sample of leaf exudate of *A. microstigma* was collected from a natural population near Worcester in the Western Cape Province of South Africa and identified by B.-E. Van Wyk.

Extraction and isolation. Leaf exudate of *A. microstigma* (10 g) was taken up in MeOH. The MeOH extract was concd and the residue was subjected to flash CC over silica gel eluting with EtOAc and MeOH gradients. The frs were further purified by applying to prep. TLC plates and Sephadex LH-20 (MeOH), which resulted in isolation of pale yellow substances: **1** (30 mg) and **2** (200 mg), respectively.

5-Hydroxyaloin A (**1**). Yellow amorphous solid. $[\alpha]_D$ −70° (MeOH; *c* 1.0). R_f 0.5 (solvent I). UV λ_{max} nm:

271, 298, 355. IR ν_{max} cm^{-1}: 3425, 1634, 1601, 1447, 1380, 1273. ^{1}H NMR (Table 1) and ^{13}C NMR (Table 2). Negative-ion FAB-MS: *m/z* 433 $[M-H]^-$; positive-ion FAB-MS: *m/z* 419 $[M-OH+H]^+$.

Microstigmin A (**2**). Yellow solid, mp 152–154°. $[\alpha]_D$ −20° (MeOH; *c* 1.0). R_f 0.6 (solvent I). UV λ_{max} nm: 245, 299, 329. IR ν_{max} cm^{-1}: 3390, 1685, 1637, 1607, 1465, 1376, 1273, 1185. ^{1}H NMR (Table 1) and ^{13}C NMR (Table 2). Negative-ion FAB-MS: *m/z* 595 $[M-H]^-$; positive-ion FAB-MS: *m/z* 619 $[M+Na]^+$, 597 $[M+H]^+$, HR-MS: 597.1602, calc. 597.1608; EIMS *m/z* (rel. int.): 596 (9), 323 (22), 309 (38), 295 (47), 272 (100), 180 (25), 163 (16), 136 (66), 123 (23), 110 (13).

Acid hydrolysis of **2**. A soln of **2** (10 mg) in 1% methanolic HCl (2 ml) was stirred for 6 hr at room temp. After removal of solvent, the reaction mixt. was neutralized with 10% $NaHCO_3$ and extracted with $CHCl_3$ to give a product (3 mg) identical to **1** (co-TLC and ^{1}H NMR).

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10-Hydroxyaloin B 6′-*O*-Acetate, an Oxanthrone from *Aloe claviflora*

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Analysis of the leaf exudate of *Aloe claviflora* resulted in the isolation of a new oxanthrone, 10-hydroxyaloin B 6′-*O*-acetate (**1**), whose structure was determined on the basis of spectral evidence as well as by conversion to the known compound 10-hydroxyaloin B (**2**).

Aloe species are known to elaborate anthrones, the most common of which is aloin or barbaloin. Recently, a number of oxanthrones based on the aloin skeleton have been discovered, in particular in leaves of *Aloe* species that belong to the series *Asperifoliae*.[1-3] *Aloe claviflora* Strydenburg (Aloaceae), which also belongs to this series, is the only species of *Aloe* that occurs in Strydenburg, Free State Province, South Africa.[4] Subjecting the methanolic extract of the leaf exudate of this species to column chromatography over reversed-phase Si gel yielded the oxanthrone (**1**), which exhibited pseudomolecular ions at *m/z* 477 ($[M + H]^+$) and 499 ($[M + Na]^+$) in its positive ion FABMS, indicating an M_r of 476. The HRESIMS of **1** revealed a $[M + Na]^+$ peak at *m/z* 499.1228, which corresponded to the molecular formula $C_{23}H_{24}O_{11}$ (see Tables 1 and 2). The IR spectrum of **1** suggested the presence of hydroxyl (3385 cm^{-1}), unconjugated ester carbonyl (1718 cm^{-1}), and chelated carbonyl (1636 cm^{-1}) functional groups.

The ^{13}C-NMR spectrum of **1**, including the DEPT measurements, showed 23 carbon atoms comprising 1 methyl (δ 20.6), 2 oxymethylenes (δ 64.6, 64.9), 10 methines, and 10 quaternary carbons, of which two are carbonyls. The presence of two chelated hydroxyl groups was further confirmed from the ^1H-NMR spectrum, which showed two singlets at δ 11.67 and 11.75. Assignments of the five aromatic protons and the other ^1H-NMR signals are shown in Table 1.

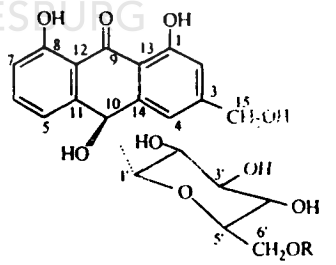
The acetate unit was placed at C-6′ of the glucose moiety due to the downfield shift of the signals of these methylene protons in **1** (δ 3.75, 4.12) relative to those in **2** (δ 3.32, 3.50). Acid hydrolysis of **1** yielded the known compound **2**, an observation that also served to prove the α orientation of the glucose group at C-10, insofar as this fact was established earlier[2] for **2** by comparing its CD spectrum with that reported by Rauwald and Lohse.[1] Thus, compound **1** was assigned as 10-hydroxyaloin B 6′-*O*-acetate.

The remaining compounds were identified as the recently described oxanthrones littoraloin and deacetyllitoraloin by comparison with authentic samples, HPLC analysis, and spectral data.[2,3] Compound **1** was reported earlier as an unknown with t_R 22.4 by HPLC, and it was also indicated that it is one of the chemotaxonomic markers for the series *Asperifoliae* of *Aloe*.[3]

Table 1. ^1H NMR Spectral Data of 10-Hydroxyaloin B 6′-*O*-acetate (**1**) and 10-Hydroxyaloin B (**2**) (300 MHz, MeOH-d_4)[a]

proton	1	2
OH-1	11.67[b](s)	11.76[b](s)
OH-8	11.75[b](s)	11.81[b](s)
2	6.99 (d, 1.1)	6.87 (d, 1.5)
4	7.56 (d, 1.1)	7.40 (d, 1.5)
5	7.45 (dd, 8.0, 0.7)	7.32 (dd, 7.8, 1.0)
6	7.67 (t, 8.0)	7.62 (t, 7.8)
7	7.02 (dd, 8.0, 0.7)	6.93 (dd, 7.8, 1.0)
H_2-15	4.58 (s)	4.60 (s)
1′	3.25 (d)	3.23 (d)
2′	3.12 (t)	3.08 (t)
3′	3.34 (t)	3.38 (t)
4′	2.81 (t)	2.92 (t)
5′	3.07 (m)	2.98 (m)
$6'_1$	4.12 (dd, 11.8, 1.9)	3.50 (dd)
$6'_2$	3.75 (dd, 11.8, 7.2)	3.32 (dd)
OAc	2.01 (s)	

[a] In parentheses are given the multiplicities of the signals and the coupling constants *J* in Hz. [b] Spectrum recorded in DMSO-d_6.



1 R = Ac
2 R = H

Experimental Section

General Experimental Procedures. The melting point was determined with Kofler apparatus and is uncorrected. The optical rotation was measured on a Perkin–Elmer 241 polarimeter. The UV spectrum was obtained on Milton Roy Spectronic 1001 Plus instrument. The IR spectrum was taken with a Perkin–Elmer 1600 series FT-IR spectrometer. The NMR spectra (MeOH-d_4, 300 MHz for ^1H and 75 MHz for ^{13}C) were recorded on a Bruker AMXR 300 NMR spectrometer with TMS as internal standard. The FABMS (positive ion mode) was conducted on a Finnigan MAT 95Q double-focusing mass spectrometer with a cesium gun: glycerin matrixes. Column chromatography was carried out over reversed-phase Si gel with PrepPAK

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Table 2. ^{13}C-nmr Spectral Data of 10-Hydroxyaloin B 6′-*O*-acetate (**1**) and 10-Hydroxyaloin B (**2**) (75 MHz, MeOH-d_4)[a]

carbon	1	2
1	162.4	162.3
2	114.9	114.5
3	152.9	152.9
4	115.4	115.4
5	118.9	118.1
6	136.3	136.1
7	118.2	117.7
8	162.8	162.5
9	194.4	194.2
10	77.3	76.7
11	146.2	146.5
12	117.7	117.2
13	116.5	115.6
14	149.8	148.8
15	64.6	64.2
1′	84.2	84.1
2′	72.8	72.7
3′	79.2	79.1
4′	71.2	71.5
5′	78.7	80.9
6′	64.9	63.0
$OCCH_3$	172.3	
$OCCH_3$	20.6	

[a] Signal assignments are based on ^1H–^{13}C COSY and DEPT.

500 (Waters Associates). The HRESIMS was recorded on MAT 95Q with API II interface and electrospray head.

Plant Material. A bulk sample of leaf exudate of *Aloe claviflora* was collected at Strydenburg, Free State Province, South Africa, in January 1996, and identified by B.-E.V.W. A voucher specimen has been deposited at the Botany Department, Rand Afrikaans University.

Extraction and Isolation. The MeOH-soluble portion of the leaf exudate (5 g) of *A. claviflora* was subjected to column chromatography over reversed-phase Si gel eluting with MeOH and H_2O gradients. The fourth fraction, which was eluted by MeOH–H_2O (1:1), resulted in the isolation of a pale yellow substance (**1**, 80 mg) after removal of H_2O by freeze-drying. The remaining fractions were further purified by preparative TLC ($CHCl_3$–MeOH, 4:1), which gave the yellow substances littoraloin, deacetyllitoraloin, and 10-hydroxyaloin B (**2**).

10-Hydroxyaloin B 6′-*O*-acetate (1): yellow amorphous solid; mp 296–298 °C; $[\alpha]^{23}_D$ −41° (*c* 1.0, MeOH); UV (MeOH) λ_{max} (log ϵ) 270 (3.62), 300 (4.20), 370 (4.43) nm; IR (KBr) λ_{max} 3385 (br), 2924, 1718, 1636, 1616, 1560, 1456, 1422 cm^{-1}; ^1H NMR (Table 1) and ^{13}C NMR (Table 2); FABMS (positive ion mode) *m/z* 499 [M + Na]$^+$ (10), 477 [M + H]$^+$ (1), 459 [M + H − H_2O]$^+$ (9), 272 [M + H − Glc − 6′-OAc]$^+$ (14); HRESIMS [M + Na]$^+$ at *m/z* 499.1228, calcd for $C_{23}H_{24}O_{11}$, 499.1216, R_f 0.6 ($CHCl_3$–MeOH, 4:1).

Hydrolysis of Compound 1 to 10-Hydroxyaloin B (2). A solution of **1** (8 mg) in 1% methanolic HCl (2 mL) was stirred for 6 h at room temperature. After removal of the solvent, the reaction mixture was neutralized with 10% $NaHCO_3$ and extracted with EtOAc to give a product (4 mg) identical with **2** (co-TLC and ^1H NMR).

Acknowledgment. We thank Professor W. Steglich, Ms V. Hellwig, and Mr W. Spahl of the University of Munich (Germany) for NMR and FAB measurements.

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PII: S0031-9422(96)00302-0

Phytochemistry, Vol. 43, No. 4, pp. 867–869, 1996

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ALOERESINS E AND F, TWO CHROMONE DERIVATIVES FROM *ALOE PEGLERAE*

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(*Received in revised form* 28 *March* 1996)

Key Word Index—*Aloe peglerae*; Asphodelaceae; 5-methylchromone; aloesin; cinnamoyl esters.

Abstract—The structures of two new aloesin derivatives isolated from *Aloe peglerae*, *viz.*, 2-acetonyl-8-(2-*O*-cinnamoyl-β-D-glucopyranosyl)-7-β-D-glucopyranosyloxy-5-methylchromone (aloeresin E) and 2-acetonyl-8-(2-*O*-cinnamoyl-β-D-glucopyranosyl)-7-hydroxy-5-methylchromone (aloeresin F) were determined by spectroscopic methods.

INTRODUCTION

According to Reynolds [1], *Aloe peglerae* occupies a taxonomic position in *Aloe* series *Longistylae* Berger. However, morphological and chemotaxonomic evidence has shown that *Aloe* series *Longistylae* is an unnatural group and that the three species constituting this group, *A. peglerae*, *A. longistyla* and *A. broomii*, have different leaf exudate compositions and morphological characters (B.-E. van Wyk and A. M. Viljoen, unpublished results). HPLC analysis of the methanol extract of the leaves of *A. peglerae* revealed, apart from the known metabolites, aloesin (**1**), homonataloin A and homonataloin B, the presence of two unidentified compounds that are of particular importance in the chemotaxonomic study of the genus *Aloe*. We now report the isolation and identification of these two compounds.

RESULTS AND DISCUSSION

Aloesin (**1**), homonataloin A and homonataloin B were identified by comparison with authentic samples (HPLC, retention times and UV data). The UV spectra of the two unknown compounds were closely related to that of aloesin (**1**) and these two compounds were named aloeresin E (**2**) and aloeresin F (**3**), respectively. The M_r of aloeresin F (**3**) was determined by FAB-mass spectrometry ($[M]^+$ *m/z* 524). The fragmentation pattern observed in the EI-mass spectrum suggested the presence of a cinnamoyl ester (*m/z* 147, 131 and 77). The ^1H and ^{13}C NMR data of the key structural features of aloeresin E, *viz.*, the acetonyl, γ-pyrone, 5-Me, 7-OH and 8-*C*-glucoside, were in close agreement with those reported for aloesin [2, 3], confirming the similarity between the two compounds. In addition, the NMR data also revealed the presence of a cinnamoyl ester residue (δ_H 6.37 and 7.37, $J = 16$ Hz, *trans*-α,β-unsaturated carbonyl; δ_H 7.37 and 6.60, monosubstituted phenyl; δ_C 165.1, ester carbonyl). The remaining ambiguity, i.e. the position of the cinnamoyl group, was resolved by chemical shift considerations. The triplet at δ_H 5.49 collapsed upon irradiation of the signal at δ_H 4.92 (*d*, assigned to H-1′) and was assigned to H-2′. The chemical shift of this signal is characteristic of a proton influenced by the anisotropic effect of an ester carbonyl; the cinnamoyl group was, therefore, located at C-2 of the carbohydrate moiety. On the basis of this evidence, structure **3** was assigned unequivocally to aloeresin F.

The M_r of aloeresin E (*m/z* 686) was determined by FAB-mass spectrometry. This information, with support of NMR data, suggested that the only difference between the structures of aloeresins E (**2**) and F (**3**) was the presence of an additional *O*-glucoside moiety in aloeresin E (**2**). The differences in chemical shifts observed for the aromatic carbons of aloeresin E (**2**) and of aloeresin F (**3**) indicated that the 7-hydroxyl group, and not one of the carbohydrate hydroxyl functions, had been subjected to glucosidation. Structure **2** was, therefore, assigned to aloeresin E. The close agreement of the spectroscopic data of aloeresin E (**2**) with those of aloeresin C, another 7-*O*-β-D-glucosyl derivative of aloesin [4], confirmed the assigned structure.

Although cinnamic acid derivatives are present in other *Aloe* metabolites, e.g. in the aloin series [5],

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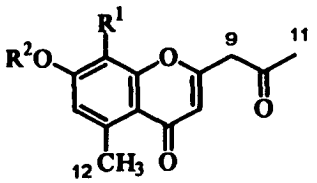
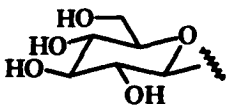


1: R^1 = 

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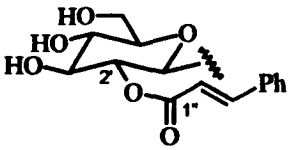
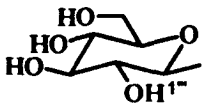
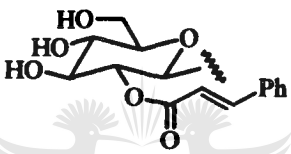
2: R^1 = 

R^2 = 

3: R^1 = 

R^2 = H

aloeresin E (2) and aloeresin F (3) represent the first cinnamic acid derivatives in the aloeresin series of metabolites.

EXPERIMENTAL

Analytical HPLC analysis was performed on a C_{18} column (5μ, 4.5 × 250 mm, flow 1 ml min^{-1}) with the following gradient system: 30% MeOH in H_2O (1 min), 30%–60% MeOH in H_2O (25 min) and 60%–100% MeOH (2 min). Peaks were detected with a photodiode array detector. For prep. HPLC a C_{18} column (5μ, 10 × 250 mm, flow 4.5 ml min^{-1}) was used with the following gradient system: 30%–50% MeOH in H_2O (4 min), 50% MeOH in H_2O (9 min) and 50%–100% MeOH (2 min).

Isolation of metabolites. Fresh, chopped leaves (771 g) of *A. peglerae* were soaked in MeOH (24 hr, room.temp.) to dissolve the exudate. After filtration and evapn, a dark brown residue (12 g) was obtained. Analysis of the sample by analytical HPLC revealed the presence of aloesin (R_f 6.9, 30%), aloeresin E (R_f 20.1, 22%), aloeresin F (R_f 25.1, 12%), homonataloin B (R_f 26.1, 7%) and homonataloin A (R_f 27.8, 10%). A portion of the extract (0.95 g) was subjected to prep. HPLC to afford aloeresins E (11 mg) and F (5 mg).

Table 1. ^{13}C NMR data of compounds 2 and 3 (50 MHz, DMSO-d_6)

C	2	3	C	2	3
2	160.7	160.7	4′	70.1	70.8
3	112.6	112.6	5′	81.5	81.9
4	178.5	179.0	6′	61.7	61.9
4a	115.1	114.7	1″	165.1	165.4
5	141.3	141.2	2″	118.1	118.0
6	116.6	116.1	3″	143.7	144.5
7	157.4	158.7	4″	134.2	134.1
8	112.1	109.1	5″,9″	128.8	129.2
8a	158.1	159.8	6″,8″	128.1	128.4
9	47.9	48.2	9″	130.2	130.7
10	202.1	202.8	1‴	101.0	—
11	29.5	29.8	2‴	73.2	—
12	22.8	22.8	3‴	76.4	—
1′	69.6	70.8	4‴	70.8	—
2′	72.4	72.8	5‴	77.1	—
3′	74.9	76.1	6‴	60.5	—

Aloeresin E. Amorphous solid. $[\alpha]_D^{20}$ −126° (MeOH, *c* 1.4). UV λ_{max}^{MeOH} (nm) 285, 250, 215. ^1H NMR (200 MHz, DMSO-d_6): δ 2.26 (3H, *s*, H-11), 2.61 (3H, *s*, H-12), 3.2–3.8 (13H, *m*, sugar-H), 3.80 (2H, *s*, H-9), 4.46 (1H, *br s*, OH), 4.58 (1H, *br s*, OH), 4.74 (1H, *d*, *J* = 7.5 Hz, H-1‴), 5.1–5.3 (3H, *m*, H-1′, 2 × OH), 5.44 (1H, *t*, *J* = 9 Hz, H-2′), 5.78 (1H, *br s*, OH), 6.21 (1H, *s*, H-3), 6.33 (1H, *d*, *J* = 16 Hz, H-2″), 6.95 (1H, H-6), 7.38 (3H, *m*, H-6″, 7″, 8″), 7.48 (1H, *d*, *J* = 16 Hz, H-3″), 7.62 (2H, *m*, H-5″, 9″). ^{13}C NMR: see Table 1. EIMS: *m/z* (rel. int.): 376 (4), 245 (5), 163 (10), 147 (21), 131 (20), 103 (24), 85 (20), 73 (53), 71 (41), 60 (47), 43 (100). FAB-MS: *m/z* 687 $[M + 1]^+$.

Aloeresin F. Amorphous solid. $[\alpha]_D^{20}$ −120° (MeOH, *c* 0.8). UV λ_{max}^{MeOH} (nm) 285, 250, 215. ^1H NMR (200 MHz, DMSO-d_6): δ 2.25 (3H, *s*, H-11), 2.55 (3H, *s*, H-12), 3.2–3.6 (6-H, *m*, sugar-H), 3.77 (2H, *s*, H-9), 4.46 (1H, *br s*, OH), 4.92 (1H, *d*, *J* = 10 Hz, H-1′), 5.20 (1H, *br s*, OH), 5.26 (1H, *br s*, OH), 5.49 (1H, *t*, *J* = 10 Hz, H-2′), 6.14 (1H, *s*, H-3), 6.37 (1H, *d*, *J* = 16 Hz, H-2″), 6.57 (1H, *s*, H-6), 7.37 (4H, *m*, H-3″, 6″, 7″, 8″), 7.60 (2H, *m*, H-5″, 9″). ^{13}C NMR: see Table 1. EIMS: *m/z* (rel. int.): 524 (8), 376 (34), 298 (10), 285 (12), 261 (33), 257 (43), 245 (28), 219 (25), 215 (24), 147 (100), 131 (78), 103 (66), 91 (27), 77 (46), 51 (27), 43 (84). FAB-MS: *m/z* 547 $[M + Na]^+$, 525 $[M + 1]^+$.

Acknowledgement—We gratefully acknowledge the financial support of the Foundation for Research Development.

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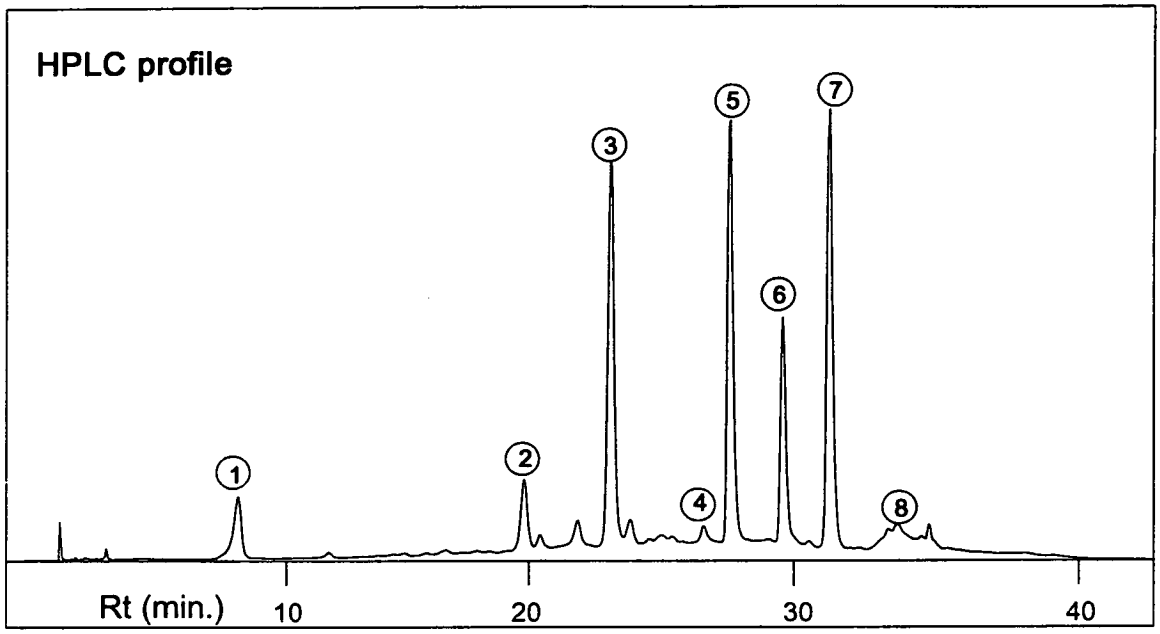
Appendix 2

A chromatographic atlas of species analysed

Aloe aageodonta L.E. Newton



Peak number	Retention time	Compound	Percentage
1	7.8	7-*O*-methyl aloesin	5
2	18.84	unidentified chromone	4
3	22.15	aloeresin D	22
4	25.67	aloin B	1
5	26.66	aloin A	22
6	28.71	aloinoside B	11
7	30.46	aloinoside A	23

The leaf exudate of *A. aageodonta* contains three chromones and the anthrones aloin A and B with the corresponding aloinosides. Note the quantitative imbalance between the isomers. The 'peak' denoted by 8 is most probably low concentrations of microdontins A and B.

Distribution

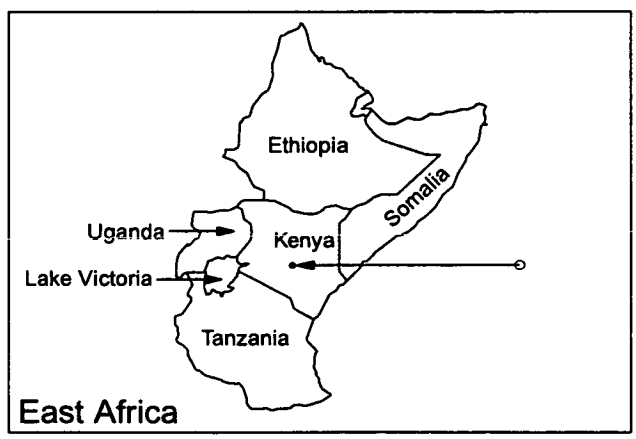
- Taxonomic position:

  Allied to *A. lensayuensis* (Newton, 1993).

- Samples analysed:

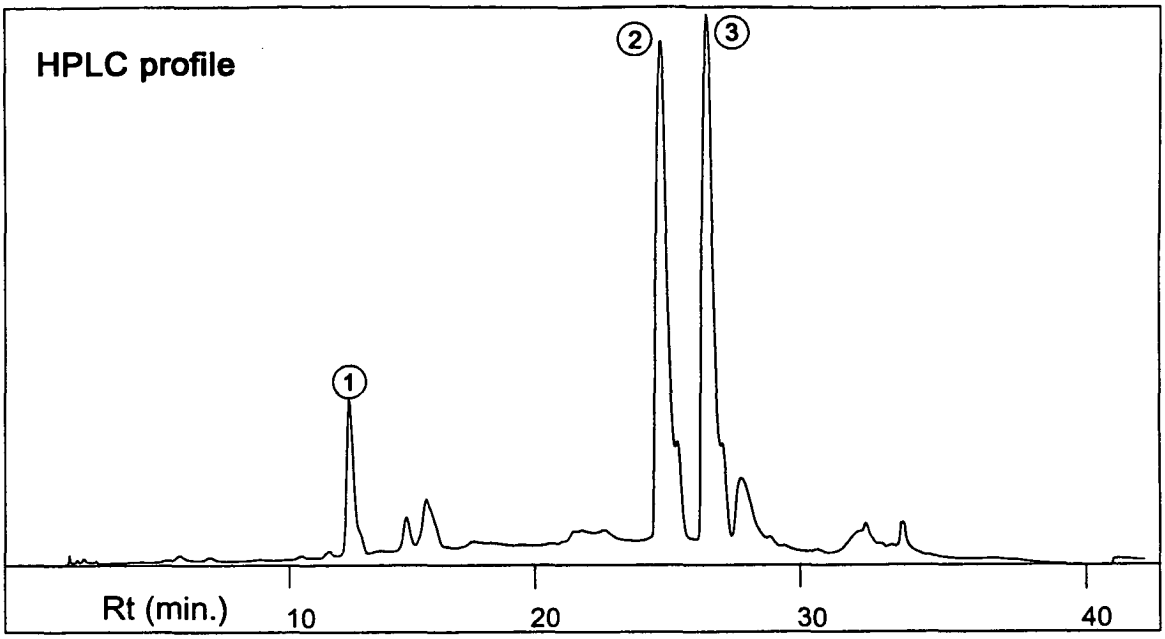
  The leaf exudate was investigated:

  - L. E. Newton 3643 (type specimen)



This species is only known from the Muvaroa and Waita Hills in the Eastern Province of Kenya.

Aloe abyssicola Lavranos & Bilaidi



Peak number	Retention time	Compound	Percentage
1	13.10	Homonataloside B	7.0
2	25.32	Homonataloin B	32.6
3	27.10	Homonataloin A	34.7

The novel anthrone recently isolated from *A. lutescens*, homonataloside B, co-occurs with homonataloin A and B.

- Taxonomic position:

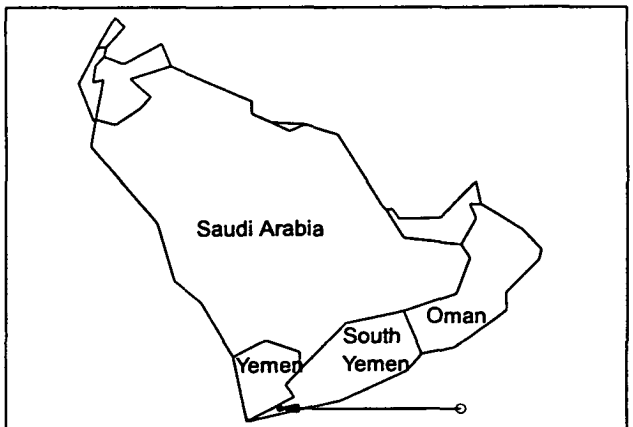
  Group 6, 7 or 10 of the tropical aloes, (Lavranos & Bilaidi, 1971).

- Samples analysed:

  The leaf exudate was investigated:

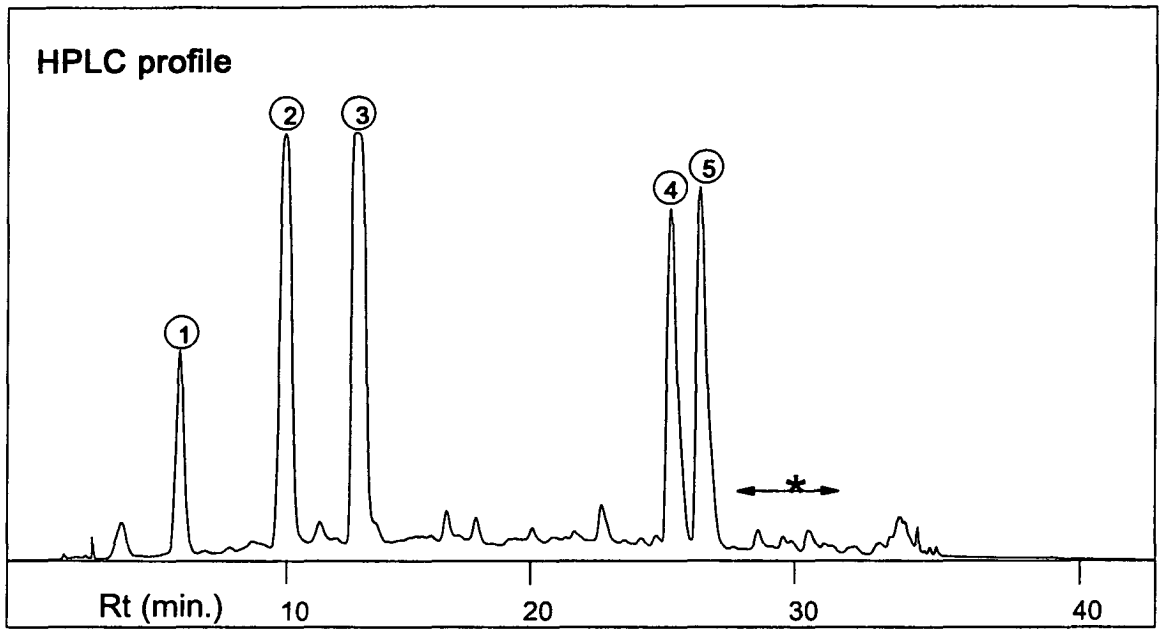
  - NBI 15813

Distribution



Aloe abyssicola is known to occur at Jabal al Arays in south Yemen.

Aloe aculeata Pole-Evans



Peak number	Retention time	Compound	Percentage
1	6.51	aloesin	7
2	10.49	unidentified chromone 1	22
3	13.14	aloeresin C	25
4	25.00	aloin B	16
5	26.09	aloin A	17

The sample from the Witwatersrand Botanical Garden did not contain aloeresin C. The peaks in the area marked * show UV absorbance spectra similar to that for aloin and could possibly be low concentrations of aloinoside A and B.

- Taxonomic position:

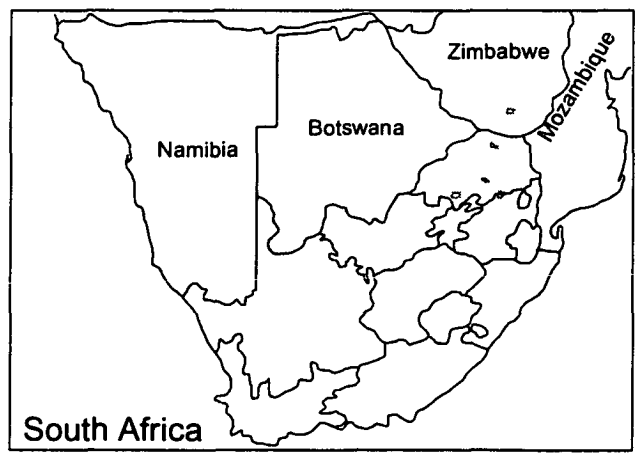
  Aloe section *Pachydendron* (Reynolds, 1950).

- Samples analysed:

  The leaf exudate was investigated:

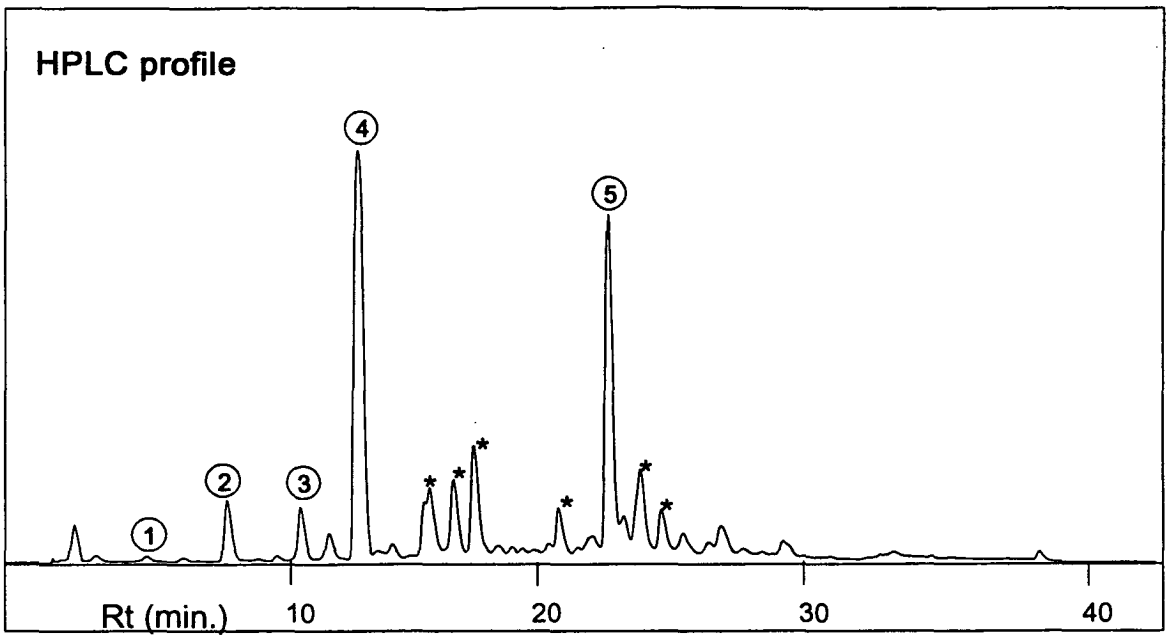
  - NBG 786/69
  - ex hort WBG

Distribution



This species is widely distributed in the Mpumalanga and Northern Province of South Africa and in the southern parts of Zimbabwe.

Aloe acutissima H. Perrier var. *acutissima*



Peak number	Retention time	Compound	Percentage
1	5.21	aloesin	tr
2	8.20	unidentified chromone 1	4
3	10.98	unidentified chromone 2	3
4	13.09	unidentified chromone 3	33
5	22.51	unidentified chromone 4	21

All the compounds in the leaf exudate of *A. acutissima* are coumaroyl chromones derivatives (including peaks denoted by *). This species contains no anthrones.

- Taxonomic position:

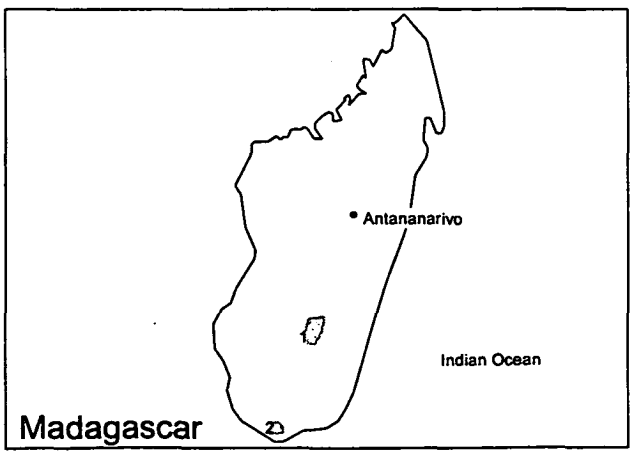
  Group 8 (Reynolds, 1966).

- Samples analysed:

  The leaf exudate was investigated:

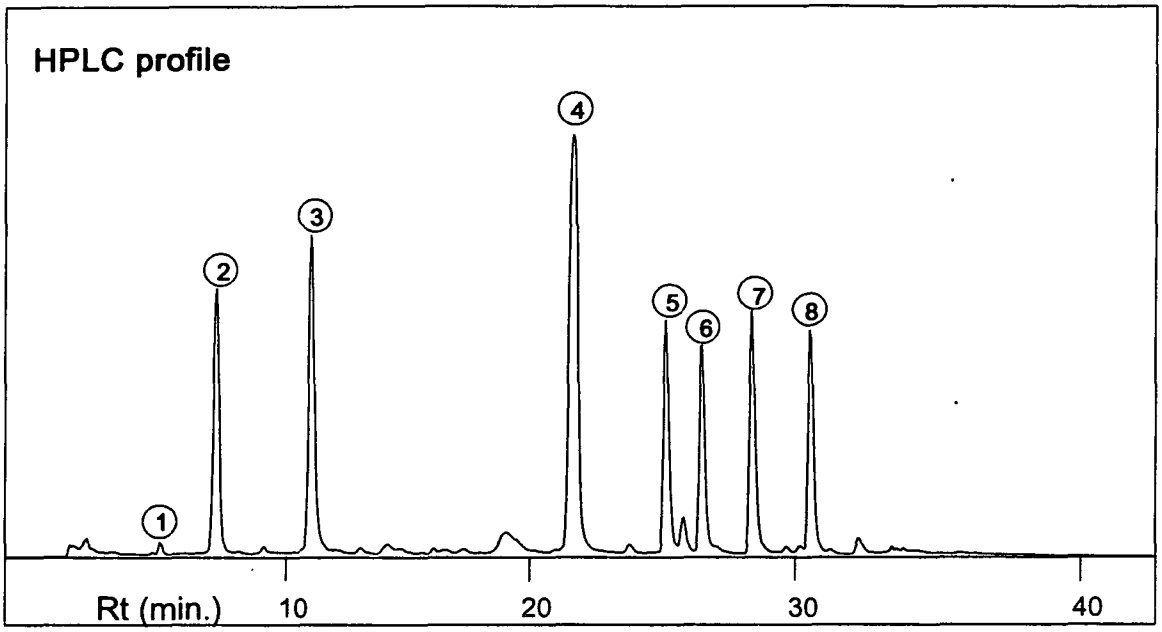
  - Lavranos *et al.* 30009

Distribution



This species is restricted to rocky places near Ambalavao (1) and Tranoroa (2) in the southern parts of Madagascar.

Aloe africana Miller



Peak number	Retention time	Compound	Percentage
1	5.91	aloesin	1
2	8.02	unidentified chromone 1	11
3	11.81	unidentified chromone 2	4
4	21.55	africana chromone*	26
5	25.18	aloin B	4
6	26.48	aloin A	5
7	28.36	aloinoside B	10
8	30.55	aloinoside A	8

Aloe africana is the species from which the compounds denoted by 4 has been isolated and characterised *(E-2-acetonyl-8-(2'-*O*-feruloyl)-β-D-gluco-pyranosyl-7-methoxy-5-methylchromone). The unidentified chromone 2 displays the same UV absorbance spectra as peak 4 indicating that it could possibly be a feruoyl chromone.

- Taxonomic position:

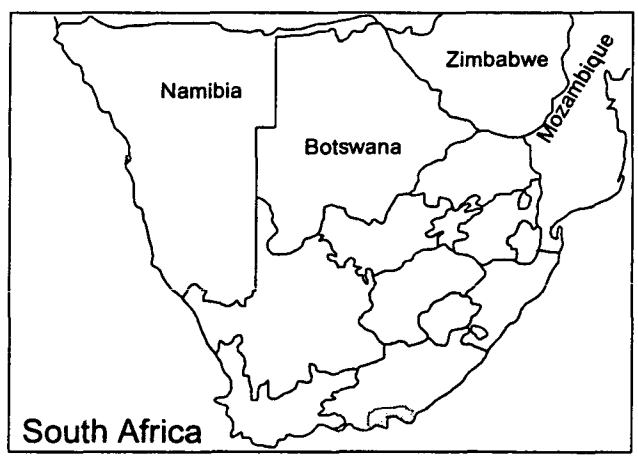
  Aloe section *Pachydendron* (Reynolds, 1950).

- Samples analysed:

  The leaf exudate was investigated:

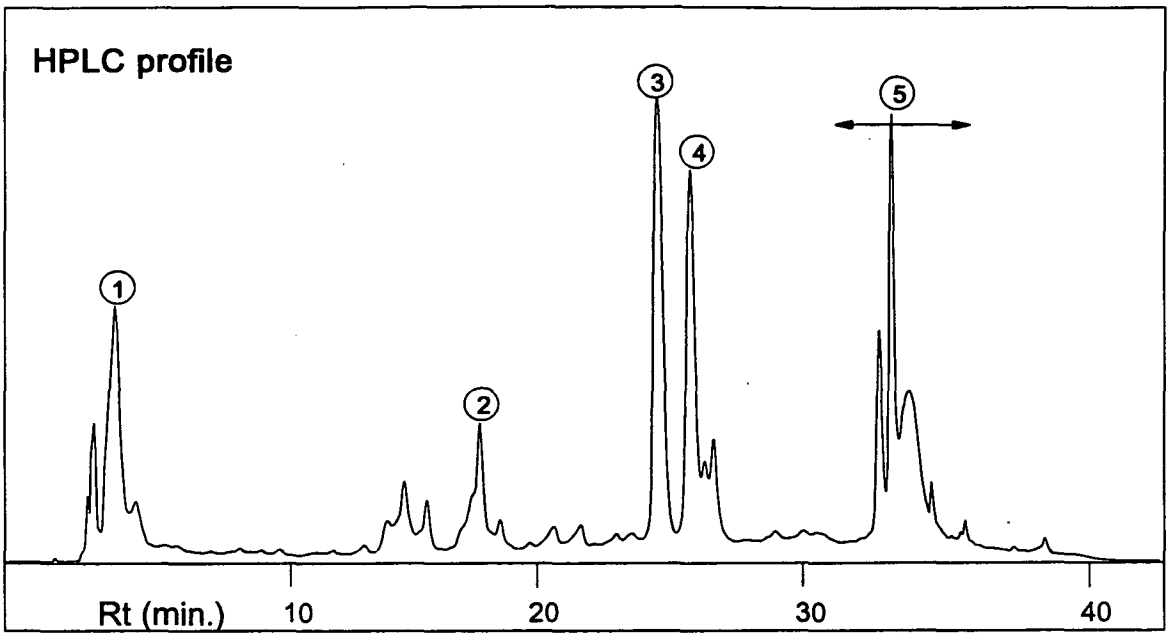
  - Aloes, Port Elizabeth
  - Tipper's Creek
  - Fort Brown
  - Ann's Villa

Distribution



Aloe africana follows a coastal distribution from the Gamtoos River in the west to Port Alfred in the east.

Aloe aldabrensis (Marais) L. E. Newton & G. D. Rowley



Peak number	Retention time	Compound	Percentage
1	4.09	unidentified compound	7
2	17.70	unidentified flavone	6
3	24.29	aloin B	19
4	25.50	aloin A	15
5	33.00	unidentified anthrones	24

A. aldabrensis, like all the other species previously placed in the genus *Lomatophyllum* produces a combination of anthrones (aloin) and flavones. The series of peaks denoted by 5 is a series of peaks which all show UV spectra resembling that of aloin.

- Taxonomic position:

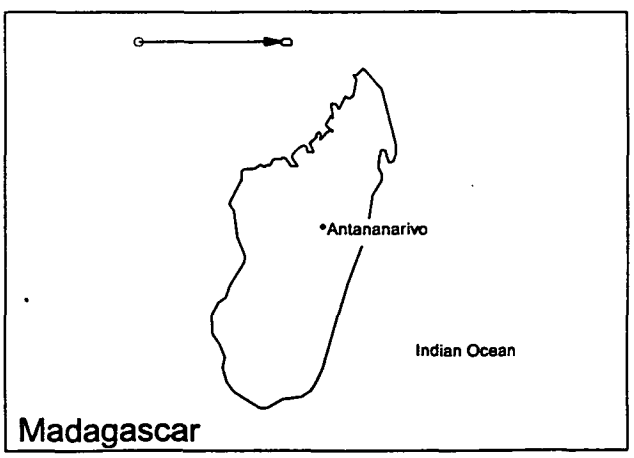
  Aloe section *Lomatophyllum* (Rowley, 1996).

- Samples analysed:

  The leaf exudate was investigated:

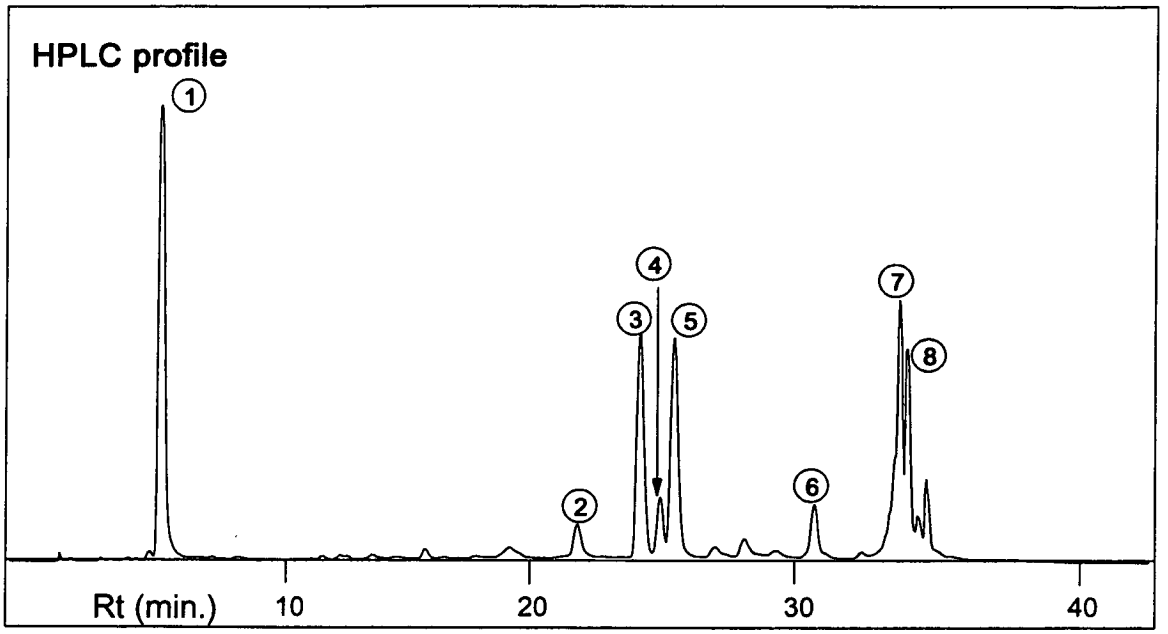
  - Wikens 3519 (ex hort NBI)

Distribution



Aloe aldabrensis is found on Aldabra Island, north-west of Madagascar.

Aloe alooides (Bolus) van Druten



Peak number	Retention time	Compound	Percentage
1	5.74	aloesin	27
2	21.59	unidentified chromone 1	2
3	23.95	aloin B	15
4	24.72	6'-*O*-coumaroylaloesin	4
5	25.24	aloin A	15
6	30.50	unidentified chromone 2	3
7	33.68	unidentified anthrone 1	14
8	33.84	unidentified anthrone 2	11

All species placed in *Aloe* section *Anguialoe* have the characteristic chromone eluting between the two aloin isomers. This chromone shows a UV absorbance spectra characteristic of the coumaroyl chromones, while peak 6 represents a chromone with UV absorbance characteristic of the cinnamoyl range of chromones.

- Taxonomic position:

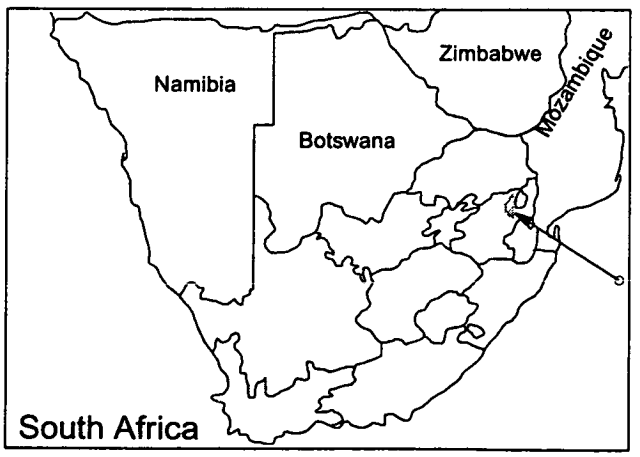
  Aloe section *Anguialoe* (Reynolds, 1950).

- Samples analysed:

  The leaf exudate was investigated:

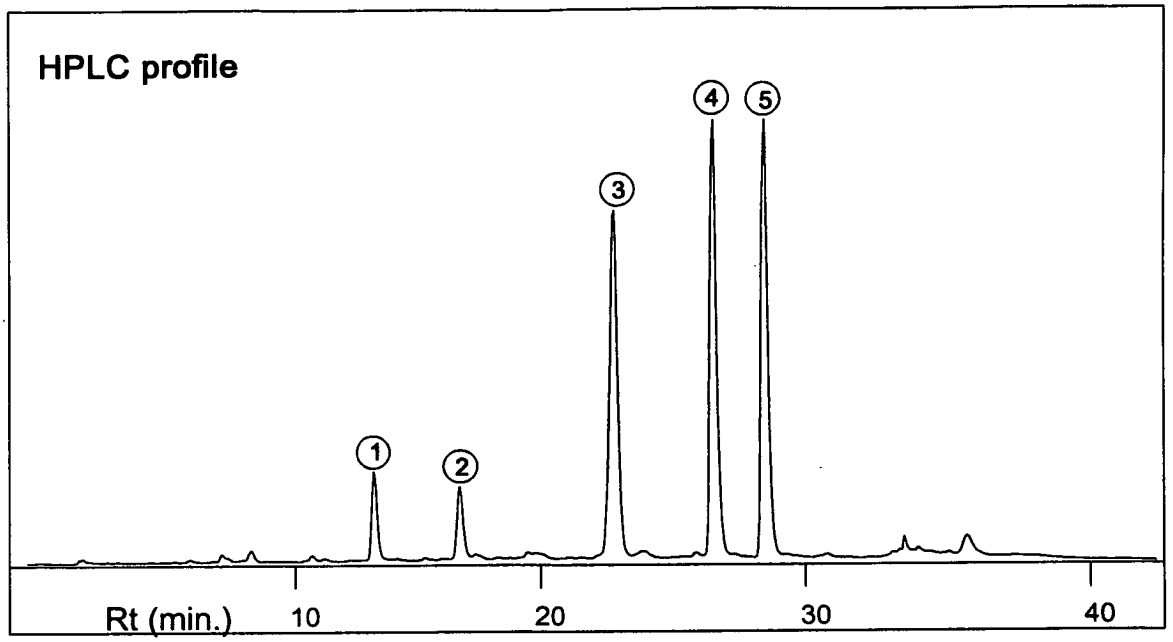
  - The Bonnet, Mpumalanga

Distribution



Aloe alooides is usually associated with dolomite ridges in the northern parts of Mpumalanga.

Aloe amicorum L.E. Newton



Peak number	Retention time	Compound	Percentage
1	13.19	homonataloside B	5
2	16.45	aloeresin A	4
3	22.37	aloeresin D	28
4	26.13	homonataloin B	30
5	28.09	homonataloin A	30

The only di-glucoside anthrone, homonataloside B, has been isolated from *A. lutescens* and its presence confirmed by HPLC co-injection in *A. amicorum*.

Distribution

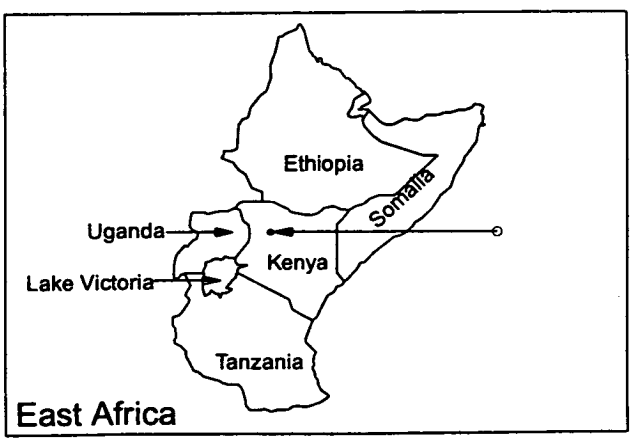
- Taxonomic position:

  Allied to *A. inermis* (Newton, 1991).

- Samples analysed:

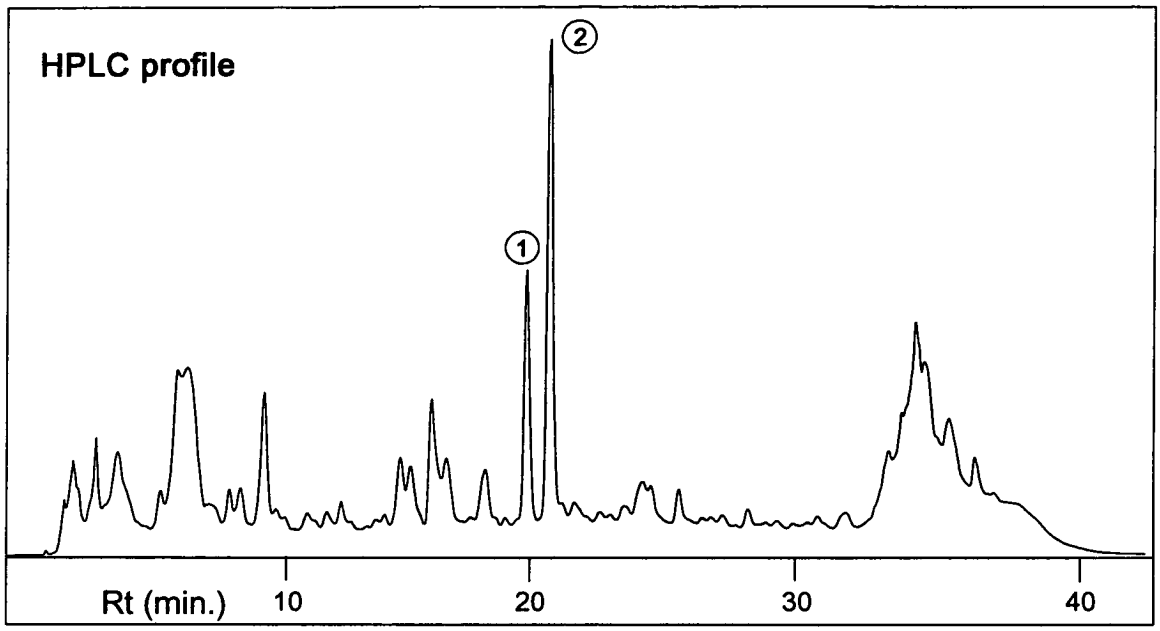
  The leaf exudate was investigated:

  - L.E. Newton (type specimen)



This species is only known from Mount Kulal in the Marsabit District in the Eastern Province of Kenya.

Aloe amudatensis Reynolds



Peak number	Retention time	Compound	Percentage
1	19.79	unidentified anthrone 1	22
2	20.66	unidentified anthrone 2	42

Aloe amudatensis shows the general pattern for the maculate aloes. The phenolic compounds are present in very low quantities. The anthrones display the UV absorbance spectra similar to that of nataloin and its derivative, 7-hydroxyaloin.

Distribution

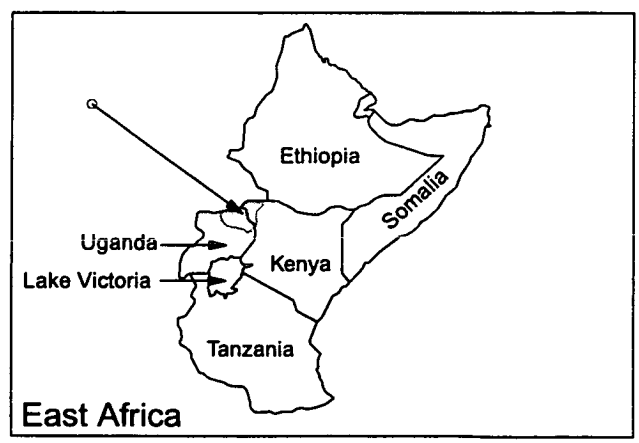
- Taxonomic position:

  Group 6 of the tropical aloes (Reynolds, 1966).

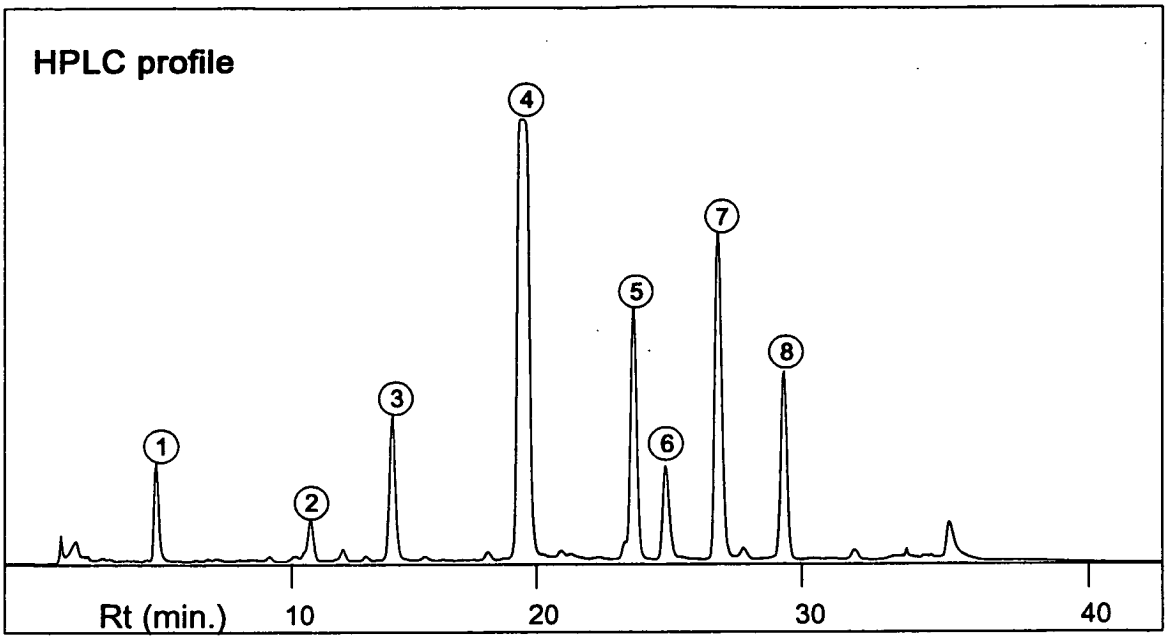
- Samples analysed:

  The leaf exudate was investigated:

  - A. Ellert 16



Aloe amudatensis is common in the sandy soils of the Karamoja District in Uganda and the West Suk District in Kenya.



Peak number	Retention time	Compound	Percentage
1	5.54	aloesin	5
2	11.07	unidentified compound	tr
3	14.37	aloeresin A	7
4	19.23	aloeresin E	32
5	23.36	aloeresin F	13
6	24.56	homonataloin B	7
7	26.52	homonataloin A	18
8	28.99	unidentified chromone	13

The general chromatographic pattern recorded for species in the *Mitriformes*-group is repeated in *A. angelica*. The unidentified chromone (peak 8) could possibly be a cinnamoyl chromone.

- Taxonomic position:

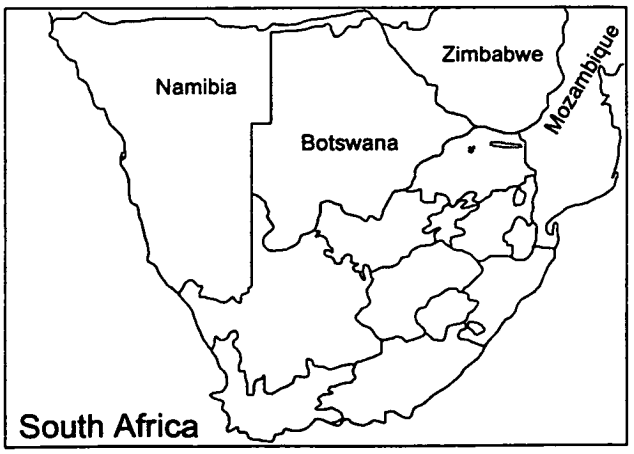
  Aloe section *Pachydendron* (Reynolds, 1950).

- Samples analysed:

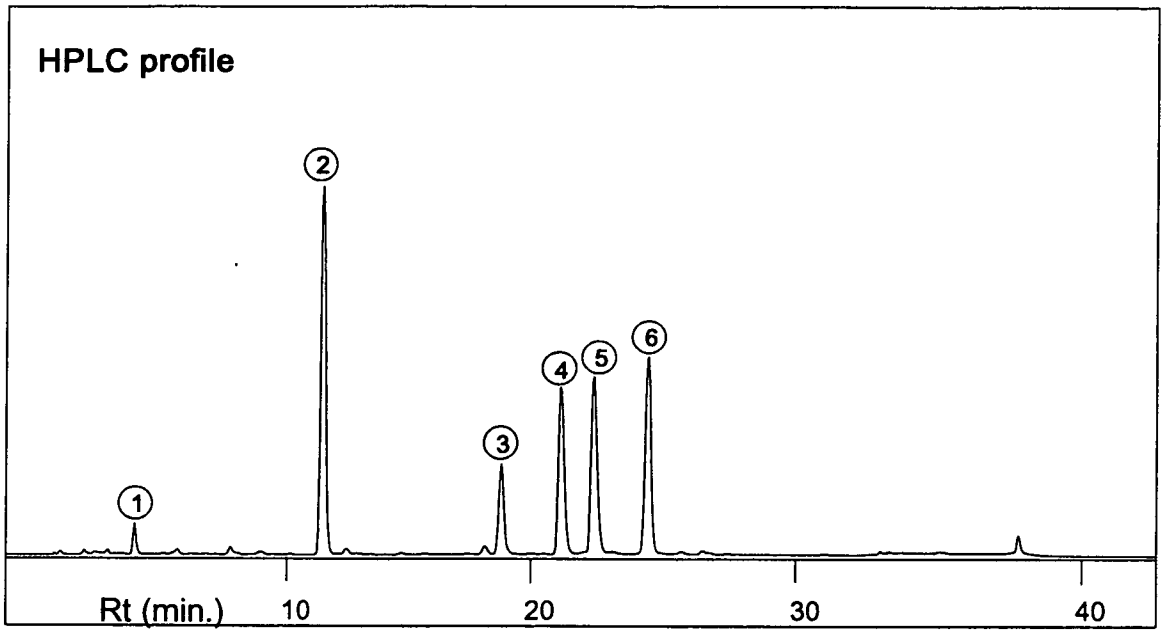
  The leaf exudate was investigated:

  - Waterpoort (3 samples)

Distribution



Aloe angelica is restricted to Soutpansberg and Blouberg in theNorthern Province of Southern Africa.



Peak number	Retention time	Compound	Percentage
1	4.80	aloesin	2
2	11.92	aloenin	32
3	18.68	aloeresin D	8
4	20.86	aloin B	17
5	22.08	aloin A	18
6	24.12	unidentified chromone	20

Due to the wide range of distribution several populations were sampled. Peaks 1 to 5 were present in all samples but the unidentified chromone (peak 6) occurred erratically between different populations. No variation was found within a population.

- Taxonomic position:

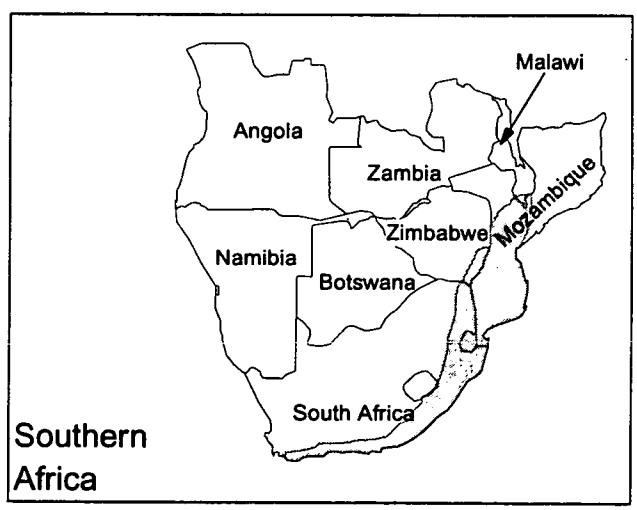
Aloe series *Arborescentes* (Reynolds, 1950).

- Samples analysed:

The leaf exudate was investigated:

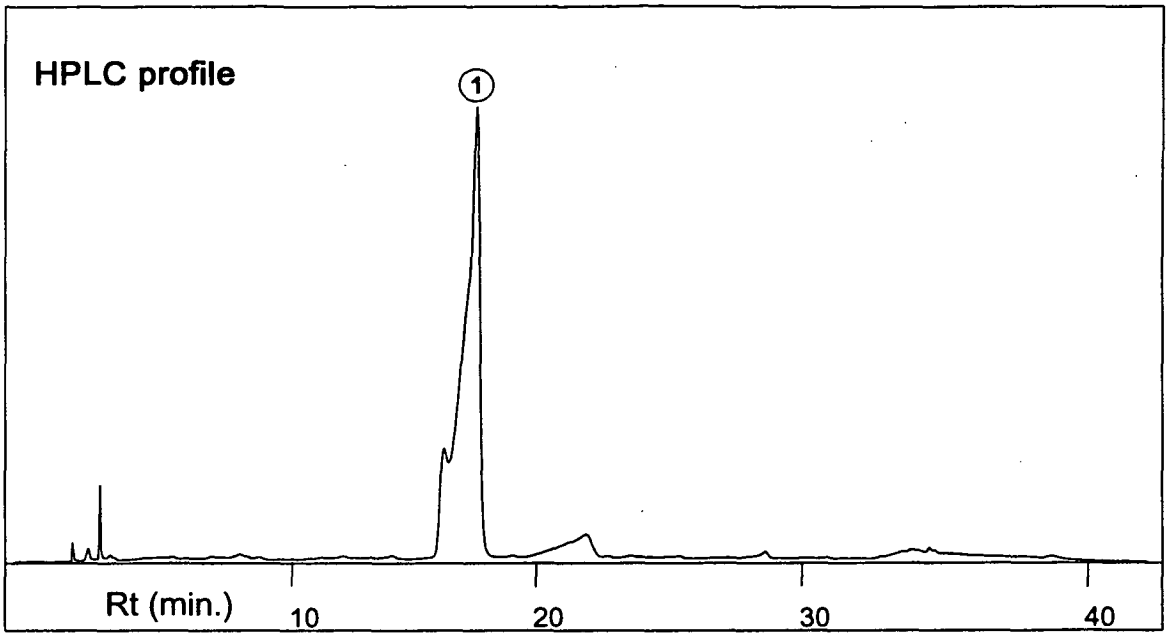
- Jozini, Pongola
- Storms river
- Blyde River
- Bizana
- Kaapsche Hoop
- Tradouws Pass
- Swellendam
- Gouritz river mouth
- Swellendam
- Mosselbay
- Stilbay
- Flagstaff
- Howick Falls
- Malalotja
- Umtamvuna Valley
- Ngome
- Herbert's Dale
- Vumba

Distribution



Aloe arborescens is the most widely distributed of all the South African species. It extends from the southern Cape coastally to the southern parts of Malawi.

Aloe archeri Lavranos amend. L.E. Newton



Peak number	Retention time	Compound	Percentage
1	17.21	plicataloside	87

The only compound detected in the leaf exudate of *A. archeri* is plicataloside. The poor peak symmetry could be ascribed to an interfering substance influencing the elution of this naphthalene-like compound.

Distribution

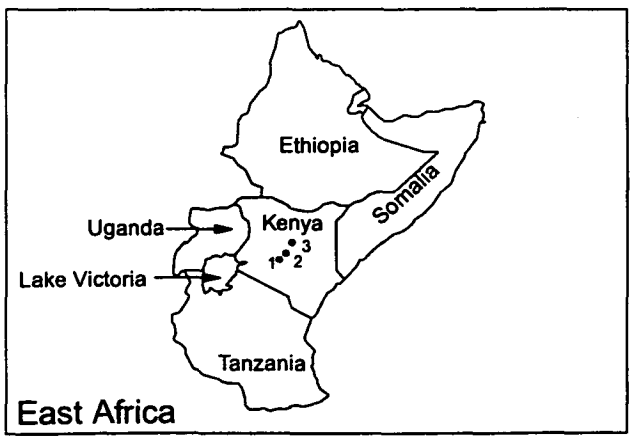
- Taxonomic position:

  Allied to *A. tugenensis* (Newton, 1992).

- Samples analysed:

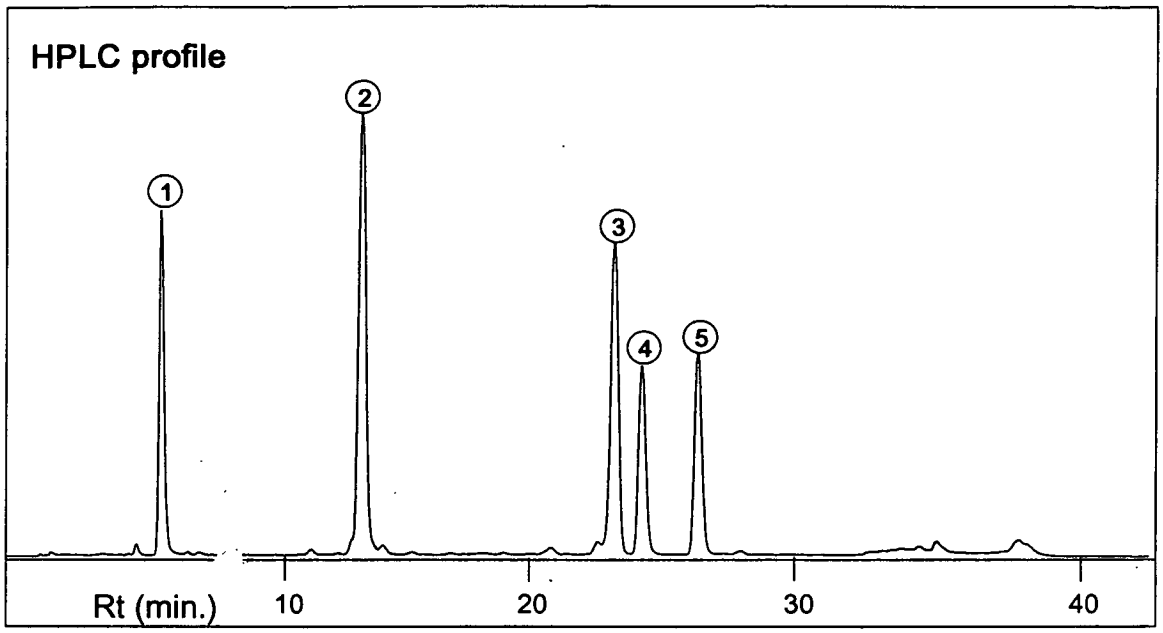
  The leaf exudate was investigated:

  - L.E. Newton 3118 (neotype plant)



Aloe archeri is restricted to the Rift Valley Province in Kenya. It has been collected at Kirimun (1), NE of Phumuruti (2) and Ol Doinyo Lenkiyio (3).

Aloe arenicola Reynolds



Peak number	Retention time	Compound	Percentage
1	5.58	aloesin	16
2	14.33	aloeresin A	30
3	23.03	aloeresin F	23
4	24.07	homonataloin B	13
5	26.18	homonataloin A	14

This is a characteristic profile for all the species belonging to *Aloe* series *Mitriformes*. In addition to aloeresin F most of the species in the group also contain the diglucoside analogue, aloeresin E.

- Taxonomic position:

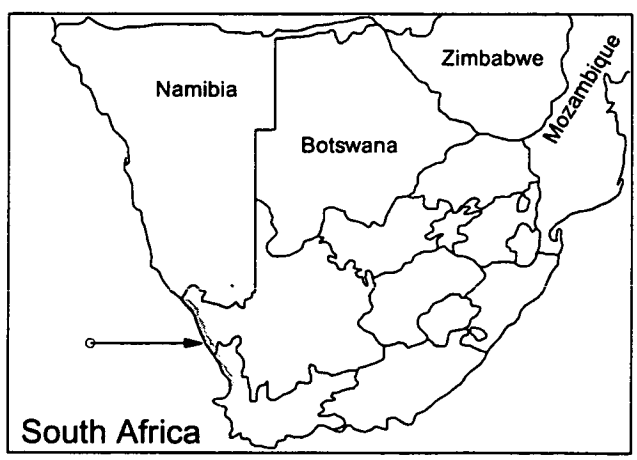
  Aloe series *Mitriformes* (Reynolds, 1950).

- Samples analysed:

  The leaf exudate was investigated:

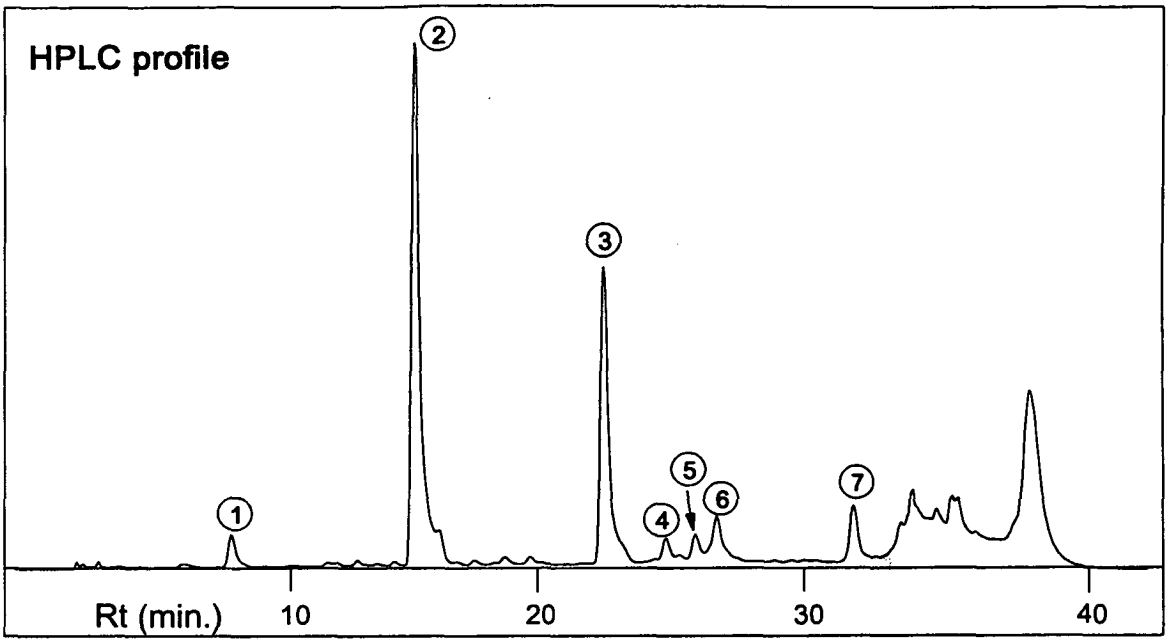
  - ex hort JBG
  - NBI 1283/92

Distribution



As suggested by the name, *A. arenicola* occupies sandy habitats on the west coast of South Africa.

Aloe argenticauda Merxmüller & Giess



Peak number	Retention time	Compound	Percentage
1	7.6	7-*O*-methylaloesin	2
2	15.1	10-hydroxyaloin B	32
3	22.4	10-hydroxyaloin-6'-mono-acetate B	22
4	25.6	aloin B	1
5	26.1	deacetyllittoraloin	3
6	26.7	aloin A	1
7	31.9	littoraloin	3

The chemical marker for *Aloe* series *Asperifoliae*, 10-hydroxyaloin B is the main compound co-occurring with the other compounds in the *Asperifoliae*-group.

- Taxonomic position:

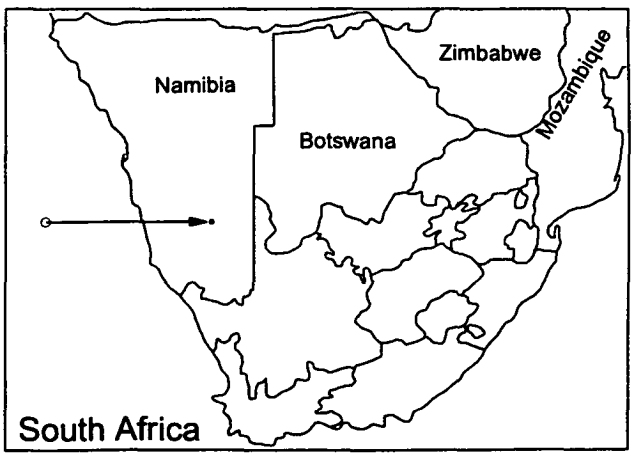
  Aloe series *Asperifoliae* (Reynolds, 1950 and Merxmüller & Giess, 1974).

- Samples analysed:

  The leaf exudate was investigated:

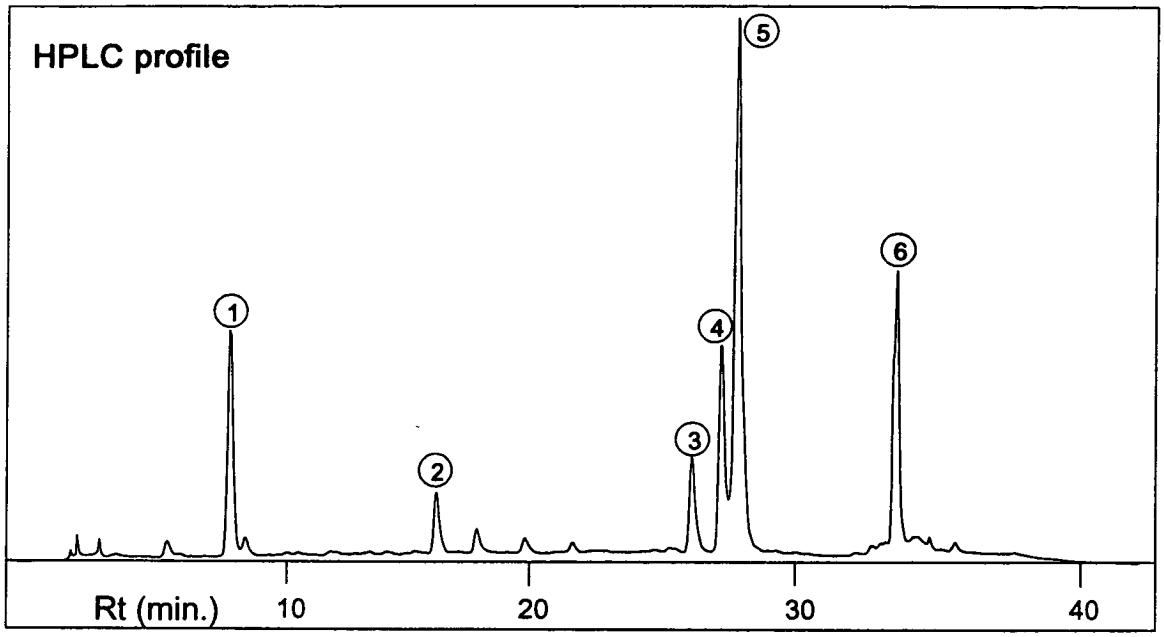
  - ex hort JBG

Distribution



Aloe argenticauda is restricted to the Witputz area in Namibia.

Aloe asperifolia A. Berger



Peak number	Retention time	Compound	Percentage
1	7.6	7-*O*-methylaloesin	15
2	15.1	10-hydroxyaloin B	4
3	25.5	aloin B	7
4	26.6	aloin A	14
5	26.1	deacetyllittoraloin	42
6	33.7	unidentified derivative of aloin	18

In addition to the chemotaxonomic marker 10-hydroxyaloin B (peak 2) this species also contains an unidentified derivative of the anthrone-*C*-glycosyl aloin.

- Taxonomic position:

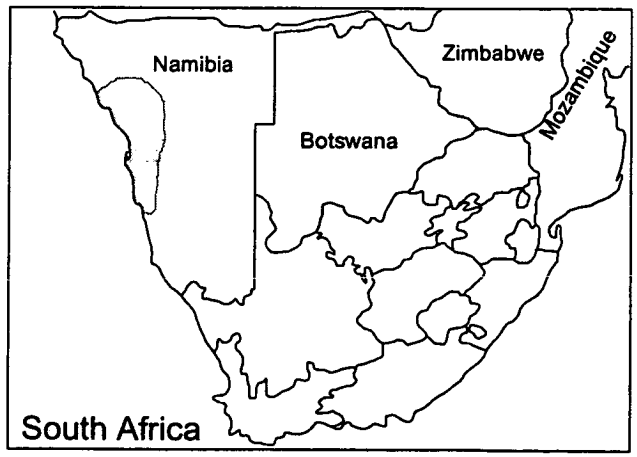
  Aloe series *Asperifoliae* (Reynolds, 1950).

- Samples analysed:

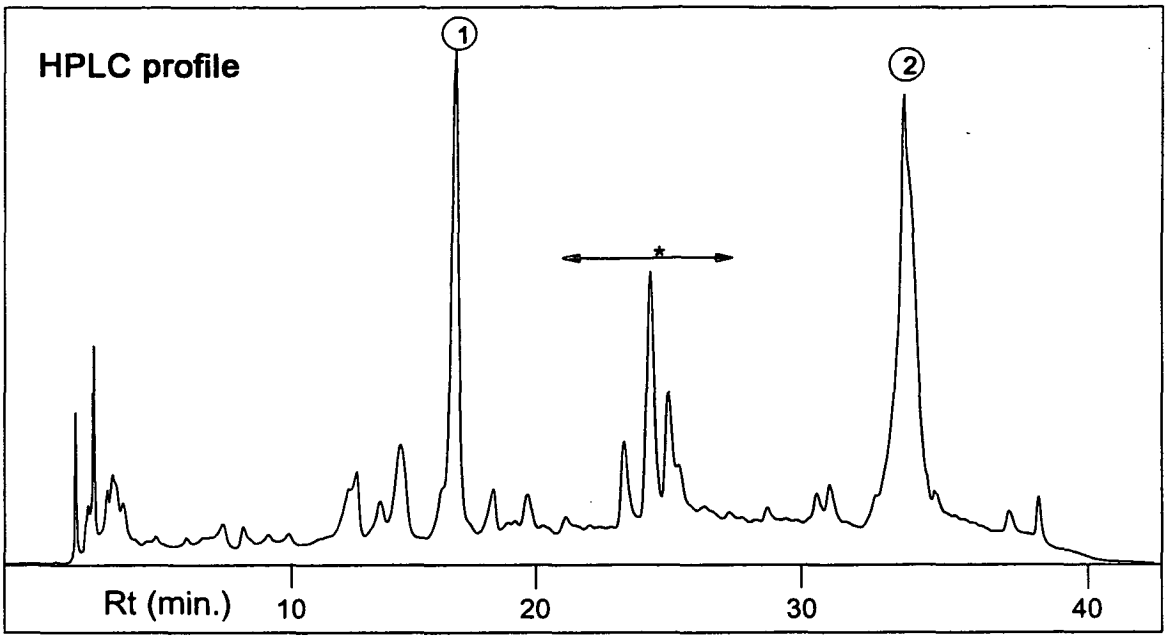
  The leaf exudate was investigated:

  - Van Jaarsveld 2850
  - ex hort JBG
  - NBI 432/72

Distribution



Aloe asperifolia occurs in large numbers on the open gravel flats from Swakopmund and northwards.



Peak number	Retention time	Compound	Percentage
1	16.83	plicataloside	20
2	33.67	unidentified compound	38

The leaf extract contains plicataloside and possibly low concentrations of unidentified flavones (indicated by *).

Distribution

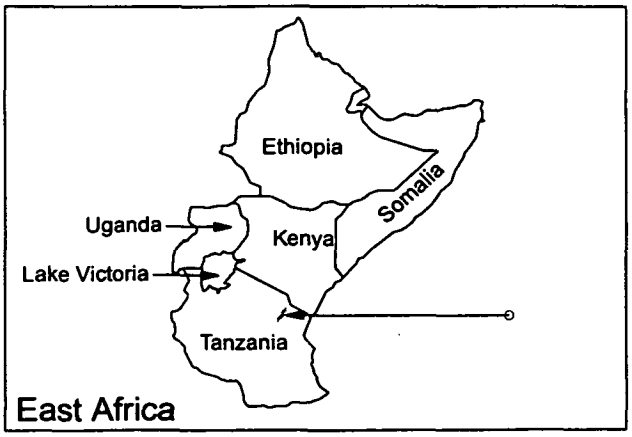
- Taxonomic position:

  Group 19 of the tropical aloes (Reynolds, 1966).

- Samples analysed:

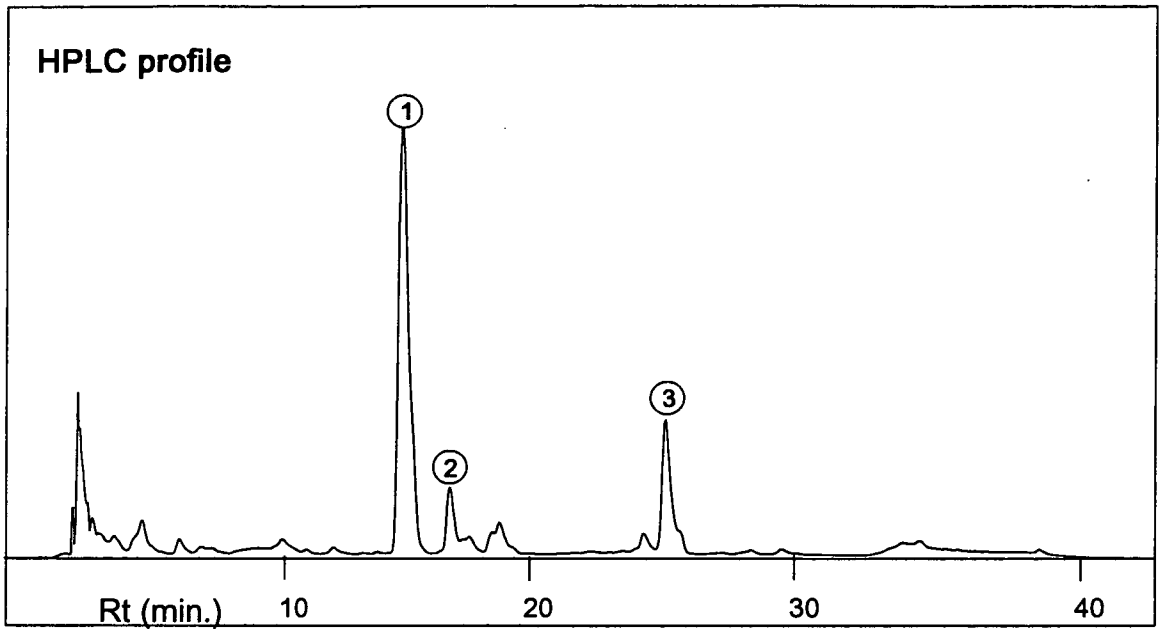
  The leaf extract was investigated:

  - RBG, Kew 1974-4463



Aloe babatiensis is restricted to the Mbulu Highlands in the Masai and Mbulu Districts of northern Tanzania.

Aloe bakeri Scott-Elliot



Peak number	Retention time	Compound	Percentage
1	15.03	unidentified flavonoid 1	57
2	16.84	unidentified flavonoid 2	6
3	24.91	unidentified flavonoid 3	17

Aloe bakeri represents one of the few species of *Aloe* which are devoid of any anthrones and chromones but instead contain various flavanones or dihydroflavonols.

- Taxonomic position:

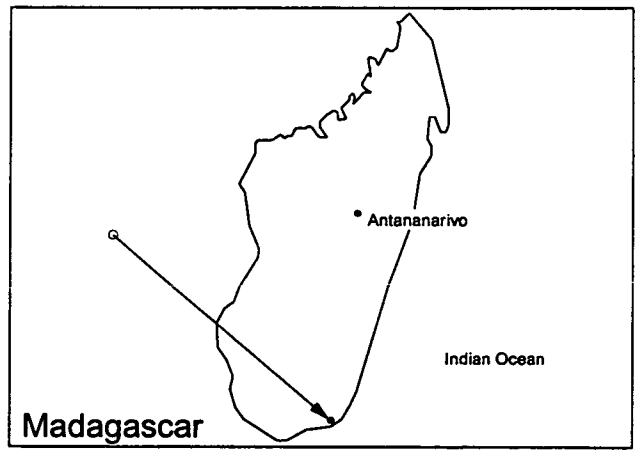
  Group 1 (Reynolds, 1966).

- Samples analysed:

  The leaf extract was investigated:

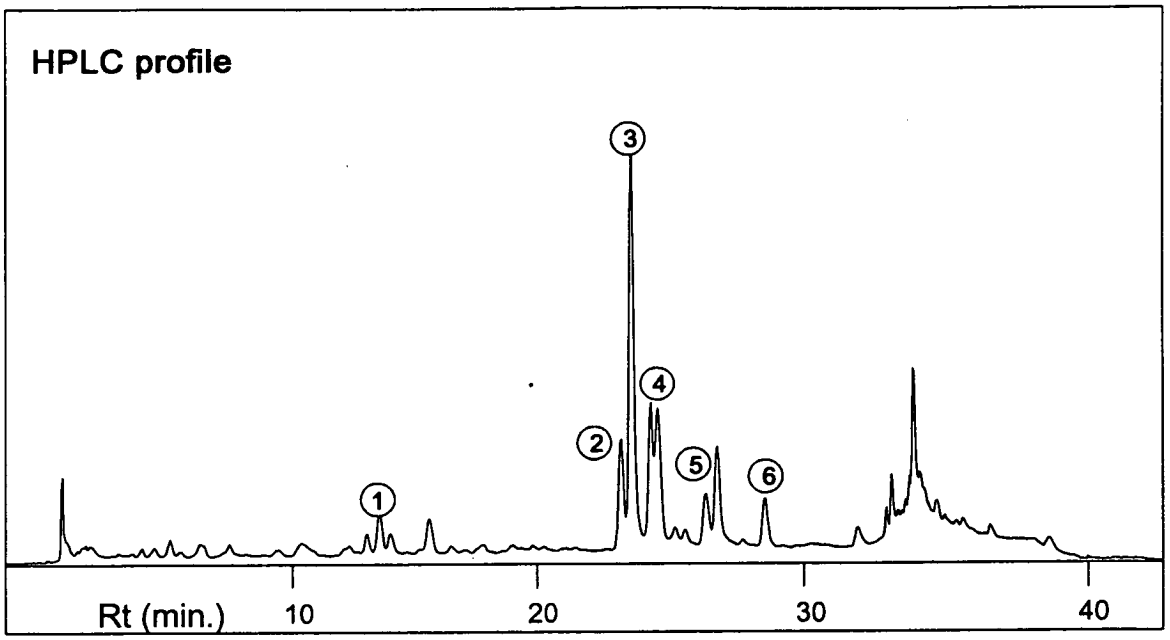
  - NBI 31548

Distribution



Aloe bakeri occurs in large numbers near Fort Dauphin in southern Madagascar.

Aloe barberae Dyer



Peak number	Retention time	Compound	Percentage
1	13.21	unidentified anthrone 1	tr
2	22.87	unidentified anthrone 2	9
3	23.26	unidentified compound	30
4	24.00	unidentified anthrone 3	12
5	26.03	unidentified anthrone 4	5
6	28.24	unidentified anthrone 5	4

All the 'tree-like' aloes have a unique chemical profile. The concentration level of the phenolics are extremely low. The unidentified anthrones all display the UV spectra characteristic of the aloin isomers.

- Taxonomic position:

  Aloe section *Aloidendron* (Reynolds, 1950).

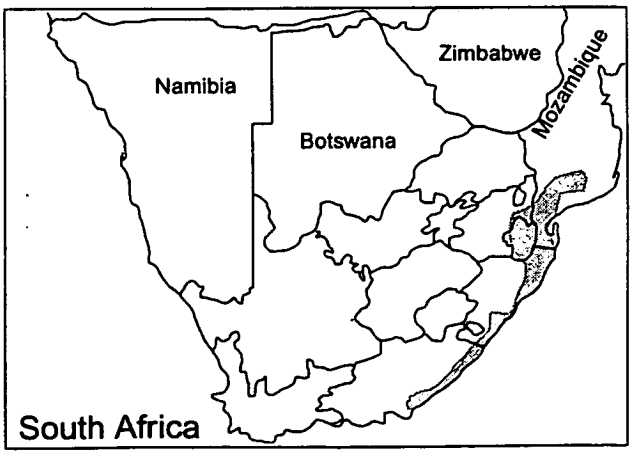
  Syn. *A. bainsii* (Smith *et al.* 1994).

- Samples analysed:

  The leaf exudate was investigated:

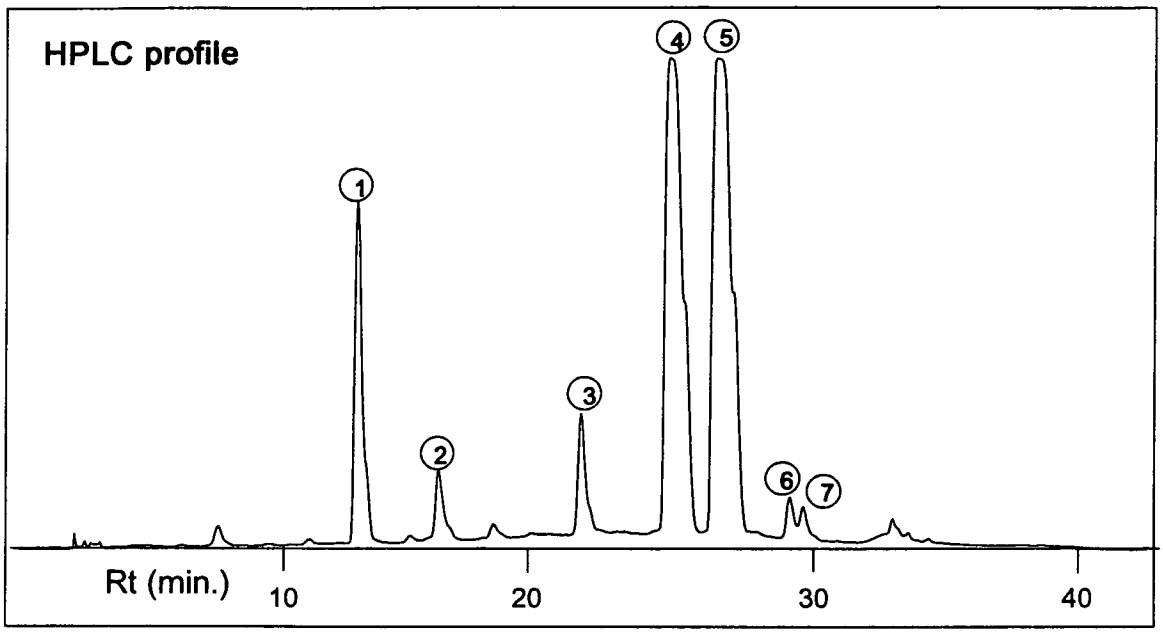
  - ex hort NBI
  - ex hort NBG

Distribution



Aloe barberae is mostly associated with a forest habitat. It is widely distributed along the eastern coast of South Africa.

Aloe bargalensis Lavranos



Peak number	Retention time	Compound	Percentage
1	12.65	homonataloside B	9
2	15.80	unidentified compound 1	8
3	21.22	aloeresin D	14
4	24.67	homonataloin B	21
5	26.39	homonataloin A	37
6	29.50	unidentified chromone 2	1
7	29.82	unidentified chromone 3	1

The unidentified compound (peak 2) could possibly be a 'mixed peak' containing aloeresin A and another compound. The retention time and uv absorbance of peak 6 corresponds to 3',-6'-di-*O*-coumaroylaloesin isolated from *Aloe lutescens* (together with homonataloside).

Distribution

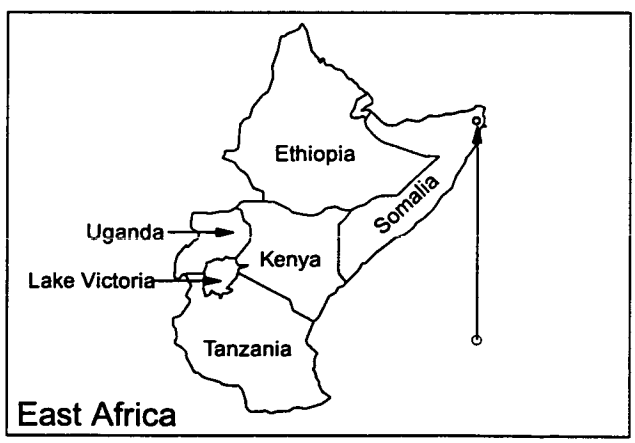
- Taxonomic position:

  Unknown (Lavranos, 1973).

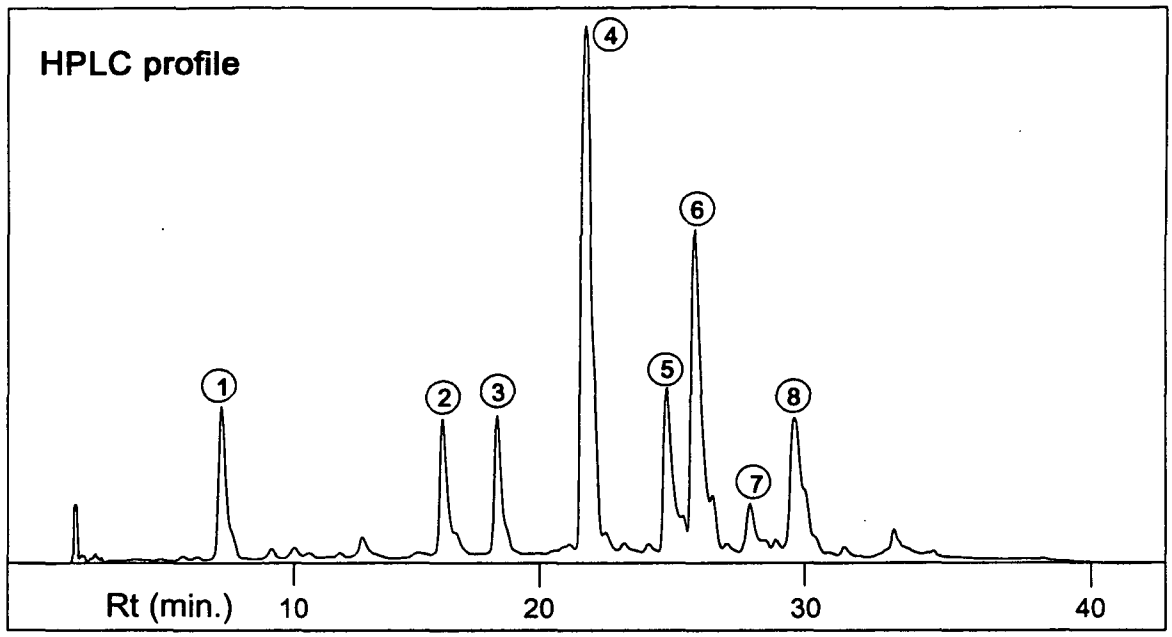
- Samples analysed:

  The leaf exudate was investigated:

  - NBI 16949



Aloe bargalensis inhabits the extreme north-eastern corner of Africa. It is restricted to the Basaso region west of Bargal in Somalia.



Peak number	Retention time	Compound	Percentage
1	7.69	7-*O*-methylaloesin	7
2	16.11	dihydroisocoumaringlucoside	7
3	18.18	unidentified chromone 1	6
4	21.28	aloeresin D	31
5	24.66	aloin B	9
6	25.71	aloin A	18
7	27.82	unidentified anthrone	3
8	29.53	unidentified chromone 2	8

The unidentified chromone 1 displays an UV absorbance spectrum resembling the caffeoyl derivative of aloesin isolated from *A. broomii* while peak 8 could possibly be related to the cinnamoyl group of chromones.

- Taxonomic position:

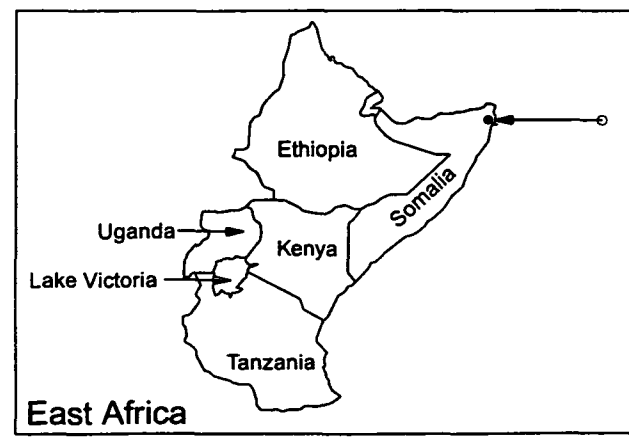
  Allied to *A sinkatana* and *A. elegans* (Lavranos, 1973).

- Samples analysed:

  The leaf exudate was investigated:

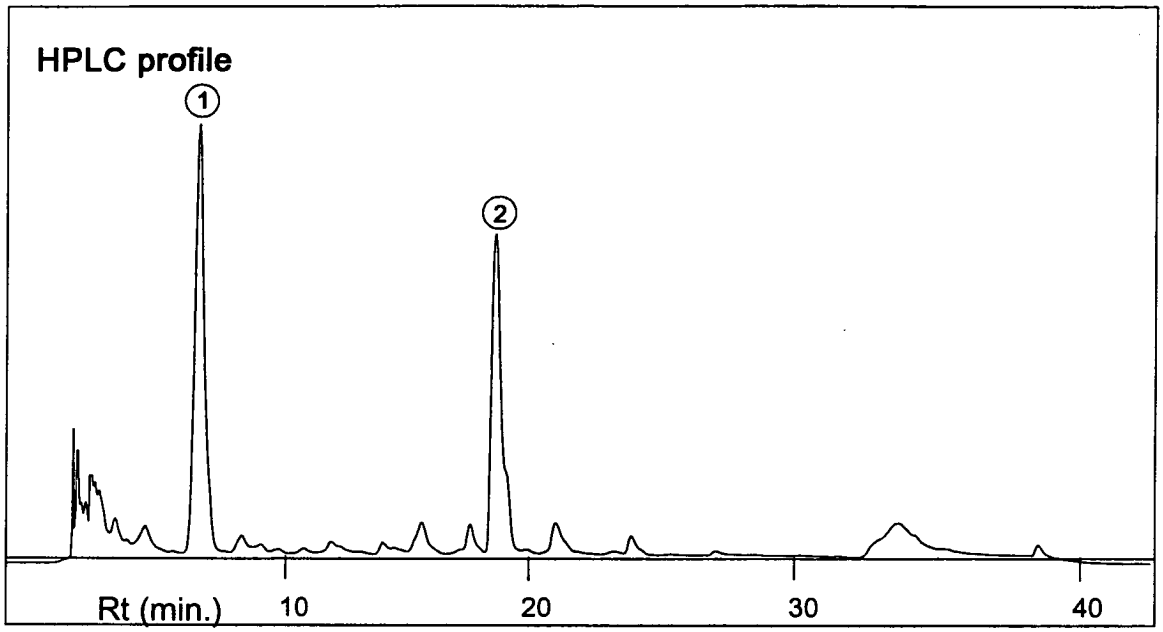
  - NBI 31546

Distribution



Aloe bella inhabits the coastal plain between Eil Libah and God Ad in the Basaso Region of Somalia.

Aloe bellatula Reynolds



Peak number	Retention time	Compound	Percentage
1	7.34	unidentified flavonoid 1	41
2	18.58	unidentified flavonoid 2	33

As is the case in *A. bakeri*, *A. bellatula* is another 'miniature Malagasy aloe' displaying an unique chromatographic profile showing flavanones / dihydroflavonols as the main compounds in the leaf extract.

- Taxonomic position:

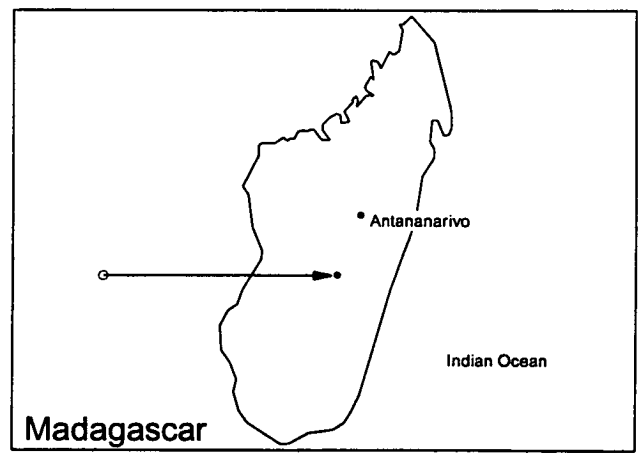
  Group 1 (Reynolds, 1966).

- Samples analysed:

  The leaf extract was investigated:

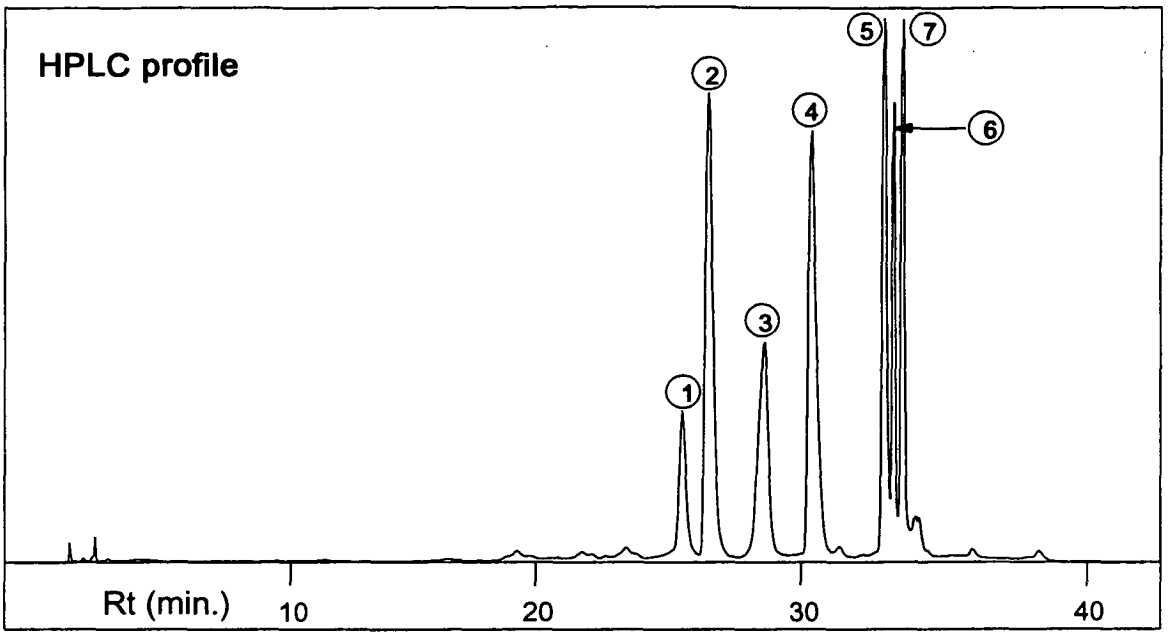
  - NBI 16648

Distribution



Aloe bellatula was described from a locality near Itremo Village which is south-west of Ambatofinandrahana in the central region of Madagascar.

Aloe boscawenii Christian



Peak number	Retention time	Compound	Percentage
1	25.39	aloin B	7
2	26.38	aloin A	21
3	28.54	aloinoside B	12
4	30.33	aloinoside A	20
5	33.11	microdontin B	15
6	33.46	microdontin A	8
7	33.80	unidentified anthrone	12

This HPLC profile is typical of a large number of species in tropical east Africa. Peaks 5 - 7 are often not completely separated, but *A. boscawenii* clearly shows three fully resolved peaks. Co-injection with a microdontin standard confirmed peak 5 and 6 to correspond to microdontin B and A respectively. The third peak in the series displays the same UV properties as peak 5 and 6.

Distribution

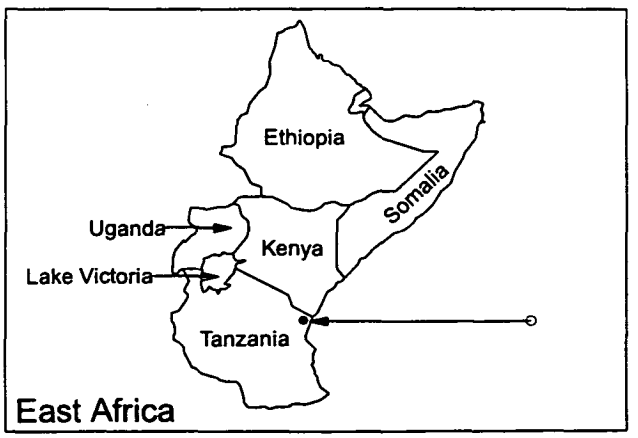
- Taxonomic position:

  Group 19 of the tropical aloes (Reynolds, 1966).

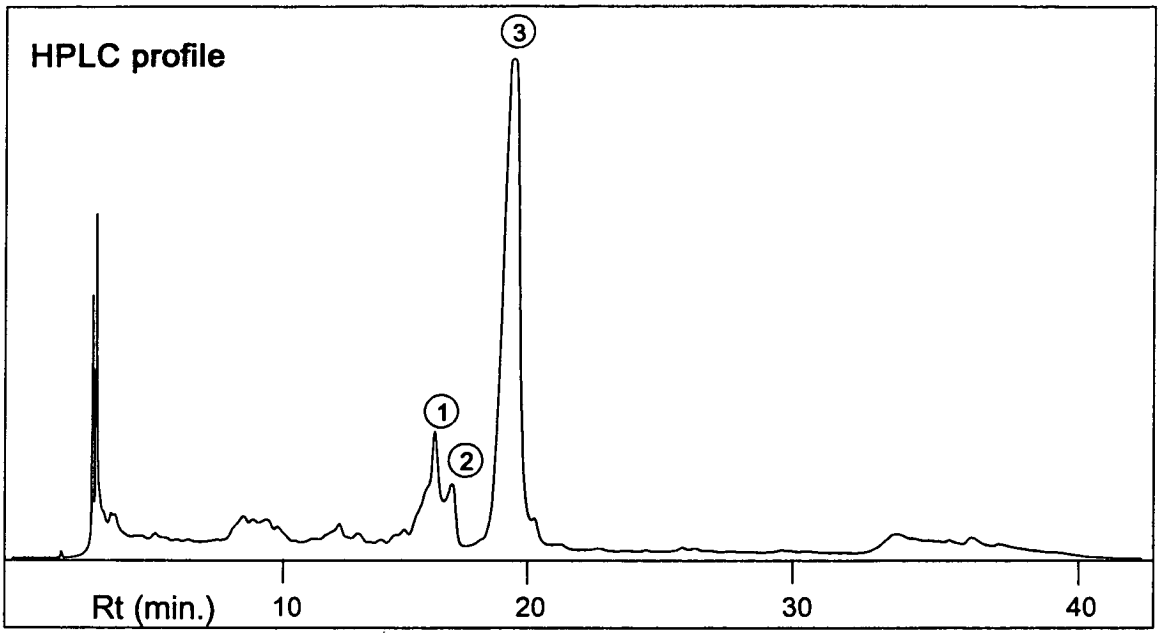
- Samples analysed:

  The leaf exudate was investigated:

  - ex hort P. Favell



Aloe boscawenii is only known from the Tanga Coast in the north-eastern corner of Tanzania.



Peak number	Retention time	Compound	Percentage
1	16.2	unidentified flavone 1	13
2	17.6	unidentified flavone 2	5
3	18.5	isovitexin (a flavone)	71

The major compound is the flavone, isovitexin. Two minor constituents were detected which have an UV spectrum identical to that of isovitexin.

- Taxonomic position:

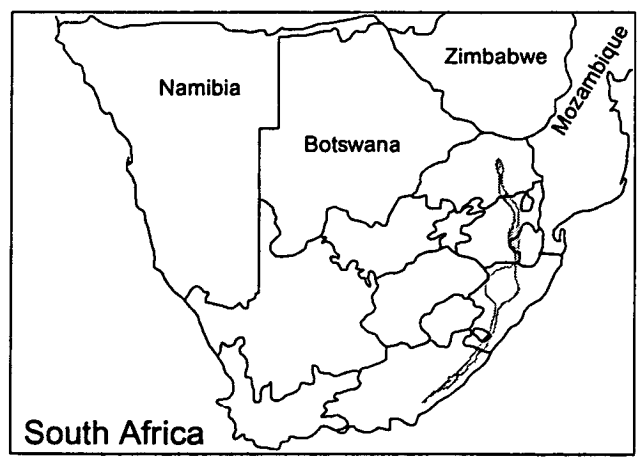
Aloe section *Leptoaloe* (Reynolds, 1950).

- Samples analysed:

The leaf extract was investigated:

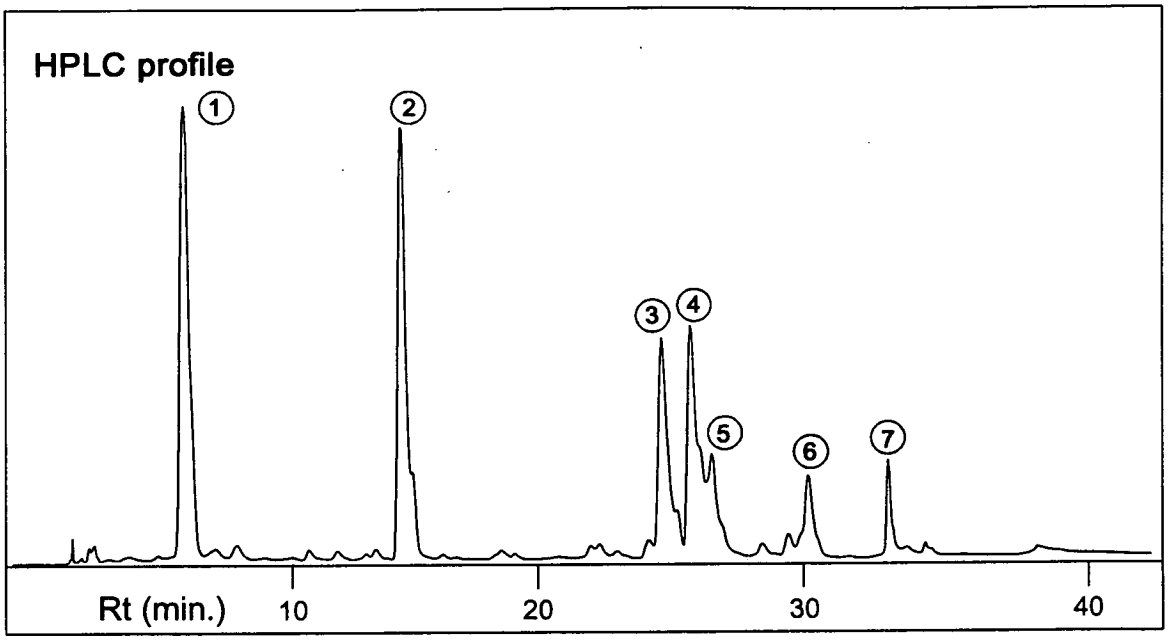
- ex hort C. Craib (collected near Piet Retief)
- NBI 31524

Distribution



Aloe boylei is widely distributed along the eastern parts of South Africa, from East London in the south to Magoebaskloof in the north.

Aloe brachystachys Baker



Peak number	Retention time	Compound	Percentage
1	6.39	aloesin	25
2	14.61	aloenin	21
3	24.48	aloin B	12
4	25.56	aloin A	15
5	26.38	unidentified chromone 1	7
6	30.1	unidentified chromone 2	5
7	33.0	unidentified chromone 3	3

The three unidentified chromones all display the UV spectra typical of the coumaroyl chromones.

- Taxonomic position:

  Unknown, (Lavranos, 1970).

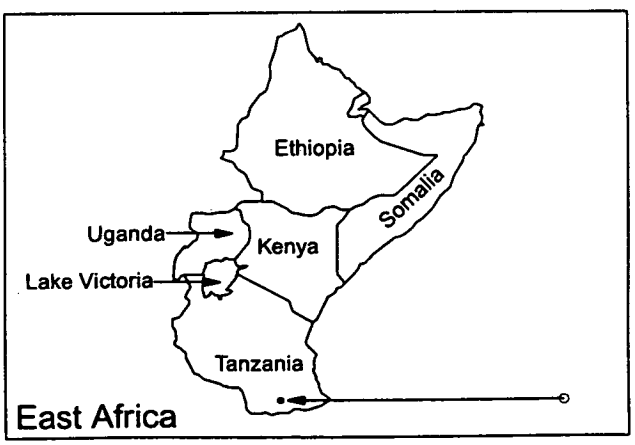
- Samples analysed:

  The leaf exudate was investigated:

  - NBI 17388*

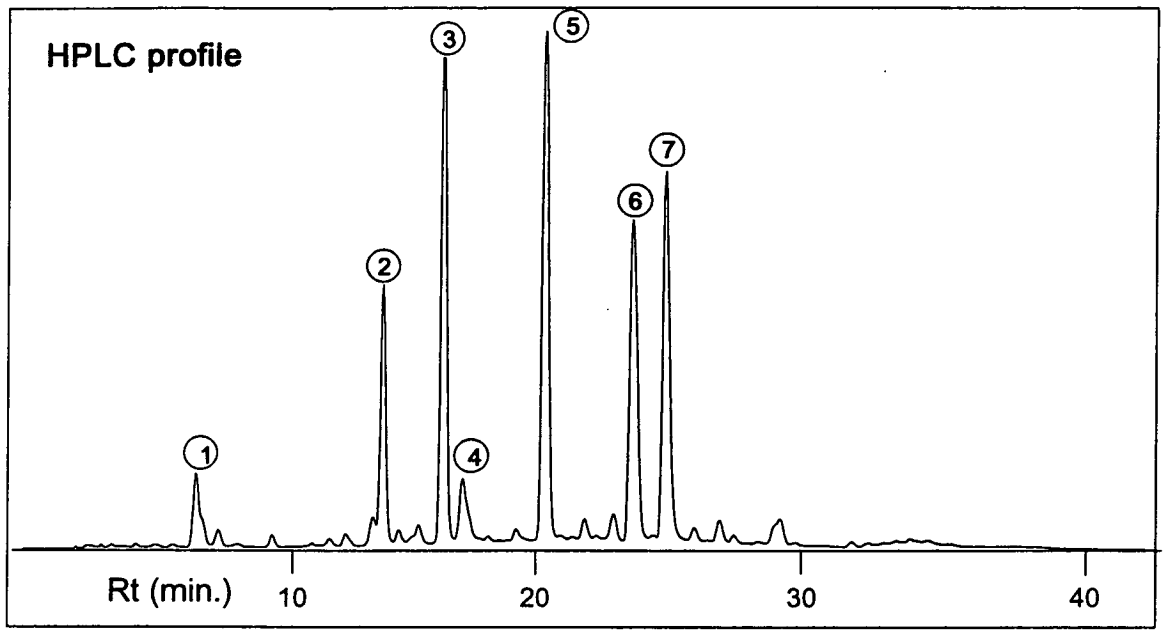
* This sample was collected under the name of *Aloe schliebenii* Lavranos but was renamed as *A. brachystachys* Baker. (Lavranos, 1993).

Distribution



Aloe brachystachys is only known from the type locality which is in the Unguru Mountains in southern Tanzania.

Aloe brandhamii S. Carter



Peak number	Retention time	Compound	Percentage
1	6.69	aloesin	3
2	13.91	aloenin	9
3	16.24	unidentified compound	20
4	17.01	unidentified chromone	3
5	20.16	aloeresin D	22
6	23.51	aloin B	16
7	24.76	aloin A	16

The unidentified compound, peak 3, has also been detected in *A. bussei*, *A. secundiflora* and *A. dorotheae* and various other species. Observations on the peak purity indicates a compound co-eluting with aloin B (this is also the case in the species mentioned above).

Distribution

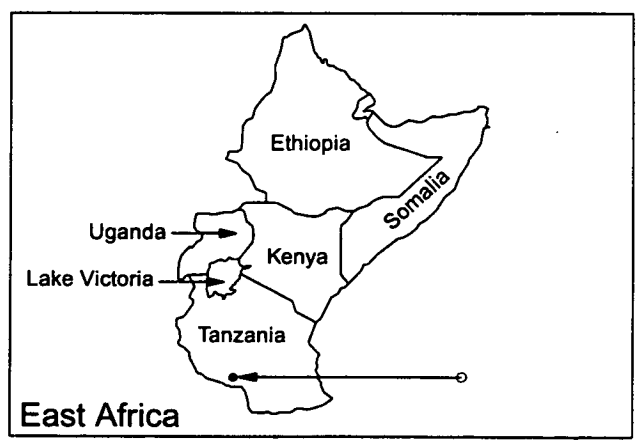
- Taxonomic position:

  Allied to *A. secundiflora* (Carter, 1994).

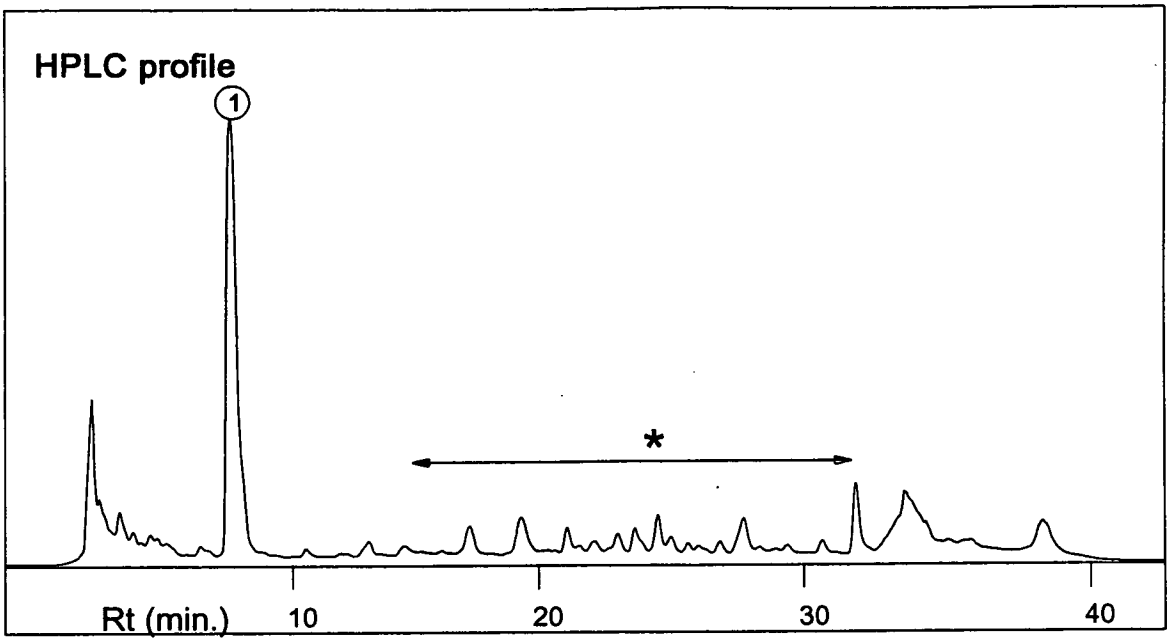
- Samples analysed:

  The leaf exudate was investigated:

  - Carter, Abdallah, Brandham & Newton 2600 (type material)



This species is only known from the Iringa District in Tanzania.



Peak number	Retention time	Compound	Percentage
1	8.23	unidentified chromone	44

Concentration of leaf phenolics are very low. The UV spectra of the series of peaks denoted by * display a similar UV absorbance spectra to that of 5-hydroxyaloin. A similar pattern was found in *A. longistyla*.

- Taxonomic position:

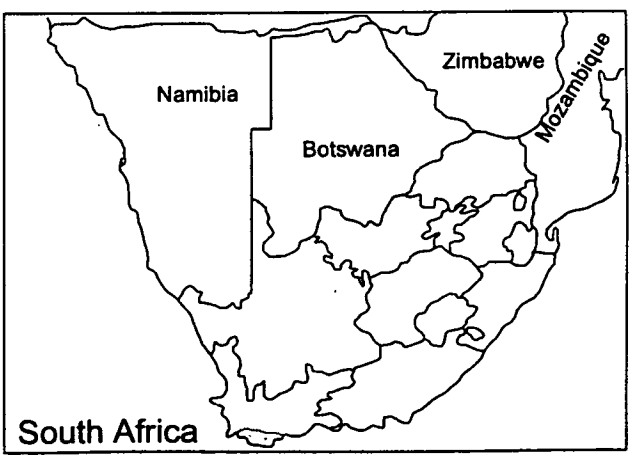
  Aloe series *Proliferae* (Reynolds, 1950).

- Samples analysed:

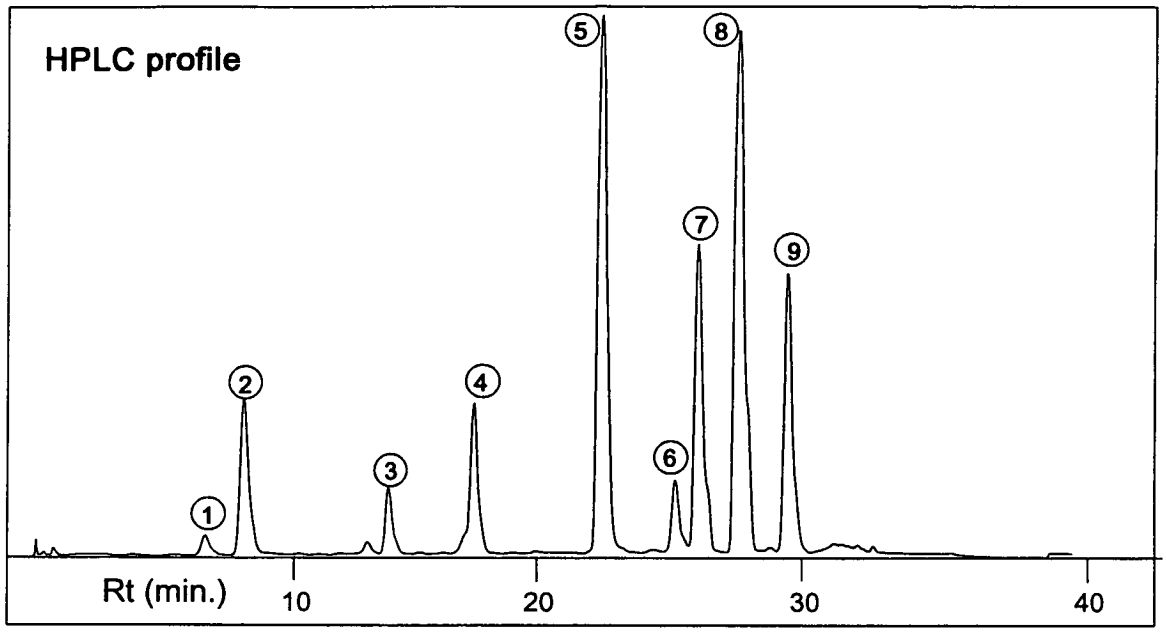
  The leaf extract was investigated:

  - ex hort JBG

Distribution



With a preference for clay soil this species is found in the Caledon and Bredasdorp area in the Western Cape Province.



Peak number	Retention time	Compound	Percentage
1	6.65	aloesin	1
2	8.56	7-*O*-methylaloesin	7
3	13.90	homonataloside B	2
4	17.30	aloeresin A	6
5	22.22	aloeresin D	26
6	25.33	unidentified chromone 1	3
7	26.02	homonataloin B	14
8	27.58	homonataloin A	27
9	29.58	unidentified chromone 2	12

The two unidentified chromones (peak 6 & 9), display the UV absorbance spectra typical of the cinnamoyl group of chromones.

- Taxonomic position:

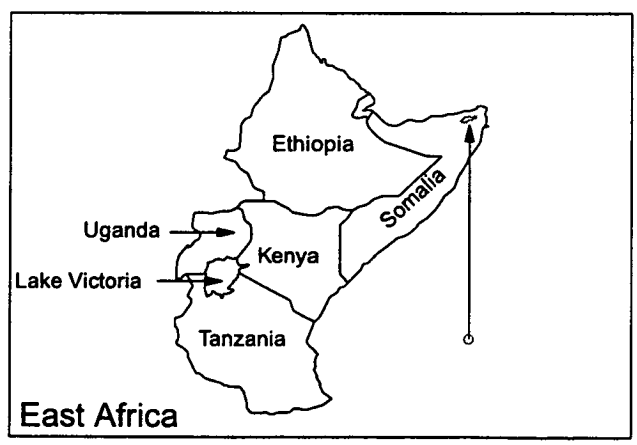
  Group 16 of the tropical aloes (Reynolds, 1966).

- Samples analysed:

  The leaf exudate was investigated:

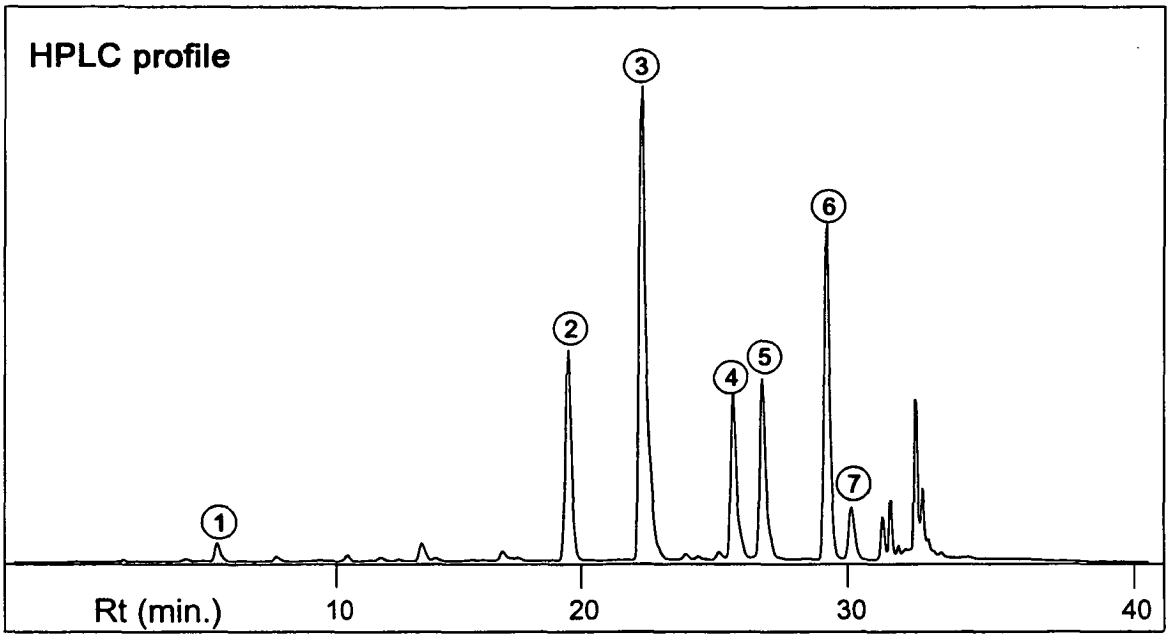
  - NBI 17034

Distribution



Aloe breviscapa is common on the gypsum plains between Erigavo and Buran in northern Somalia.

Aloe broomii Schönland



Peak number	Retention time	Compound	Percentage
1	6.24	aloesin	1
2	19.56	broomii chromone 1	8
3	21.87	5-hydroxyaloin B	33
4	25.00	aloin B	6
5	26.07	aloin A	7
6	28.27	microstigmin	17
7	29.27	broomii chromone 2	6

Aloe broomii is the species from which compounds donated by peak 2 and 7 have been isolated (Holtzapfel *et al.* 1997).
broomii chromone 1 = (E)-acetonyl-8-(2'-*O*-caffeoyl-β-D-glucopyranosyl-7-methoxy-5-methylchromone, broomii chromone 2 = (E)-acetonyl-8-(2'-*O*-cinnamoyl-β-D-glucopyranosyl-7-methoxy-5-methylchromone.

Distribution

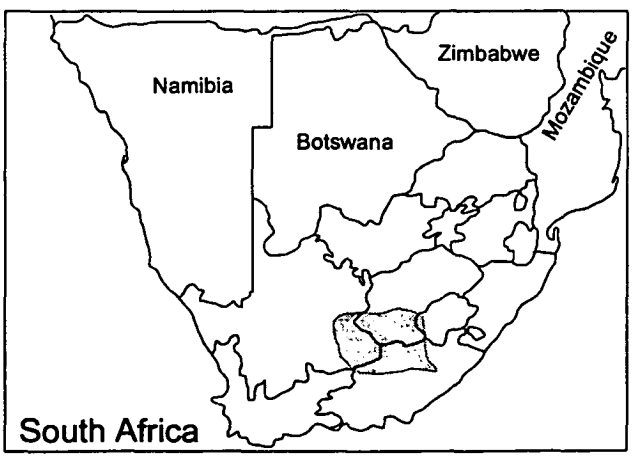
- Taxonomic position:

  Aloe series *Longistylae* (Reynolds, 1950).

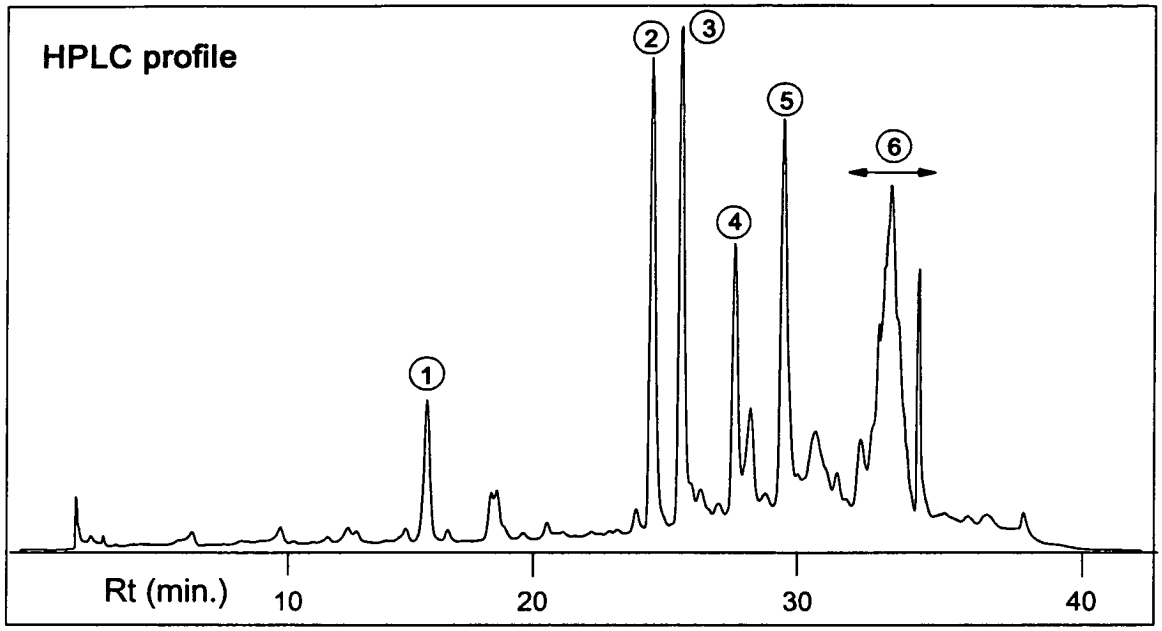
- Samples analysed:

  The leaf exudate was investigated:

  - 162 km south of Bloemfontein
  - Middelburg
  - Bethulie



Aloe broomii is widely distributed throughout the central region of South Africa and extends marginally into the south western parts of Lesotho.



Peak number	Retention time	Compound	Percentage
1	15.76	dihydroisocoumaringlucoside	4
2	24.39	aloin B	12
3	25.49	aloin A	14
4	27.57	aloinoside B	7
5	29.40	aloinoside A	13
6	33.17	microdontin A & B	20

Peak 6 represents the microdontins A and B which have not separated completely under the chromatographic conditions.

Distribution

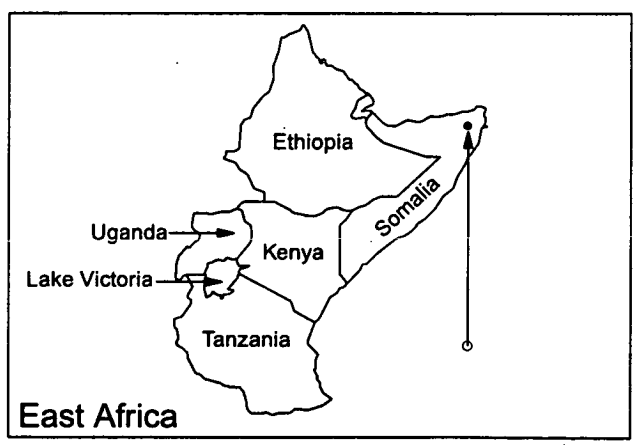
- Taxonomic position:

  Most closely allied to *A. inermis* and *A. luntii* (Lavranos & Carter, 1992).

- Samples analysed:

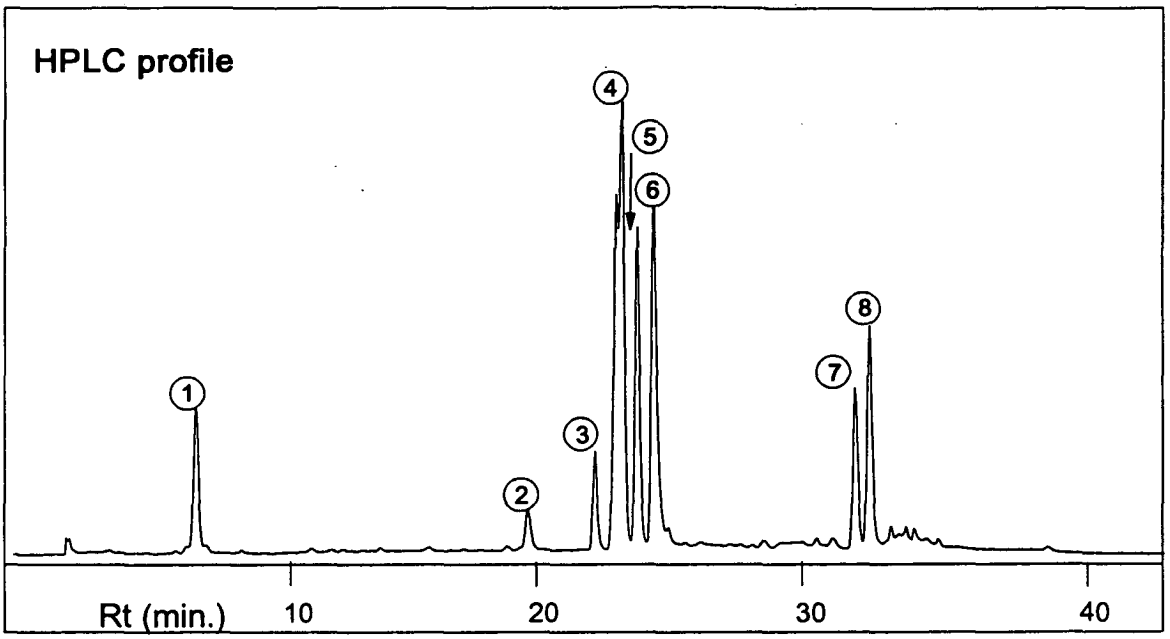
  The leaf exudate was investigated:

  - ex hort NBI



Aloe brunneostriata occurs in the Bari Region near Gardo in Somalia.

Aloe buchlohii Rauh



Peak number	Retention time	Compound	Percentage
1	6.77	unidentified chromone 1	6
2	19.25	unidentified chromone 2	2
3	21.75	unidentified compound 1	4
4	22.75	aloin B & unidentified compound 2	34
5	23.34	unidentified compound 3	14
6	23.95	aloin A	19
7	31.47	microdontin B	7
8	32.00	microdontin A	10

The unidetified compounds (peaks 4 & 5) display an UV absorbance spectra unique to this species. *Aloe buchlohii* is the only Malagasy species containing microdontins. This isomeric pair usually co-occurs with aloinosides which are absent in *A. buchlohii*.

- Taxonomic position:

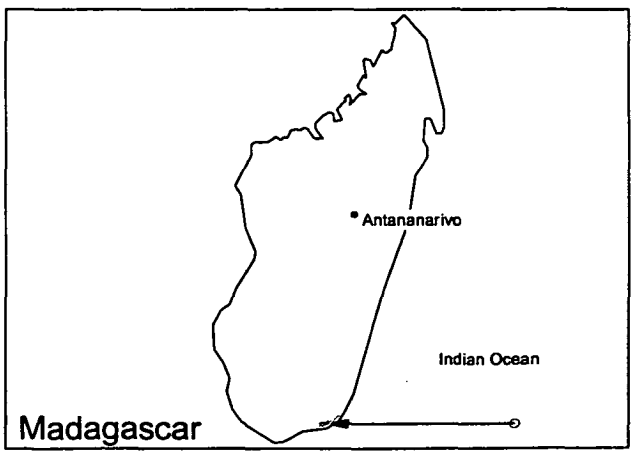
  Group 3 (Reynolds, 1966).

- Samples analysed:

  The leaf extract was investigated:

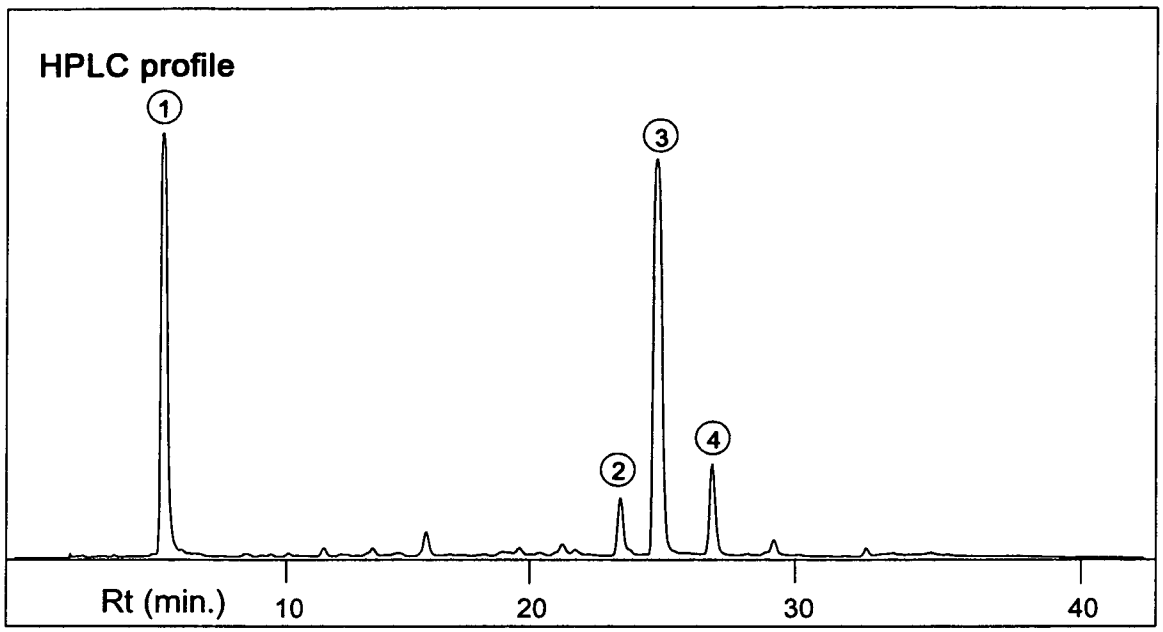
  - ex hort D. Hardy (Tzimbazaza)
  - NBI 14645

Distribution



Aloe buchlohii grows in the Fort Dauphin area in the southern parts of Madagascar.

Aloe bukobana Reynolds



Peak number	Retention time	Compound	Percentage
1	5.69	aloesin	37
2	23.24	unidentified chromone 1	5
3	24.62	homonataloin B & unidentified chromone 2	45
4	26.71	homonataloin A	7

Both the unidentified chromone 1 and 2 (co-eluting with homonataloin B) are probably related to the cinnamoyl chromones.

- Taxonomic position:

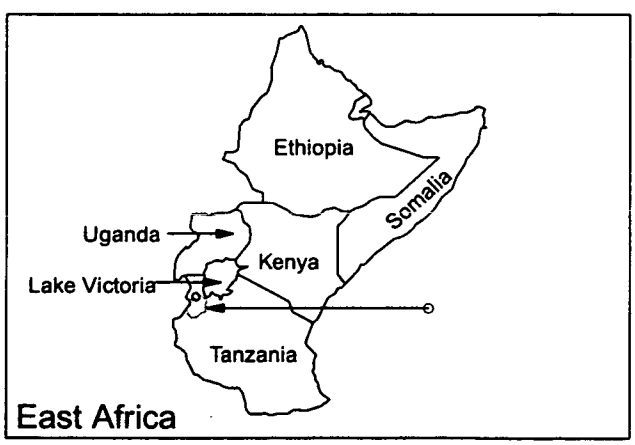
  Group 8 of the tropical aloes (Reynolds, 1966).

- Samples analysed:

  The leaf exudate was investigated:

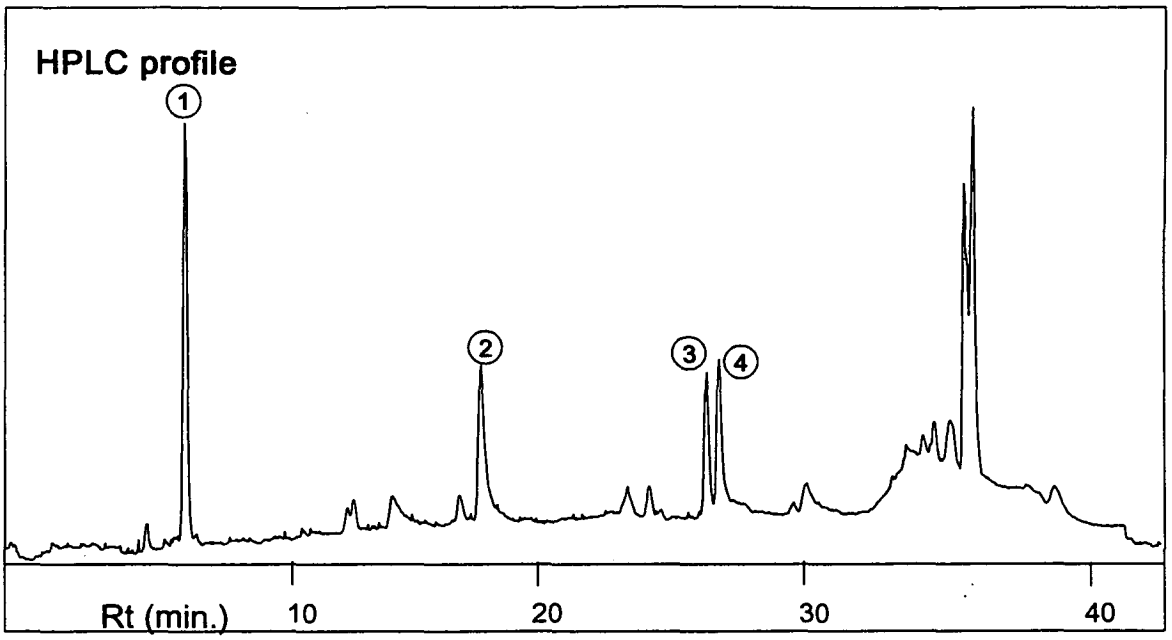
  - RBG, Kew 1990-1816

Distribution



This species has been reported from the Biharamulo, Kigoma and Mpanda Districts of Tanzania.

Aloe bulbillifera H. Perrier var. *bulbillifera*



Peak number	Retention time	Compound	Percentage
1	6.65	unidentified chromone	25
2	17.71	unidentified anthrone 1	11
3	26.12	unidentified anthrone 2	10
4	26.59	unidentified compound	10

The leaf exudate yielded a series of unidentified compounds all in very low concentrations.

- Taxonomic position:

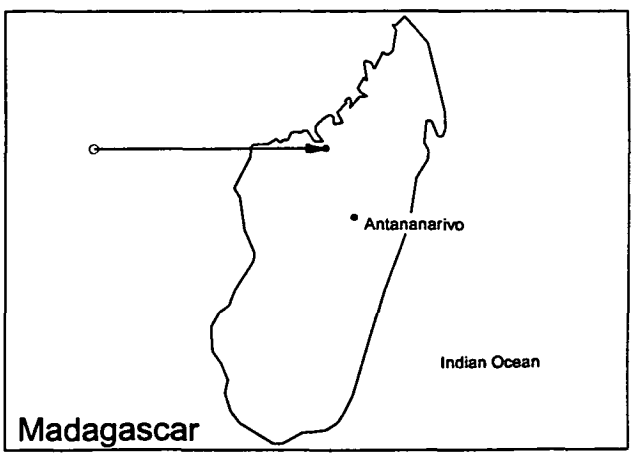
  Group 5 (Reynolds, 1966).

- Samples analysed:

  The leaf exudate was investigated:

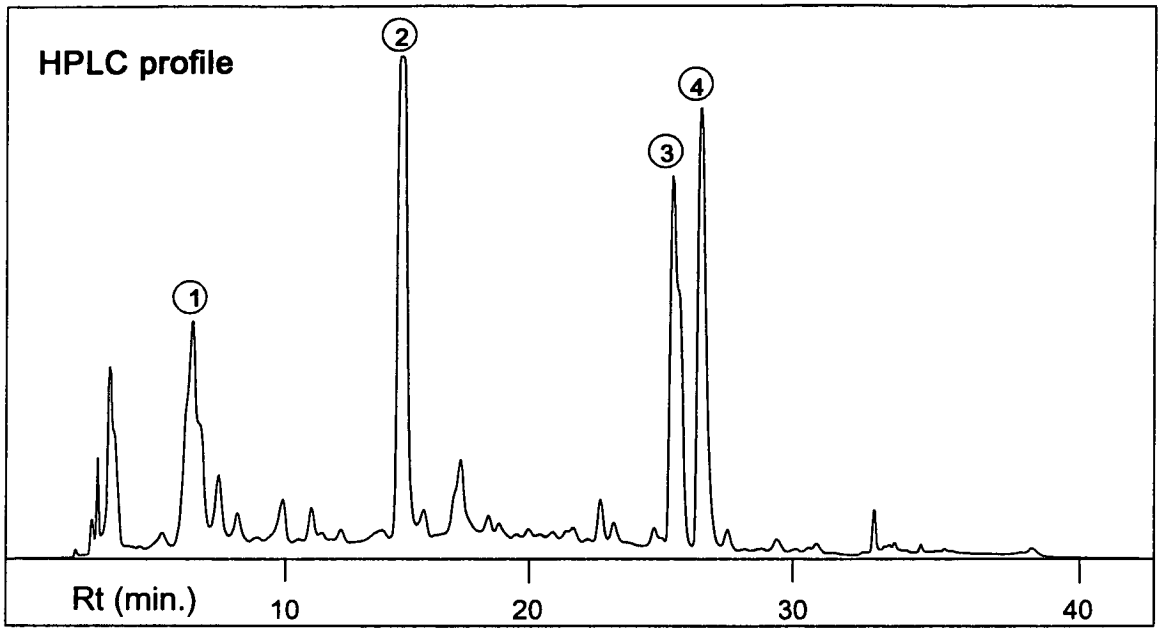
  - ex hort D. Hardy

Distribution



Aloe bulbillifera is restricted to the Analamaitso region in the Majunga Province in the NW of Madagascar.

Aloe bussei A. Berger



Peak number	Retention time	Compound	Percentage
1	6.82	aloesin	13
2	14.95	aloenin	24
3	25.31	aloin B	18
4	26.36	aloin A	18

Two exudate samples of *A. bussei* were analysed. The sample (ex Favell) contained high quantities of the anthrone aloin. In the second sample (RBG, Kew) aloin A and B were absent and contained a number of unidentified chromones. Both samples contained high quantities of the phenylpyrone, aloenin

- Taxonomic position:

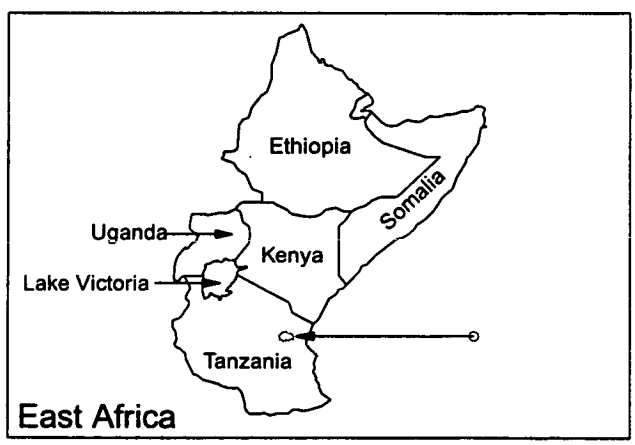
  Group 5 of the tropical aloes (Reynolds, 1966). (syn. *A. morogoroensis*)

- Samples analysed:

  The leaf exudate was investigated:

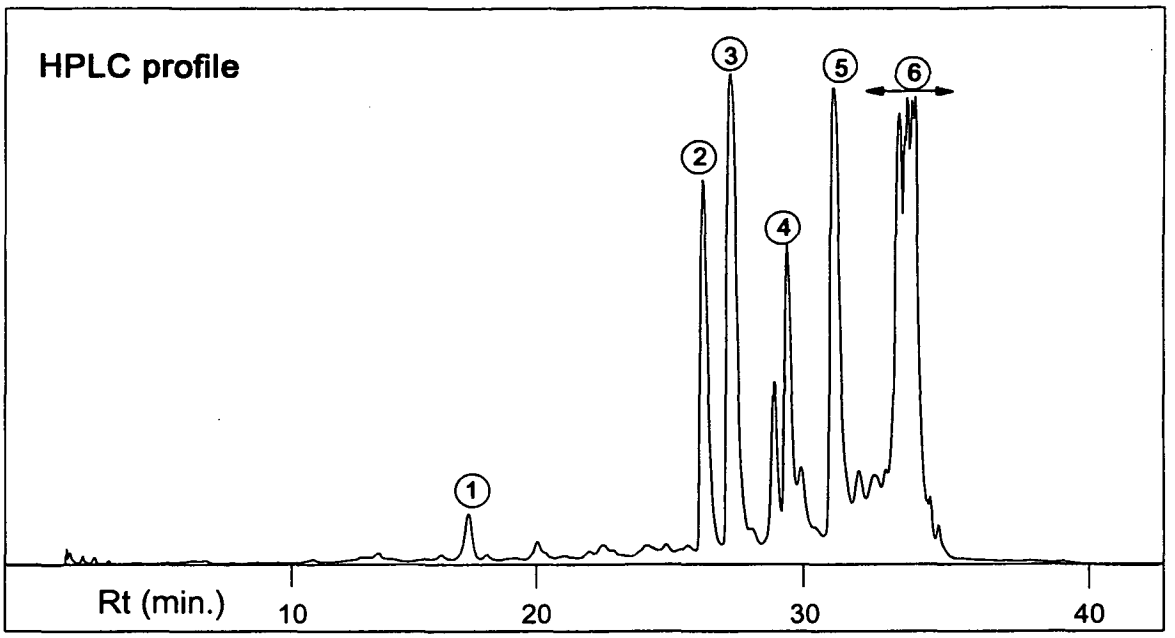
  - ex hort P. Favell
  - RBG, Kew 1990-1816

Distribution



Aloe bussei, occurs in the Morogoro, Kilosa and Iringa Districts of Tanzania.

Aloe calidophila Reynolds



Peak number	Retention time	Compound	Percentage
1	17.23	dihydroisocoumaringlucoside	1
2	25.94	aloin B	9
3	26.94	aloin A	14
4	29.09	aloinoside B	7
5	30.82	aloinoside A	16
6	33.29	microdontins A & B	33

The high quantities of the microdontins (6) results in incomplete separation of the compounds. (See *A. boscawenii*).

Distribution

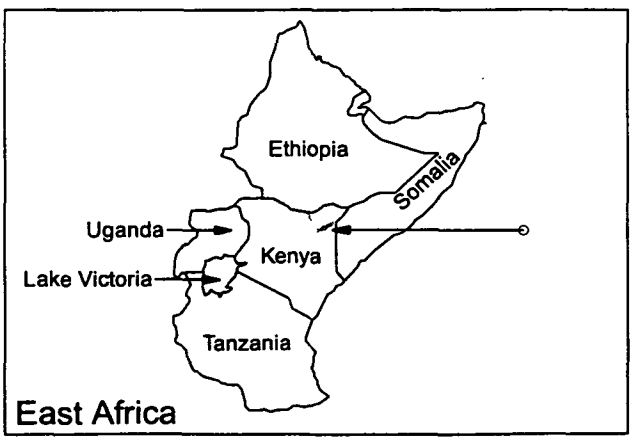
- Taxonomic position:

  Group 13 of the tropical aloes (Reynolds, 1966).

- Samples analysed:

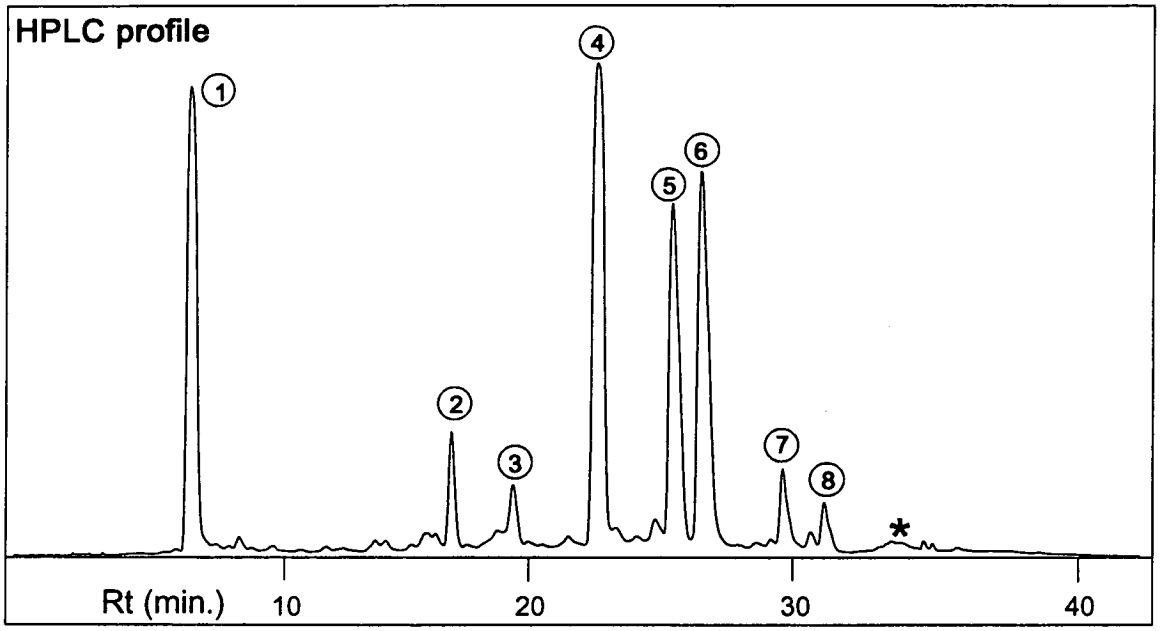
  The leaf exudate was investigated:

  - RBG, Kew 1974-4199



Aloe calidophila is abundant in the Northern Frontier Province (Moyale) in Kenya from where it extends northwards into the southern parts of Ethiopia. This species also occurs north of Wajir in the north eastern parts of Kenya

Aloe cameronii Hemsley



Peak number	Retention time	Compound	Percentage
1	6.80	aloesin	21
2	16.85	aloeresin A	4
3	19.21	unidentified chromone	2
4	22.40	aloeresin D	24
5	25.29	aloin B	16
6	26.40	aloin A	18
7	29.51	aloinoside B	3
8	31.09	aloinoside A	2

This sample represents an unusual combination of compounds as the aloinosides in the aloes of east Africa usually co-occur with the microdontins in the absence of chromones. The deflection in the baseline indicated by * could be ascribed to a low concentration of the microdontins.

- Taxonomic position:

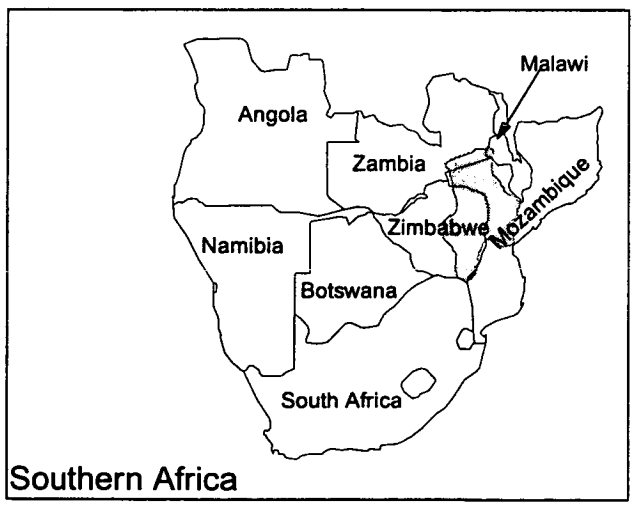
  Group 19 of the tropical aloes (Reynolds, 1996).

- Samples analysed:

  The leaf exudate was investigated:

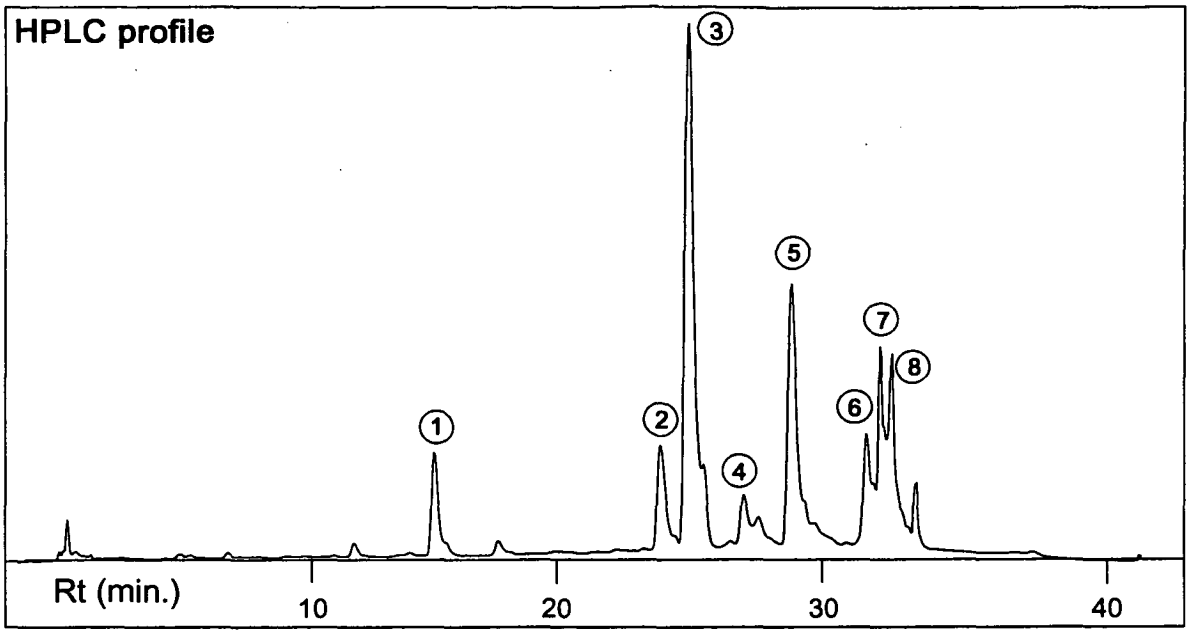
  - NBI 15231
  - A. Ellert

Distribution



Aloe cameronii is widely distributed in Malawi, Zambia, Zimbabwe and Mozambique.

Aloe camperi Schweinfurth



Peak number	Retention time	Compound	Percentage
1	16.23	dihydroisocoumaringlucoside	5
2	24.87	aloin B	5
3	25.91	aloin A	38
4	28.03	aloinoside B	3
5	29.83	aloinoside A	17
6	32.68	microdontin B	8
7	33.19	microdontin A	12
8	33.63	unidentified anthrone	10

Both samples investigated were identical in leaf exudate composition.

Distribution

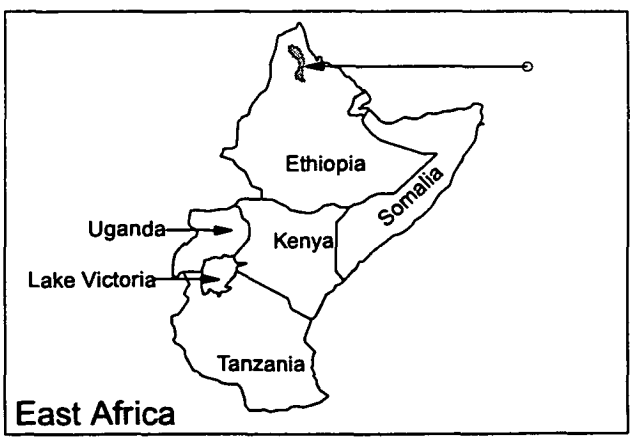
- Taxonomic position:

  Group 13 of the tropical aloes (Reynolds, 1996).

- Samples analysed:

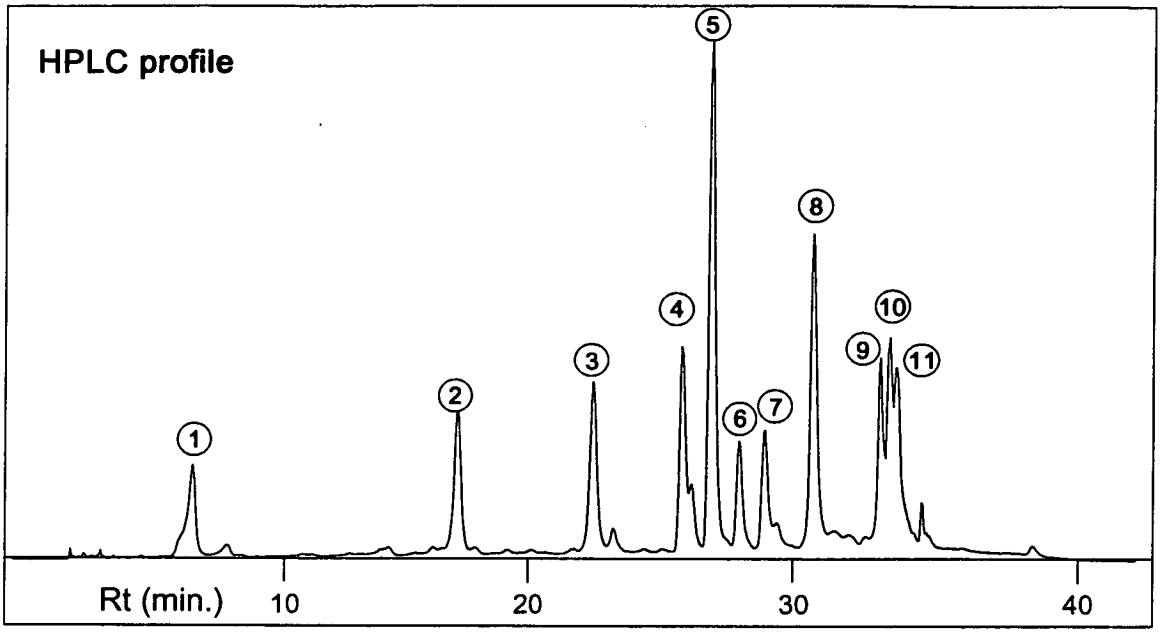
  The leaf exudate was investigated:

  - EDS 208
  - ex hort NBI



Aloe camperi is widely distributed in the northern parts of Ethiopia near Dessye.

Aloe canarina S. Carter



Peak number	Retention time	Compound	Percentage
1	6.97	aloesin	5
2	17.21	unidentified chromone	7
3	22.40	aloeresin D	8
4	25.81	aloin B	8
5	26.88	aloin A	21
6	27.98	unidentified compound	4
7	28.95	aloinoside B	5
8	30.77	aloinoside A	13
9	33.34	microdontin B	7
10	33.70	microdontin A	7
11	33.85	unidentified anthrone	8

This HPLC profile is virtually identical compared to that recorded for *A. microdonta*.

- Taxonomic position:

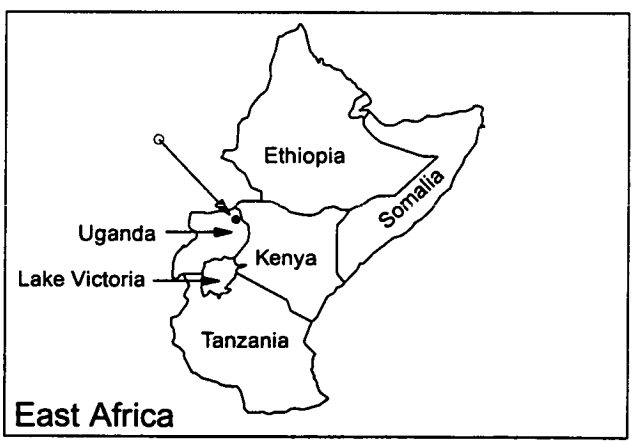
  Allied to *A. microdonta* (Carter, 1994).

- Samples analysed:

  The leaf exudate was investigated:

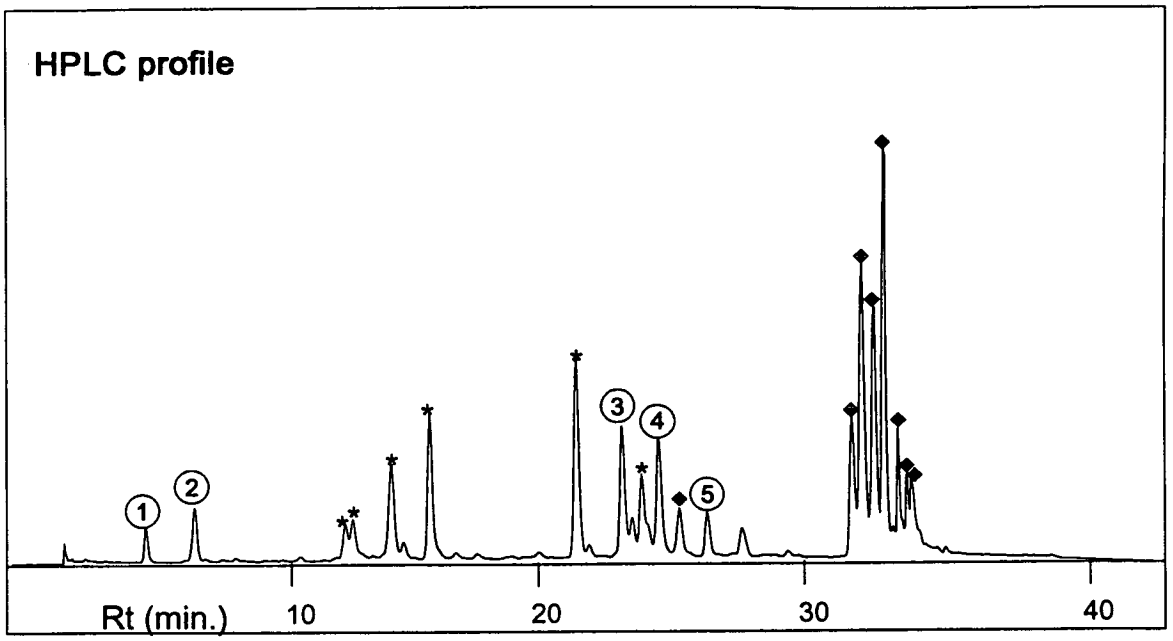
  - RBG, Kew 1977-3888

Distribution



Aloe canarina is found near Loyoro in the north east of Uganda. Unconfirmed reports of this species has been documented in Sudan

Aloe capitata var. *gneissicola* H. Perrier



Peak number	Retention time	Compound	Percentage
1	4.99	aloesin	1
2	6.82	7-*O*-methylaloesin	2
3	22.86	aloin B	6
4	24.23	aloin A	5
5	26.01	unidentified anthrone	2

This species contains a series of coumaroyl chromones (*) and an equally complex mixture of anthrones (◆) which display identical UV absorbance when compared to aloin.

- Taxonomic position:

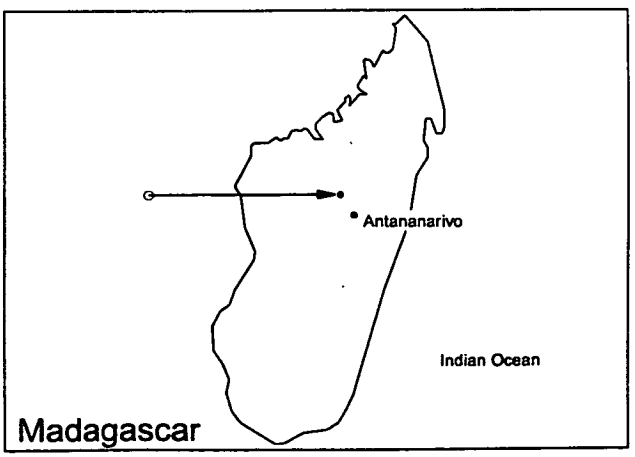
  Group 6 (Reynolds, 1966).

- Samples analysed:

  The leaf exudate was investigated:

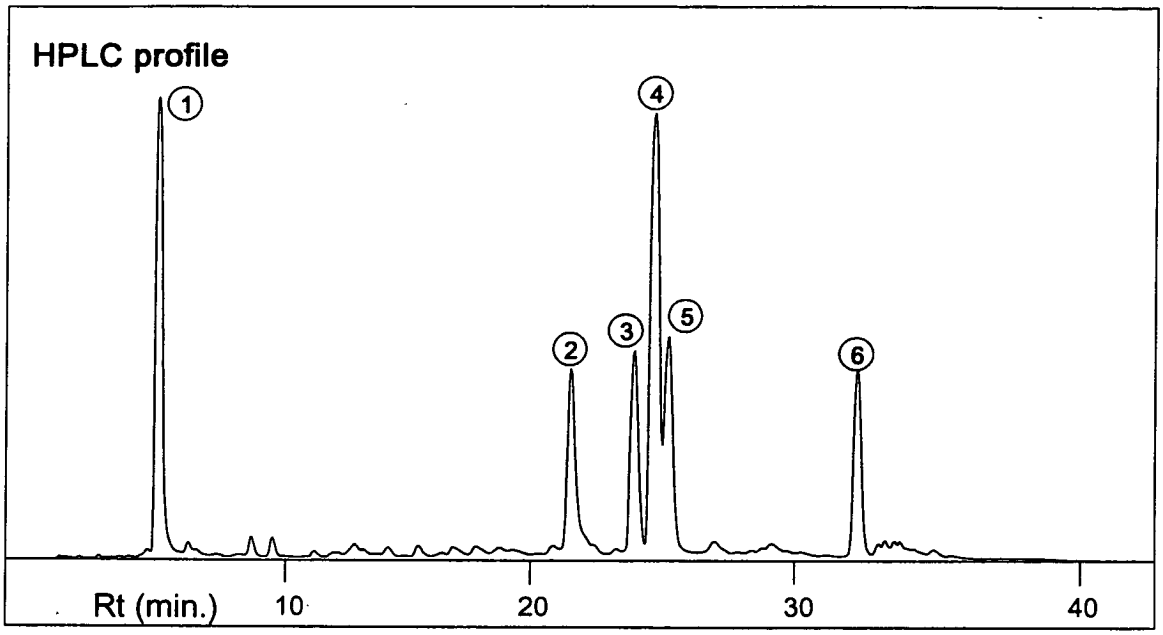
  - NBI 16218

Distribution



As suggested by the name this species has a preference for the gneissic rock near Ankazobe to the north of Antananarivo.

Aloe castanea Schönland



Peak number	Retention time	Compound	Percentage
1	5.62	aloesin	22
2	21.31	unidentified chromone 1	10
3	23.71	aloin B	11
4	24.42	6'-*O*-coumaroylaloesin	27
5	24.99	aloin A	13
6	32.12	unidentified chromone 2	10

This spectrum is almost identical to that recorded for A. *alooides*. This is the species from which 6'-*O*-coumaroylaloesin was isolated.

(See *A. alooides*)

- Taxonomic position:

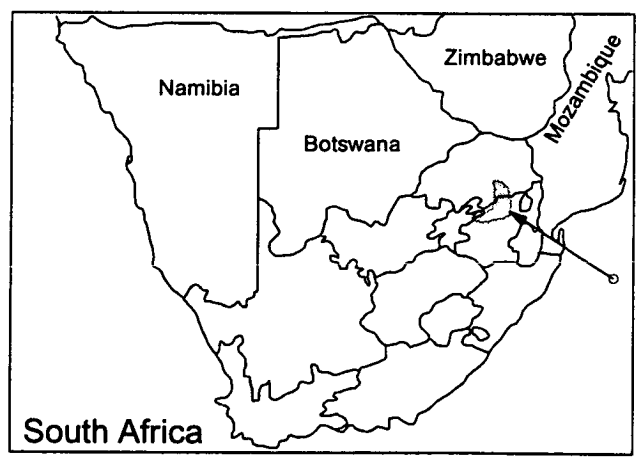
  Aloe section *Anguialoe* (Reynolds, 1950).

- Samples analysed:

  The leaf exudate was investigated:

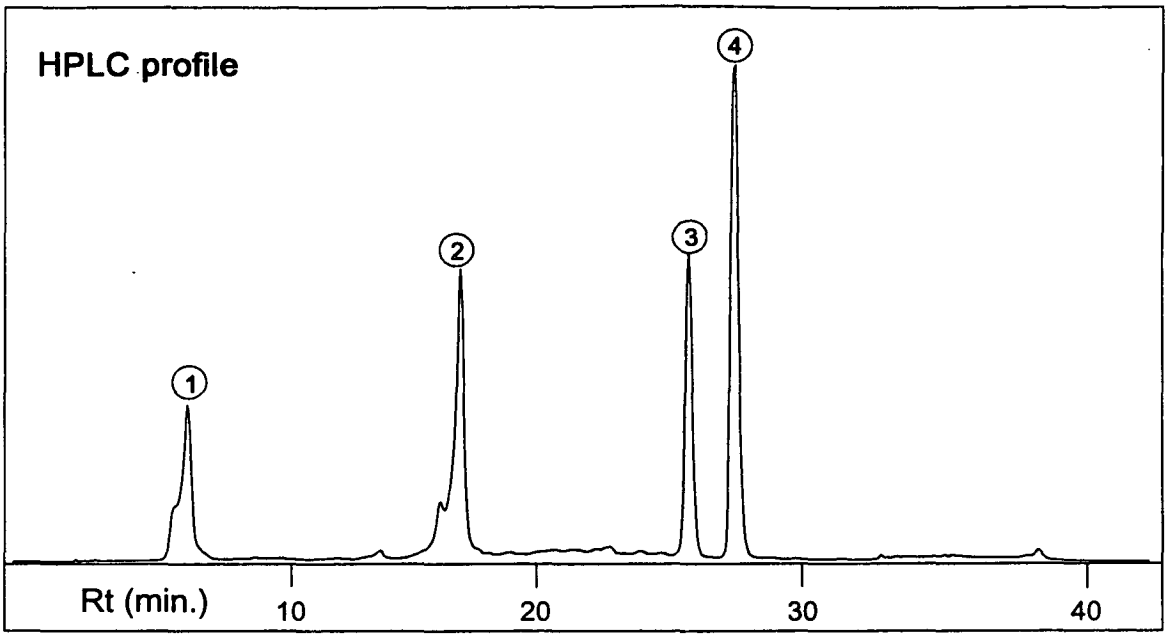
  - Three Rondawels view site, Mpumalanga
  - Elandslaagte

Distribution



This aloe is a common feature in the Lydenburg area (Mpumalanga) and near Pietersburg in the Northern Province of South Africa.

Aloe catengiana Reynolds



Peak number	Retention time	Compound	Percentage
1	6.56	aloesin	16
2	16.93	aloeresin A	29
3	25.59	homonataloin B	19
4	27.28	homonataloin A	35

Aloe catengiana only has four main compounds in the leaf exudate. Both samples (see below), are identical in exudate composition.

- Taxonomic position:

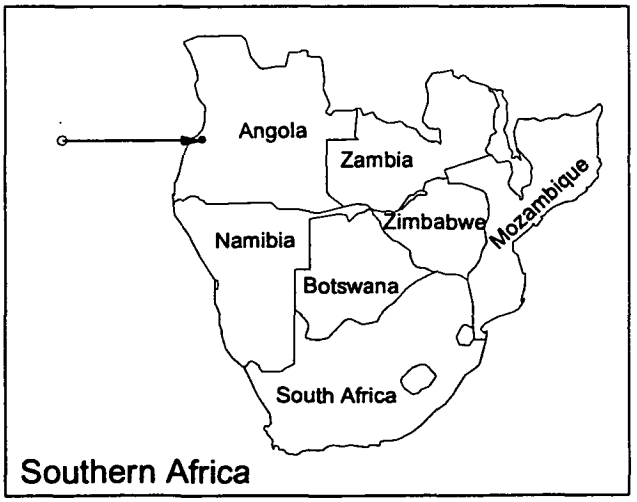
  Group 19 of the tropical aloes (Reynolds, 1996).

- Samples analysed:

  The leaf exudate was investigated:

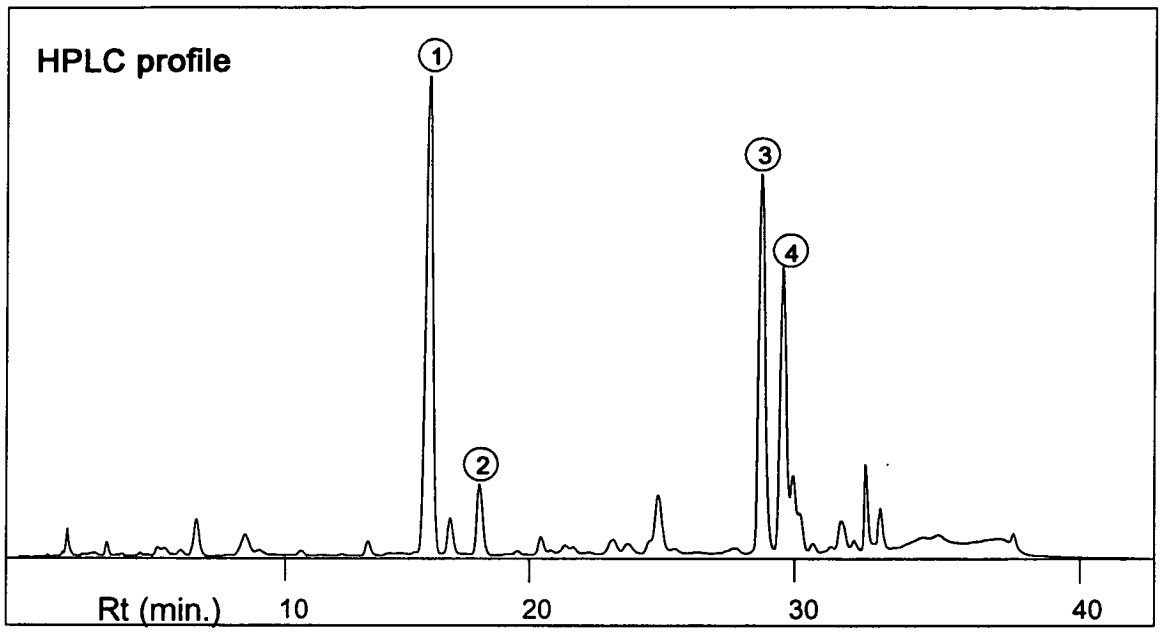
  - ex hort P. Favell
  - RBG, Kew 1960-70602

Distribution



Aloe catengiana is only known to occur at Catengue in the Benguele District of Angola.

Aloe chabaudii Schönland



Peak number	Retention time	Compound	Percentage
1	15.59	plicataloside	33
2	17.94	unidentified compound 1	4
3	28.74	unidentified compound 2	23
4	29.95	unidentified compound 3	17

The three unidentified compounds display an unique UV spectra which does not correlate to any of the known classes of compounds detected in *Aloe.*

- Taxonomic position:

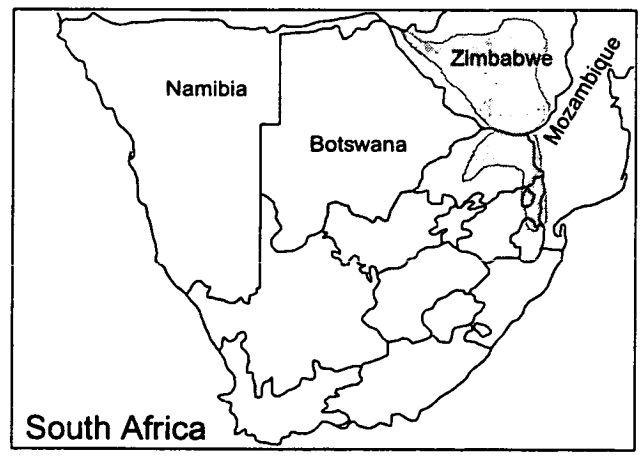
  Aloe series *Aethiopicae* (Reynolds, 1950).

- Samples analysed:

  The leaf exudate was investigated:

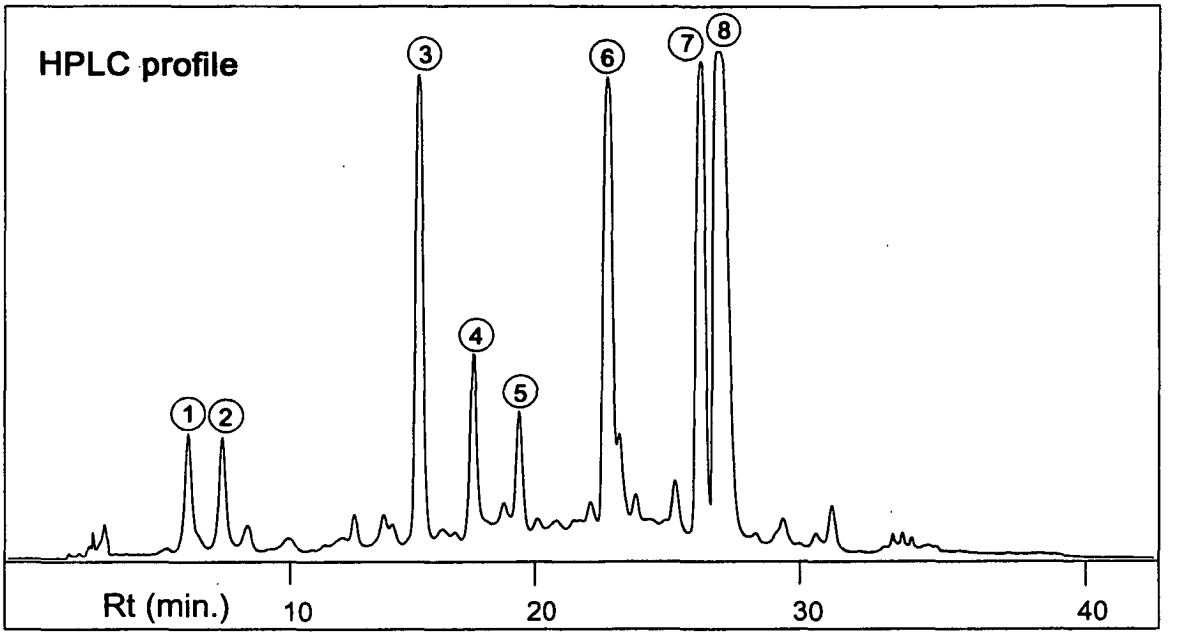
  - A. Ellert 32 (ex Zimbabwe)
  - Steelpoort
  - ex Zimbabwe (Tony de Castro)

Distribution



Aloe chabaudii is widely distributed throughout Zimbabwe. It also occurs in the northern parts of South Africa and extends southwards to Swaziland.

Aloe cheranganiensis S. Carter & Brandham



Peak number	Retention time	Compound	Percentage
1	6.73	aloesin	6.73
2	8.00	7-*O*-methylaloesin	8.00
3	15.73	aloenin	15.73
4	17.44	aloeresin A	17.44
5	19.18	unidentified chromone	19.18
6	22.51	aloeresin D	22.51
7	25.96	aloin B (impure peak)	25.96
8	26.66	aloin A	26.66

The leaf exudate of *A. cheranganiensis* is a highly complex mixture of chromones (peaks 1,2,4,5 & 6) together with anthrones (7 & 8), and the phenylpyrone, aloenin (3). Both samples (see below) analysed were virtually identical.

- Taxonomic position:

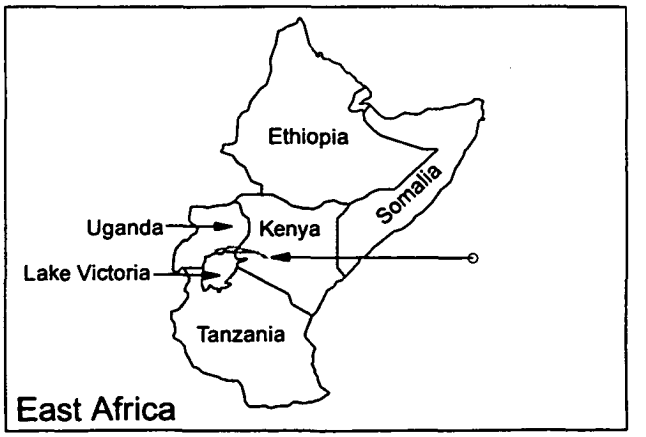
  Allied to *A. dawei*, *A. elgonica*, *A nyeriensis* *A. ngobitiensis* and *A. kedongensis* (Carter & Brandham, 1979).

- Samples analysed:

  The leaf exudate was investigated:

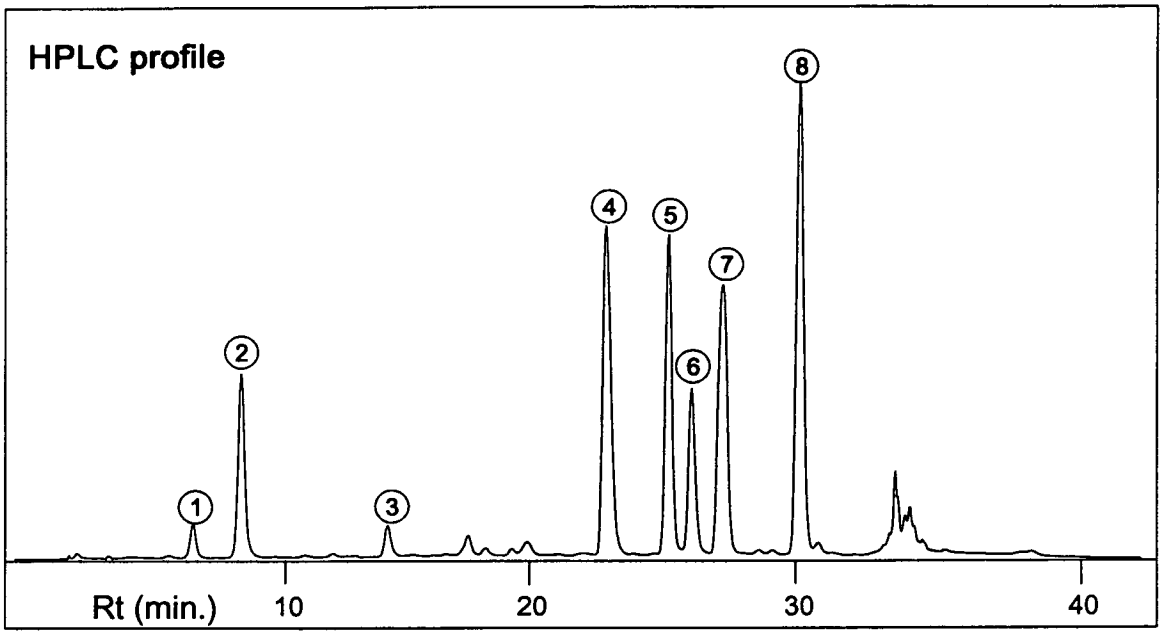
  - ex hort P. Favell
  - ex hort B. Kemble

Distribution



Aloe cheranganiensis is known to grow on the summit of Mt. Toror in Uganda and on the Cherangani Hills in the West Suk District of Kenya.

Aloe chlorantha Lavranos



Peak number	Retention time	Compound	Percentage
1	6.86	aloesin	1
2	8.73	7-*O*-methylaloesin	9
3	14.40	unidentified chromone 1	1
4	22.75	5-hydroxyaloin B	18
5	25.12	unidentified chromone 2	14
6	25.99	aloin B	8
7	27.19	aloin A	16
8	30.11	unidentified chromone 3	23

The unidentified chromones (peaks 5 & 8) could possibly be cinnamoyl chromones as their UV spectra is identical when compared to that of aloeresin E and F.

- Taxonomic position:

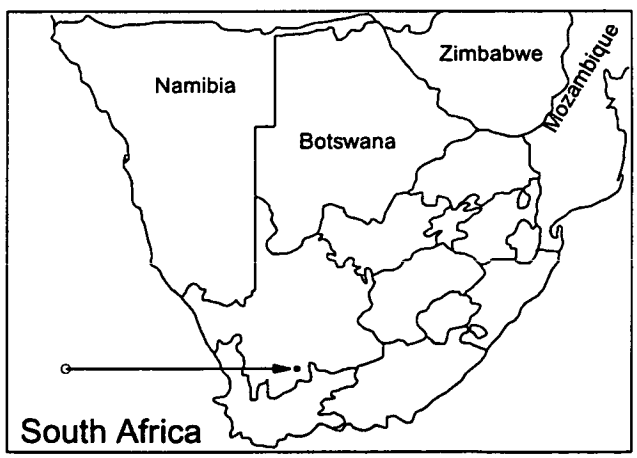
  Allied to *A. broomii* (Lavranos, 1973).

- Samples analysed:

  The leaf exudate was investigated:

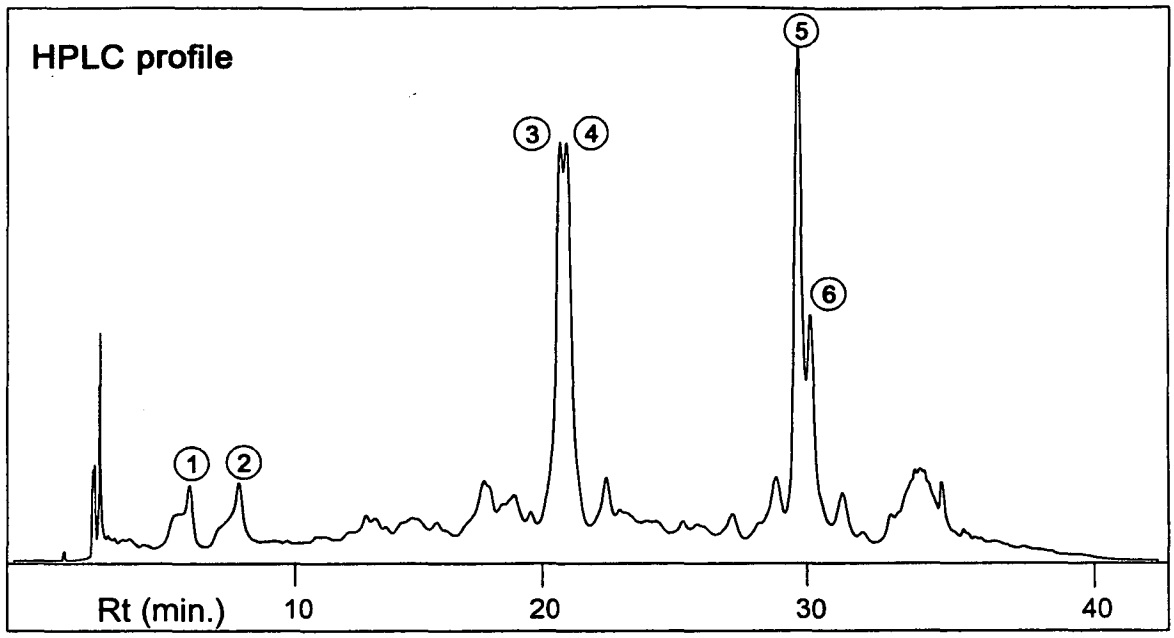
  - Lavranos 10024 (type material)

Distribution



Aloe chlorantha is only known from the type locality which is near Fraserburg in the Northern Cape Province.

Aloe chortolirioides var. *chortolirioides* A. Berger



Peak number	Retention time	Compound	Percentage
1	6.3	aloesin	2
2	8.4	unidentified chromone	3
3	20.4	unidentified anthrone 1	14
4	20.7	unidentified anthrone 2	14
5	29.4	nataloin B	19
6	29.9	nataloin A	9

The major compounds are the two anthrones, nataloin A and B. Two peaks (3 & 4) show UV spectra similar to nataloin and 7-hydroxyaloin.

- Taxonomic position:

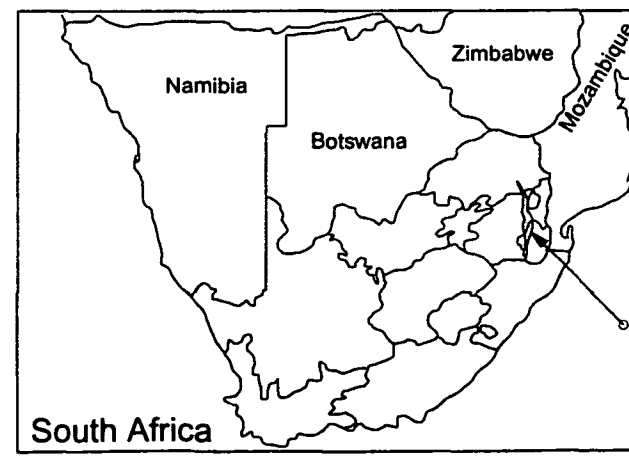
Aloe section *Leptoaloe* (Reynolds, 1950 and Glen & Hardy, 1987).

- Samples analysed:

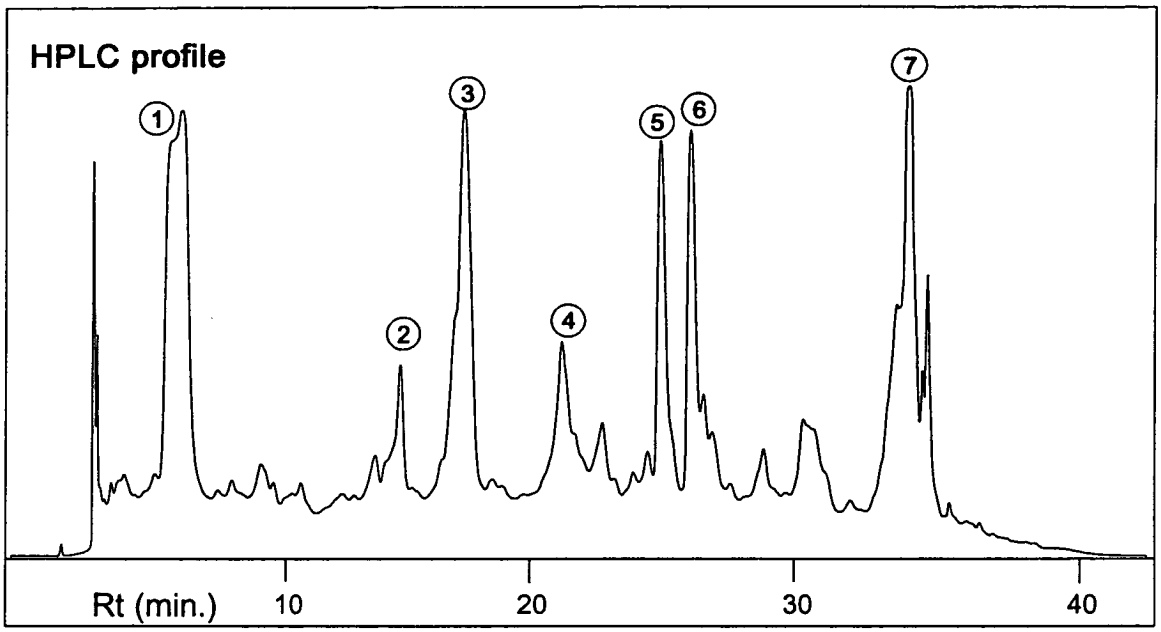
The leaf extract was investigated:

- ex hort C. Craib (collected on Saddleback Mountain, Barberton)
- NBI 29453

Distribution



This grass aloe is abundant in the Barberton area (Mpumalanga) and in the northern parts of Swaziland.



Peak number	Retention time	Compound	Percentage
1	6.3	aloesin (& unidentified cmpd)	18
2	14.9	unidentified flavone	3
3	17.3	unidentified anthrone	10
4	21.0	unidentified compound	5
5	24.7	aloin B	7
6	25.8	aloin A	7
7	34.0	unidentified compounds	15

This species of the grass-like aloes deviates from the general chemical pattern for the group as is the only member to contain the anthrones aloin A and B.

- Taxonomic position:

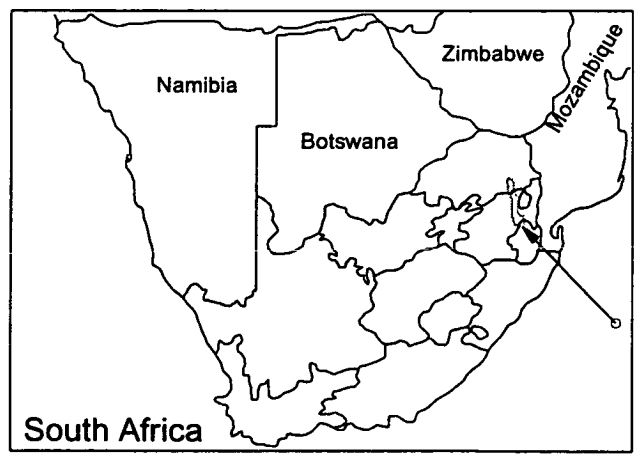
  Aloe section *Leptoaloe* (Reynolds, 1950 and Glen & Hardy, 1987).

- Samples analysed:

  The leaf extract was investigated:

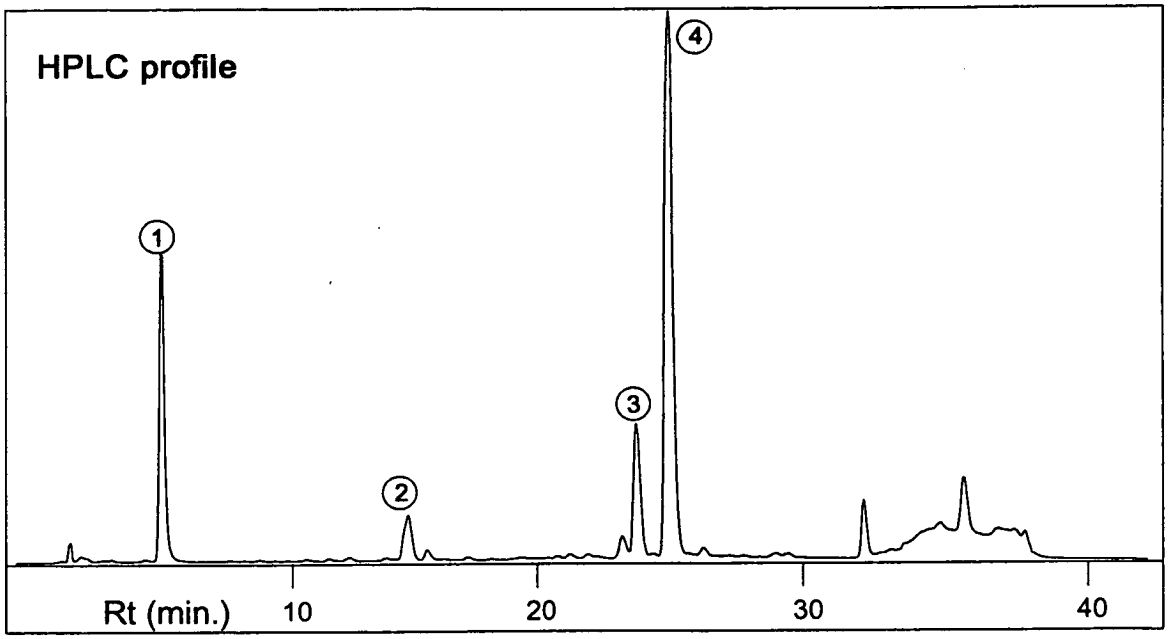
  - ex hort C. Craib (collected near Sabia)

Distribution



This species is found in the mountainous area of northern Swaziland and round the Sabie arae (Mpumalanga).

Aloe christianii Reynolds



Peak number	Retention time	Compound	Percentage
1	5.49	aloesin	19.1
2	14.88	8-*O*-methyl-7-hydroxyaloin	4.3
3	23.61	aloin B	11.1
4	24.81	aloin A and unidentified chromone	52.4

The unidentified chromone co-eluting with aloin A shows an UV spectrum typical of the coumaroyl class of chromones. Two samples of this species were injected. The second sample was from a plant collected in Zambia and showed a different HPLC profile from the one depicted above. As the sample above has valid voucher details it has been selected.

Distribution

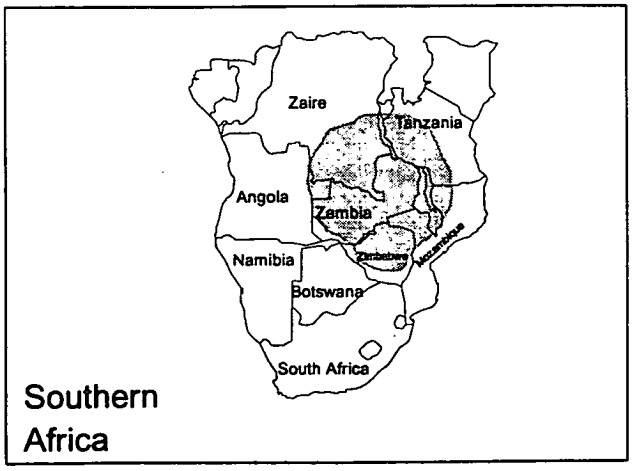
- Taxonomic position:

  Aloe series *Superpositae* (Reynolds, 1950).

- Samples analysed:

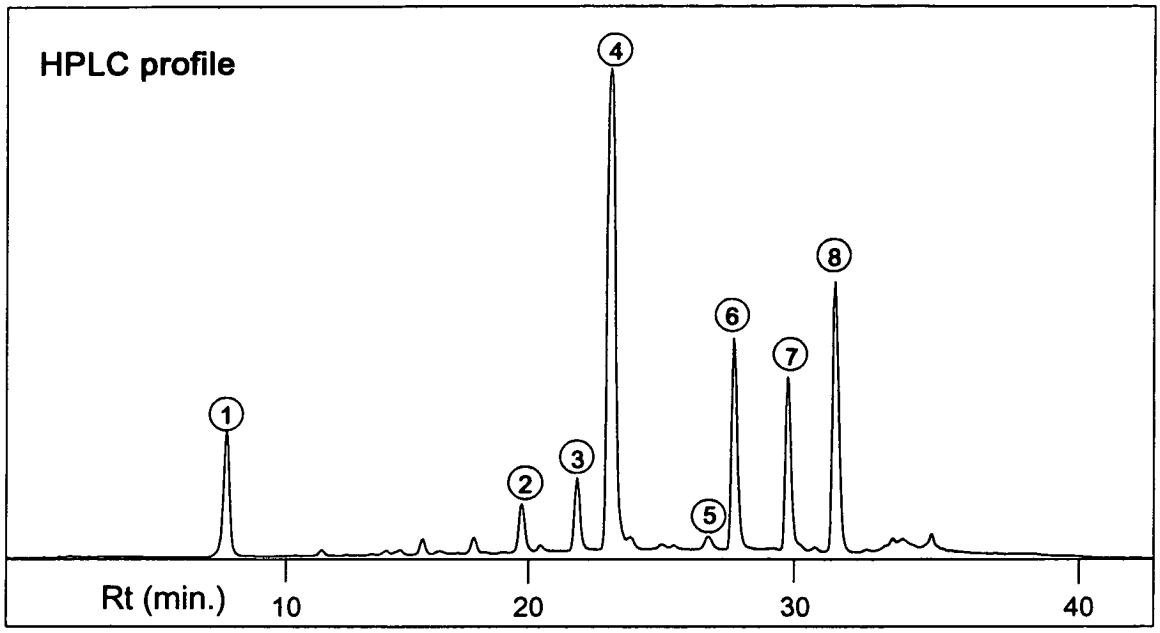
  The leaf exudate was investigated:

  - A. Ellert 591



Aloe christianii has been recorded Zimbabwe, Zambia, Malawi, Mozambique, Tanzania & Zaire.

Aloe chrysostachys Lavranos & L. Newton



Peak number	Retention time	Compound	Percentage
1	8.35	7-*O*-methylaloesin	8
2	19.50	unidentified chromone 1	3
3	21.56	unidentified chromone 2	4
4	22.80	aloeresin D	38
5	26.43	aloin B	1
6	27.39	aloin A	12
7	29.40	aloinoside B	10
8	31.17	aloinoside A	16

The chromones constitute 53 % of the exudate composition. It is interesting to note the 'abnormal' imbalance between the two aloin isomers.

- Taxonomic position:

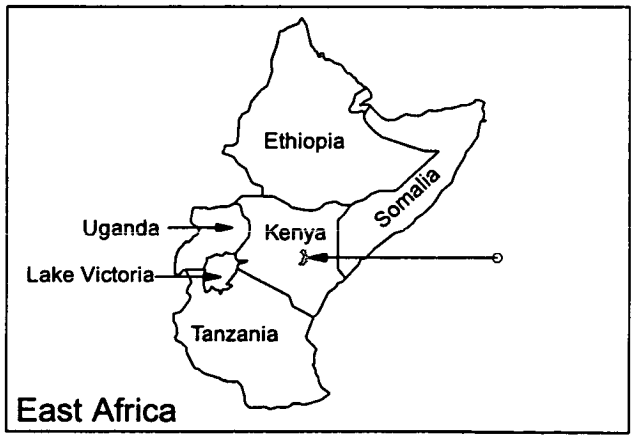
  Allied to *A. rivae* (Lavranos & Newton, 1976).

- Samples analysed:

  The leaf exudate was investigated:

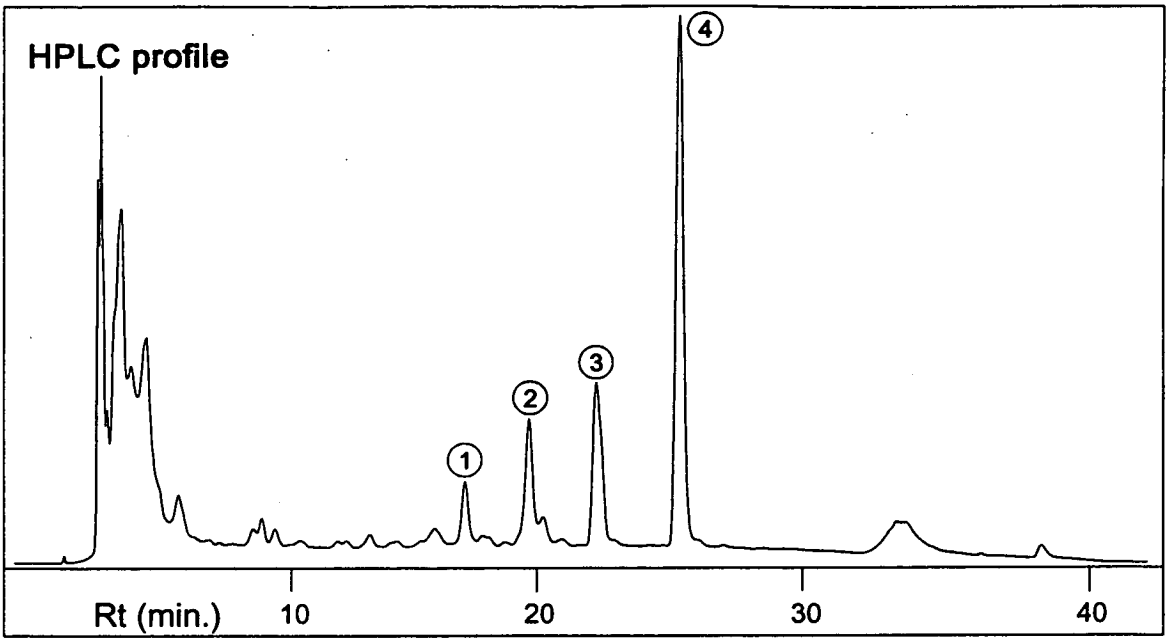
  - L. Newton (type locality)

Distribution



Aloe chrysostachys occurs on the Kijegge and Ngomeni Hills in the Meru and Kitui Districts of Kenya.

Aloe ciliaris Haworth



Peak number	Retention time	Compound	Percentage
1	15.9	unidentified flavone 1	2
2	19.4	unidentified flavone 2	9
3	22.0	unidentified flavone 3	14
4	25.2	unidentified flavone 4	37

The four main components in the methanolic leaf extract all display the UV absorbance pattern characteristic of the flavone group of flavonoids.

- Taxonomic position:

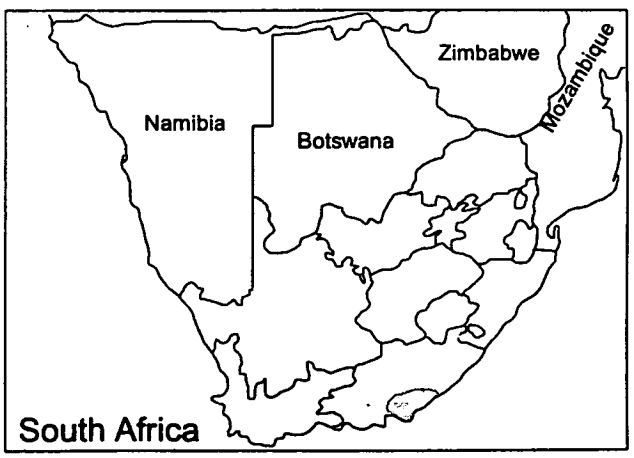
  Aloe series *Macrifoliae* (Reynolds, 1950).

- Samples analysed:

  The leaf extract was investigated:

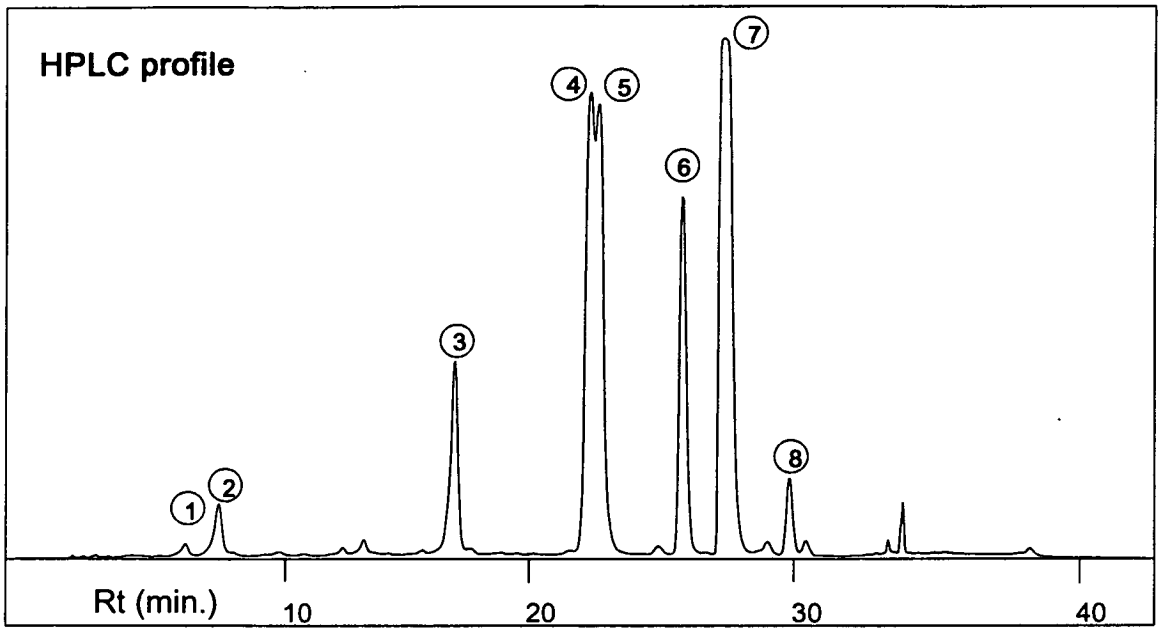
  - ex hort NBG
  - NBI 10674

Distribution



Aloe ciliaris is abundant along the coastal regions of the Eastern Cape Province.

Aloe citrina S. Carter & Brandham



Peak number	Retention time	Compound	Percentage
1	6.56	aloesin	1
2	7.84	7-*O*-methylaloesin	3
3	13.48	homonataloside B	1
4	16.99	aloeresin A	8
5	22.14	aloeresin D & unidentified chromone 1	37
6	25.65	homonataloin B	12
7	27.19	homonataloin A	33
8	29.78	unidentified chromone 2	3

The unidentified chromone co-eluting with aloeresin D (peak 5), is most probably a derivative of this coumaroyl chromone. Peak 8 displays the same UV absorbing properties of the cinnamoyl class of chromones.

Distribution

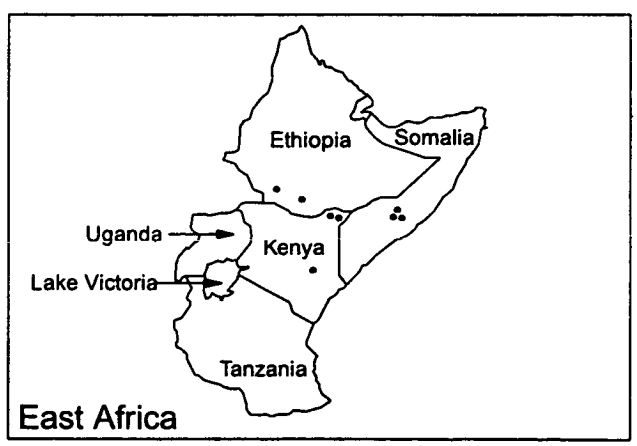
- Taxonomic position:

  Allied to *A. trichosantha* (Carter & Brandham, 1976).

- Samples analysed:

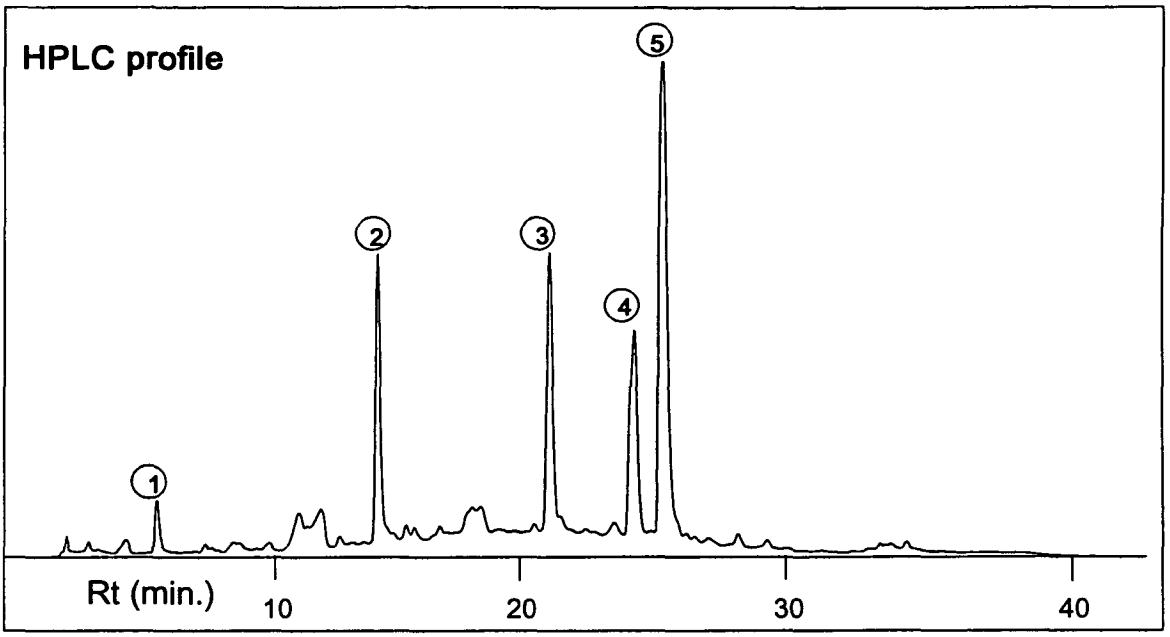
  The leaf exudate was investigated:

  - ex hort P. Favell



Aloe citrina is distributed in the southern parts of Ethiopia, central Somalia and in the Northern Frontier Province of Kenya.

Aloe classenii Reynolds



Peak number	Retention time	Compound	Percentage
1	5.61	aloesin	2
2	14.05	aloenin	12
3	20.62	aloeresin D	14
4	23.86	aloin B & unidentified compound 1	10
5	24.86	aloin A	37

The unidentified compound co-eluting with aloin B (down slope of peak), has an UV absorbance spectrum identical to the series of unidentified compounds in *A. dorotheae*, co-elution of this same compound also occurs in *A. dorotheae*.

- Taxonomic position:

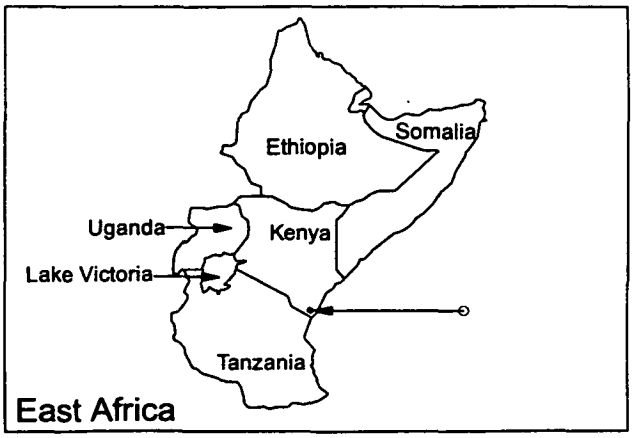
  Group 16 of the tropical aloes (Reynolds, 1966).

- Samples analysed:

  The leaf exudate was investigated:

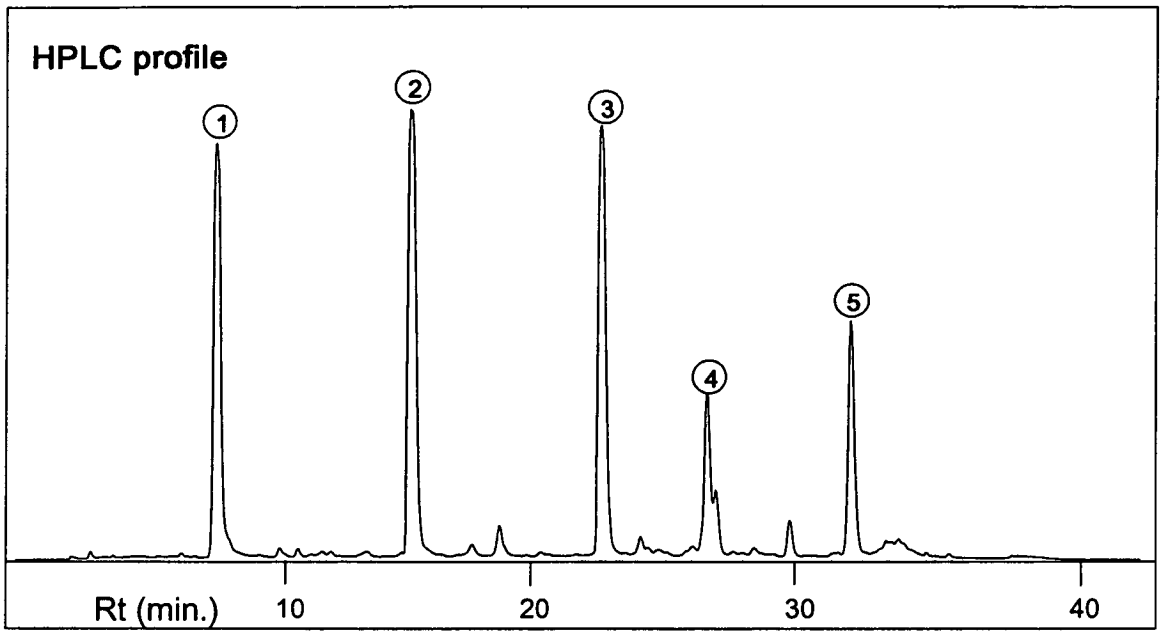
  - L. Newton 3910

Distribution



Aloe classenii is distributed in the Teita District of Kenya where it is usually found on rocky outcrops.

Aloe claviflora Burchell



Peak number	Retention time	Compound	Percentage
1	7.6	7-*O*-methylaloesin	22
2	15.1	10-hydroxyaloin B	25
3	22.4	10-hydroxyaloin-6'-mono-acetate B	23
4	26.1	deacetyllittoraloin	7
5	31.9	littoraloin	11

Aloe claviflora provides the diagnostic fingerprint for *Aloe* series *Asperifoliae.* Other samples of *A. claviflora* in addition to the compounds above also contained aloin. This is the species from which 10-hydroxyaloin-6'-mono-acetate B has been isolated.

- Taxonomic position:

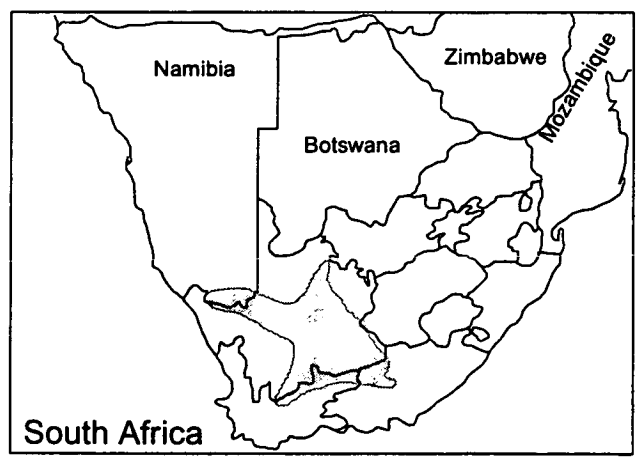
  Aloe series *Asperifoliae* (Reynolds, 1950).

- Samples analysed:

  The leaf exudate was investigated:

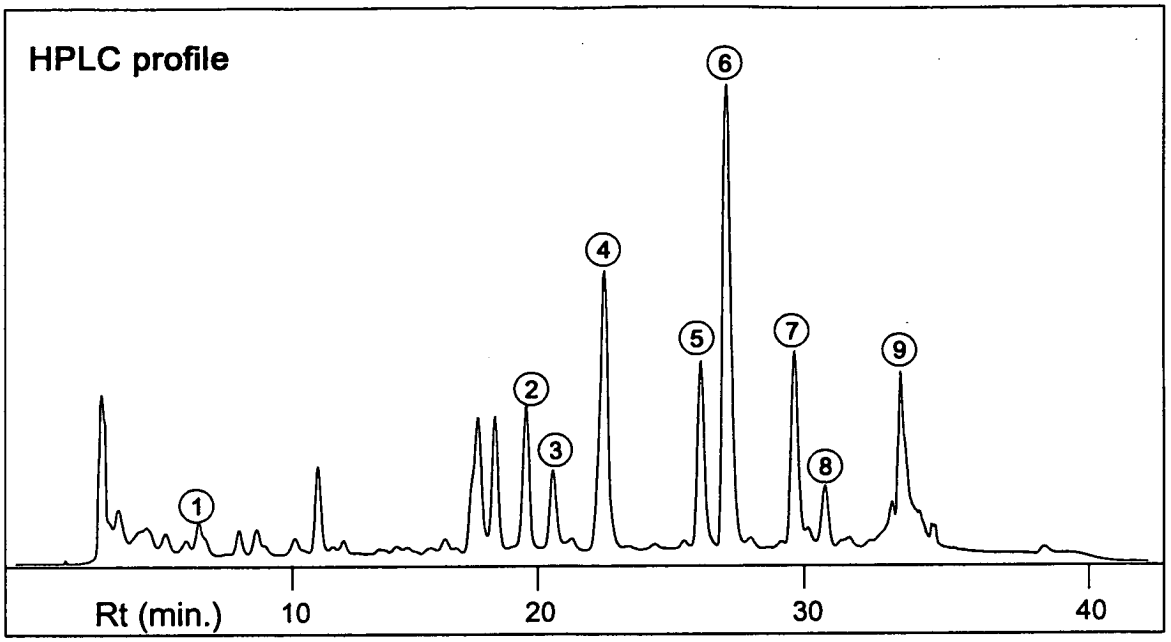
  - Strydenberg,
  - Graaff-Reinet
  - Beaufort West
  - Namibia

Distribution



Aloe claviflora is abundant in the dry interior of South Africa and the southern parts of Namibia

Aloe commixta A. Berger



Peak number	Retention time	Compound	Percentage
1	6.4	aloesin	1
2	19.3	unidentified flavone 1	6
3	20.4	isovitexin	3
4	22.3	unidentified flavone 2	13
5	26.0	aloin B	7
6	27.0	aloin A	20
7	29.5	unidentified anthrone 1	8
8	30.7	unidentified anthrone 2	3
9	33.6	unidentified anthrone 3	9

The analysis above is rather 'unusual' as all the classes of compounds detected in the genus *Aloe* co-occur in this species. Trace amounts of the chromone, aloesin co-occurs with various flavones, including isovitexin.

- Taxonomic position:

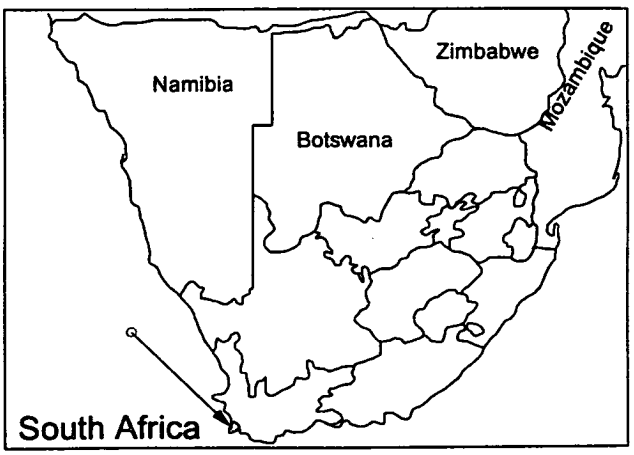
  Aloe series *Macrifoliae* (Reynolds, 1950).

- Samples analysed:

  The leaf extract was investigated:

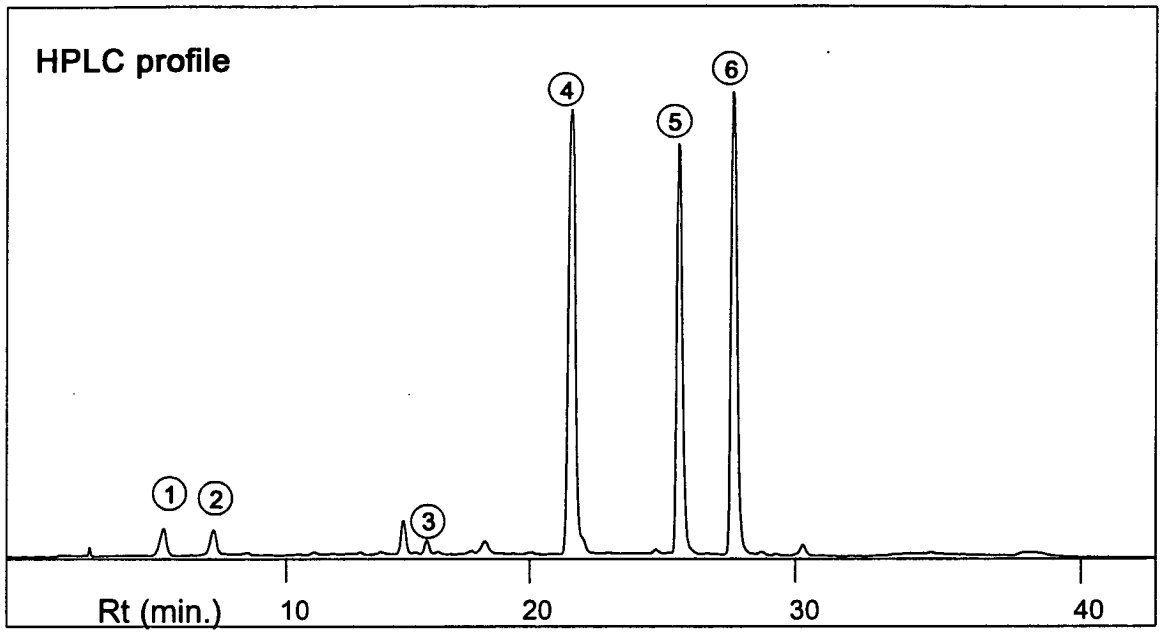
  - ex hort NBG
  - NBI 29455

Distribution



Aloe commixta is restricted in distribution to the Cape Peninsula.

Aloe comosa Marloth & A. Berger



Peak number	Retention time	Compound	Percentage
1	5.95	aloesin	2
2	7.85	7-*O*-methylaloesin	2
3	15.86	dihydroisocoumaringlucoside	1
4	21.28	aloeresin D	35
5	25.32	homonataloin B	25
6	27.32	homonataloin A	31

Aloe comosa represents one of the few South African species in which the chromone aloeresin D is found.

- Taxonomic position:

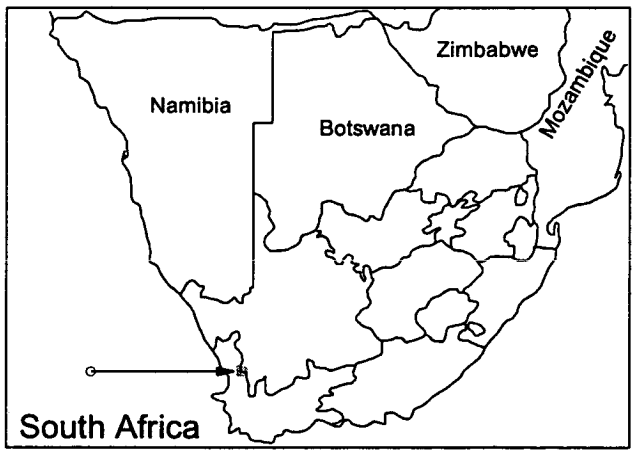
  Aloe series *Comosae* (Reynolds, 1950).

- Samples analysed:

  The leaf exudate was investigated:

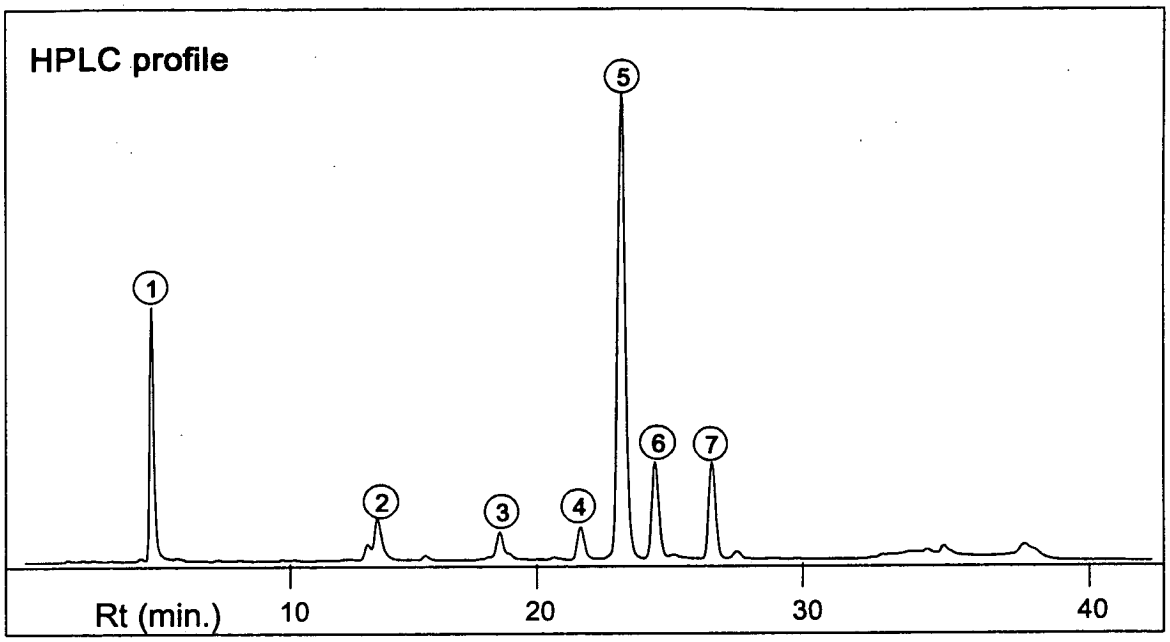
  - Pakhuis Pass

Distribution



Aloe comosa is only found around Clanwilliam in the Western Cape Province.

Aloe comptonii Reynolds



Peak number	Retention time	Compound	Percentage
1	4.83	aloesin	15
2	13.48	unidentified chromone 1	1
3	18.15	unidentified chromone 2	4
4	21.26	unidentified chromone 3	3
5	22.81	aloeresin F	52
6	24.10	homonataloin B	10
7	26.24	homonataloin A	10

The unidentified chromones 1 and 2 have a similar UV spectrum, while the unidentified chromone 3 displays an UV absorbance spectrum identical to aloeresin F. In addition to these compounds, the Perdepoort sample also contained aloeresin A.

- Taxonomic position:

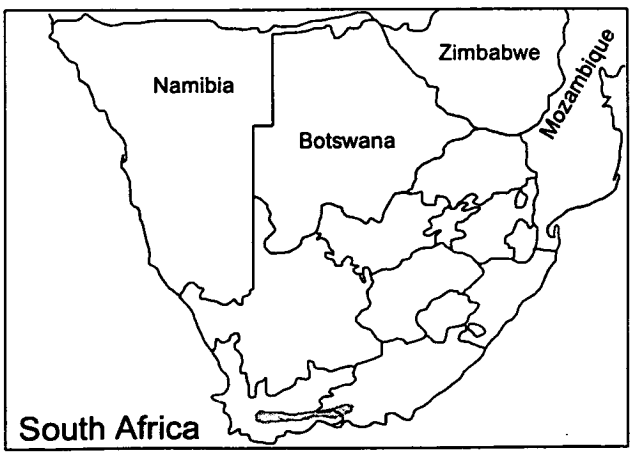
  Aloe series *Mitriformes* (Reynolds, 1950).

- Samples analysed:

  The leaf exudate was investigated:

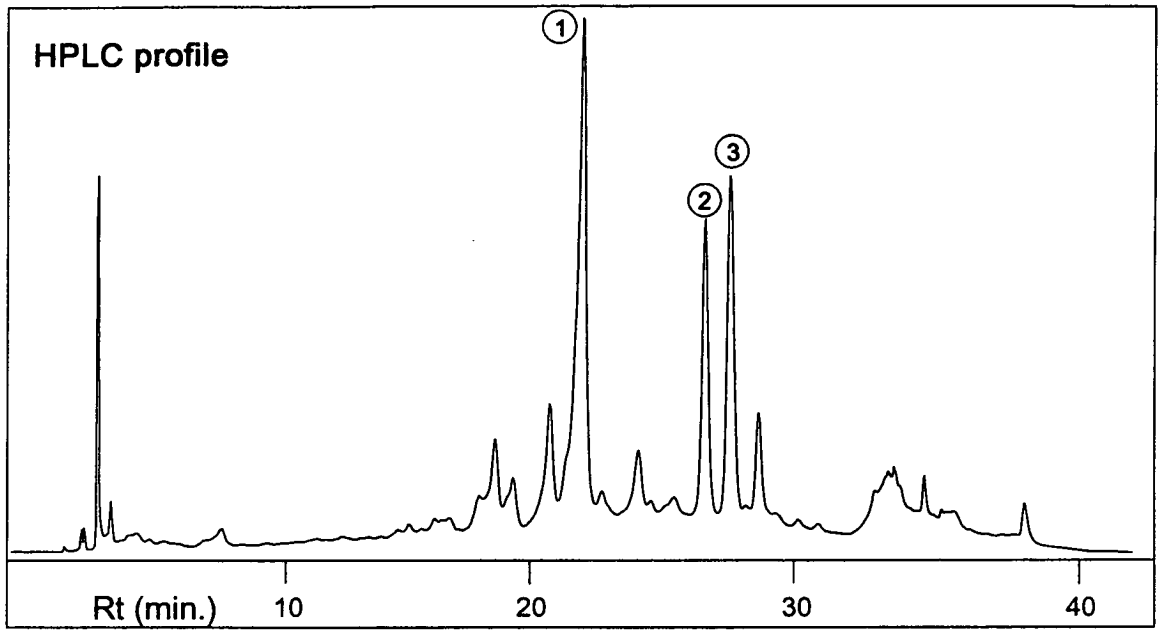
  - NBI 29356
  - Perdepoort

Distribution



This species grows in the central Karoo region. It stretches from Montaqu in the west to Uitenhage in the east.

Aloe confusa Engler



Peak number	Retention time	Compound	Percentage
1	22.07	aloeresin D	31
2	26.75	unidentified anthrone 1	13
3	27.73	unidentified anthrone 2	17

The two unidentified anthrones (most probably isomers), display an UV absorbance identical to nataloin A & B. The retention time however is earlier than expected for nataloin A & B. The second sample of *A. confusa* proved to be quantitatively insufficient for a chromatographic analysis.

Distribution

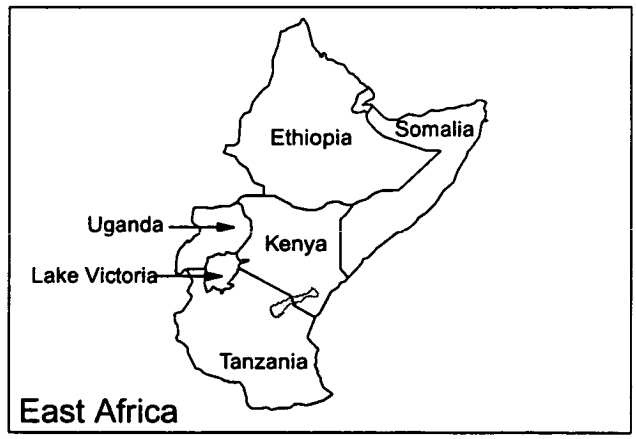
- Taxonomic position:

  Group 10 of the tropical aloes (Reynolds, 1966).

- Samples analysed:

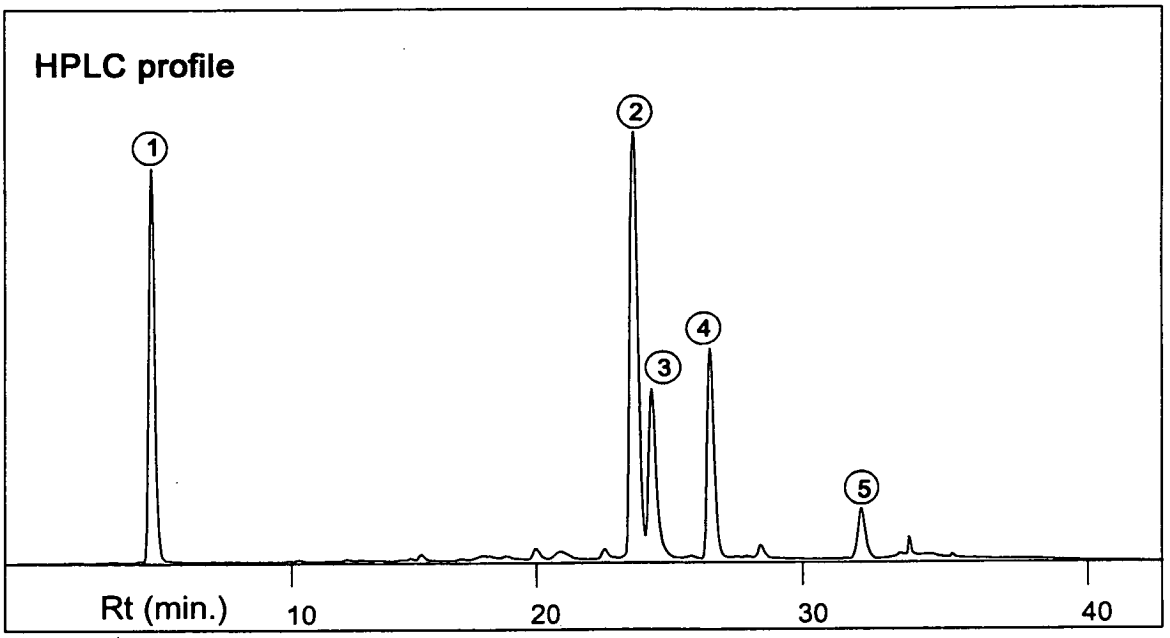
  The leaf exudate was investigated:

  - ex hort Uitenhage (BEVW & GFS)
  - RBG, Kew 1977-5436



Aloe confusa has been recorded in the Teita District of Kenya and the Moshi District of Tanzania.

Aloe congdonii S. Carter



Peak number	Retention time	Compound	Percentage
1	5.00	aloesin	25
2	23.14	unidentified chromone 1	38
3	23.84	homonataloin B	14
4	25.98	homonataloin A	16
5	31.69	unidentified chromone 2	4

Both unidentified chromones shows the same UV spectra characteristic of the coumaroyl chromones.

- Taxonomic position:

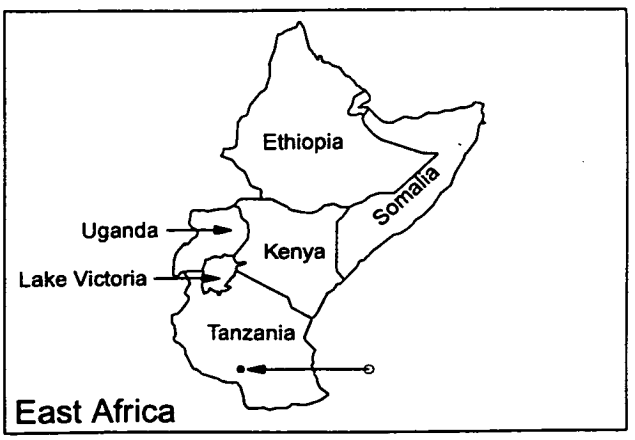
  Allied to *A. mzimbana* (Carter, 1994).

- Samples analysed:

  The leaf exudate was investigated:

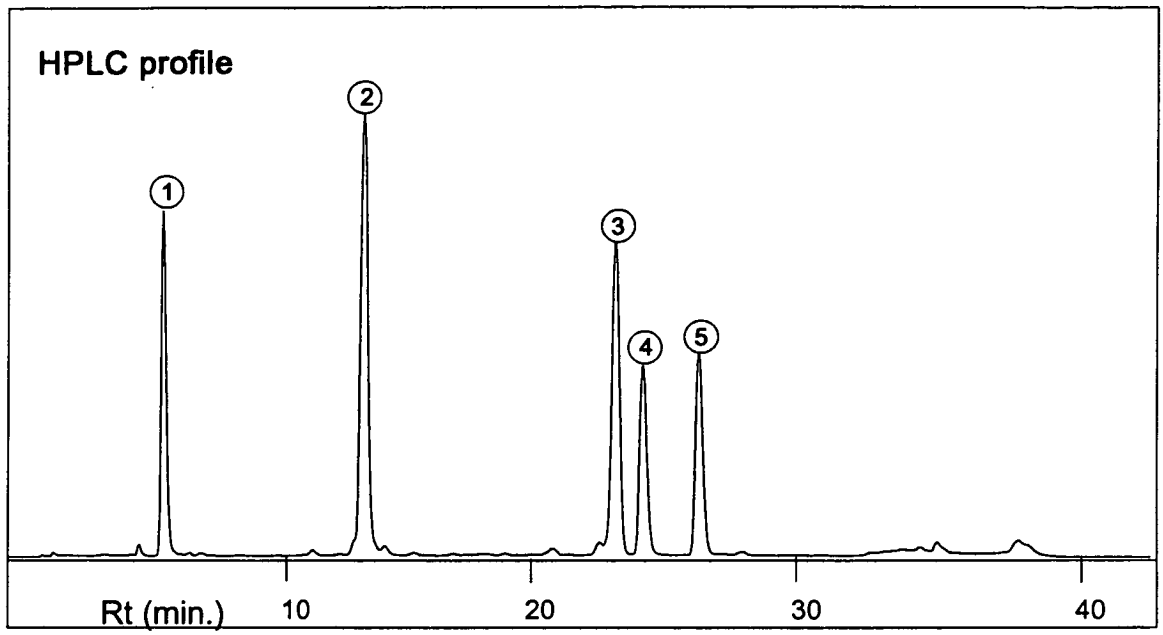
  - ex S. Carter (Collected at type locality)

Distribution



This high altitude species is known from the Kalimbali Mountain in Tanzania.

Aloe conifera H. Perrier



Peak number	Retention time	Compound	Percentage
1	5.58	aloesin	16
2	14.33	aloeresin A	30
3	23.03	unidentified chromone	23
4	24.07	homonataloin B	13
5	26.18	homonataloin A	14

The unidentified chromone displays an UV spectrum resembling the cinnamoyl class of chromones.

- Taxonomic position:

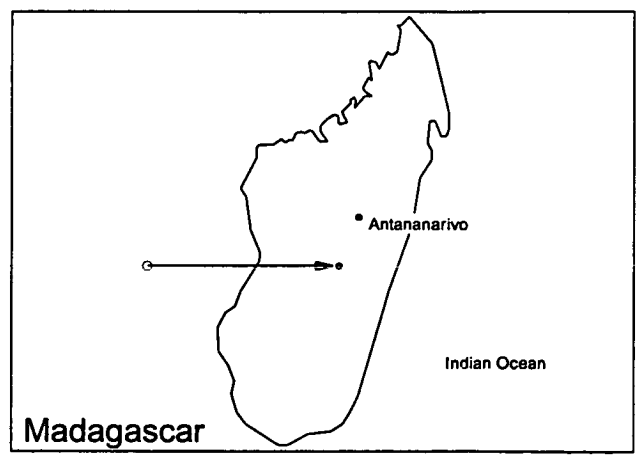
  Group 7 (Reynolds, 1966).

- Samples analysed:

  The leaf exudate was investigated:

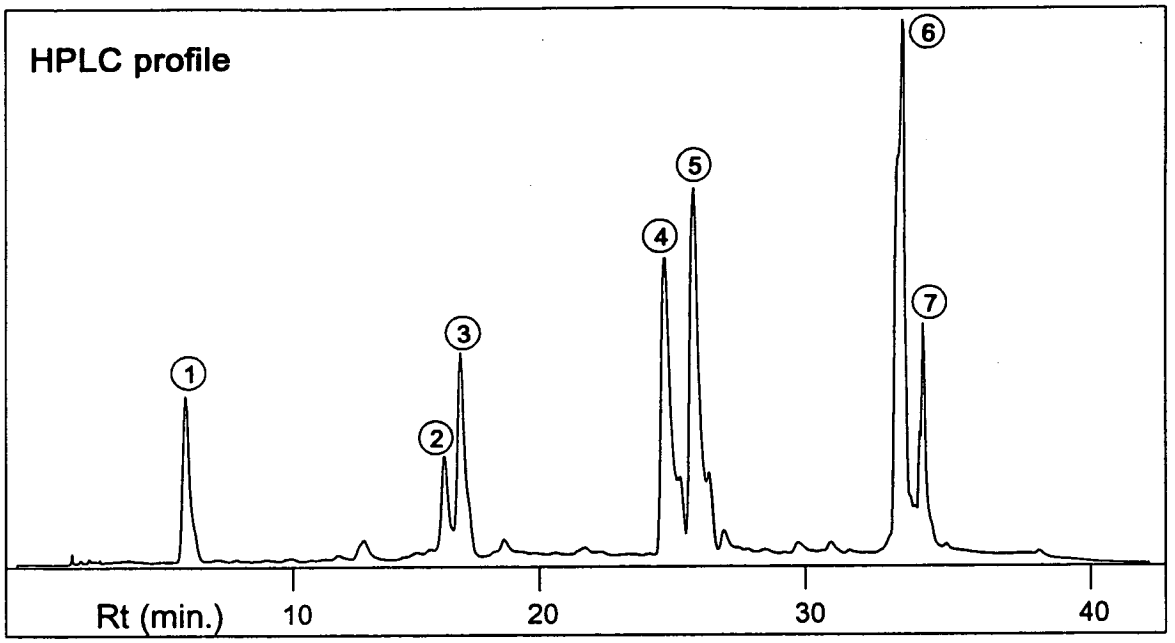
  - ex Lavranos

Distribution



Aloe conifera is abundant around Ivato near Ambatofinandrahana in central Madagascar

Aloe corallina I. Verdoorn



Peak number	Retention time	Compound	Percentage
1	6.5	aloesin	7
2	16.2	aloeresin A	5
3	16.9	unidentified chromone	9
4	25.6	aloin B	16
5	26.7	aloin A	19
6	33.6	unidentified derivative of aloin	28
7	34.4	unidentified anthrone	8

Although *A. corallina* lacks the expected 10-hydroxyaloin B, it contains an unidentified anthrone (peak 6) which also occurs in other members of the *Asperifoliae*-group; *A. dewinteri*, *A. namibensis* and *A. asperifolia*.

- Taxonomic position:

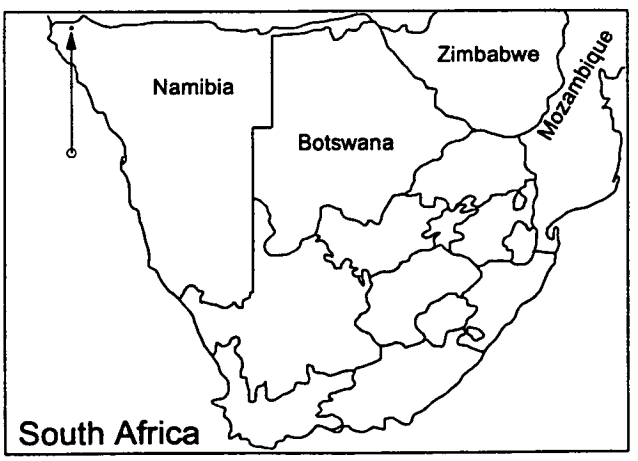
  Aloe series *Asperifoliae* (Verdoorn, 1979).

- Samples analysed:

  The leaf exudate was investigated:

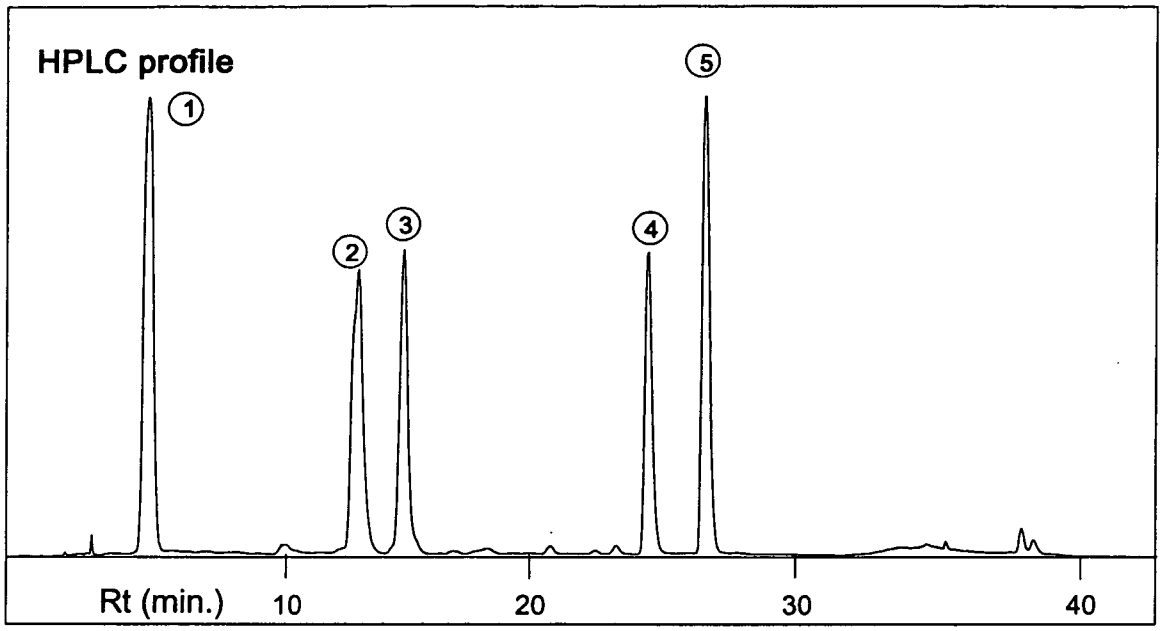
  - NBI 20079

Distribution



Aloe corallina is restricted to the slopes of the Baynes Mountains at Otjomborombonga in northern Koakaland.

Aloe cremnophila Reynolds & P.R.O. Bally



Peak number	Retention time	Compound	Percentage
1	5.01	aloesin	28
2	12.82	unidentified chromone 1	5
3	14.72	aloeresin A	16
4	23.91	homonataloin B	14
5	26.03	homonataloin A	22

The unidentified chromone shows the same UV spectrum as all the coumaroyl chromones.

- Taxonomic position:

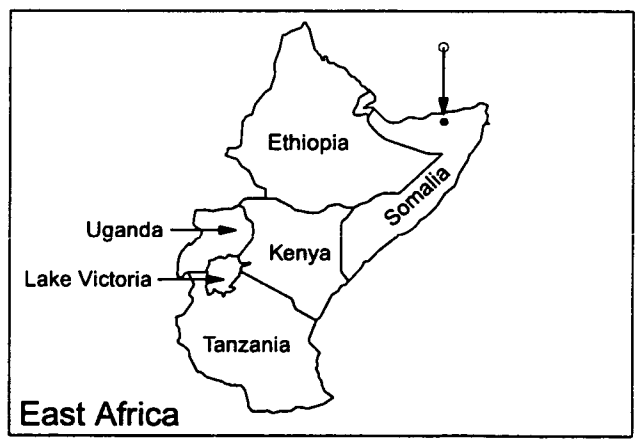
  Group 10 of the tropical aloes (Reynolds, 1966).

- Samples analysed:

  The leaf exudate was investigated:

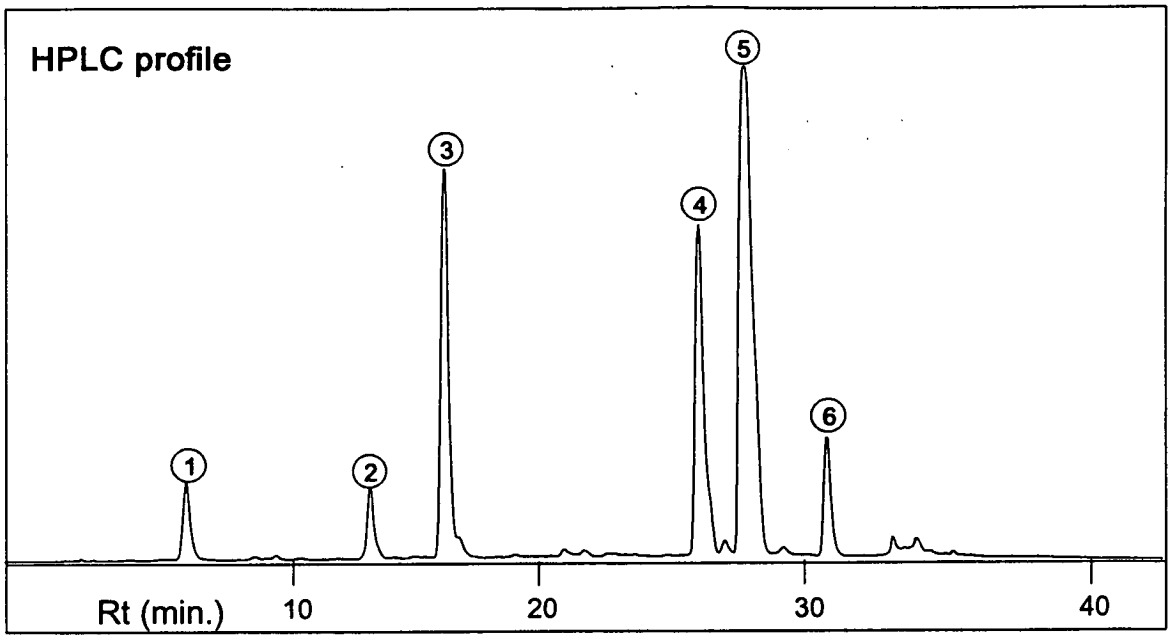
  - RBG, Kew 1958-29517

Distribution



This pendent species is found near Daloh, north of Erigavo in Somalia.

Aloe cryptopoda Baker



Peak number	Retention time	Compound	Percentage
1	6.7	aloesin	4
2	13.57	homonataloside B	3
3	16.32	3'-*O*-coumaroylaloesin	20
4	25.76	homonataloin B	19
5	27.47	homonataloin A	44
6	30.57	3',6'-di-*O*-coumaroylaloesin	5

This combination of compounds is characteristic of species pertaining to *Aloe* series *Latebracteatae*. (see *A. lutescens* and *A. wickensii*).

- Taxonomic position:

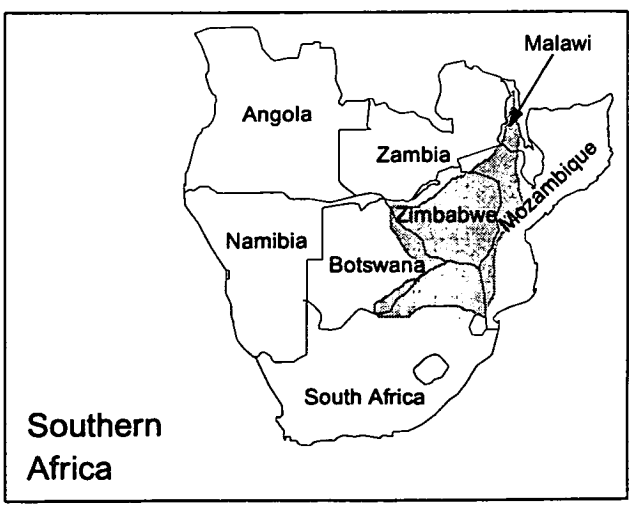
  Aloe series *Latebracteatae* (Reynolds, 1950).

- Samples analysed:

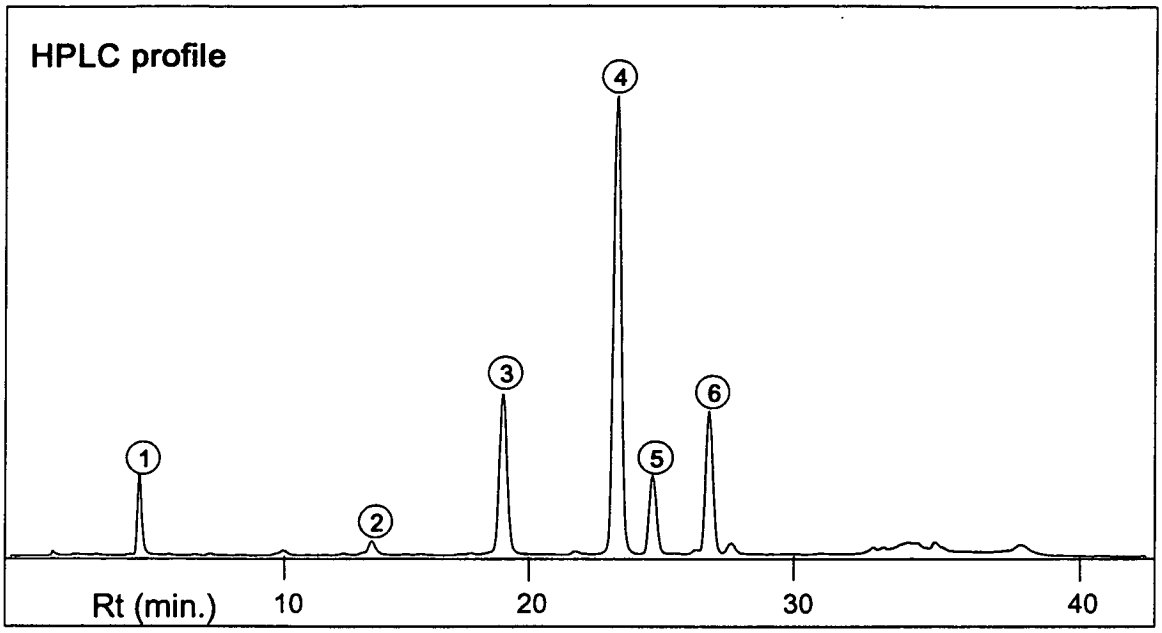
  The leaf exudate was investigated:

  - ex hort NBI (ex Venda)
  - A. Ellert 8

Distribution



Aloe cryptopoda has a northern limit in Malawi from where it extends southwards to areas of Zimbabwe, Botswana, Mozambique and South Africa.



Peak number	Retention time	Compound	Percentage
1	4.95	aloesin	5
2	13.84	unidentified chromone	1
3	18.82	aloeresin E	18
4	23.11	aloeresin F	52
5	24.46	homonataloin B	8
6	26.59	homonataloin A	15

The general chemical pattern for all species placed in *Aloe* series *Mitriformes* is represented by this HPLC profile.

- Taxonomic position:

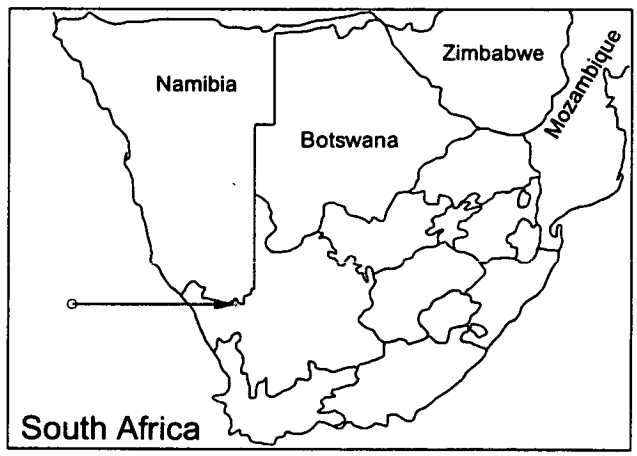
  Aloe series *Mitriformes / Macrifoliae* (Van Jaarsveld, 1982).

- Samples analysed:

  The leaf exudate was investigated:

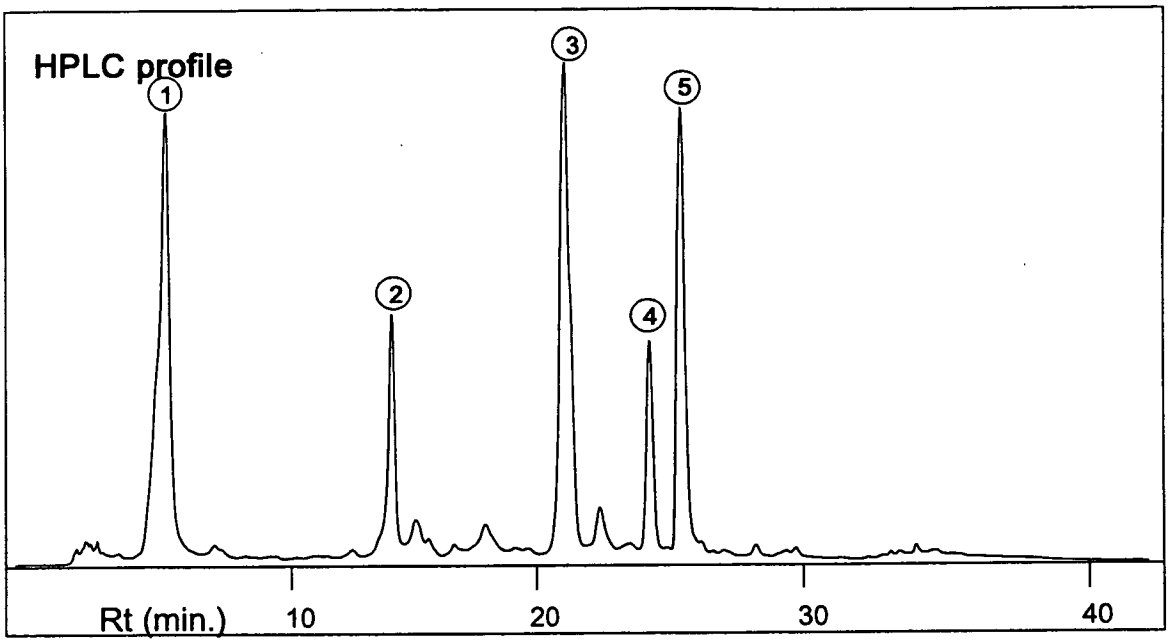
  - Dabenorisberg (type material)

Distribution



This pendant species is only known from the hard quartz peaks of the Dabenoris mountain in Northern Bushmanland

Aloe dawei Berger



Peak number	Retention time	Compound	Percentage
1	5.70	aloesin & unidentified compound 1	23
2	14.27	aloenin	9
3	20.88	aloeresin D	23
4	24.15	aloin B & unidentified compound 2	8
5	25.27	aloin A	19

The unidentified compound co-eluting with aloin B (down slope of peak), has a UV absorbance spectrum identical to the series of unidentified compounds in *A. dorotheae* and *A. classenii*, co-elution of this same compound also occurs in the two latter species.

- Taxonomic position:

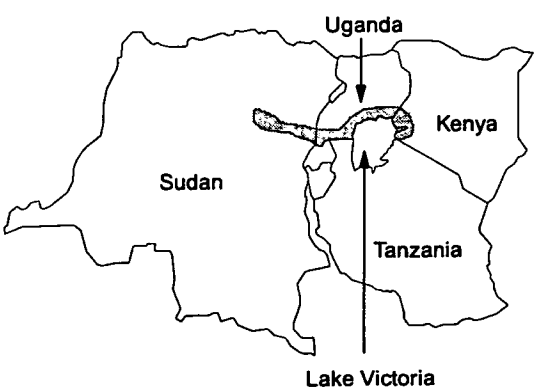
  Group 19 of the tropical aloes (Reynolds, 1966).

- Samples analysed:

  The leaf exudate was investigated:

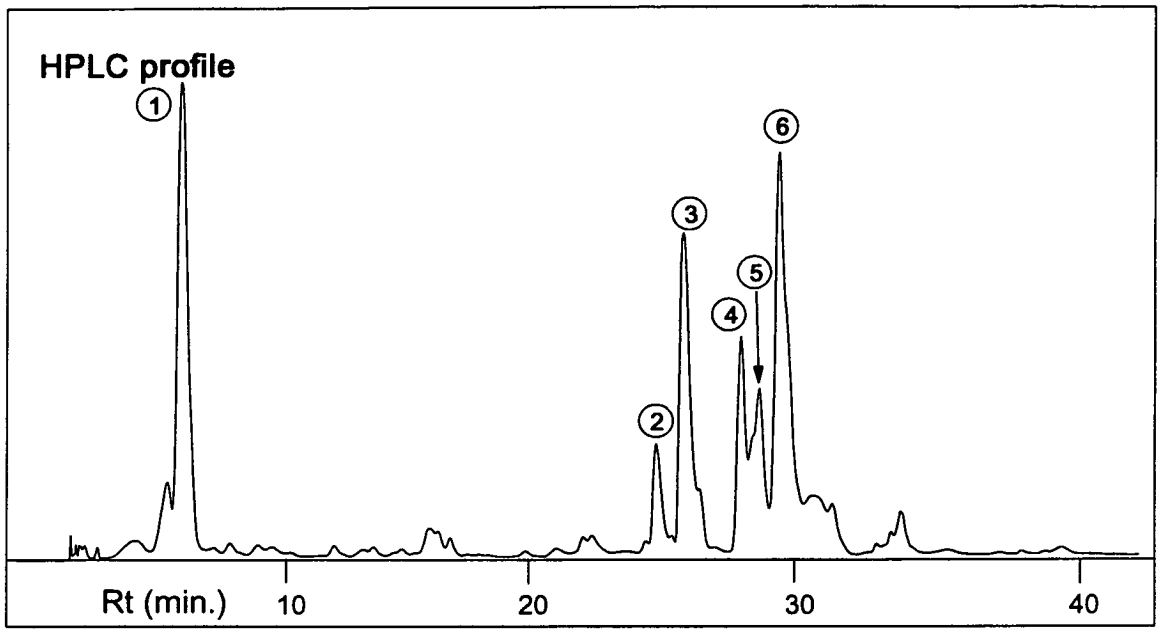
  - RBG, Kew 1951-35701
  - Bot Staats München

Distribution



East Africa

Aloe dawei is widely distributed in Uganda, Kenya, Zaire and Rwanda.



Peak number	Retention time	Compound	Percentage
1	6.39	aloesin	21
2	24.66	aloin B	5
3	25.68	aloin A	14
4	27.88	unidentified chromone 1	7
5	28.59	unidentified chromone 2	9
6	29.34	unidentified chromone 3	18

Three unidentified chromones (4-6) all have an identical UV absorbance spectrum characteristic to the cinnamoyl chromones.

Distribution

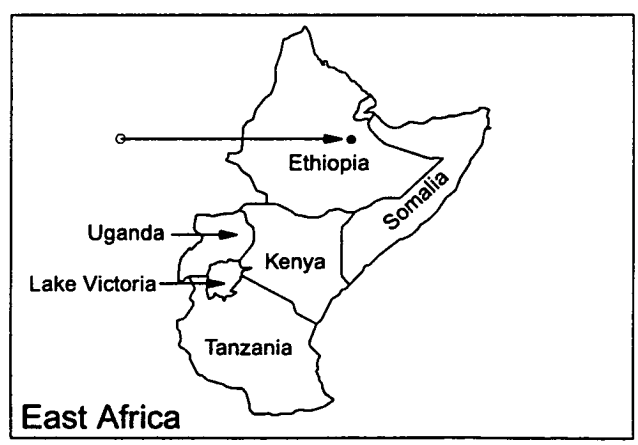
- Taxonomic position:

  Group 16 of the tropical aloes (Reynolds, 1966). (syn. *A. debrana* Reynolds)

- Samples analysed:

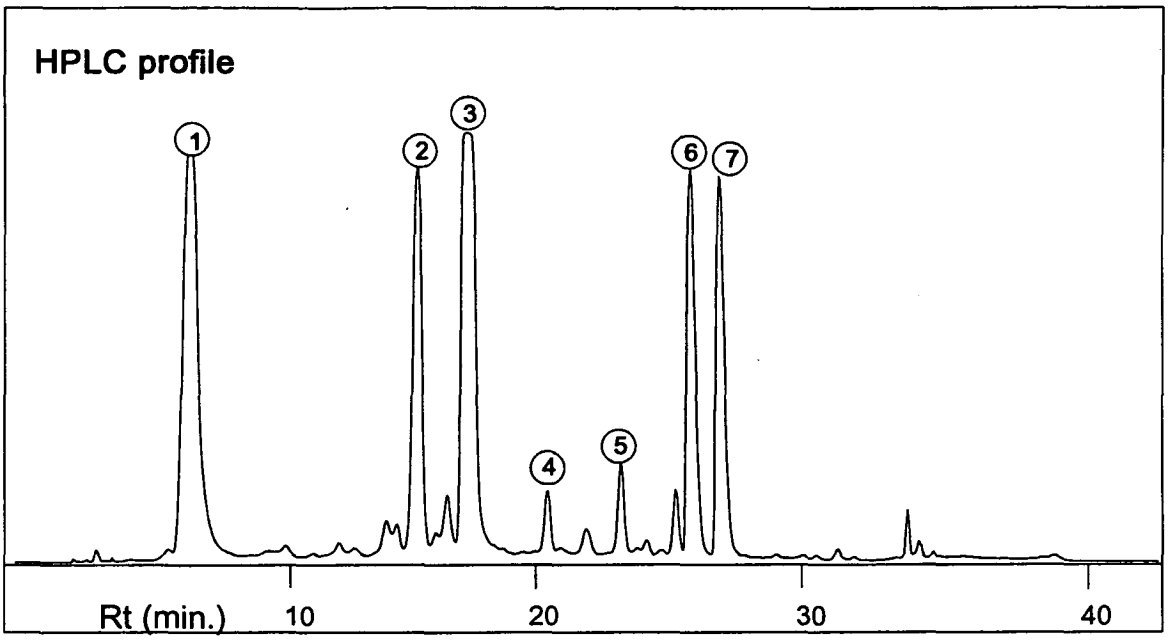
  The leaf exudate was investigated:

  - Sebsebe 288



Aloe debrana is found in the Shoa Province of Ethiopia in the vicinity of Debra Berhan northeast of Addis Ababa

Aloe decurva Reynolds



Peak number	Retention time	Compound	Percentage
1	6.53	aloesin	25
2	15.11	unidentified chromone 1	14
3	16.26	aloeresin A	23
4	20.03	unidentified chromone 2	2
5	22.82	aloeresin D	2
6	25.37	aloin B	13
7	26.48	aloin A	12

Two unidentified chromones both display an UV absorbance spectrum correlating to aloeresins A, C & D suggesting that they are related to the coumaroyl chromones.

- Taxonomic position:

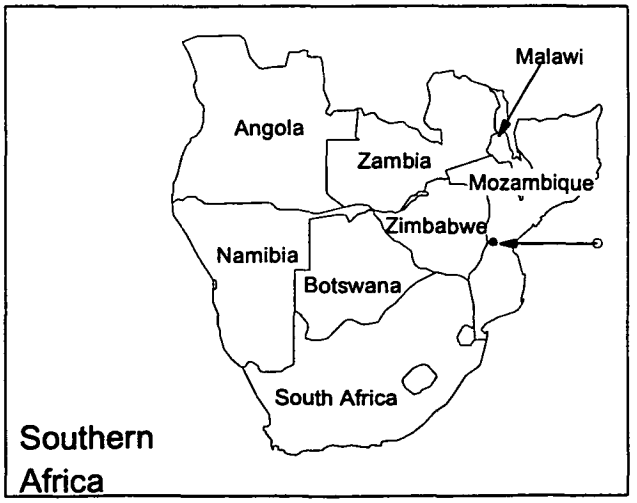
  Group 15 of the tropical aloes (Reynolds, 1996).

- Samples analysed:

  The leaf exudate was investigated:

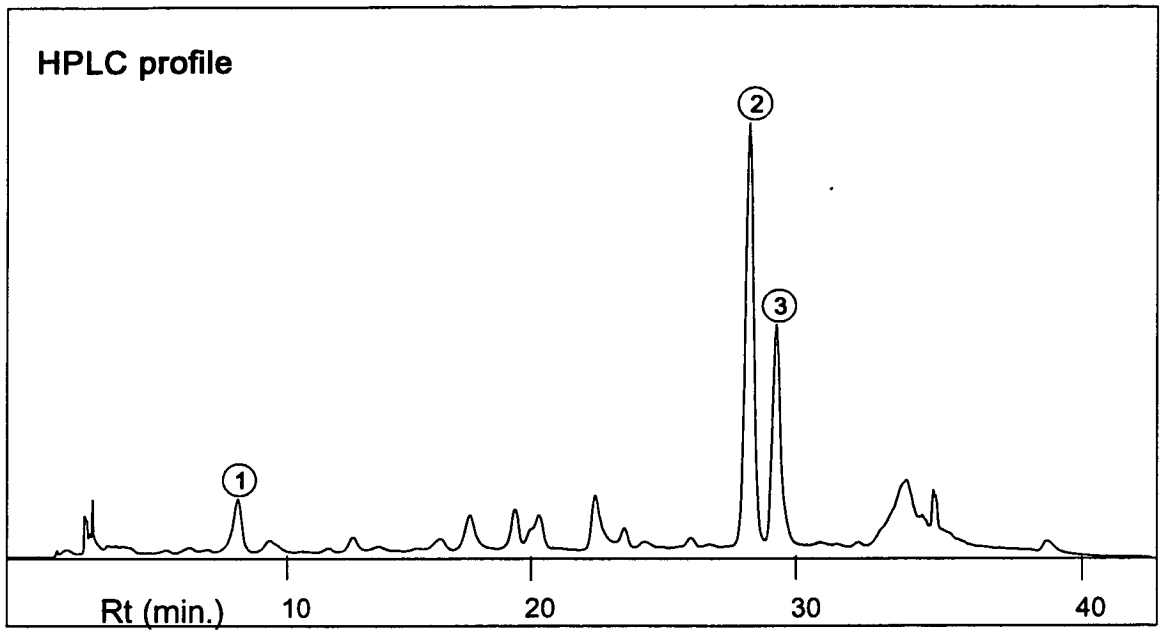
  - ex hort P. Favell

Distribution



Aloe decurva is restricted to the Zembe Mountains near Vila Pery in Mozambique.

Aloe descoingsii Reynolds ssp. *descoingsii*



Peak number	Retention time	Compound	Percentage
1	8.77	unidentified chromone 1	5
2	28.05	unidentified chromone 2	35
3	29.06	unidentified compound	19

The two unidentified chromones both show an UV spectra resembling that of the coumaroyl chromones. No class of compound could be ascribed to peak 3.

- Taxonomic position:

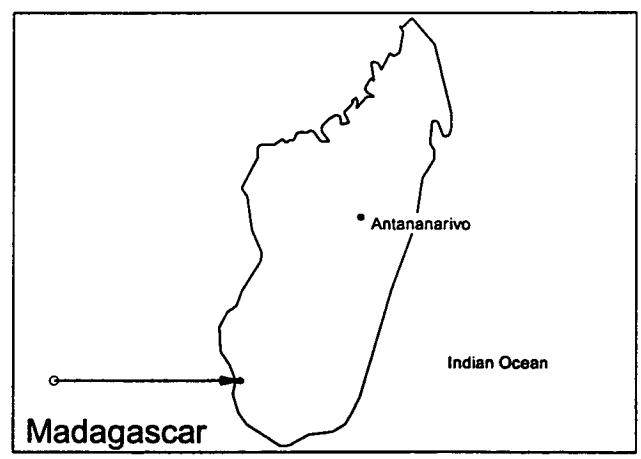
  Group 1 (Reynolds, 1966).

- Samples analysed:

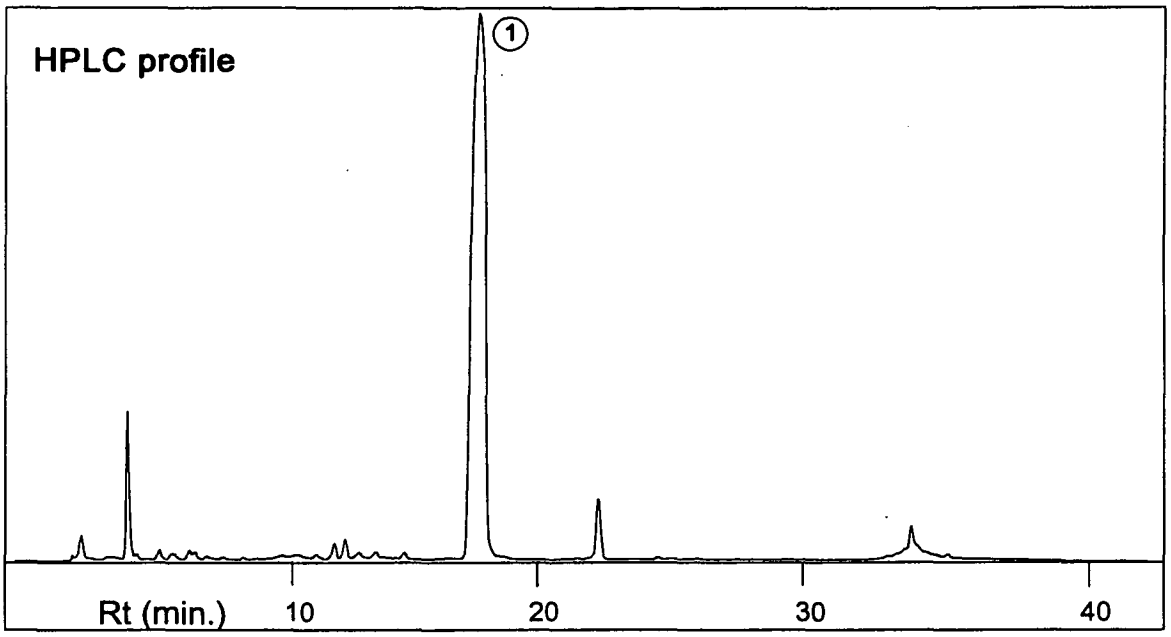
  The leaf exudate was investigated:

  - ex hort NBI

Distribution



Aloe descoingsii is known from limestone cliffs near Tulear in the south-western part of Madagascar



Peak number	Retention time	Compound	Percentage
1	17.52	plicataloside	72

As is the case in most plicataloside-containing species, this is the only compound detected in the leaf exudate with the commonly distributed chromones and anthrones being absent.

Distribution

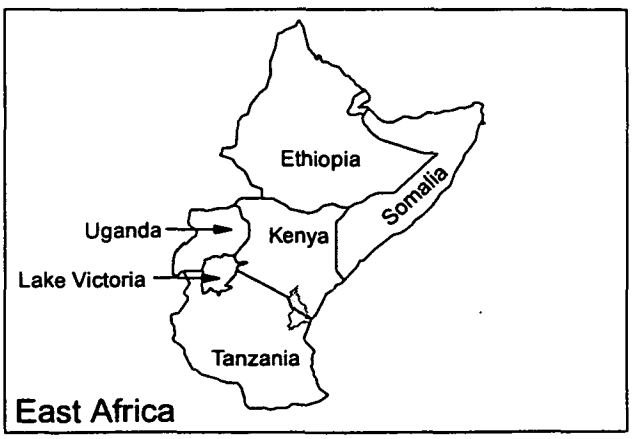
- Taxonomic position:

  Group 10 of the tropical aloes (Reynolds, 1966).

- Samples analysed:

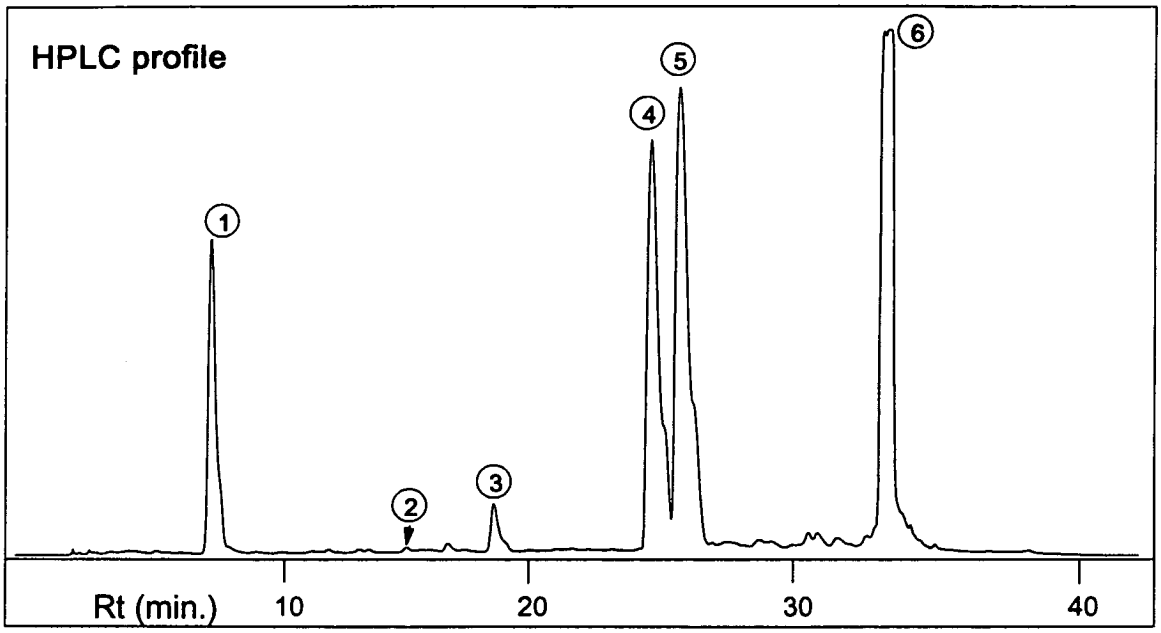
  The leaf exudate was investigated:

  - LEN 3608 (type locality)
  - RBG, Kew 16970



Aloe diserti is widely distributed in the Fort Hall, Masai and Teita Districts of Kenya from where it extends south to Lembeni in Tanzania.

Aloe dewinteri Giess



Peak number	Retention time	Compound	Percentage
1	7.5	7-*O*-methylaloesin	12
2	15.1	10-hydroxyaloin B	1
3	18.4	unidentified compound	2
4	25.6	aloin B	21
5	26.7	aloin A	27
6	33.5	unidentified anthrones (?)	31

Aloe dewinteri only has trace amounts of 10-hydroxyaloin B but lack the nilic acid esters associated with this compound (see *A. littoralis*). Peak 6 represents a mixture of two or more compounds with UV spectra identical to that of aloin.

- Taxonomic position:

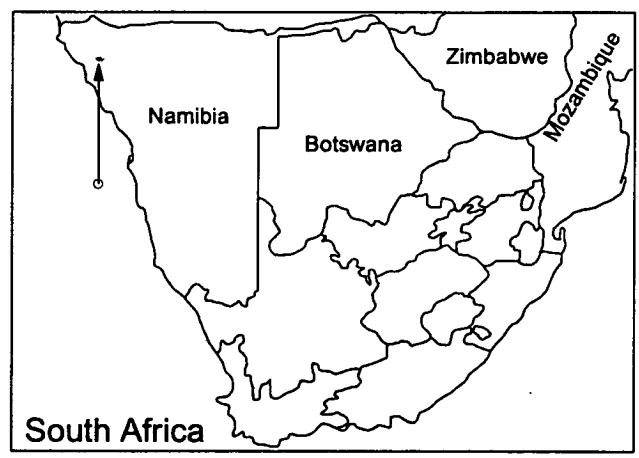
  Aloe series *Asperifoliae* (Giess, 1973).

- Samples analysed:

  The leaf exudate was investigated:

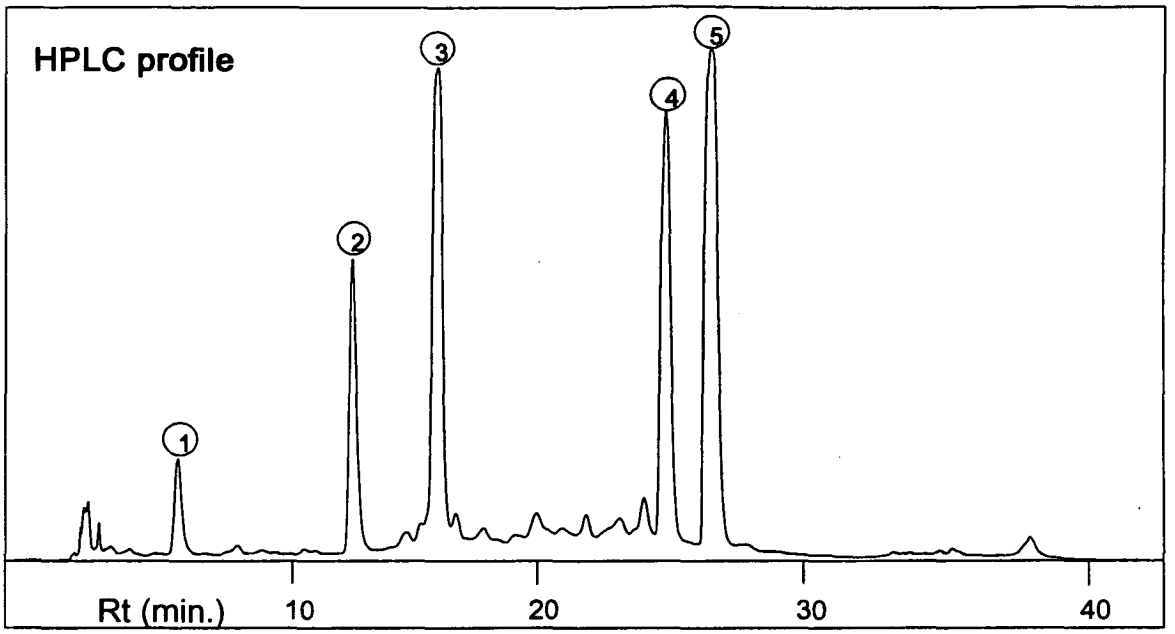
  - ex hort NBG
  - Warmbad

Distribution



Aloe dewinteri is restricted to the Sesfontein area in the remote north-east of Namibia.

Aloe dhufarensis Lavranos



Peak number	Retention time	Compound	Percentage
1	6.13	aloesin	3
2	12.74	homonataloside B	11
3	16.00	aloeresin A	23
4	24.69	homonataloin B	19
5	26.39	homonataloin A	29

Aloe dhufarensis contains homonataloside B which is restricted to a small number of species in South and east Africa. Note that this compound is always associated with the anthrone isomers, homonataloin A and B.

- Taxonomic position:

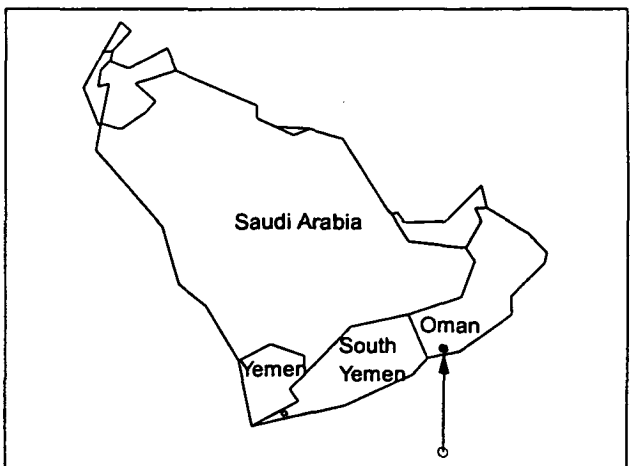
  Allied to *A. ukambensis* and *A. breviscapa* (Lavranos, 1967).

- Samples analysed:

  The leaf exudate was investigated:

  - RBG, Kew 409-77

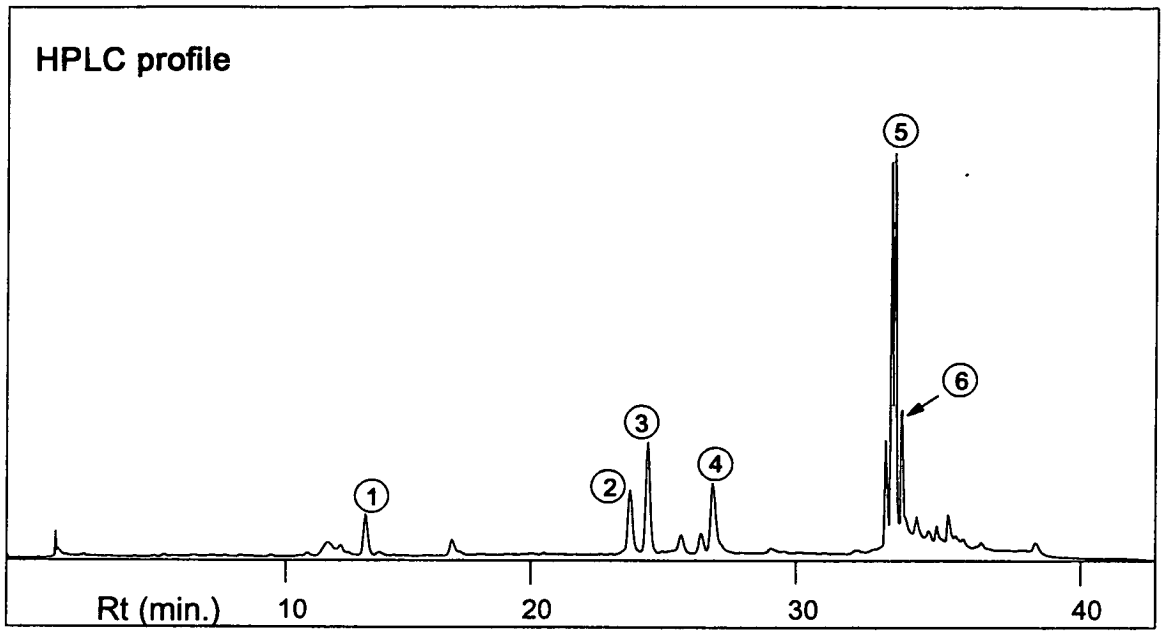
Distribution



Arabia and the horn of Africa

Aloe dhufarensis represents the most easterly distribution of the genus *Aloe*. This species inhabits the Dhufar coast of Oman in southern Arabia.

Aloe dichotoma Masson



Peak number	Retention time	Compound	Percentage
1	13.56	unidentified compound 1	4
2	23.50	unidentified compound 2	7
3	24.17	unidentified compound 3	11
4	26.60	unidentified compound 4	7
5	33.02	unidentified anthrones 1 & 2	19
6	33.23	unidentified anthrone 3	7

All the 'tree-like' aloes have a unique chemical profile. The concentration of the phenolics are extremely low. No class of compound generally found in *Aloe* could be ascribed to four unidentified compounds. The two anthrones show the same UV absorbance spectra as 5-hydroxyaloin B

- Taxonomic position:

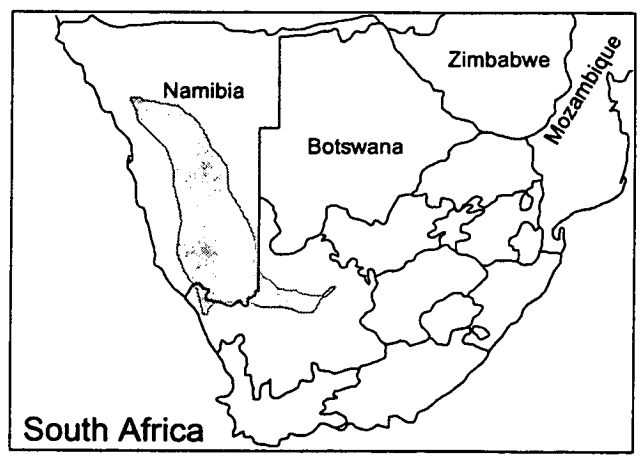
Aloe section *Dracoaloe* (Reynolds, 1950).

- Samples analysed:

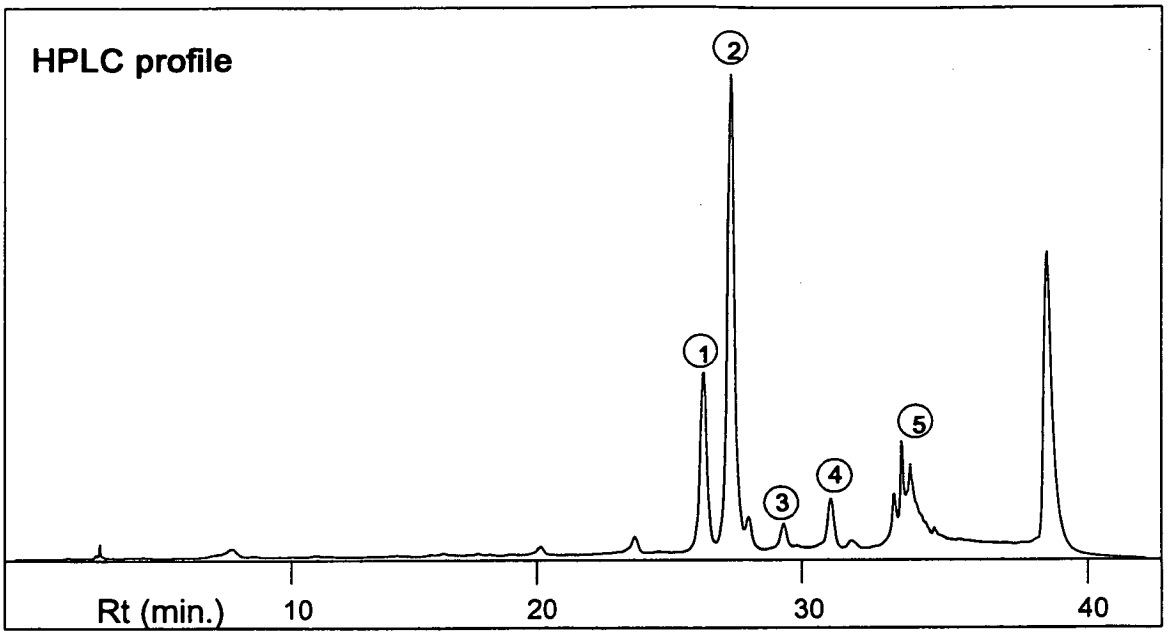
The leaf exudate and extract was investigated:

- ex hort NBG (Gannasbos)
- NBI 293322

Distribution



This species has a preference for the arid areas of South Africa and extends northwards to the Brandberg in Namibia.



Peak number	Retention time	Compound	Percentage
1	26.20	aloin B	13
2	27.22	aloin A	36
3	29.25	aloinoside B	2
4	31.02	aloinoside A	4
5	33.69	microdontin B / A	10

The microdontins have not separated completely. Three peaks could be identifoed in this area with the same UV absorbing properties characteristic of microdontin A / B.

- Taxonomic position:

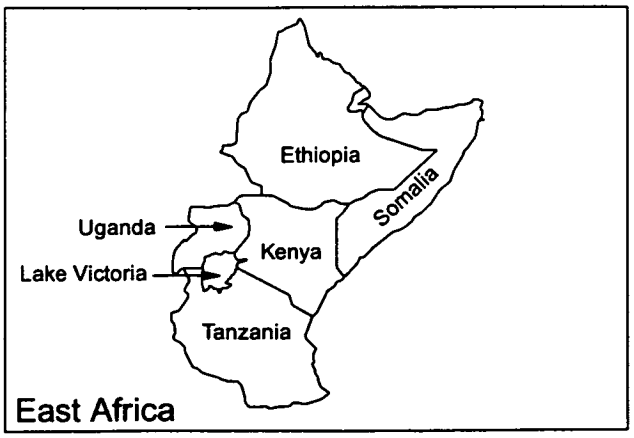
  (Newton, 1995).

- Samples analysed:

  The leaf exudate was investigated:

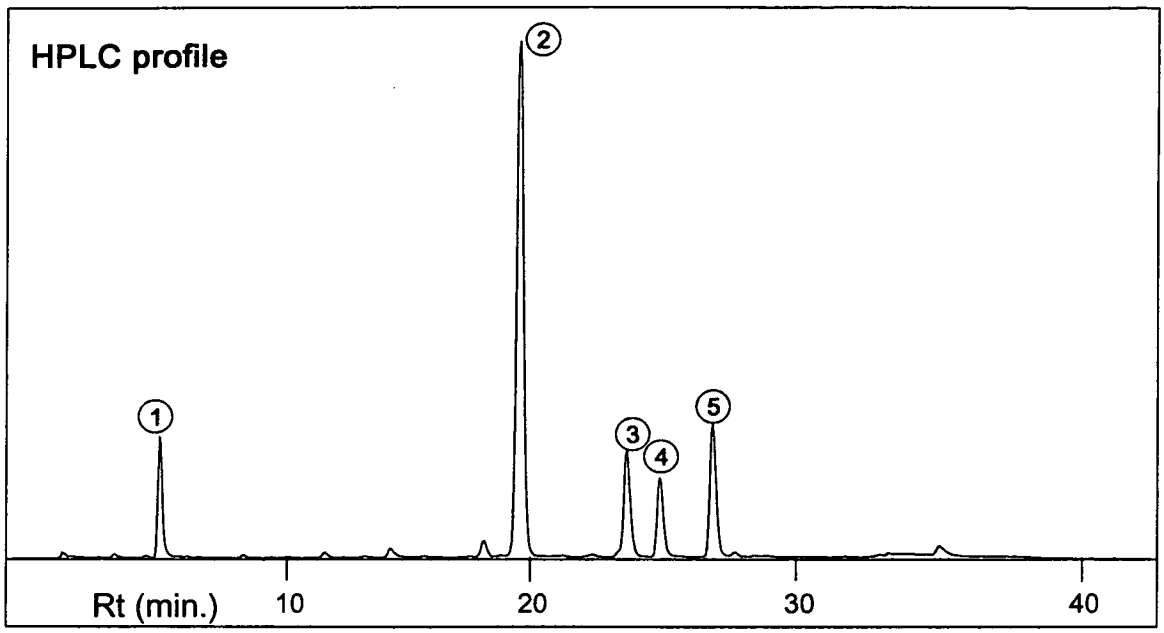
  - LEN 3508 (type plant)

Distribution



To be completed.

Aloe distans Haworth



Peak number	Retention time	Compound	Percentage
1	5.64	aloesin	8
2	19.46	aloeresin E	57
3	23.54	aloeresin F	11
4	24.80	homonataloin B	8
5	26.79	homonataloin A	13

Aloe distans displays the same HPLC profile as the related species in the *Mitriformes*-goup.

- Taxonomic position:

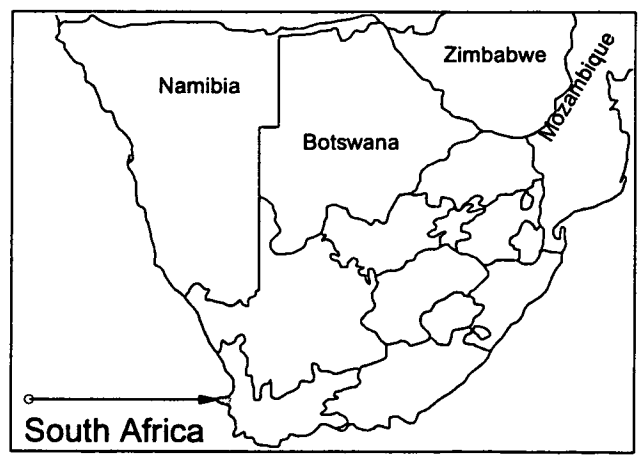
  Aloe series *Mitriformes* (Reynolds, 1950).

- Samples analysed:

  The leaf exudate was investigated:

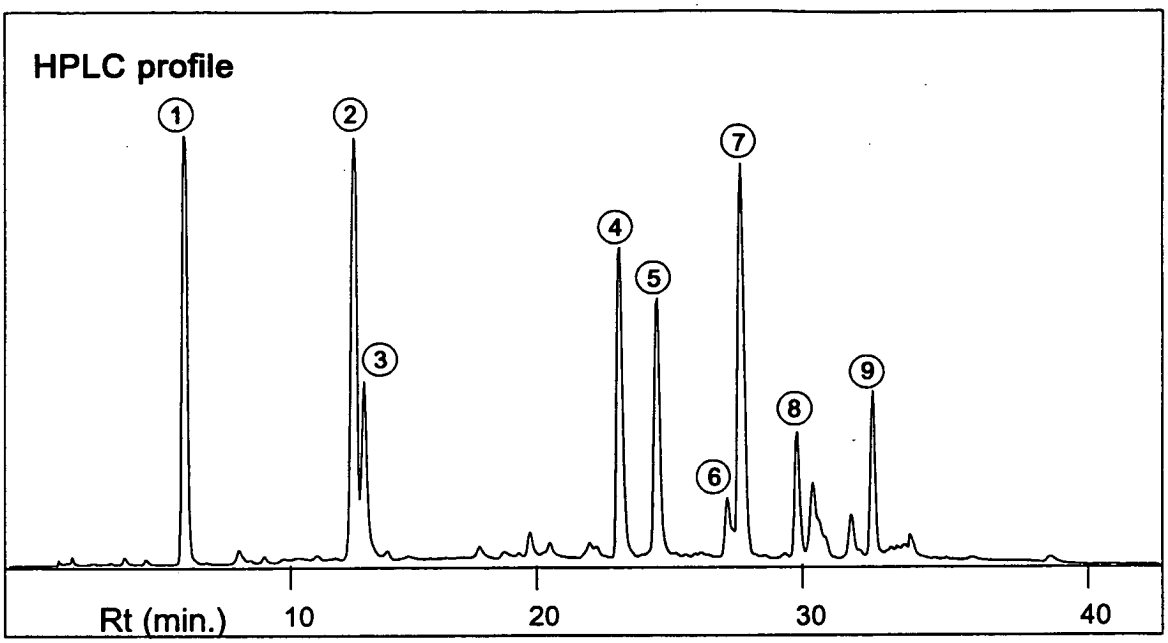
  - Saldanha

Distribution



Aloe distans is found on the west coast of southern Africa in the vicinity of Danger Point and St Helena Bay.

Aloe divaricata A. Berger var. *divaricata*



Peak number	Retention time	Compound	Percentage
1	6.48	7-*O*-methylaloesin	15
2	12.85	unidentified chromone 1	17
3	13.26	unidentified chromone 2	6
4	22.78	aloin B	12
5	24.20	aloin A	10
6	26.88	unidentified chromone 3	2
7	27.34	unidentified anthrone 1	16
8	29.00	unidentified anthrone 2	4
9	32.30	unidentified anthrone 3	5

Various unidentified anthrones characterise the leaf exudate of this species. As is the case in *A. capitata*, all these unidentified anthrones display UV spectra identical to that of aloin.

- Taxonomic position:

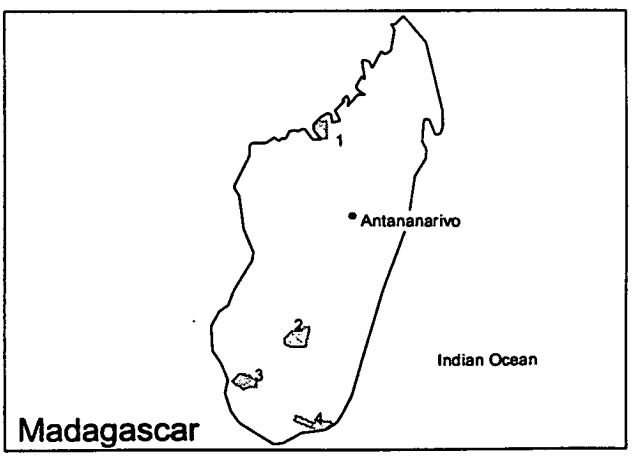
  Group 8 (Reynolds, 1966).

- Samples analysed:

  The leaf exudate was investigated:

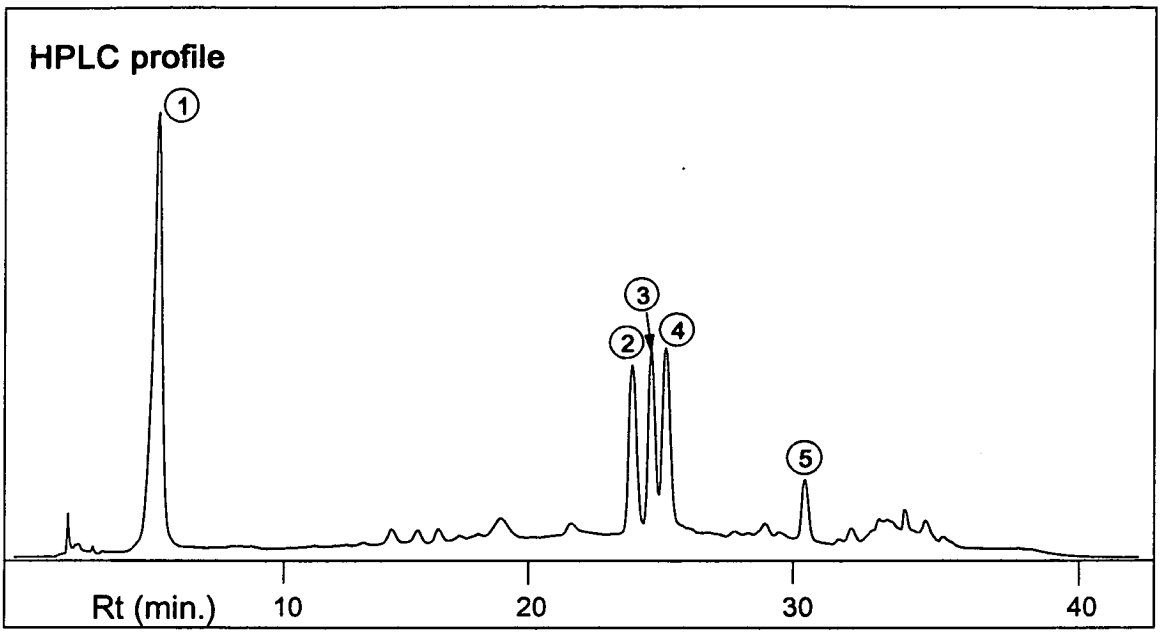
  - RBG, Kew 1988 2467
  - NBI 30617

Distribution



Aloe divaricata has been recorded at four localities; 1. near Majunga, 2. near Betsileo, 3. in the vicinity of Tulear and 4. Fort Dauphin.

Aloe dolomitica Groenewald



Peak number	Retention time	Compound	Percentage
1	5.58	aloesin	45
3	23.80	aloin B	14
4	24.53	6'-*O*-coumaroylaloesin	14
5	25.09	aloin A	16
6	30.37	unidentified chromone 1	4

(See *A. alooides* and *A. castanea*)

- Taxonomic position:

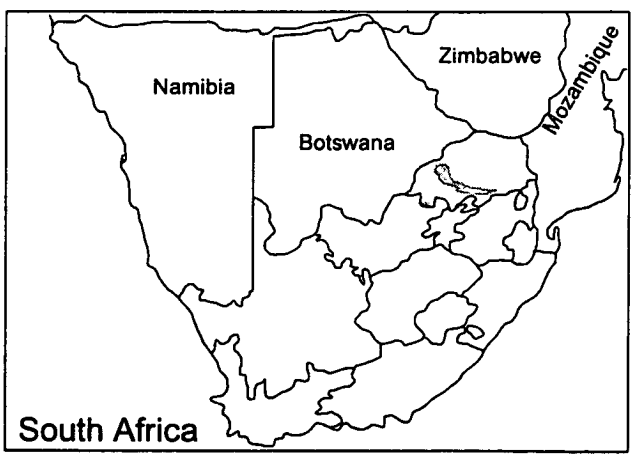
  Aloe section *Anguialoe* (Reynolds, 1950).

- Samples analysed:

  The leaf exudate was investigated:

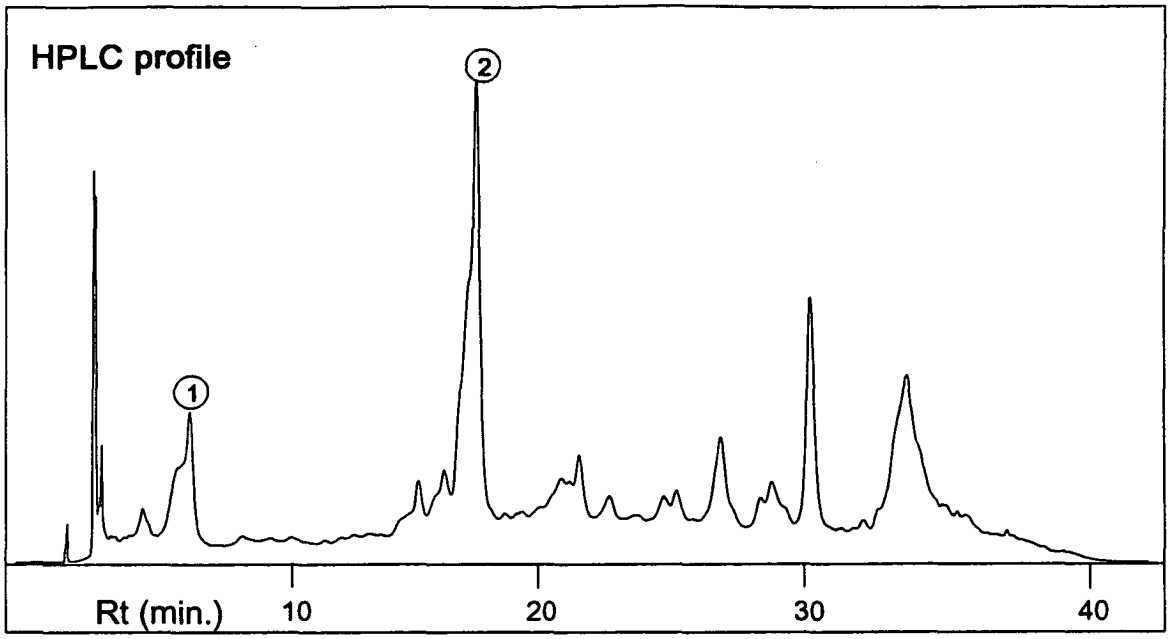
  - Wolkberg (type locality)

Distribution



With a preference for dolomite outcrops, this species is found in large numbers on the Wolkberg, Strydpoortberg and the Waterberg.

Aloe dominella Reynolds



Peak number	Retention time	Compound	Percentage
1	6.3	aloesin	2
2	17.4	unidentified flavone	18

This species has a flavone as the major compound in the leaf extract together with trace amounts of the chromone aloesin. The other peaks are unknown compounds.

- Taxonomic position:

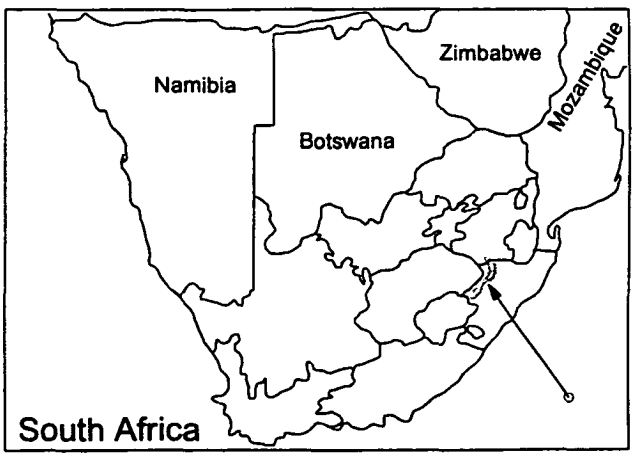
  Aloe section *Leptoaloe* (Reynolds, 1950).

- Samples analysed:

  The leaf extract was investigated:

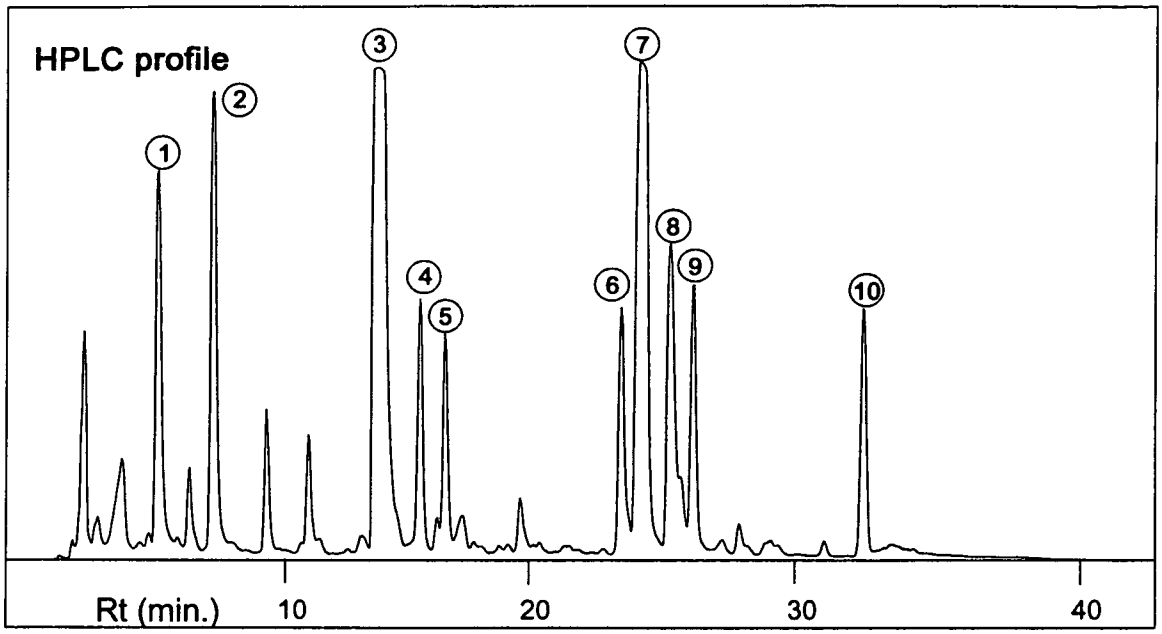
  - ex hort C. Craib (collected NE of Mooi River)

Distribution



Aloe dominella grows in and around the Mooi River area and extends to the north eastern parts (near Vryheid) of KwaZulu Natal.

Aloe dorothea Berger



Peak number	Retention time	Compound	Percentage
1	5.66	aloesin	10
2	7.75	unidentified compound 1	11
3	14.01	aloenin	29
4	15.63	unidentified compound 2	5
5	16.59	unidentified compound 3	5
6	23.26	unidentified compound 4	6
7	23.93	aloin B and unidentified compound 5	24
8	25.08	aloin A	9
9	25.95	unidentified compound 6	6
10	32.36	unidentified compound 7	6

The complex leaf extract of this species includes various unidentified compounds. There is a measure of chemical similarity between *Aloe bussei* and *A. dorotheae*, the former species also contains the unknown major compound, peak 7.

- Taxonomic position:

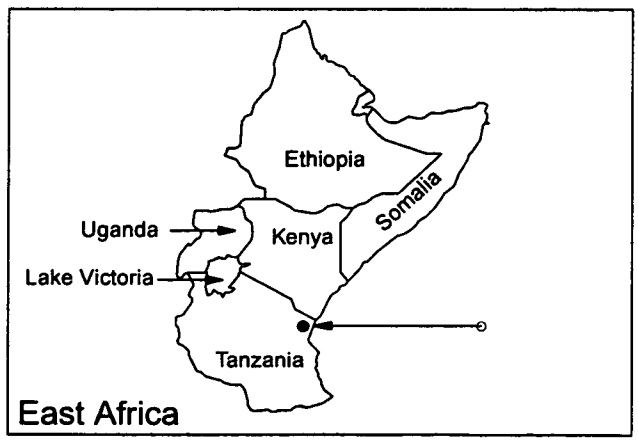
  Group 5 of the tropical aloes (Reynolds, 1966).

- Samples analysed:

  The leaf extract and exudate was investigated:

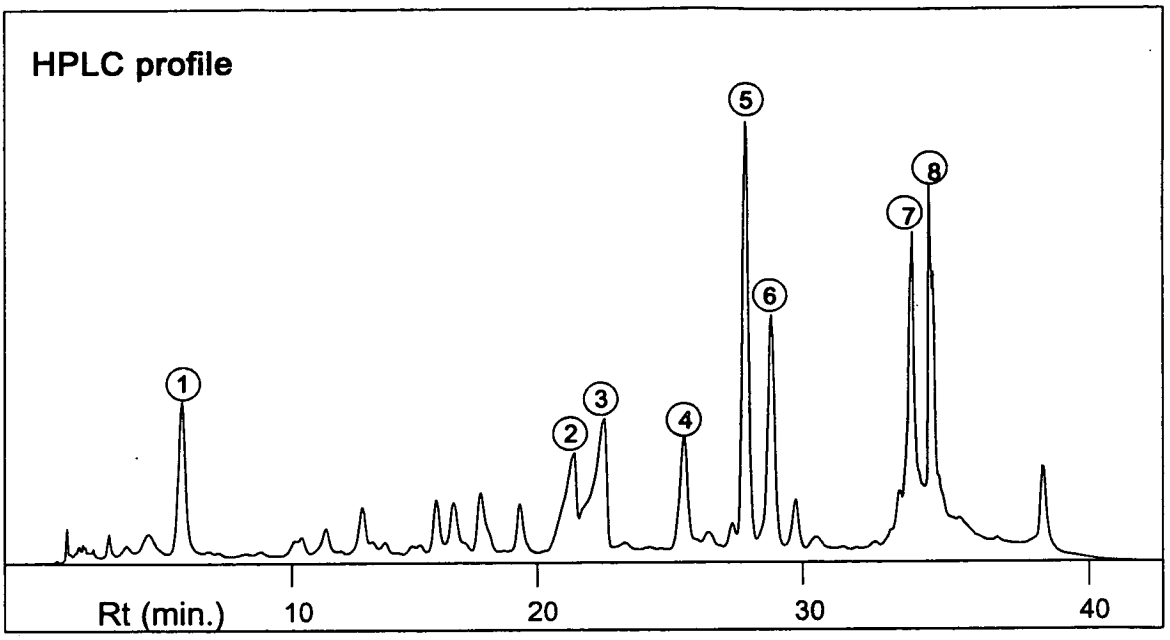
  - NBI 17305
  - RBG, Kew 295-58-29212

Distribution



This aloe is only known from Kideleko Rock in the Handeni District of Tanzania.

Aloe duckeri Christian



Peak number	Retention time	Compound	Percentage
1	6.47	aloesin	6
2	21.16	unidentified anthrone 1	7
3	22.29	unidentified anthrone 2	11
4	25.26	unidentified anthrone 3	5
5	27.56	unidentified compound 1	14
6	28.54	unidentified compound 2	9
7	33.80	unidentified compound 3	14
8	34.42	unidentified anthrone 4	14

The unidentified anthrones (peak 2,3,4 & 8) resemble the anthrones nataloin and 7-hydroxyaloin with reference to UV spectra. No class of compound could be assigned to the series of unidentified compounds.

- Taxonomic position:

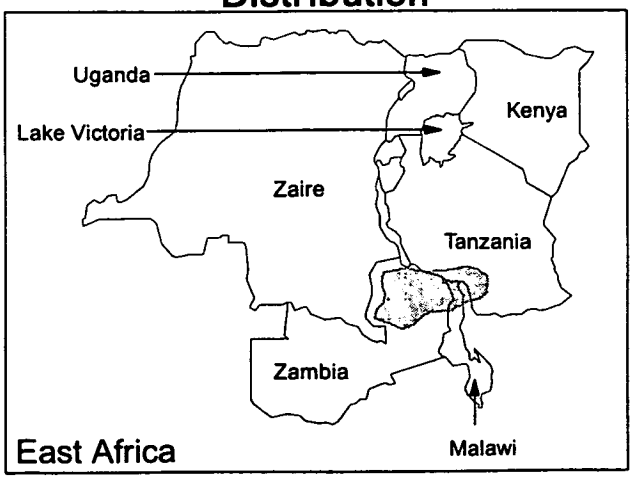
  Group 6 of the tropical aloes (Reynolds, 1966).

- Samples analysed:

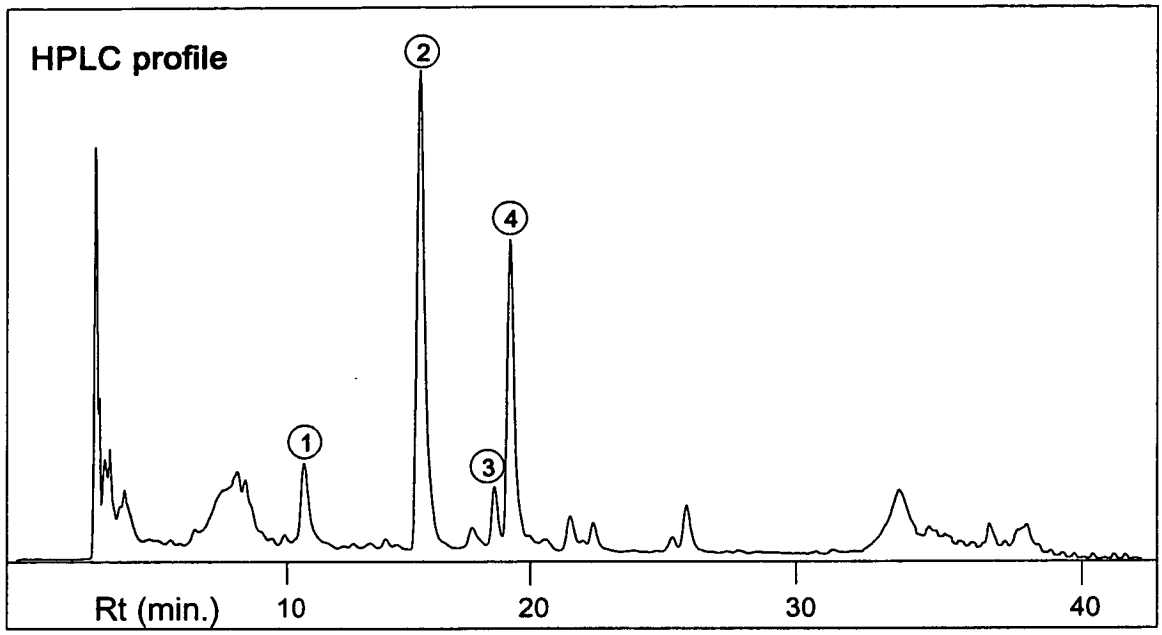
  The leaf exudate was investigated:

  - ex hort LEN

Distribution



Aloe duckeri is widely distributed in the south western parts of Tanzania, northern Malawi and in the northern areas of Zambia



Peak number	Retention time	Compound	Percentage
1	11.1	unidentified flavone 1	5
2	15.6	unidentified flavone 2	6
3	18.5	isovitexin	3
4	19.1	unidentified flavone 3	16

Based on UV spectra, the extract contains various flavones of which isovitexin was positively identified.

- Taxonomic position:

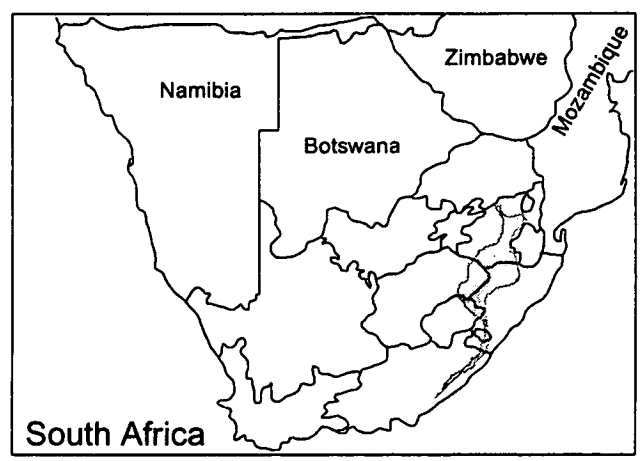
Aloe section *Leptoaloe* (Reynolds, 1950).

- Samples analysed:

The leaf extract was investigated:

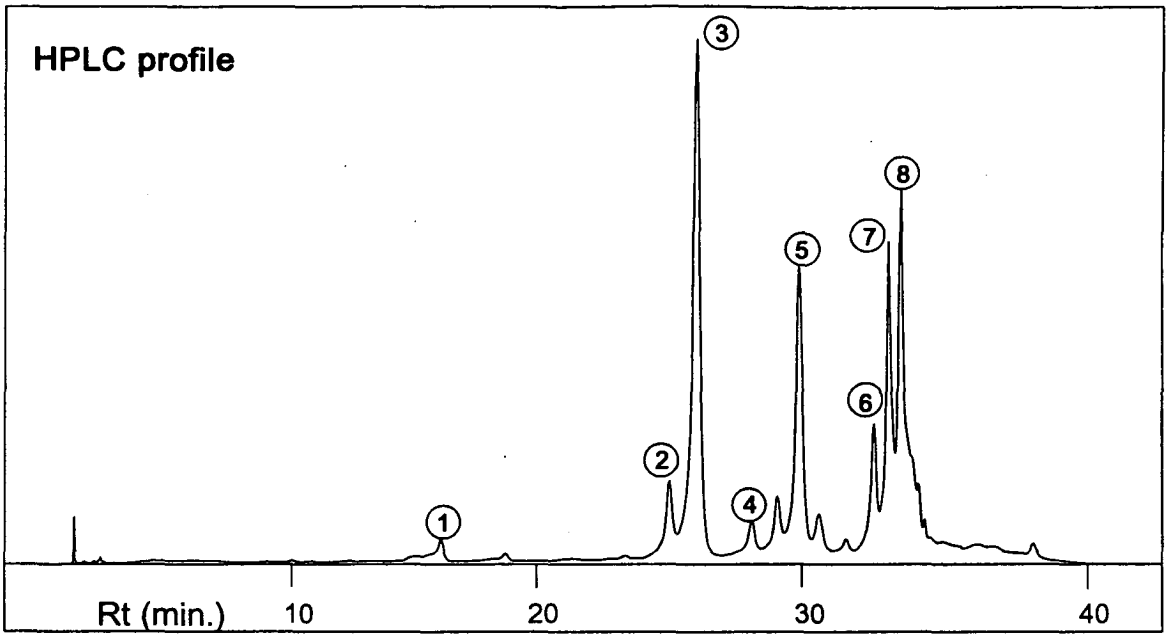
- material collected east of Middelburg
- NBI 29453

Distribution



Aloe ecklonis is the most widely distributed member of the *Leptoaloe*. It is found in the Kingwilliams Town area in the south and follows the grasslands of the eastern escarpment to Dullstroom in the north of Mpumalanga.

Aloe elegans Tod.



Peak number	Retention time	Compound	Percentage
1	16.19	dihydroisocoumarin glucoside	1
2	24.87	aloin B	4
3	25.87	aloin A	28
4	28.04	aloinoside B	3
5	29.81	aloinoside A	15
6	32.67	microdontin B	6
7	33.22	microdontin A	12
8	33.67	unidentified anthrone	19

Compounds 5 - 8 were isolated from *Aloe elegans* and the structure of these compounds were confirmed. *Aloe elegans* yielded too little of the unidentified anthrone (peak 8) to determine the structure. Based on the UV absorption spectrum this compound is structurally related to microdontins A and B.

- Taxonomic position:

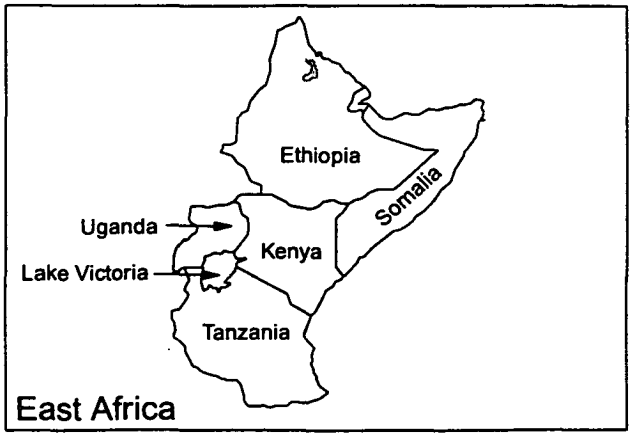
  Group 13 of the tropical aloes (Reynolds, 1966).

- Samples analysed:

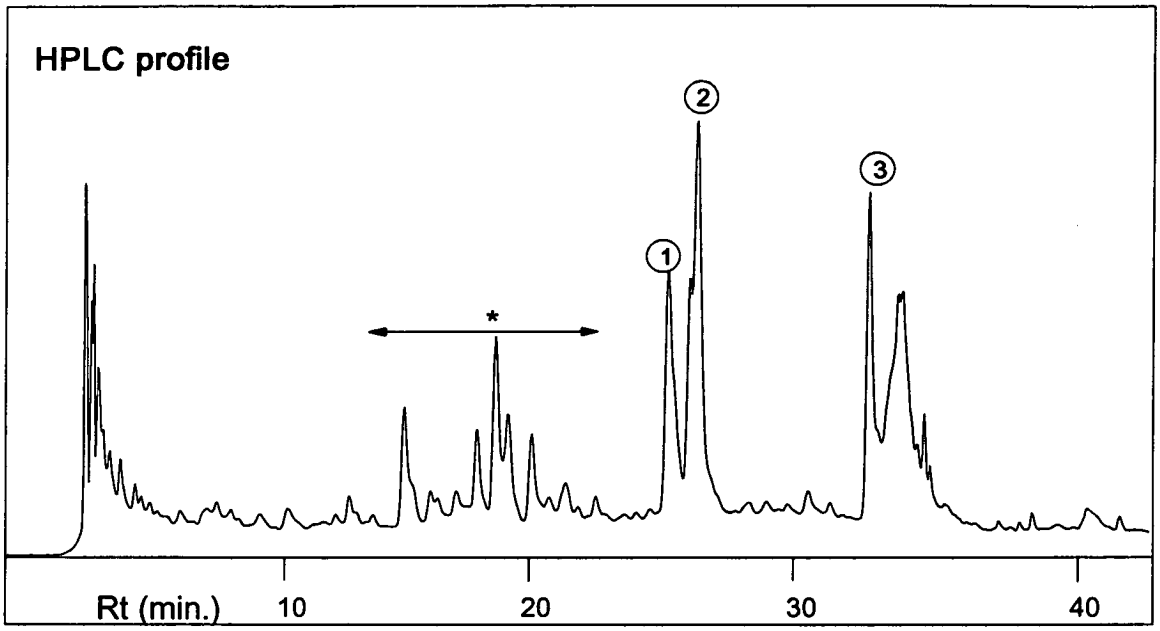
  The leaf exudate was investigated:

  - ex hort NBI

Distribution



Aloe elegans is confined to the north eastern part of Ethiopia.



Peak number	Retention time	Compound	Percentage
1	25.07	aloin B	11
2	26.11	aloin A & unidentified compound 1	22
3	32.55	unidentified compound 2	12

The two unidentified compounds have the same UV absorbance spectrum which resembles that of the dihydroisocoumarin glucoside. The series of compounds denoted by * could possible be very low concentrations of flavones.

- Taxonomic position:

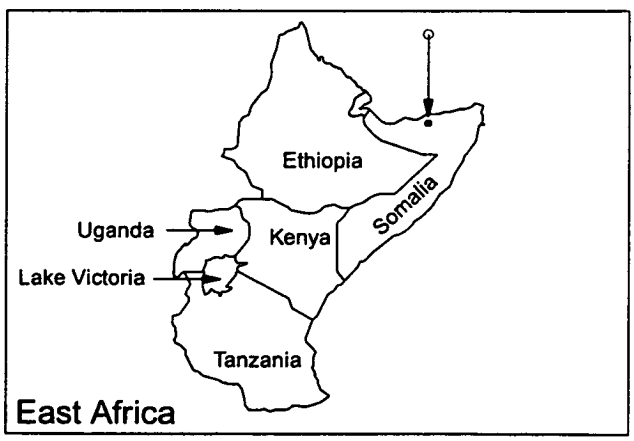
  Group 20 of the tropical aloes (Reynolds, 1966).

- Samples analysed:

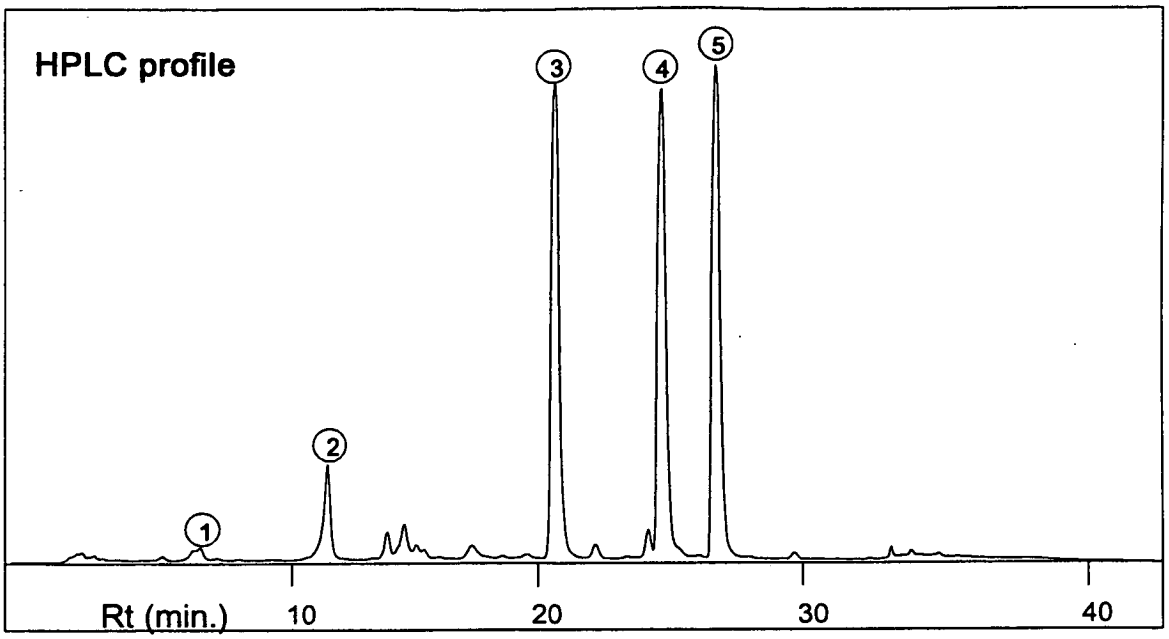
  The leaf extract was investigated:

  - ex hort NBI

Distribution



Aloe eminens is found NW of Erigavo in northern Somalia.



Peak number	Retention time	Compound	Percentage
1	7.06	7-*O*-methylaloesin	tr
2	11.84	homonataloside B	5
3	20.43	aloeresin D	29
4	24.49	homonataloin B	29
5	26.51	homonataloin A	30

The leaf exudate composition of *A. erensii* is rather simple as it only contains five major compounds. It is appropriate to mention here that aloeresin D mostly co-occurs with the anthrone homonataloin and rarely with aloin.

- Taxonomic position:

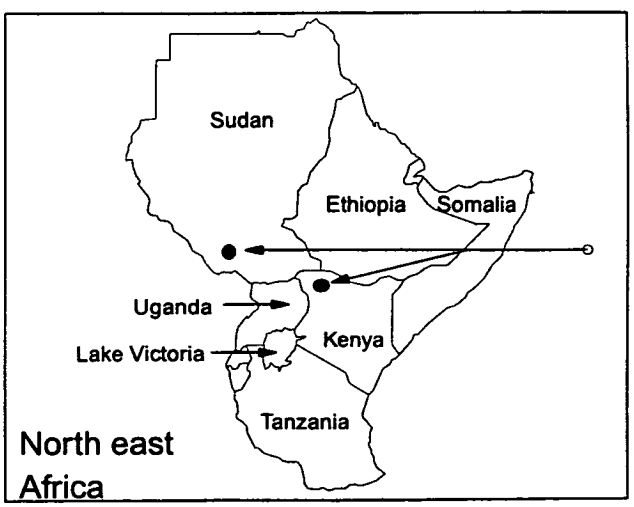
  Group 5 of the Tropical aloes (Reynolds, 1966).

- Samples analysed:

  The leaf exudate was investigated:

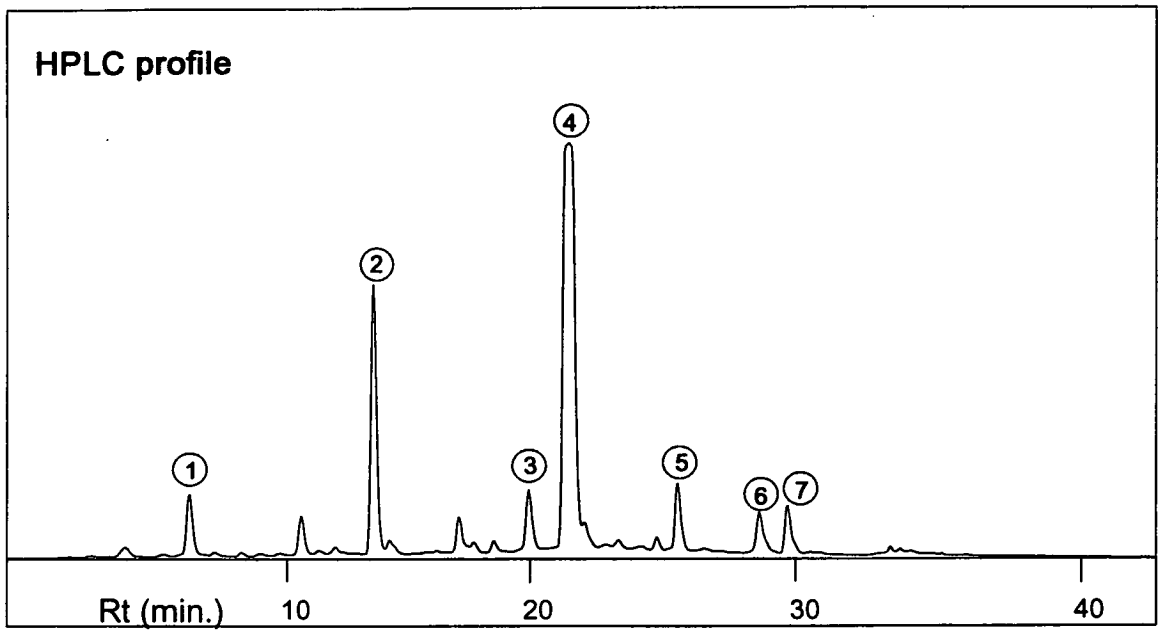
  - RBG, Kew 29558
  - ex hort NBI

Distribution



Aloe erensii occurs in the SE of Sudan and in the Turkana District of Kenya.

Aloe erinacea D.S. Hardy



Peak number	Retention time	Compound	Percentage
1	6.87	aloesin	4
2	13.83	unidentified chromone 1	17
3	18.42	unidentified chromone 2	1
4	21.23	aloeresin E	52
5	25.24	aloeresin F	4
6	28.31	nataloin B	3
7	29.37	nataloin A	3

The unidentified chromone displays the same UV absorbance spectrum as aloeresin E and F while the unidentified chromone 1 is probably a coumaroyl chromon.

- Taxonomic position:

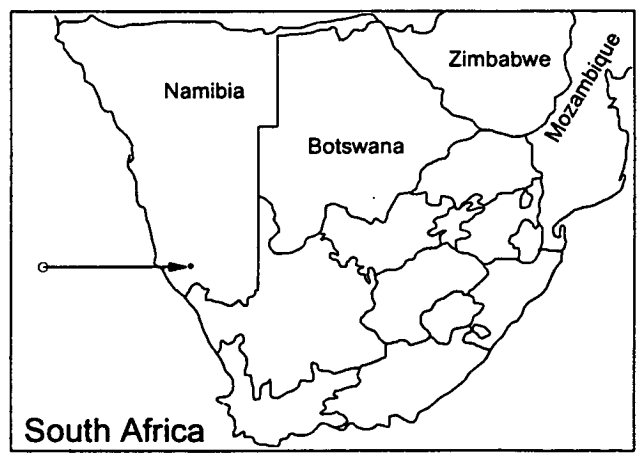
  Aloe series *Echinatae* (Hardy, 1971 & 1972).

- Samples analysed:

  The leaf exudate was investigated:

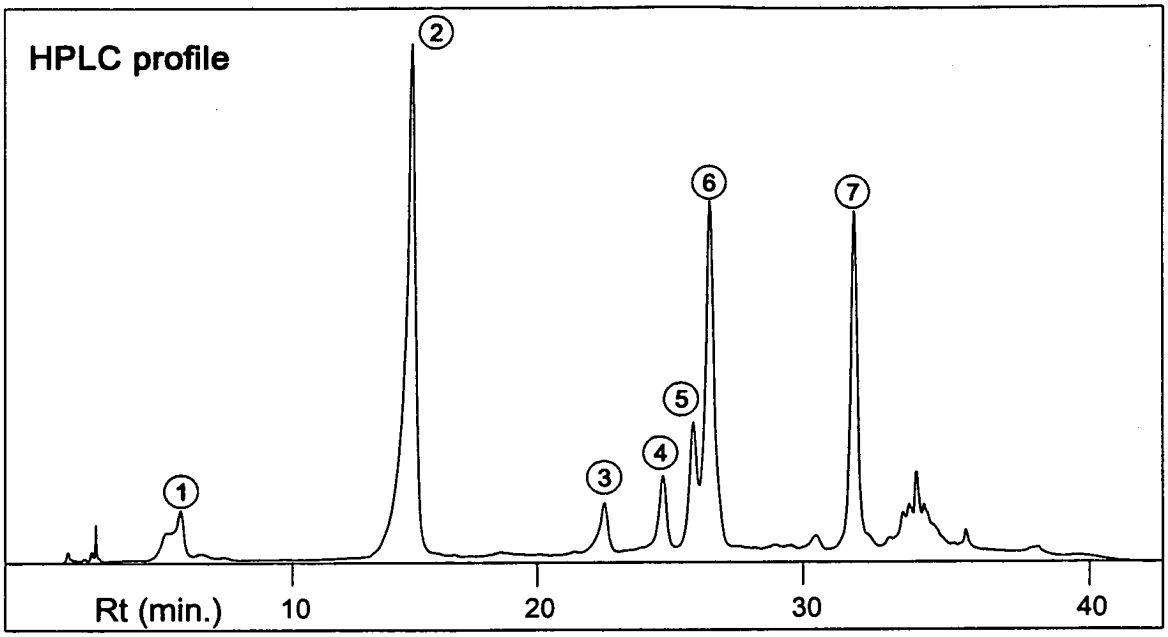
  - NBI 13426
  - NBI 24391
  - NBG 168/60

Distribution



This species is only known from the type locality which is Witputz-Suid in the southern part of Namibia.

Aloe esculenta L. C. Leach



Peak number	Retention time	Compound	Percentage
1	7.5	7-*O*-methylaloesin	tr
2	15.1	10-hydroxyaloin B	37
3	22.3	10-hydroxyaloin-6'-mono-acetate B	3
4	24.5	aloin B	4
5	25.6	aloin A	7
6	26.2	deacetyllittoraloin	21
7	31.7	littoraloin	17

The leaf exudate composition of *A. esculenta* and *A. littoralis* are virtually identical with the exception that *A. littoralis* lacks aloin and B.

- Taxonomic position:

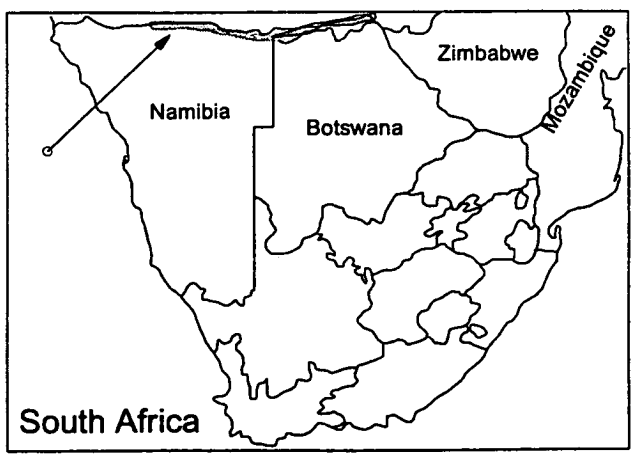
  Allied to *A. littoralis* (Leach 1971).

- Samples analysed:

  The leaf exudate was investigated:

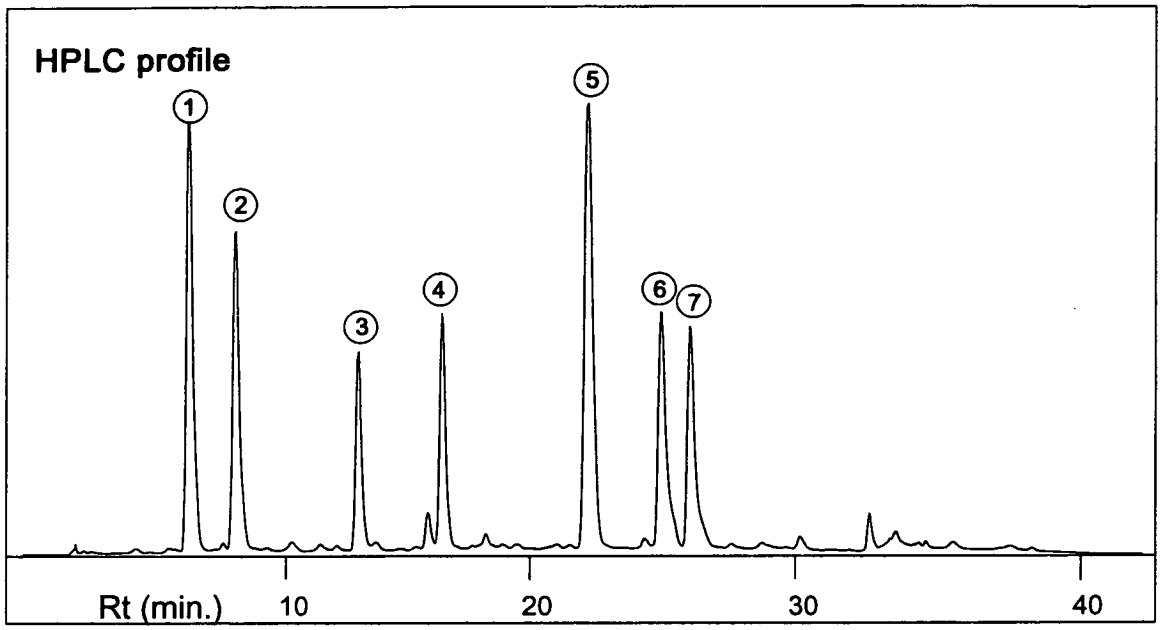
  - NBI 27823

Distribution



Aloe esculenta grows in the sandy soils along the Caprivi Strip. It has also been recorded in the Huila District of Angola, near Nangweshi in Zambia and round Mohembo in Botswana.

Aloe excelsa Berger



Peak number	Retention time	Compound	Percentage
1	6.41	aloesin	18
2	8.24	7-*O*-methylaloesin	14
3	13.04	aloeresin C	7
4	16.27	aloeresin A	9
5	21.83	aloeresin D	23
6	24.65	aloin B	12
7	26.19	aloin A	11

Aloe excelsa contains a series of coumaroyl chromones in co-occurence with the anthrones aloin A and B.

- Taxonomic position:

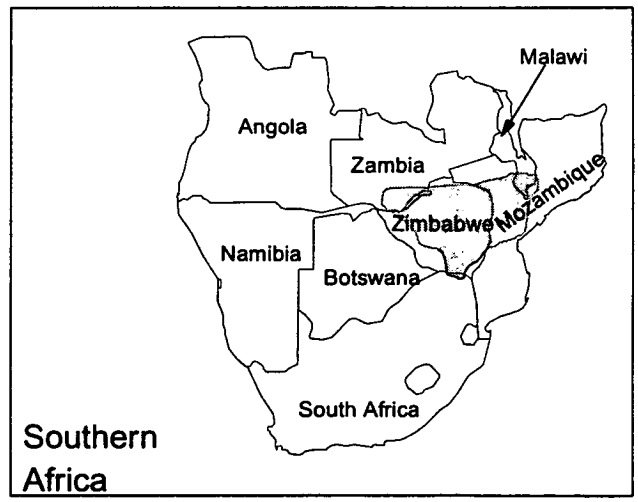
  Group 18 of the tropical aloes (Reynolds, 1996).

- Samples analysed:

  The leaf exudate was investigated:

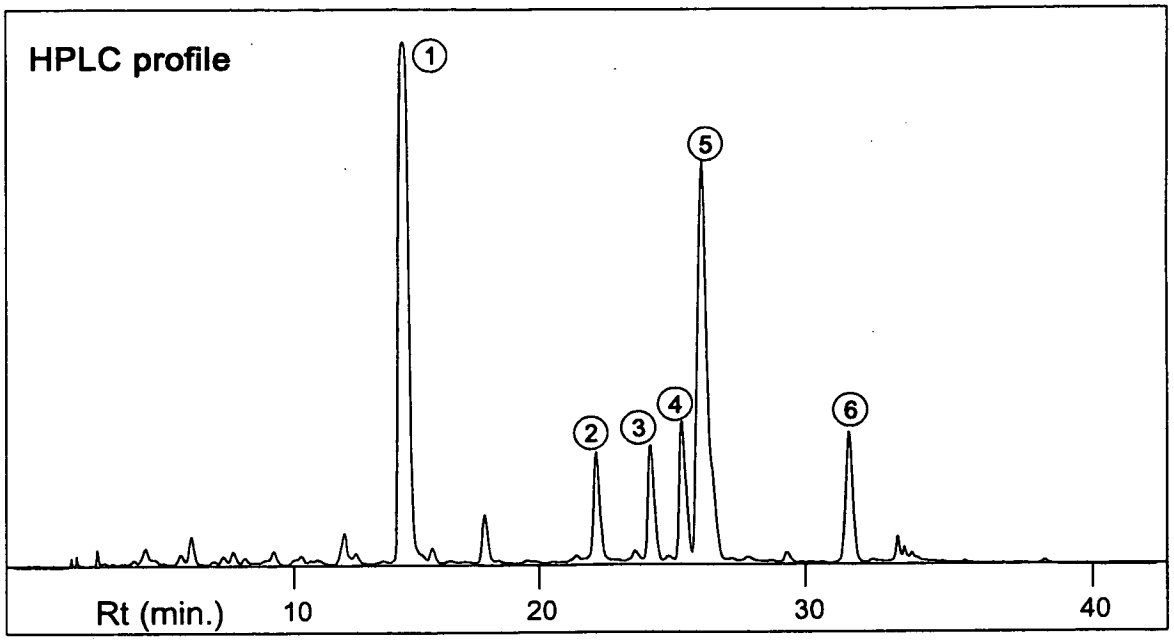
  - NBI 27286

Distribution



Aloe excelsa is widely distributed through-out Zimbabwe and marginally extends into South Africa, Zambia, Malawi and Mozambique.

Aloe falcata Baker



Peak number	Retention time	Compound	Percentage
1	14.60	10-hydroxyaloin B	37
2	21.96	10-hydroxyaloin-6'-mono-acetate B	5
3	23.89	unidentified anthrone	5
4	25.16	unidentified anthrone	7
5	25.92	deacetyllittoraloin	29
6	31.48	littoraloin	6

Aloe falcata is almost identical in leaf exudate composition when compared to *A. littoralis* and *A. claviflora*.

- Taxonomic position:

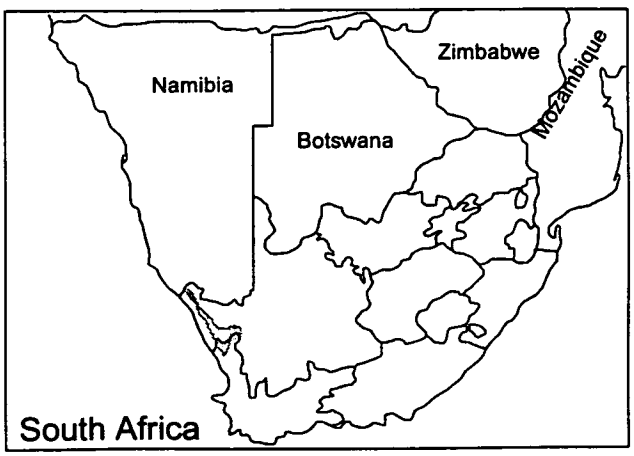
  Aloe series *Asperifoliae* (Reynolds, 1950).

- Samples analysed:

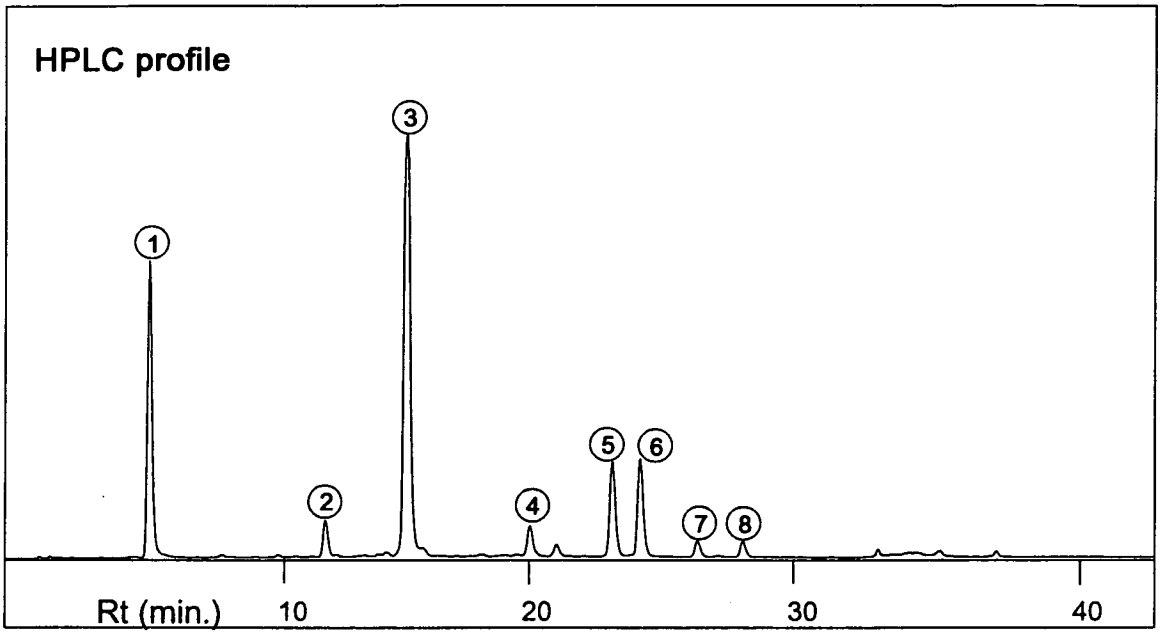
  The leaf exudate was investigated:

  - Van Rhynsdorp

Distribution



Aloe falcata occurs in large numbers from the Knersvlakte northwards to the Richtersveld.



Peak number	Retention time	Compound	Percentage
1	5.43	aloesin	23
2	12.12	aloeresin C	3
3	15.16	aloeresin A	47
4	20.80	5-hydroxyaloin B	1
5	22.87	aloin B	9
6	23.91	aloin A	10
7	26.07	aloinoside B	2
8	27.79	aloinoside A	2

Due to the commercial importance of this species several populations were investigated chemically. Only two chemotypes were defined; in the southern parts of the distribution range aloinosides co-occurred with aloin (as depicted above), in all other populations the aloinosides were absent.

- Taxonomic position:

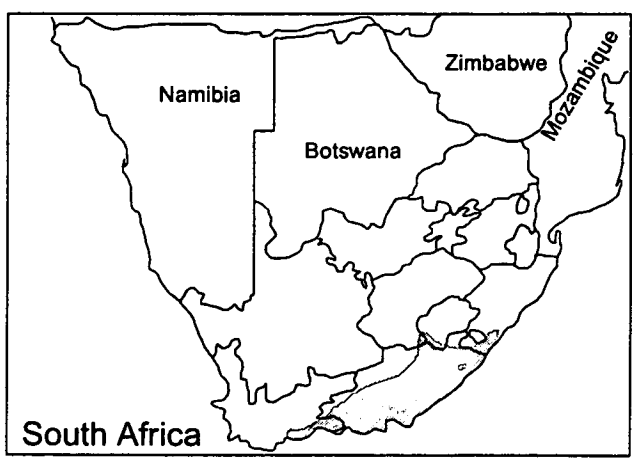
Aloe section *Pachydendron* (Reynolds, 1950).

- Samples analysed:

The leaf exudate was investigated:

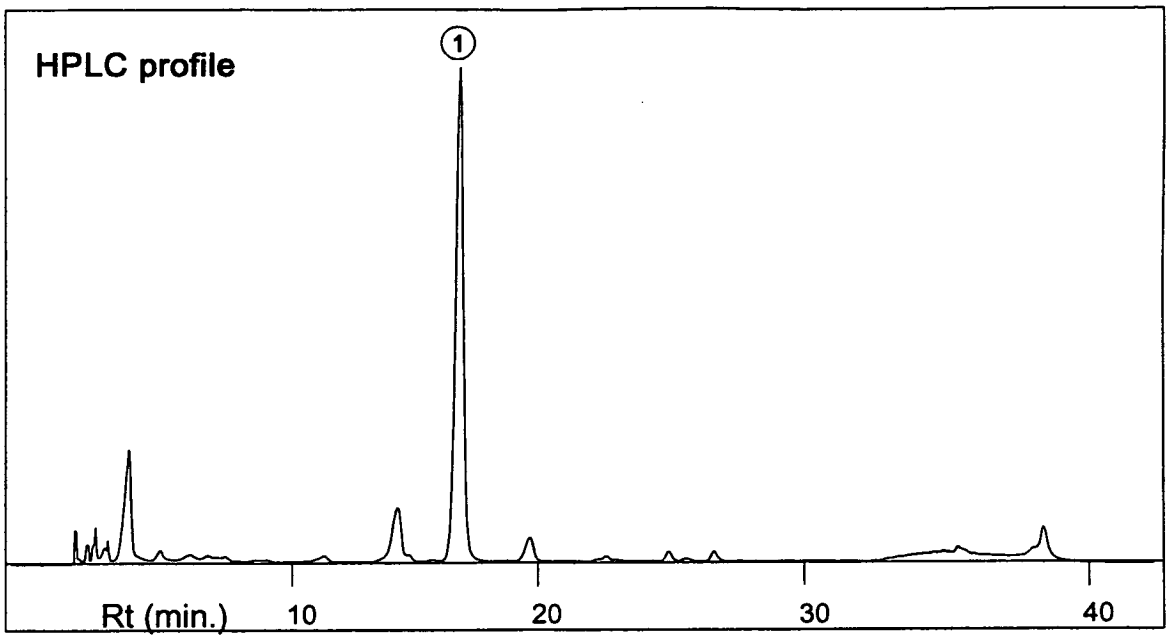
- Storms river
- Heidelberg
- Cooper
- Robinson Pass
- Moerasrivier
- George
- Meiringspoort
- Perdekraal
- Joubertina
- Aliwal North
- Coffee Bay
- Jansenville
- Graaff-Reinett
- Goliatskraal
- Pearston
- Bruintjieshoogte
- Cookhouse
- Fort Brown
- Fort Beaufort
- Queenstown
- Bizana
- Umtamvuna

Distribution



Aloe ferox is widely distributed along the eastern parts of South Africa.

Aloe fibrosa Lavranos & Newton



Peak number	Retention time	Compound	Percentage
1	16.71	plicataloside	85

(See *A. archeri*)

- Taxonomic position:

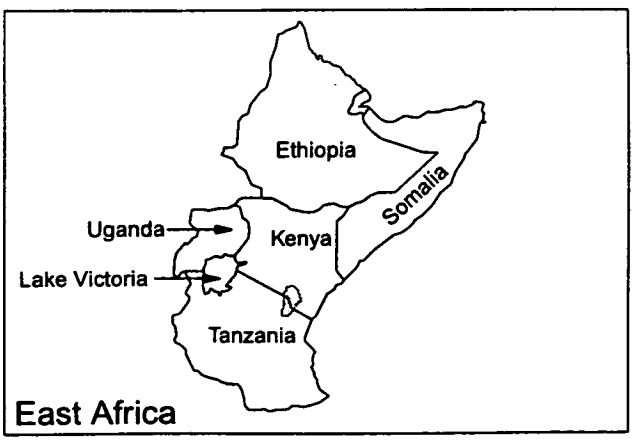
  Allied to *A. babatiensis* (Lavranos & Newton, 1976).

- Samples analysed:

  The leaf exudate was investigated:

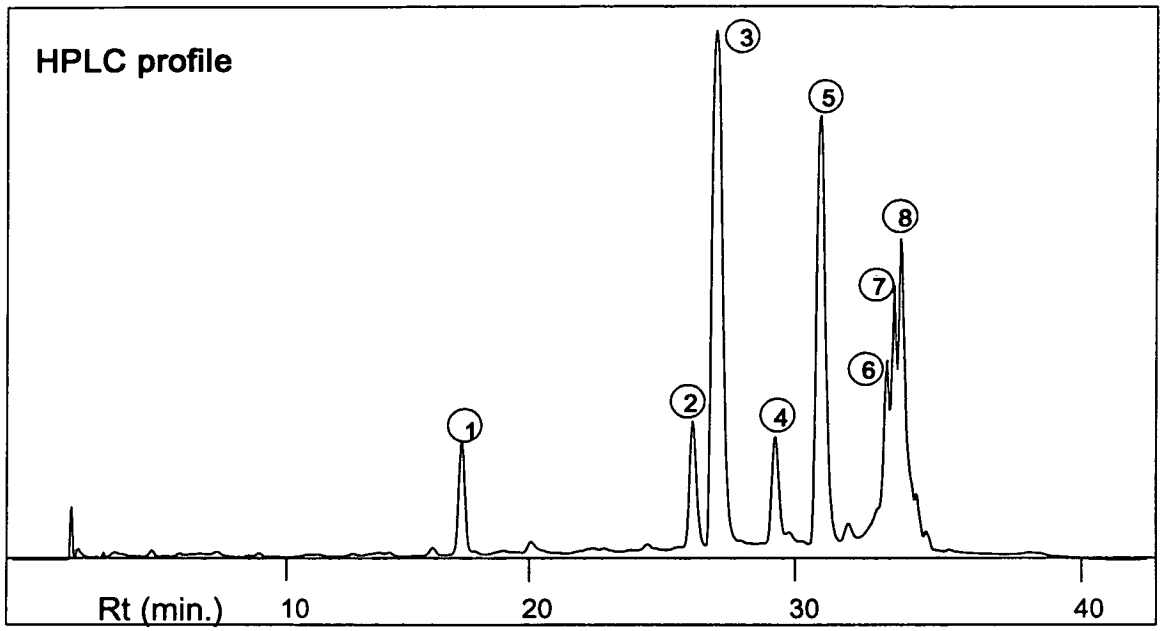
  - ex hort P. Favell

Distribution



Aloe fibrosa is known to occur in the Machakos District in Kenya, and southwards in the Moshi District of Tanzania.

Aloe fleurentinorum Lavranos & Newton



Peak number	Retention time	Compound	Percentage
1	17.24	dihydroisocumarin glucoside	4
2	25.93	aloin B	5
3	26.80	aloin A	31
4	29.08	aloinoside B	4
5	30.75	aloinoside A	22
6	33.36	microdontin B	7
7	33.61	microdontin A	6
8	33.81	unidentified anthrone	14

Aloe fleurentinorum once again illustrates the frequently detected pattern in many aloes of tropical east Africa. Chromones are usually absent in the presence of the aloinosides and microdontins. Both samples analysed were identical.

- Taxonomic position:

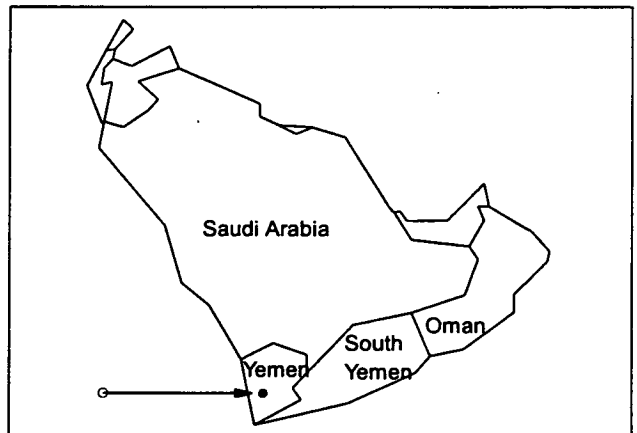
Allied to *A. inermis* (Lavranos & Newton, 1977).

- Samples analysed:

The leaf exudate was investigated:

- ex hort D. Hardy
- RBG, Kew 1977-3317

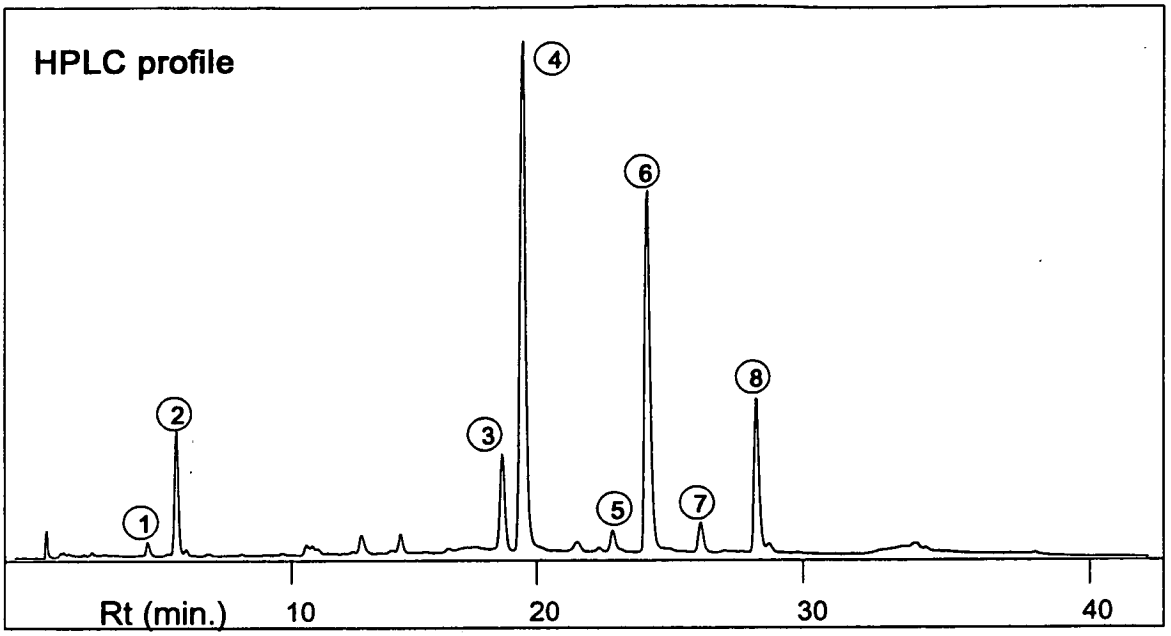
Distribution



Arabian Pininsula

The type locality of this aloe is at Sina'a in Yemen, from where it extends northwards to 'Amran and Khamer in the north.

Aloe flexilifolia Christian



Peak number	Retention time	Compound	Percentage
1	4.99	aloesin	1
2	6.08	7-O-methylaloesin	6
3	18.52	unidentified chromone 1	7
4	19.29	aloeresin D	39
5	22.70	aloin B	1
6	23.98	aloin A	27
7	26.03	aloinoside B	2
8	28.15	aloinoside A	11

Aloe flexilifolia represents the pattern found in a large number of species in tropical east Africa which is characterised by the aloin and aloinoside isomers which occur in a quantitative imbalance.

Distribution

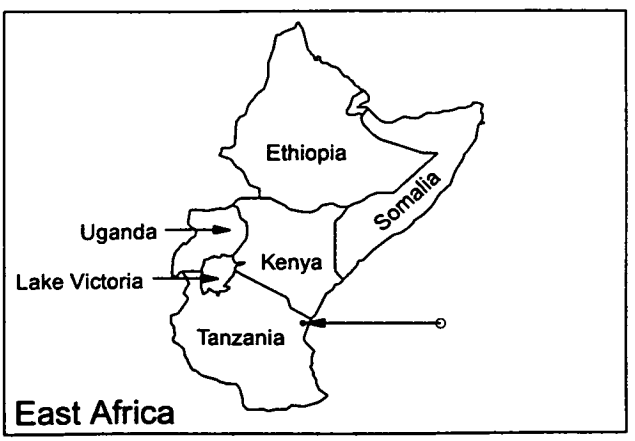
- Taxonomic position:

  Group 19 of the tropical aloes (Reynolds, 1966).

- Samples analysed:

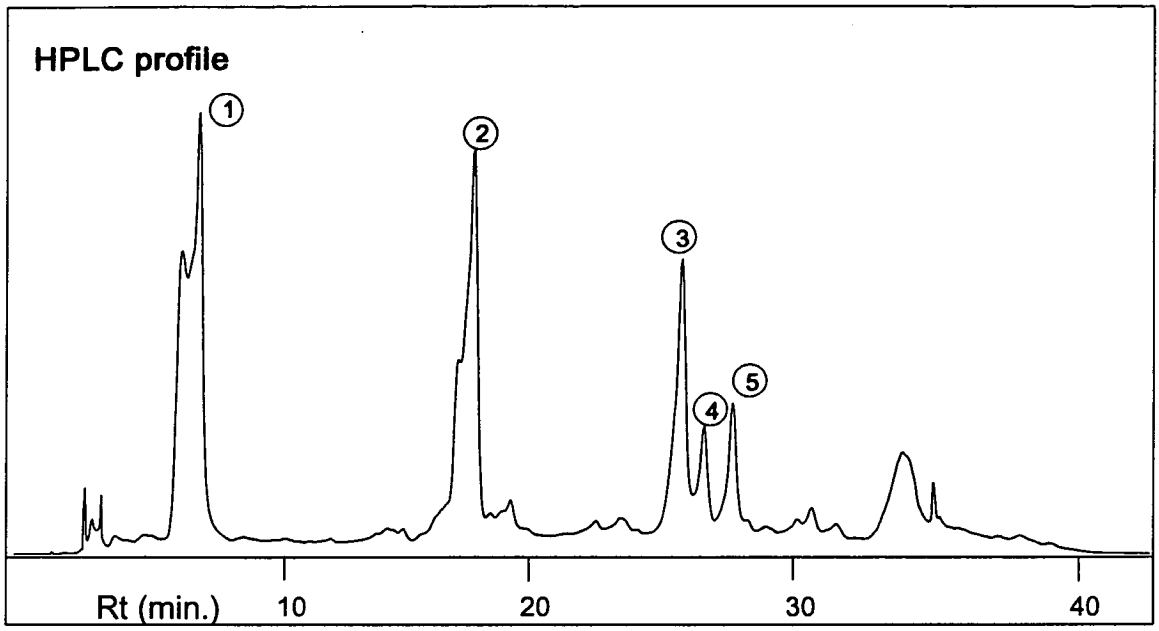
  The leaf exudate was investigated:

  - ex hort P. Favell
  - RBG, Kew 258-90-01811



Aloe flexilifolia is known to occur at Vuga and Soni in the Lushoto District of Tanzania.

Aloe forbesii Balfour



Peak number	Retention time	Compound	Percentage
1	6.08	aloesin	23
2	16.57	aloeresin A	18
3	24.51	unidentified compound	14
4	25.26	aloin B	5
5	26.35	aloin A	6

This species produces little or no exudate. For this reason an extract of the leaf was made. The levels of phenolic compounds in the leaves are extremely low.

Distribution

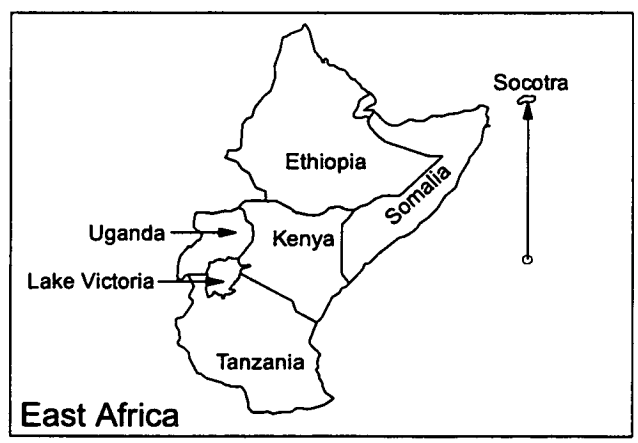
- Taxonomic position:

  Group 13 of the tropical aloes (Reynolds, 1966).

- Samples analysed:

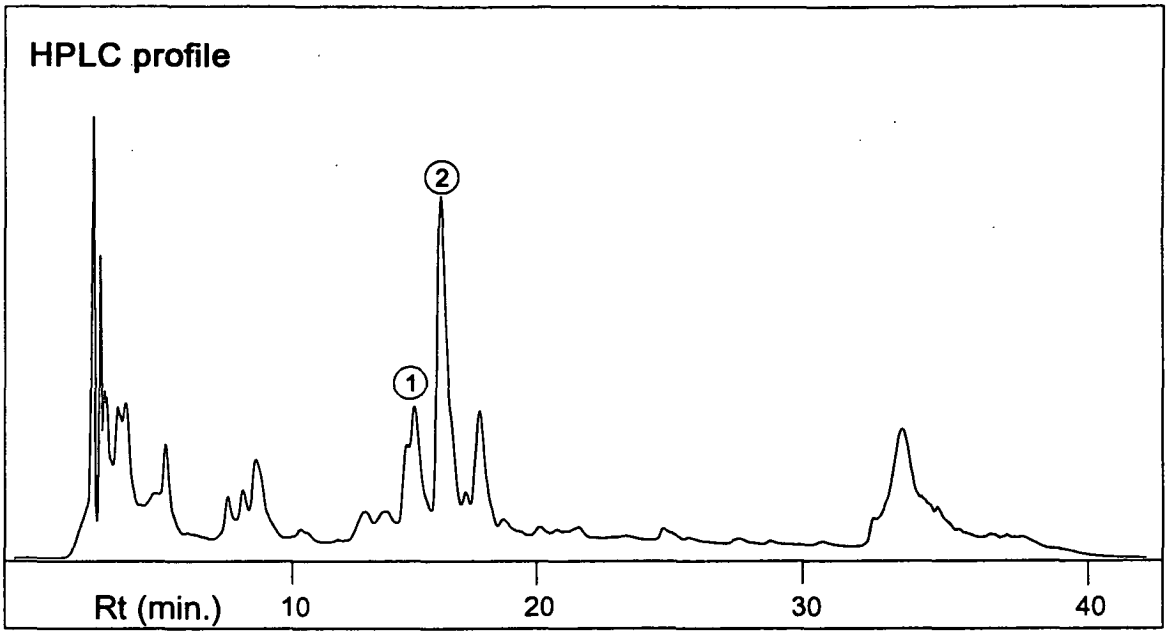
  The leaf extract was investigated:

  - NBI (ex Socotra)



Aloe forbesii grows near Bojhin on the island of Socotra.

Aloe fouriei D. S. Hardy & Glen



Peak number	Retention time	Compound	Percentage
1	15.1	unidentified flavone 1	12
2	16.1	unidentified flavone 2	27

The HPLC analysis of the leaf extract indicated flavones to be present in *A. fouriei*.

- Taxonomic position:

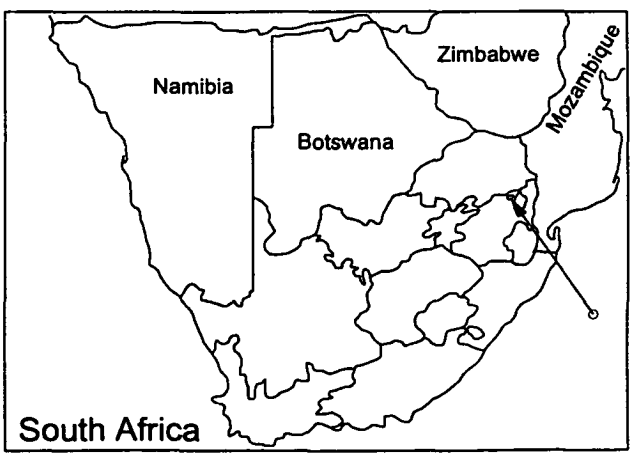
  Aloe section *Leptoaloe* (Hardy & Glen, 1987).

- Samples analysed:

  The leaf extract was investigated:

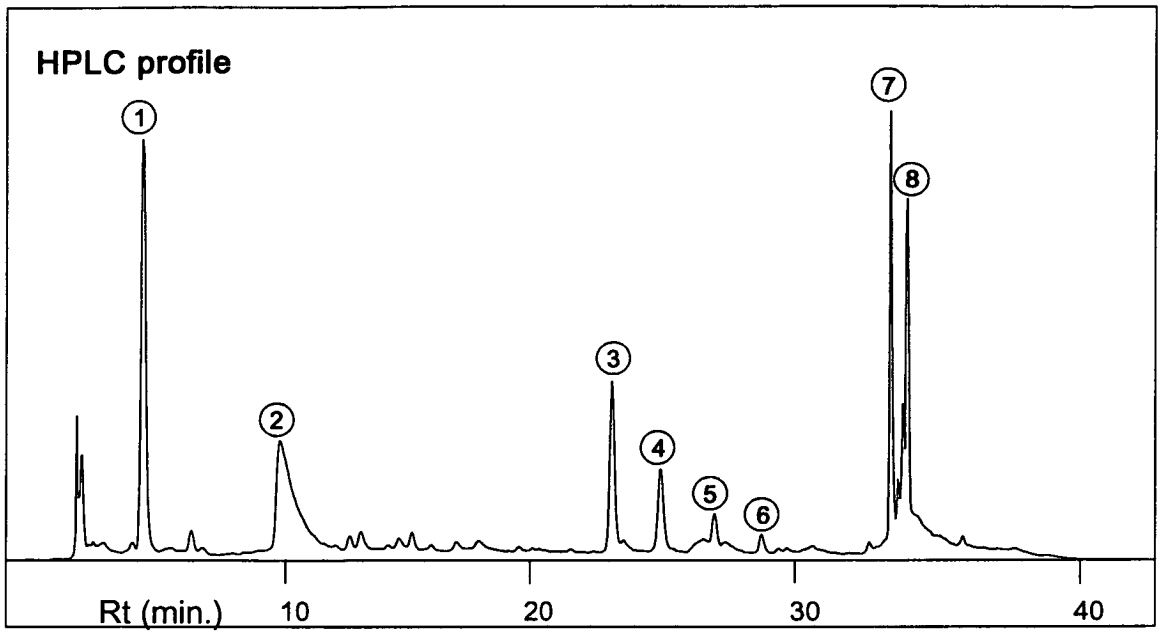
  - NBI 27652

Distribution



This species is only known to occur on the dolomite rocks in the Lydenburg and Pelgrim's Rest area (Mpumalanga).

A. fragilis Lavranos & Röösli



Peak number	Retention time	Compound	Percentage
1	5.02	aloesin	21
2	10.25	unidentified chromone 1	19
3	22.81	unidentified chromone 2	9
4	24.65	unidentified chromone 3	5
5	26.66	unidentified anthrone 1	1
6	28.41	unidentified anthrone 2	1
7	33.22	unidentified compound	12
8	33.83	unidentified chromone 4	12

The two unidentified chromones (peak 2 & 8) are probably cinnamoyl chromone derivatives which makes the occurrence of these compounds in Malagasy species unusual. The unidentified compound (peak 7) has been found in species belonging to the *Purpurascentes* group.

- Taxonomic position:

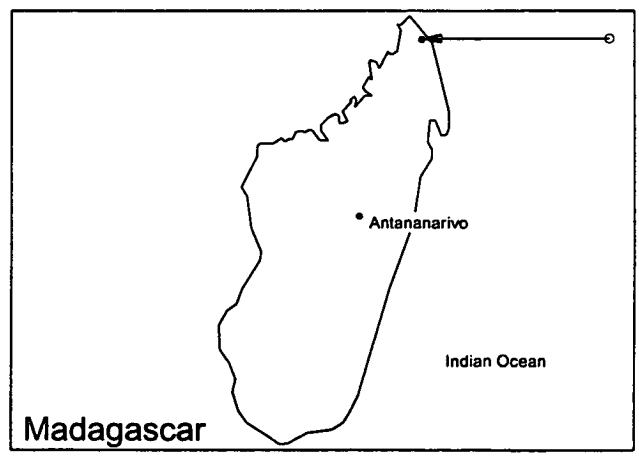
  Allied to *A. guillaumetii* / *A . rauhii* (Lavranos, 1994).

- Samples analysed:

  The leaf extract was investigated:

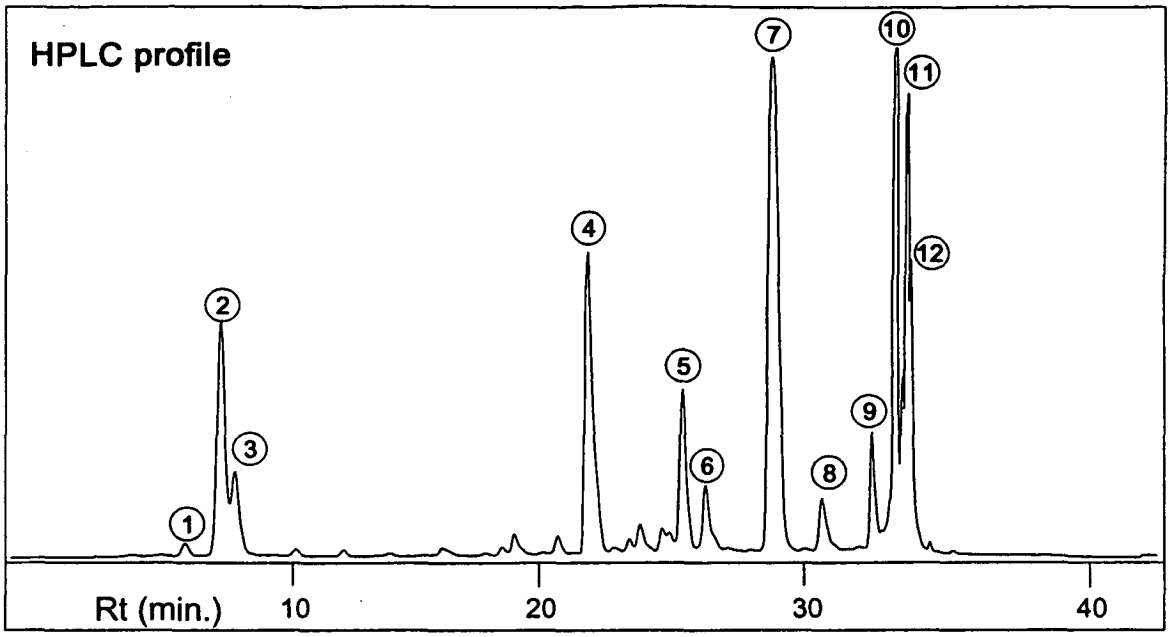
  - Lavranos 28737

Distribution



Aloe fragilis is found on the north-eastern coast of Madagascar near Cape Manambato.

Aloe framesii L. Bolus



Peak number	Retention time	Compound	Percentage
1	6.62	aloesin	1
2	7.95	7-*O*-methylaloesin	10
3	8.49	unidentified chromone 1	4
4	21.96	5-hydroxyaloin B	13
5	25.60	unidentified compound 1	5
6	26.49	unidentified compound 2	3
7	29.01	microstigmin	26
8	30.92	unidentified chromone 2	2
9	32. 81	unidentified compound 3	3
10	33.69	unidentified compound 4	14
11	34.13	unidentified chromone 3	16
12	34.12	unidentified compound 5	

Aloe framesii is the only member of the *Purpurascentes* to contain a series of compounds of which the UV spectrum does not correspond to any of the known classes of compounds detected in *Aloe*.

- Taxonomic position:

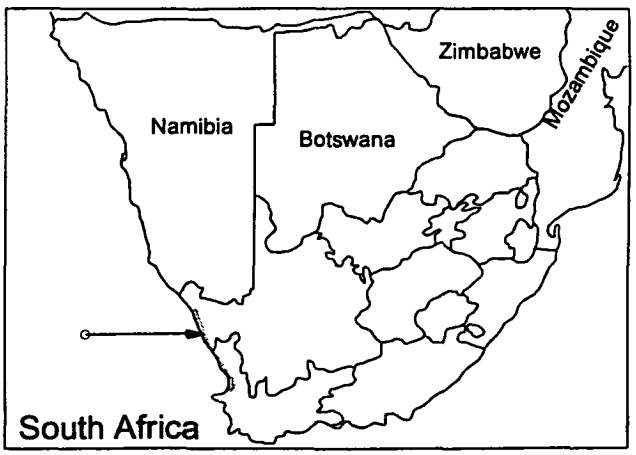
  Aloe series *Purpurascentes* (Reynolds, 1950).

- Samples analysed:

  The leaf exudate was investigated:

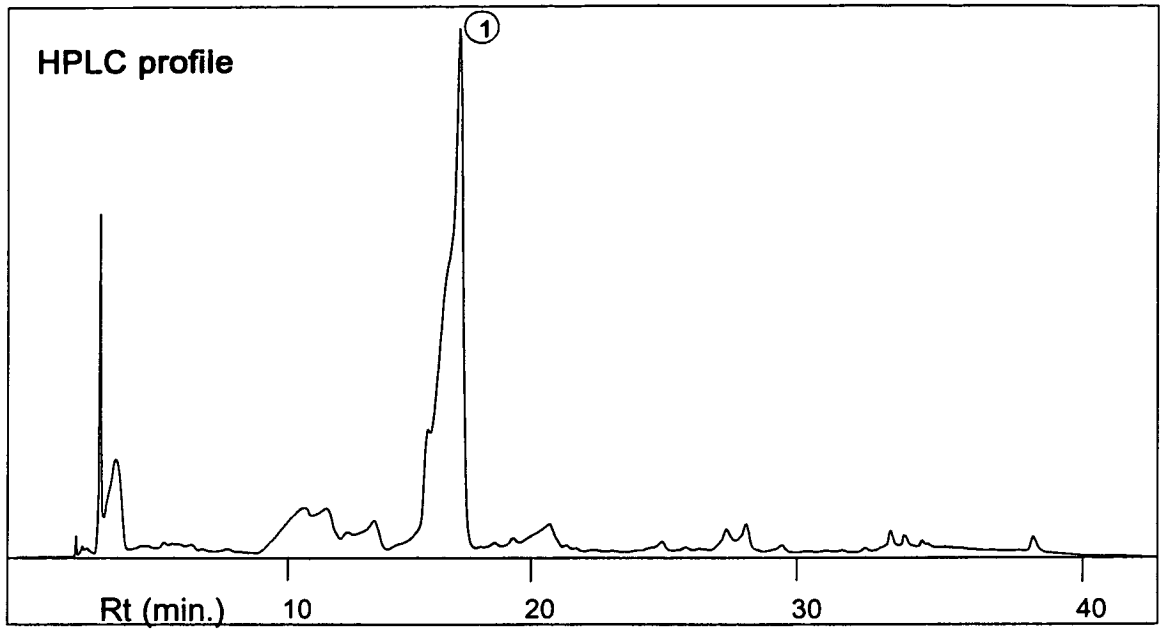
  - NBI 29271

Distribution



Aloe framesii has a coastal distribution extending from Port Nolloth in the north, southwards to Saldanha Bay.

Aloe francombei Newton



Peak number	Retention time	Compound	Percentage
1	17.10	plicataloside	78

(See *A. archeri, A. deserti, A. elgonica* etc.).

- Taxonomic position:

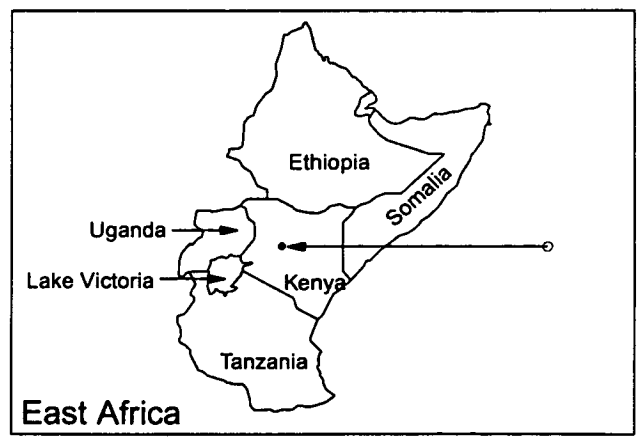
  Unknown (Newton, 1994).

- Samples analysed:

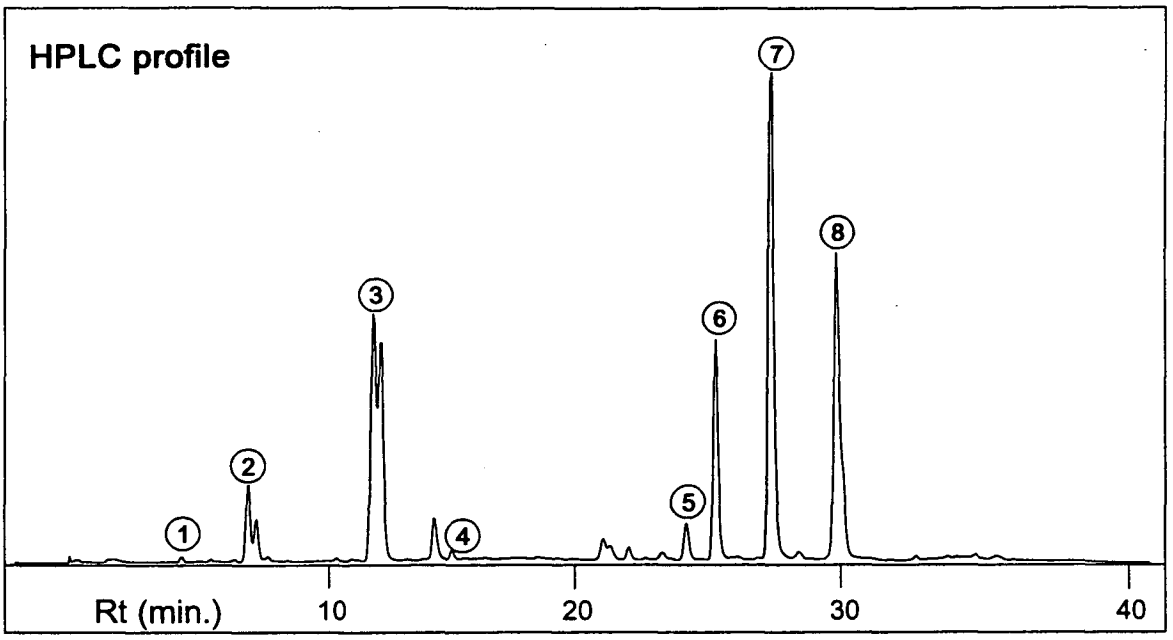
  The leaf exudate was investigated:

  - LEN 4130 (type plant)

Distribution



Aloe francombei has only been collected at Mukutan Gorge in the Laikipia District, Kenya.



Peak number	Retention time	Compound	Percentage
1	6.5	aloesin	1
2	8.3	unidentified compounds 1 & 2	9
3	12.9	unidentified compounds 3 & 4	15
4	15.7	dihydroisocoumaringlucoside	1
5	24.1	unidentified chromone 1	8
6	25.2	homonataloin B	14
7	27.2	homonataloin A	23
8	29.6	unidentified chromone 2	10

Peak 5 and 6 could possibly represent cinnamoyl chromones.

- Taxonomic position:

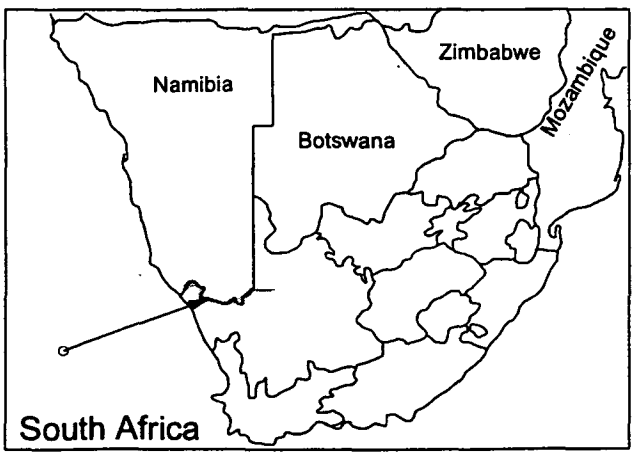
  Aloe series *Purpurascentes* (Reynolds, 1950).

- Samples analysed:

  The leaf exudate was investigated:

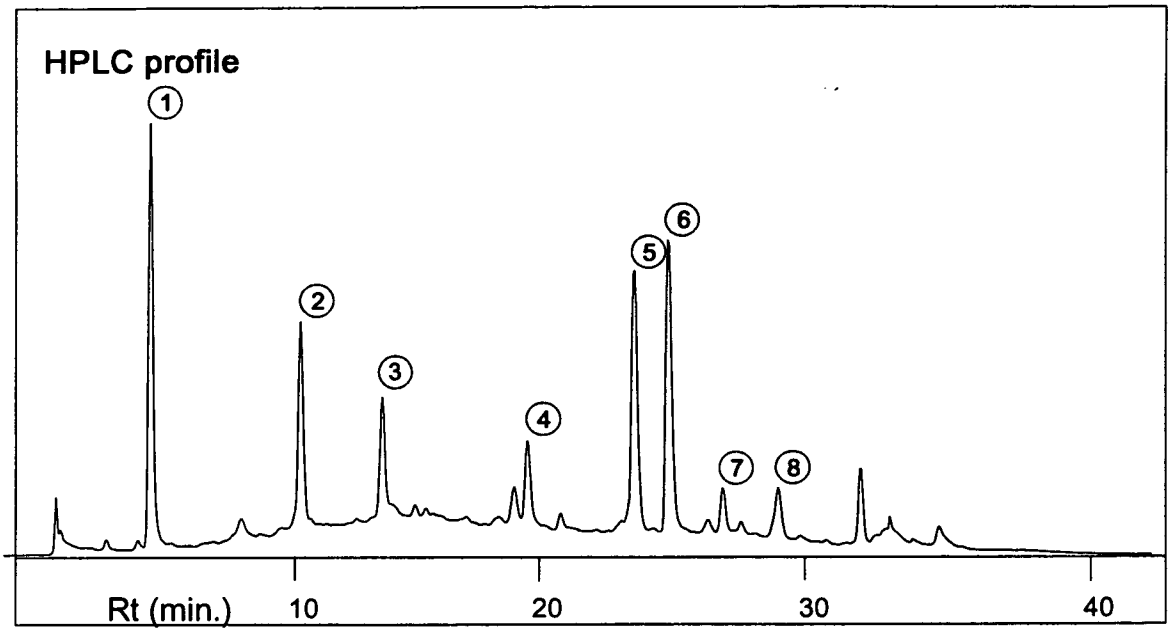
  - Lavranos 29597
  - NBI 29275

Distribution



The distribution of this species follows the route of the Orange River (previously known as the Gariep) which represents the border between South Africa and Namibia.

Aloe gerstneri Reynolds



Peak number	Retention time	Compound	Percentage
1	5.60	aloesin	21
2	11.26	unidentified chromone 1	11
3	14.34	unidentified chromone 2	6
4	19.81	unidentified chromone 3	5
5	23.78	aloin B	17
6	25.07	aloin A	19
7	27.11	unidentified anthrone 1	3
8	29.18	unidentified anthrone 2	4

The three unidentified chromones all display the typical UV absorbance spectra of the coumaroyl chromones. The two unidentified anthrones have UV spectra resembling that of aloinoside but the presence of these anthrones require confirmation.

- Taxonomic position:

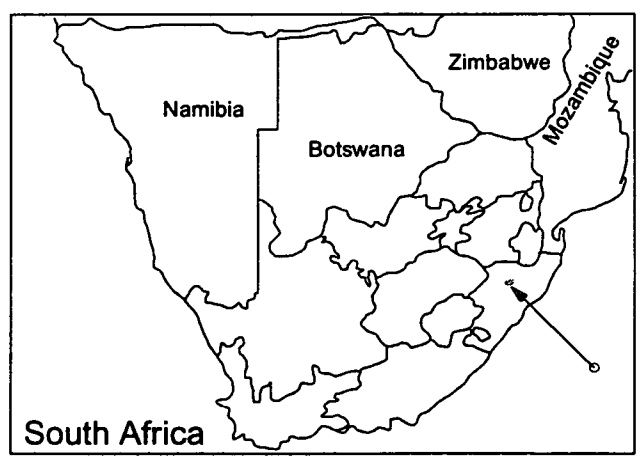
  Aloe section *Pachydendron* (Reynolds, 1950).

- Samples analysed:

  The leaf exudate was investigated:

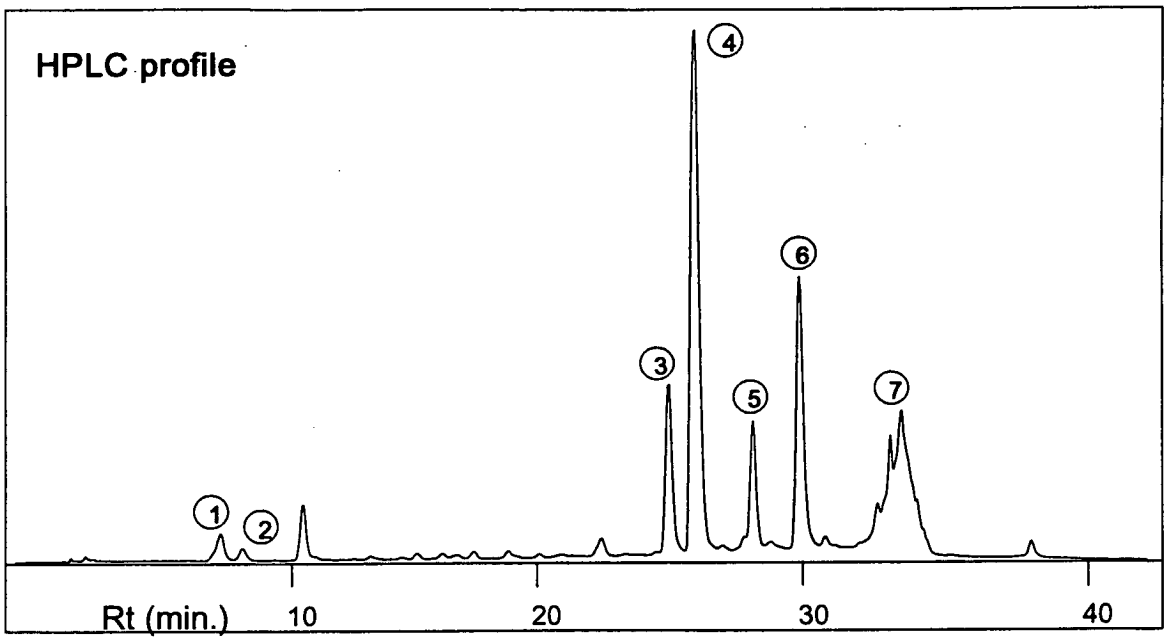
  - Bababango
  - NBG 11 96/83

Distribution



Aloe gerstneri is restricted to rocky areas around Vryheid in KwaZulu-Natal.

Aloe gilberti T. Reynolds ex Sebsebe & Brandham



Peak number	Retention time	Compound	Percentage
1	7.75	aloesin	2
2	8.56	7-*O*-methylaloesin	1
3	24.86	aloin B	9
4	25.79	aloin A	35
5	28.14	aloinoside B	7
6	29.81	aloinoside A	15
7	33.25	microdontin A / B	24

Peak 7 represents and incomplete separation of microdontin A and B.

- Taxonomic position:

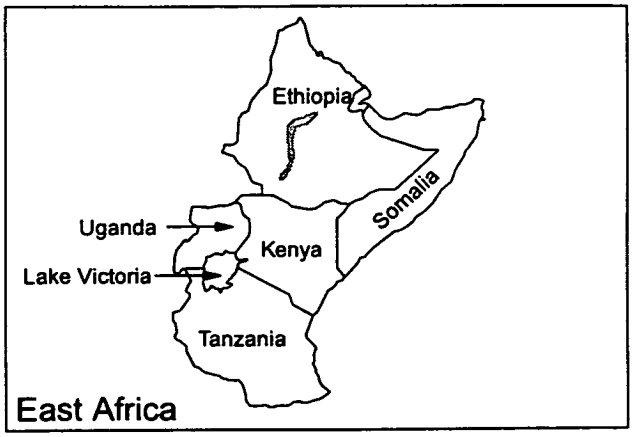
  Allied to *A. melanacantha* (Demissew & Brandham, 1992).

- Samples analysed:

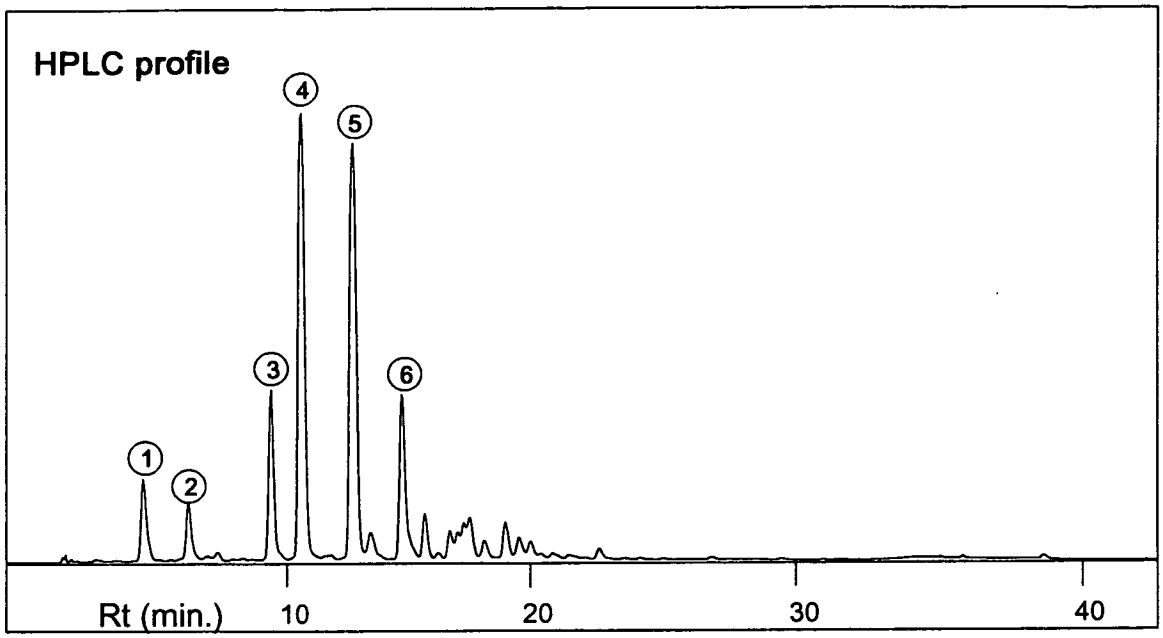
  The leaf extract and exudate was investigated:

  - RBG, Kew 1990-1301
  - EDS 226

Distribution



Aloe gilberti is distributed in the Shewa, Gamo, Gofa and Sidamo regions of Ethiopia.



Peak number	Retention time	Compound	Percentage
1	5.14	unidentified flavonoid 1	5
2	6.82	unidentified flavonoid 2	3
3	9.96	unidentified flavonoid 3	9
4	11.08	unidentified flavonoid 4	29
5	13.08	unidentified flavonoid 5	27
6	14.94	unidentified flavonoid 6	10

Aloe glauca is devoid of any anthrones or chromones in the leaf exudate. Instead this species contains complex mixtures of flavonoids (flavanones / dihydroflavanoles). Various samples were injected and each contained different flavonoid glucosides. After acid hydrolysis naringenin and dihydroisorhamnetin were present.

- Taxonomic position:

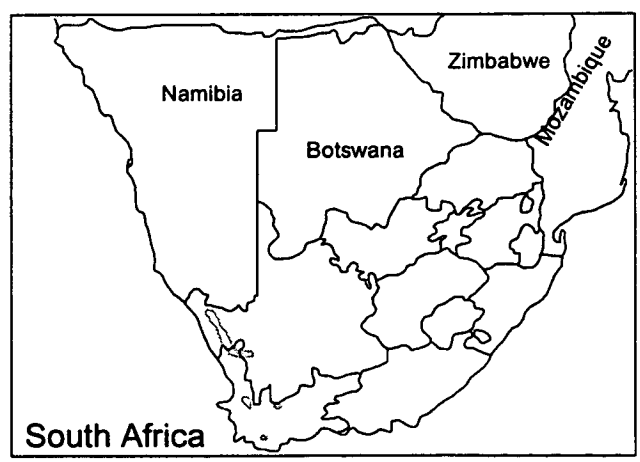
Aloe series *Rhodacanthae* (Reynolds, 1950).

- Samples analysed:

The leaf exudate was investigated:

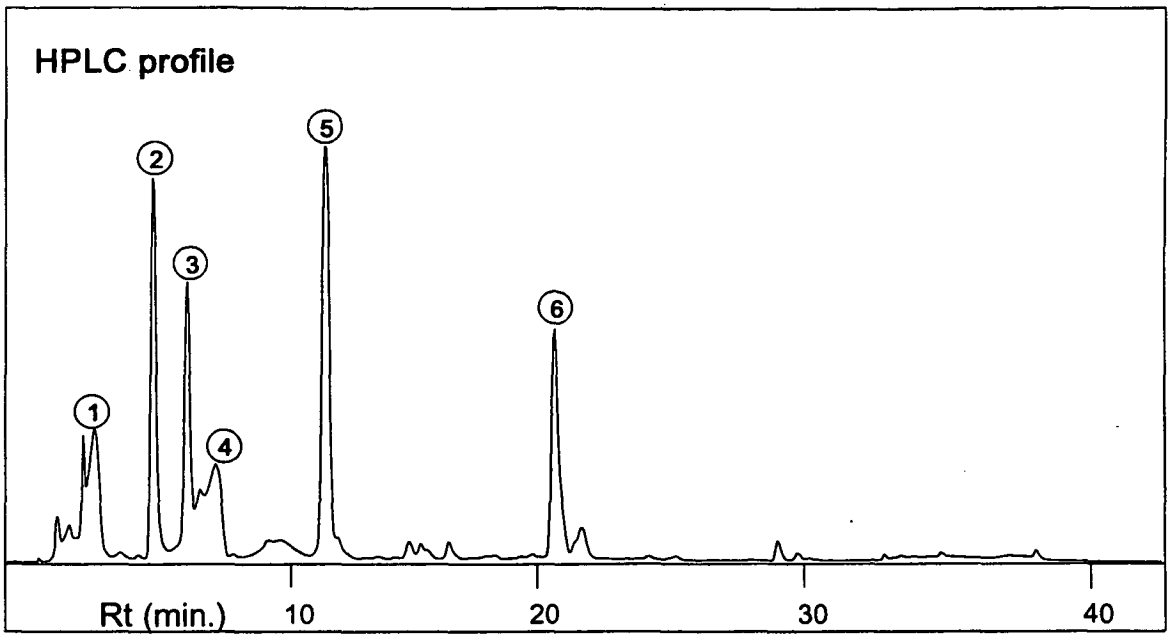
- ex hort Worcester Botanical Garden
- NBI 29866
- Bonnievale
- NBI JV 16716

Distribution



This species is sporadically distributed in the dry mountainous areas of the south western Cape.

Aloe globuligemma Pole-Evans



Peak number	Retention time	Compound	Percentage
1	2.30	unidentified chromone 1	12
2	5.35	aloesin	19
3	6.62	7-*O*-methylaloesin	15
4	7.72	unidentified chromone 2	12
5	11.78	unidentified chromone 3	27
6	20.41	aloeresin D	16

All the samples of *Aloe globuligemma* contained a series of chromones and were devoid of anthrones.

- Taxonomic position:

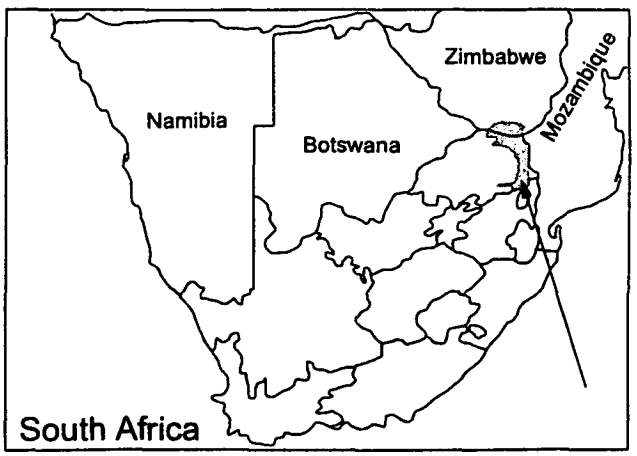
Aloe section *Pachydendron* (Reynolds, 1950).

- Samples analysed:

The leaf exudate was investigated:

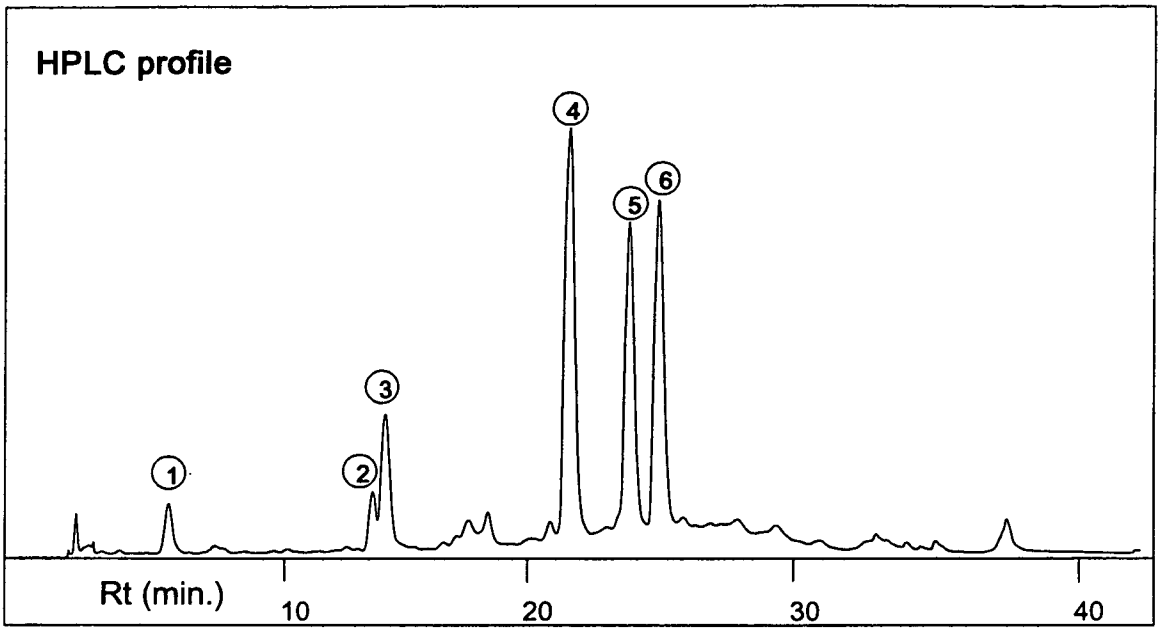
- A. Ellert 606 (ex Zimbabwe)
- A. De Castro 147
- Brandfort

Distribution



Aloe globuligemma occurs in the bushveld of Mpumalanga, the Northern Province and in the southern parts of Zimbabwe.

Aloe gossweileri Reynolds



Peak number	Retention time	Compound	Percentage
1	6.08	aloesin	3
2	13.95	aloenin	3
3	14.45	10-hydroxyaloin B	9
4	21.55	unidentified anthrone	29
5	23.84	aloin B	20
6	24.96	aloin A	22

Aloe gossweileri is chemically unique in leaf exudate composition. It is the only species to display this combination of compounds (ie. aloenin together with 10-hydroxyaloin B).

- Taxonomic position:

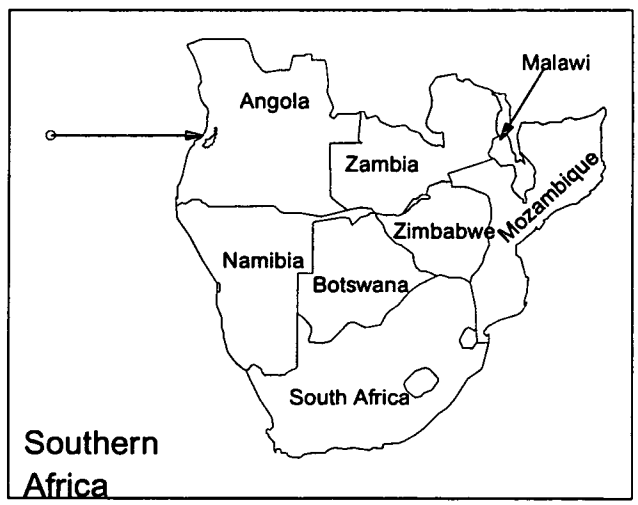
  Group 19 of the tropical aloes (Reynolds, 1996).

- Samples analysed:

  The leaf exudate was investigated:

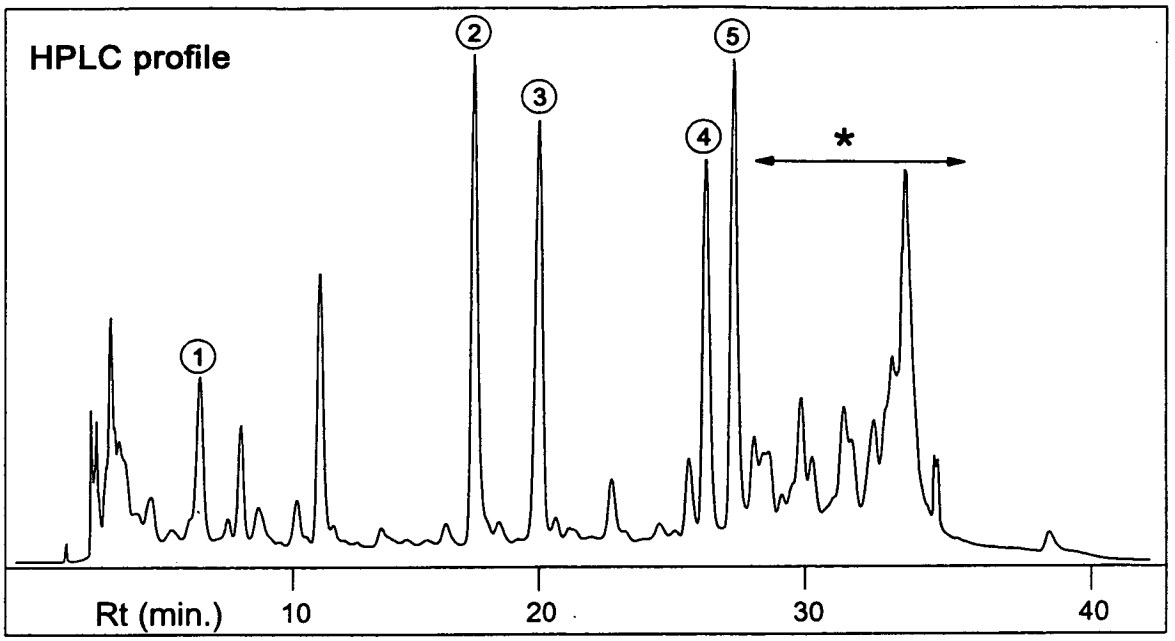
  - RBG, Kew

Distribution



Aloe gossweileri is found near Amboira and Lobito in the west of Angola.

Aloe gracilis Haworth



Peak number	Retention time	Compound	Percentage
1	6.9	aloesin	4
2	17.3	unidentified flavone 1	10
3	19.8	unidentified flavone 2	9
4	26.1	aloin B	8
5	27.1	aloin A	10

The four major compounds are two flavones (peak 2 & 3) and the anthrones aloin A and B (peak 4 & 5). All peaks in the area *, display UV absorbance spectra identical to the aloin anthrones. This pattern (indicated by *) has also been found in *A. striatula*.

- Taxonomic position:

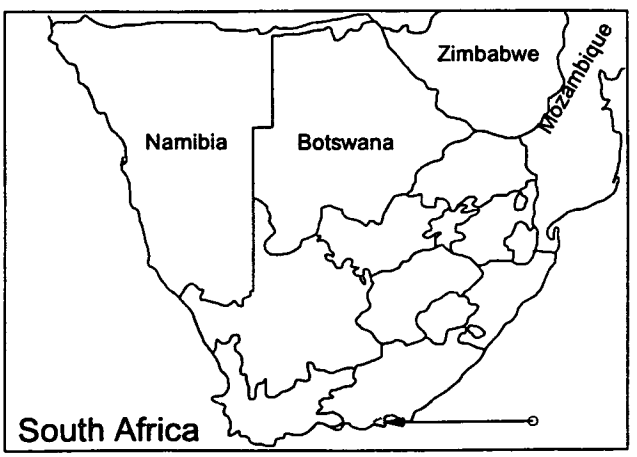
  Aloe series *Macrifoliae* (Reynolds, 1950).

- Samples analysed:

  The leaf extract was investigated:

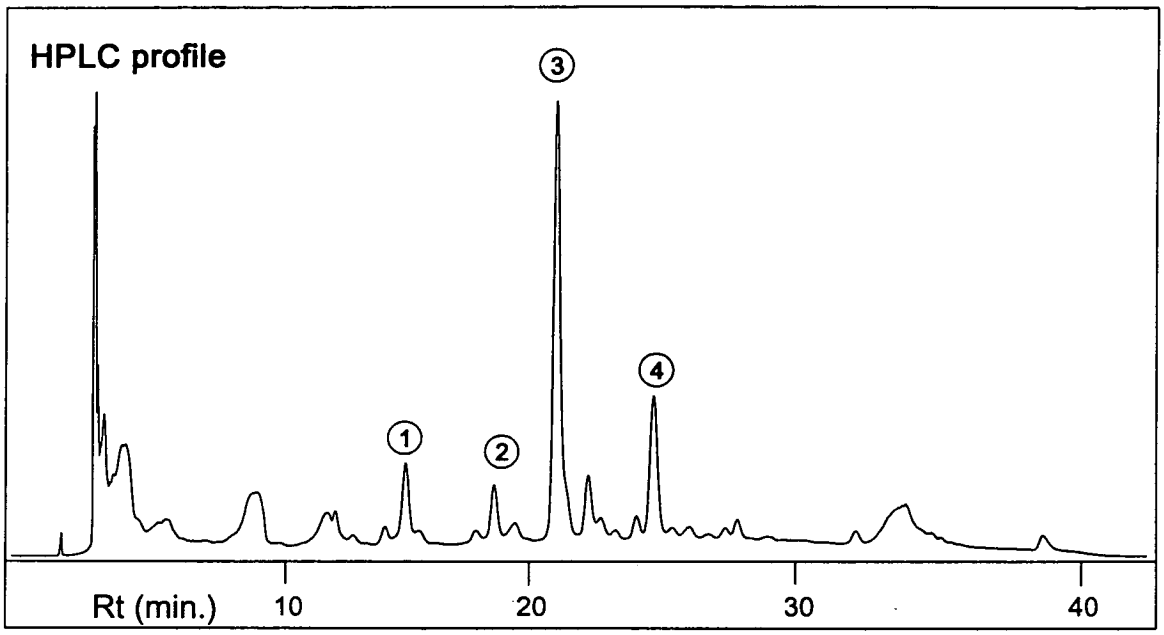
  - ex hort NBG

Distribution



Aloe gracilis is confined to the Port Elizabeth and Uitenhage area in the Eastern Cape Province.

Aloe gracilis var. *decumbens* Reynolds



Peak number	Retention time	Compound	Percentage
1	15.1	unidentified flavone 1	7
2	18.4	unidentified flavone 2	3
3	20.8	unidentified flavone 3	33
4	22.3	unidentified flavone 4	2

All the major compounds have the characteristic UV absorbance spectrum of the flavone class of flavonoids.

- Taxonomic position:

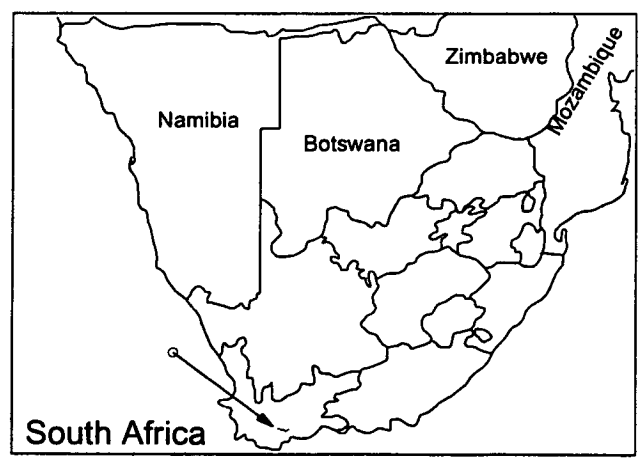
  Aloe series *Macrifoliae* (Reynolds, 1950).

- Samples analysed:

  The leaf extract was investigated:

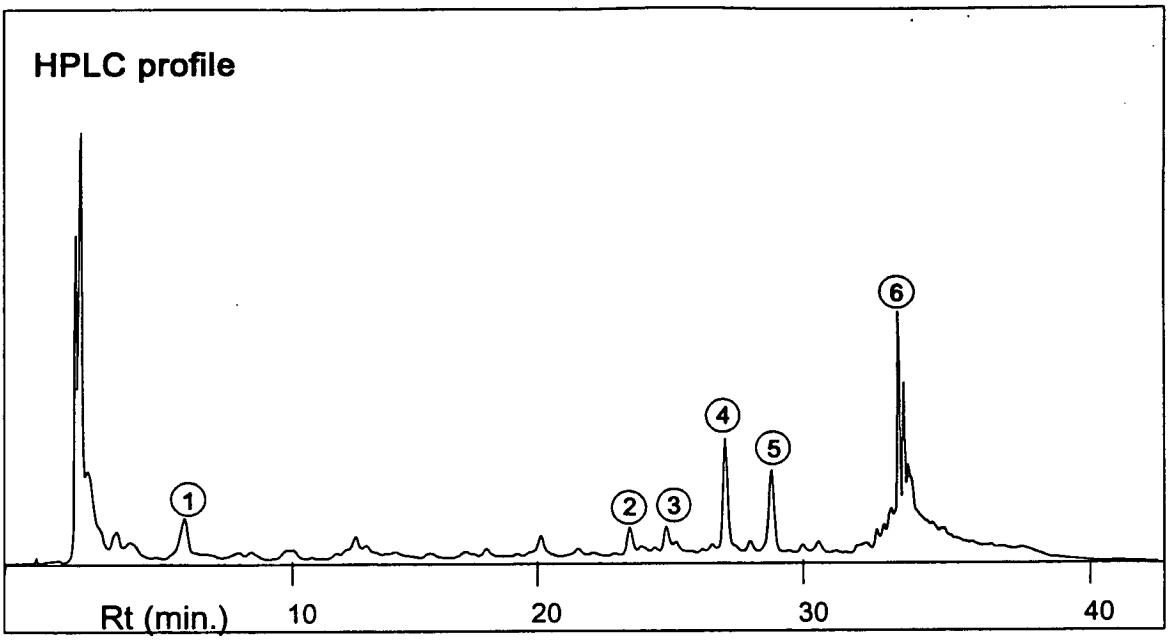
  - ex hort NBG

Distribution



Aloe gracilis var. *decumbens* is found along the Langeberg, especially in the vicinity of Garcias Pass.

A. guillaumetii Cremers



Peak number	Retention time	Compound	Percentage
1	6.63	7-*O*-methylaloesin	7
2	23.28	aloin B	3
3	24.65	aloin A	2
4	26.88	aloinoside B	12
5	28.62	aloinoside A	11
6	33.35	unidentified anthrones	25

This Malagasy species is an exception, as the aloinoside isomers are not detected in any other species in Madagascar. The unidentified anthrones show the same UV spectra as aloin and the aloinosides.

- Taxonomic position:

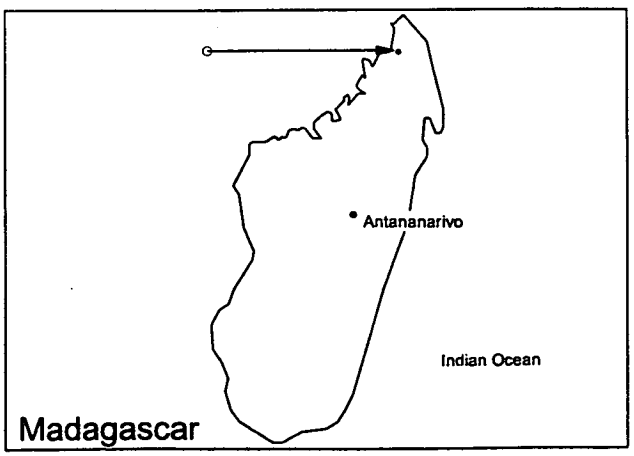
  Allied to *A. deltoideodonta* / *A. viguieri* (Cremers, 1976).

- Samples analysed:

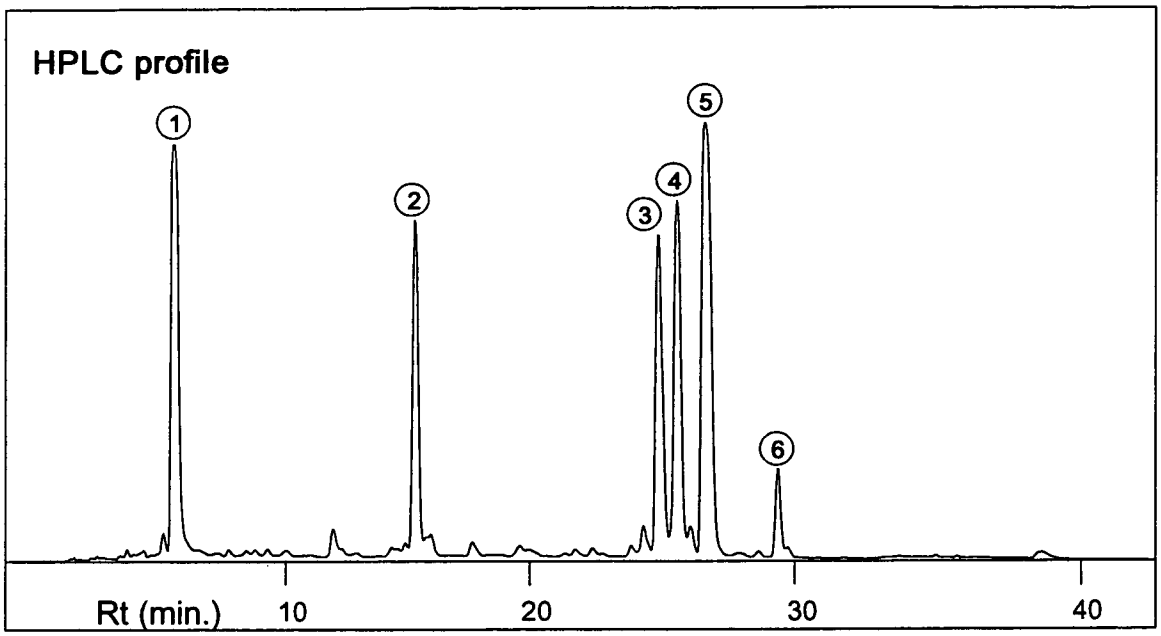
  The leaf extract was investigated:

  - Lavranos 28738

Distribution



Aloe guillaumetii is found 10 km east of Ambilobe in the north of Madagascar.



Peak number	Retention time	Compound	Percentage
1	6.21	aloesin	20
2	15.48	aloeresin A	12
3	24.06	homonataloin B	14
4	24.61	unidentified chromone 1	15
5	26.36	homonataloin A	26
6	29.16	unidentified chromone 2	3

The two unidentified chromones show UV spectra corresponding to the coumaroyl class of chromones.

- Taxonomic position:

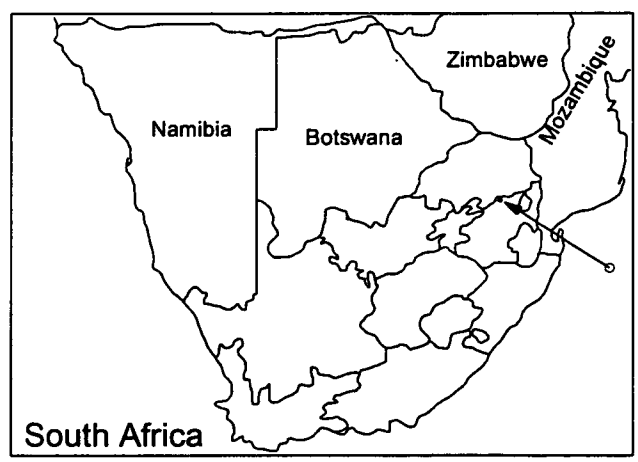
  Possibly related to *A. arborescens* and *A. mutabilis* (Glen, 1987).

- Samples analysed:

  The leaf exudate was investigated:

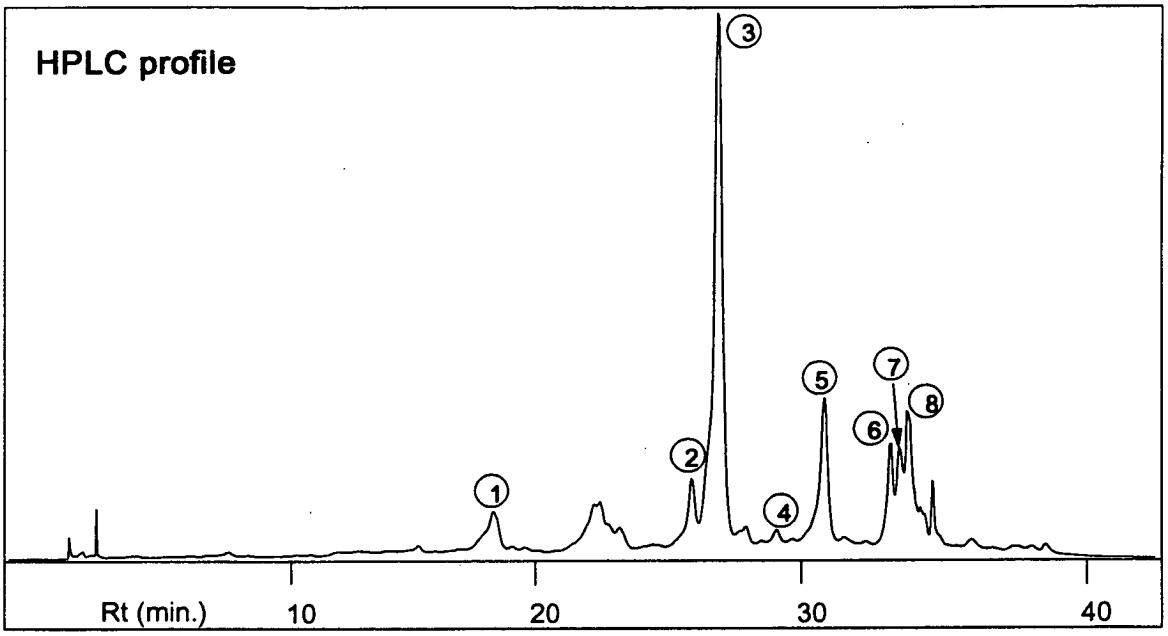
  - ex hort D. Hardy
  - ex E. Van Jaarsveld (ex Blouberg)

Distribution



This pendent species is only found near Lydenberg in the Mpumalanga Province of South Africa.

Aloe harlana Reynolds



Peak number	Retention time	Compound	Percentage
1	17.81	7-hydroxyaloin	4
2	24.22	aloin B	5
3	25.19	aloin A	42
4	27.43	aloinoside B	1
5	29.22	aloinoside A	10
6	32.12	microdontin B	5
7	32.92	microdontin A	4
8	33.54	unidentified anthrone	10

The presence of 7-hydroxyaloin is unuasual, as this is the only example where this compound occurs with the aloinosides and microdontins.

- Taxonomic position:

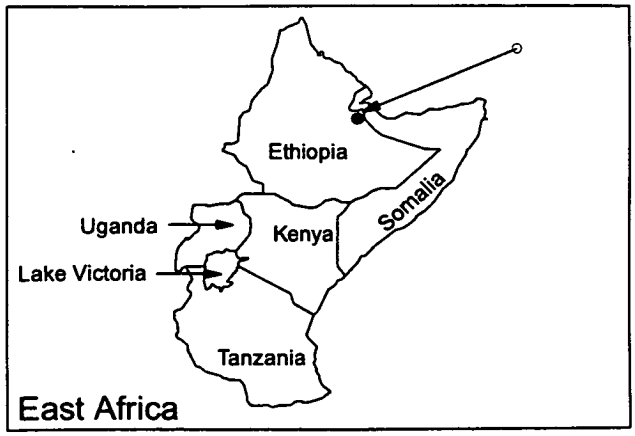
  Group 16 of the tropical aloes (Reynolds, 1966).

- Samples analysed:

  The leaf exudate was investigated:

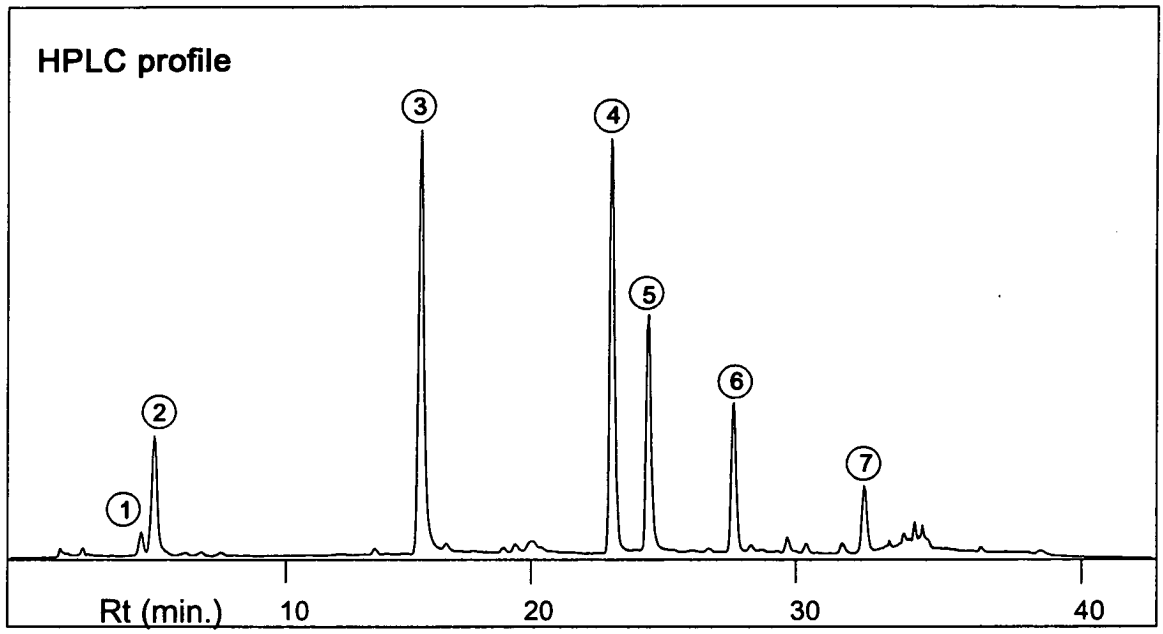
  - ex hort Bot. Staats München

Distribution



Aloe harlana grows near the Harla Village in the Harar Province of Ethiopia.

Aloe helenae Danguy



Peak number	Retention time	Compound	Percentage
1	5.01	aloesin	1
2	5.52	unidentified flavanone 1	9
3	15.59	unidentified flavanone 2	30
4	22.82	aloin B	27
5	24.20	aloin A	15
6	27.41	unidentified anthrone 1	10
7	32.27	unidentified anthrone 2	4

Aloe helenae is chemically unique as it is one of two aloes where anthrones co-occur with flavanones. The unidentified anthrones (peak 6 & 7) have UV spectra identical to that of aloin.

- Taxonomic position:

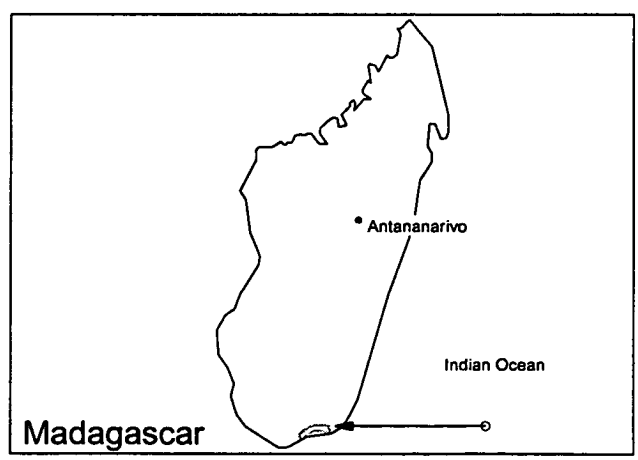
  Group 9 (Reynolds, 1966).

- Samples analysed:

  The leaf exudate was investigated:

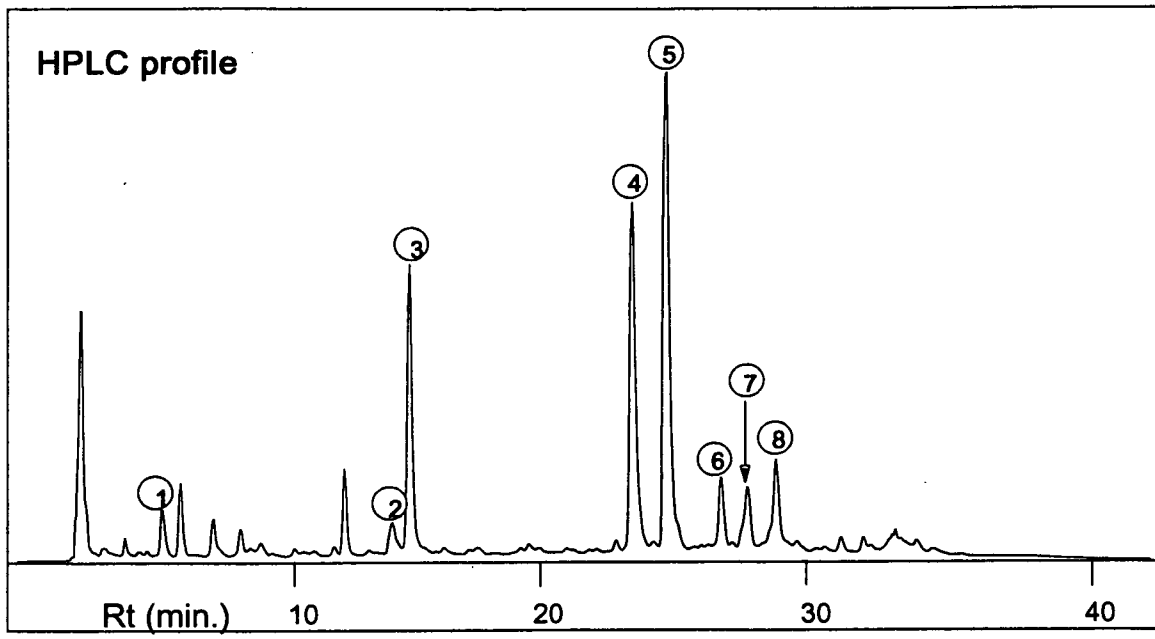
  - ex hort D. Hardy

Distribution



Aloe helenae is found near Fort Dauphin and Ambovombe in the south of Madagascar.

Aloe hemmingii Reynolds



Peak number	Retention time	Compound	Percentage
1	5.44	aloesin	2
2	14.19	8-*O*-methyl-7-hydroxyaloin	2
3	14.84	dihydroisocoumarin glucoside	14
4	23.34	aloin B	22
5	24.61	aloin A	30
6	26.73	aloinoside B	4
7	27.73	unidentified chromone	3
8	28.80	aloinoside A	4

This is the only species where 8-*O*-methyl-7-hydroxyaloin (peak 2) co-occurs with the anthrones, aloinosides A and B. Both samples injected (see below) are identical in composition.

- Taxonomic position:

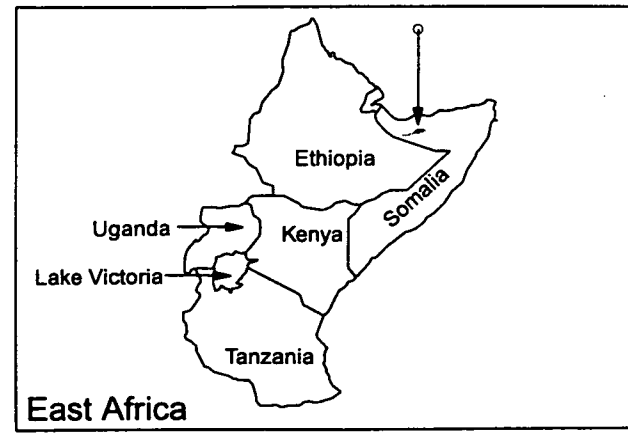
  Group 4 of the tropical aloes (Reynolds, 1966).

- Samples analysed:

  The leaf exudate was investigated:

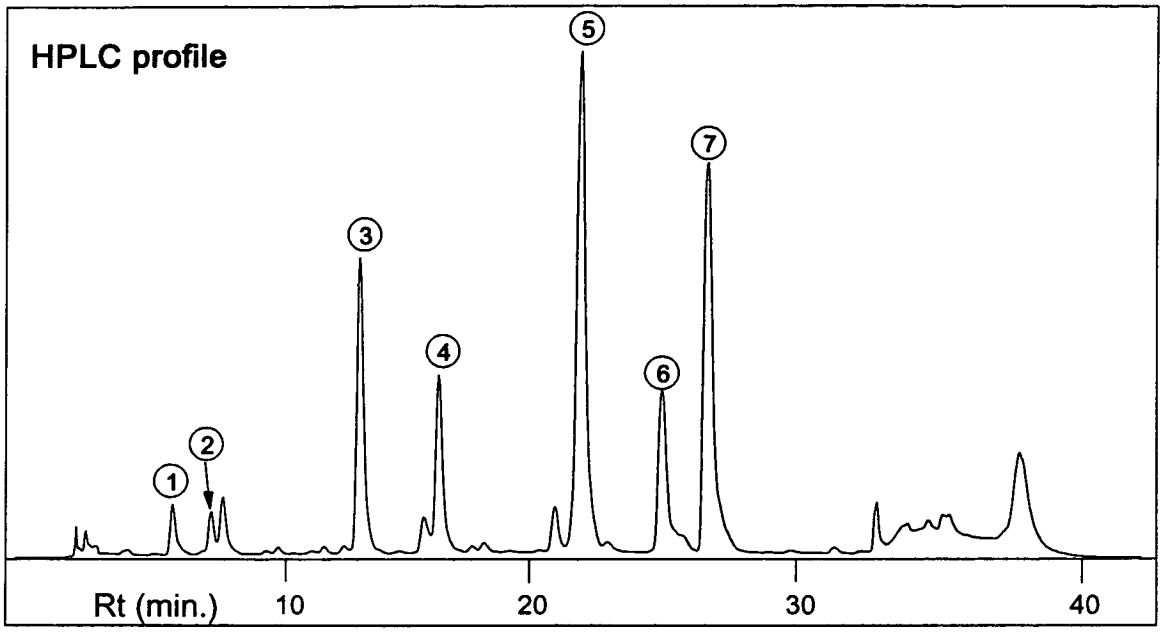
  - NBI 11170
  - RBG, Kew 08481-01059

Distribution



Aloe hemmingii grows on Sheikh Pass and near Borama in northern Somalia.

Aloe hereroensis Engler



Peak number	Retention time	Compound	Percentage
1	6.5	aloesin	2
2	7.5	7-*O*-methylaloesin	2
3	13.29	unidentified compound 1	13
4	16.35	unidentified compound 2	8
5	21.74	unidentified compound 3	25
6	24.85	homonataloin B	9
7	26.85	homonataloin A	21

The three unknown compounds display identical UV absorbance spectra and could probably be related to the chromone class of compounds.

- Taxonomic position:

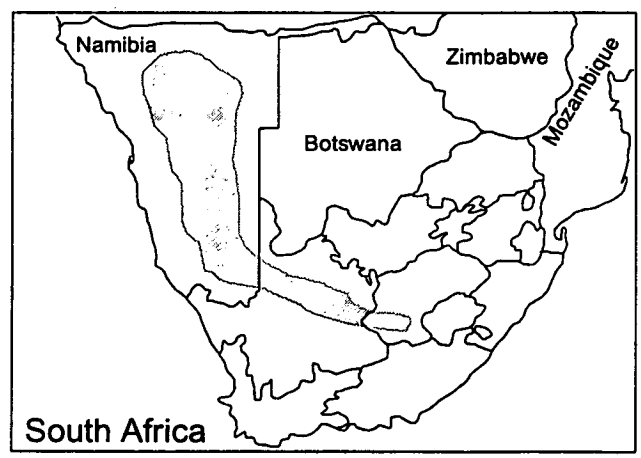
  Aloe series *Hereroenses* (Reynolds, 1950).

- Samples analysed:

  The leaf exudate was investigated:

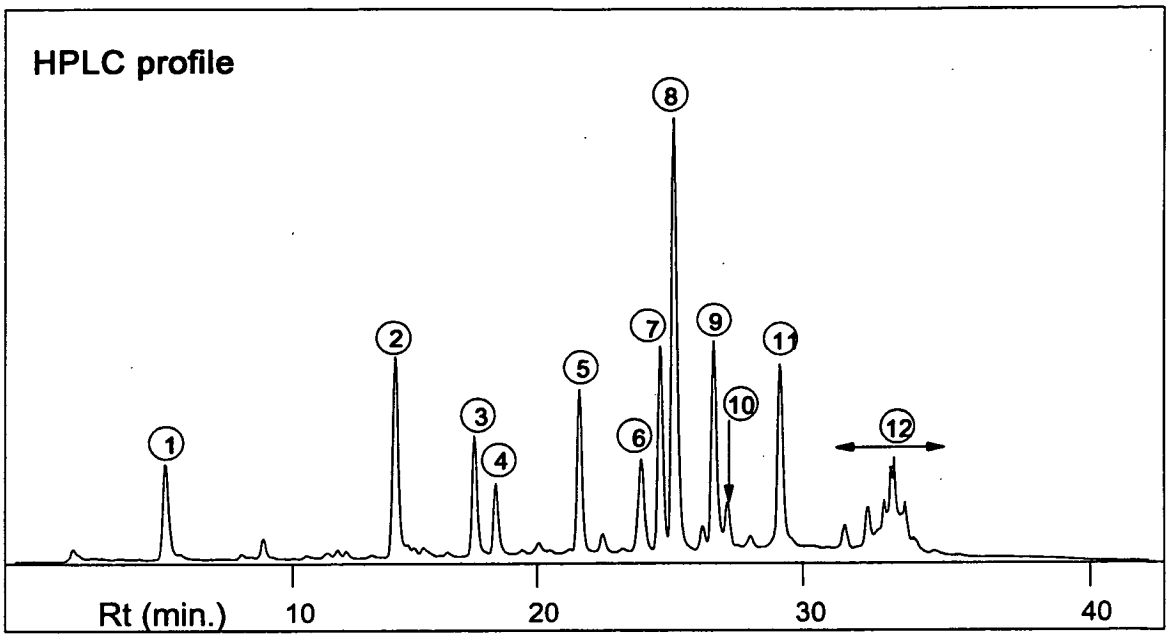
  - NBI 28966
  - ex hort JBG

Distribution



This species is widely distributed in the central part of Namibia from where it extends in a south-easterly direction to Free State Province in South Africa.

Aloe hildebrandtii Baker



Peak number	Retention time	Compound	Percentage
1	5.65	aloesin	5
2	14.39	aloeresin A	9
3	17.22	dihydroisocoumarin glucoside	5
4	18.25	unidentified anthrone 1	3
5	21.42	unidentified anthrone 2	7
6	23.76	aloin B	5
7	24.48	unidentified compound	9
8	24.97	aloin A	21
9	26.50	unidentified anthrone 3	9
10	27.03	unidentified anthrone 4	2
11	29.06	unidentified anthrone 5	9
12	33.20	unidentified anthrones 6	2

The leaf exudate of this species is rather complex and resembles that of *A. jacksonii*. The unidentified anthrones 1,2 & 3 display the UV absorbance spectra characteristic of homonataloin while peaks 10 & 11 correlate to that of aloin.

- Taxonomic position:

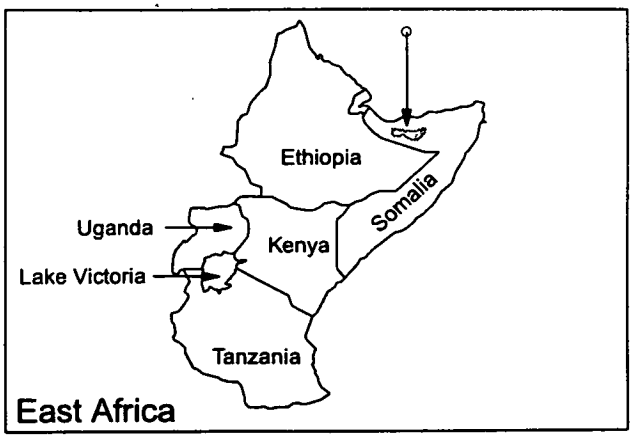
  Group 19 of the tropical aloes (Reynolds, 1966).

- Samples analysed:

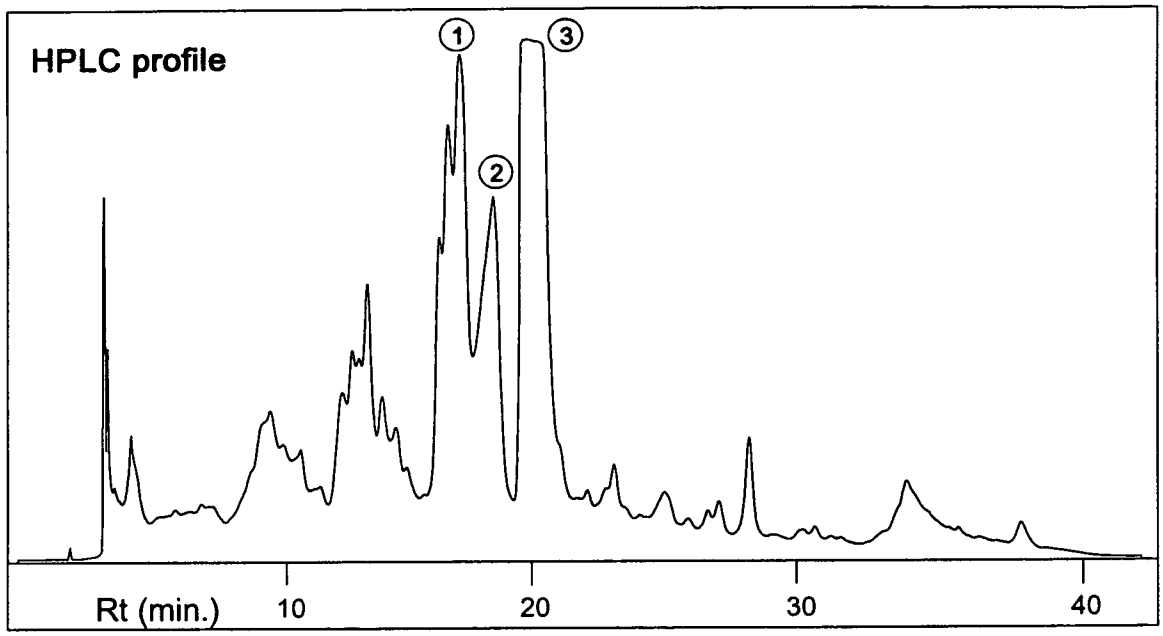
  The leaf exudate was investigated:

  - RBG, Kew 144-73-01211
  - RBG, Kew 1981-886

Distribution



Aloe hildebrandtii is found in the vicinity of Erigavo and Ghor in Somalia.



Peak number	Retention time	Compound	Percentage
1	17.0	unidentified flavone 1	11
2	18.3	unidentified flavone 2	13
3	19.6	isovitexin	26

As is the case in most of the grass-like aloes, *A. hlangapies* contains flavones. Isovitexin isolated and identified from *A. verecunda* is the major compound in *A. hlangapies*.

- Taxonomic position:

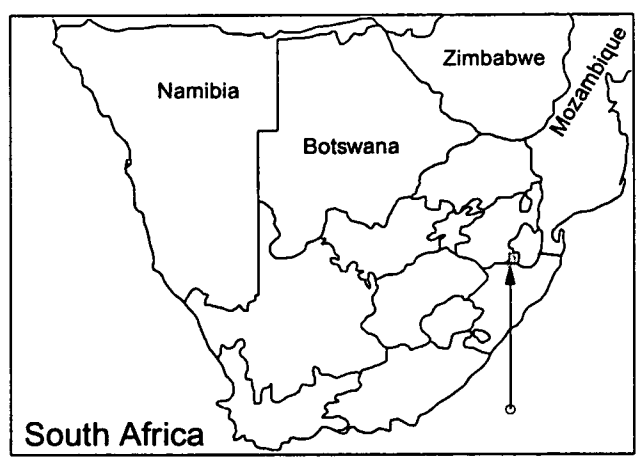
  Aloe section *Leptoaloe* (Reynolds, 1950).

- Samples analysed:

  The leaf extract was investigated:

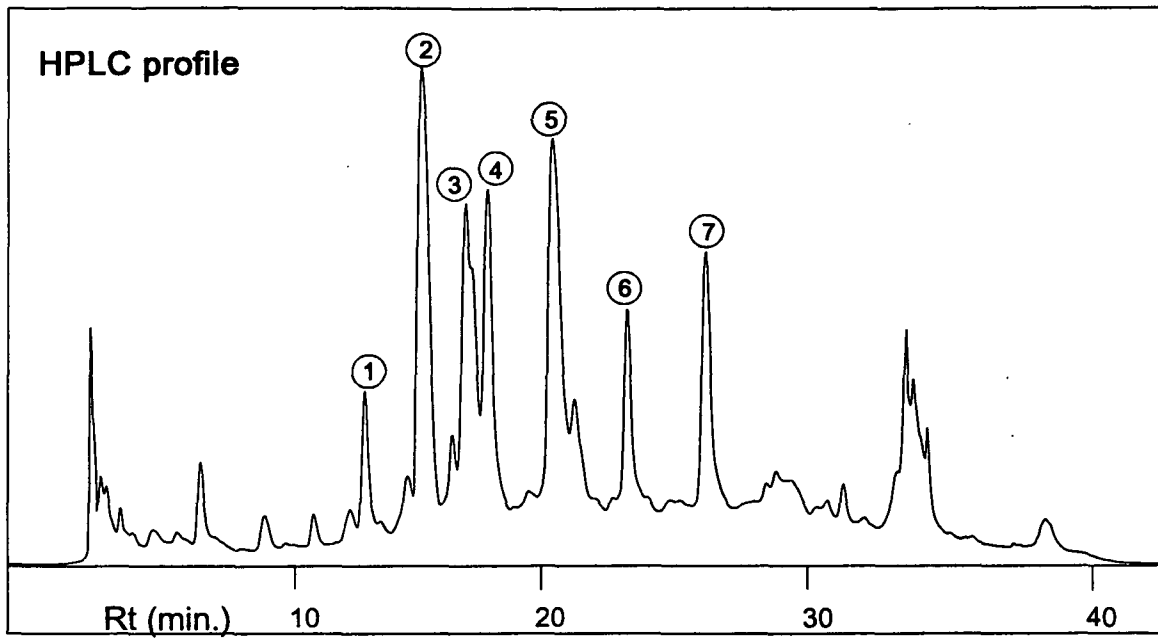
  - ex hort C. Craib (collected near Piet Retief)

Distribution



This species is restricted to the Piet Retief and Vryheid area.

Aloe humilis (L.) Miller



Peak number	Retention time	Compound	Percentage
1	13.21	unidentified flavonoid 1	3
2	15.26	unidentified flavonoid 2	16
3	16.92	unidentified flavonoid 3	12
4	17.74	unidentified flavonoid 4	10
5	20.16	unidentified flavonoid 5	15
6	22.98	unidentified flavonoid 6	5
7	25.91	unidentified flavonoid 7	7

As described for *Aloe glauca, A. humilis* also lacks chromones and anthrones and instead produces a range of flavonoids (flavanones / dihydroflavonols).

- Taxonomic position:

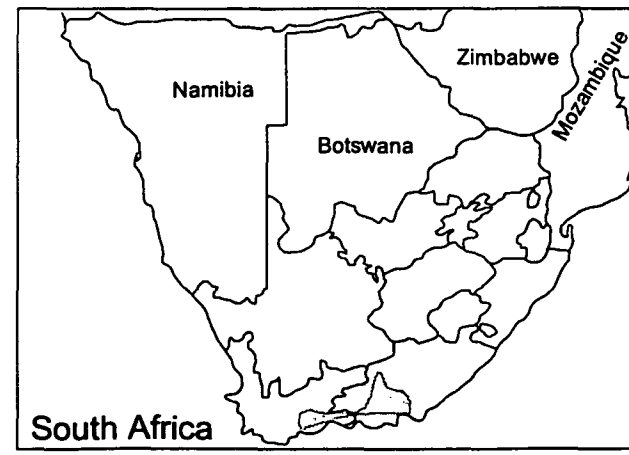
  Aloe series *Echinatae* (Reynolds, 1950).

- Samples analysed:

  The leaf exudate was investigated:

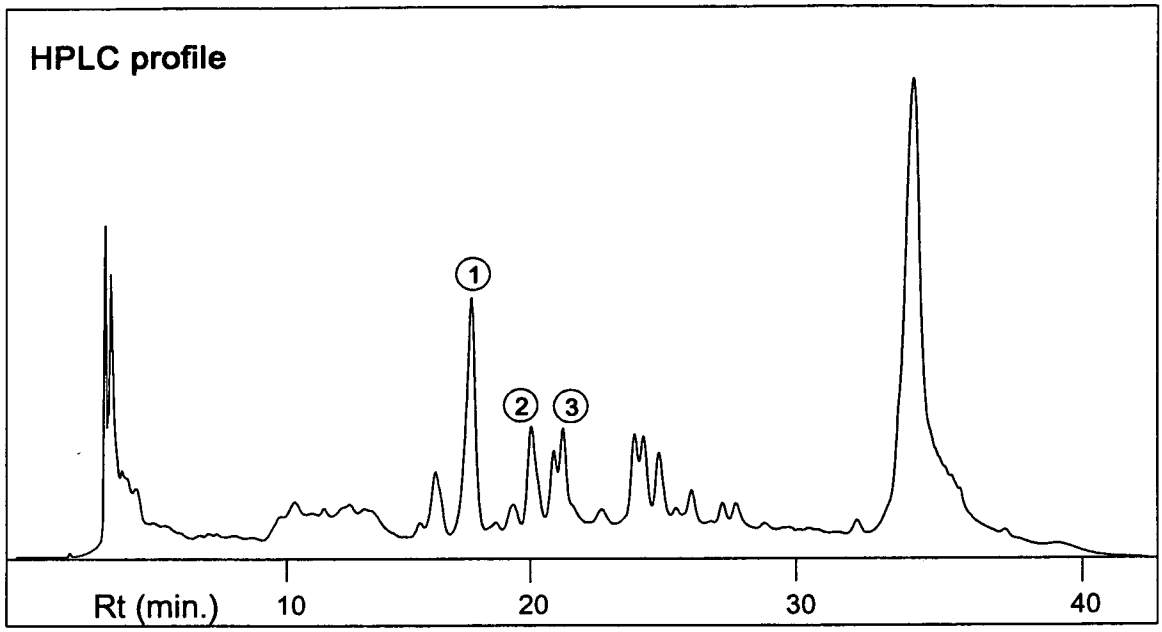
  - NBI 27971

Distribution



This species follows a karoid distribution from Mossel Bay in the west to Grahamstown in the east.

Aloe inconspicua Plowes



Peak number	Retention time	Compound	Percentage
1	17.5	unidentified flavone 1	12
2	19.8	unidentified flavone 2	5
3	21.0	unidentified flavone 3	4

Peak 1 - 3 have the characteristic UV spectra of the flavone class of flavonoids.

- Taxonomic position:

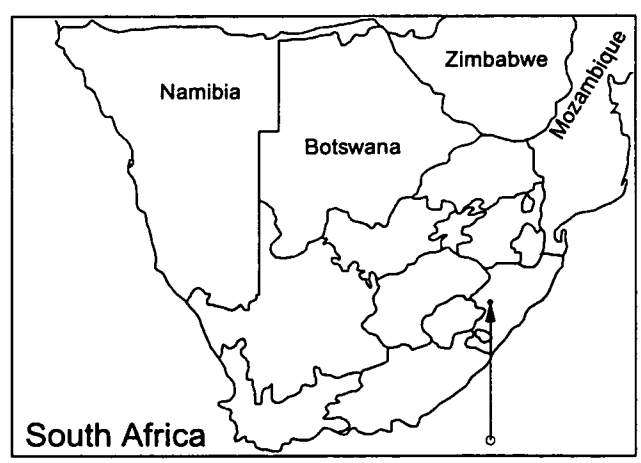
  Aloe section *Graminialoe* (Plowes, 1986).

- Samples analysed:

  The leaf extract was investigated:

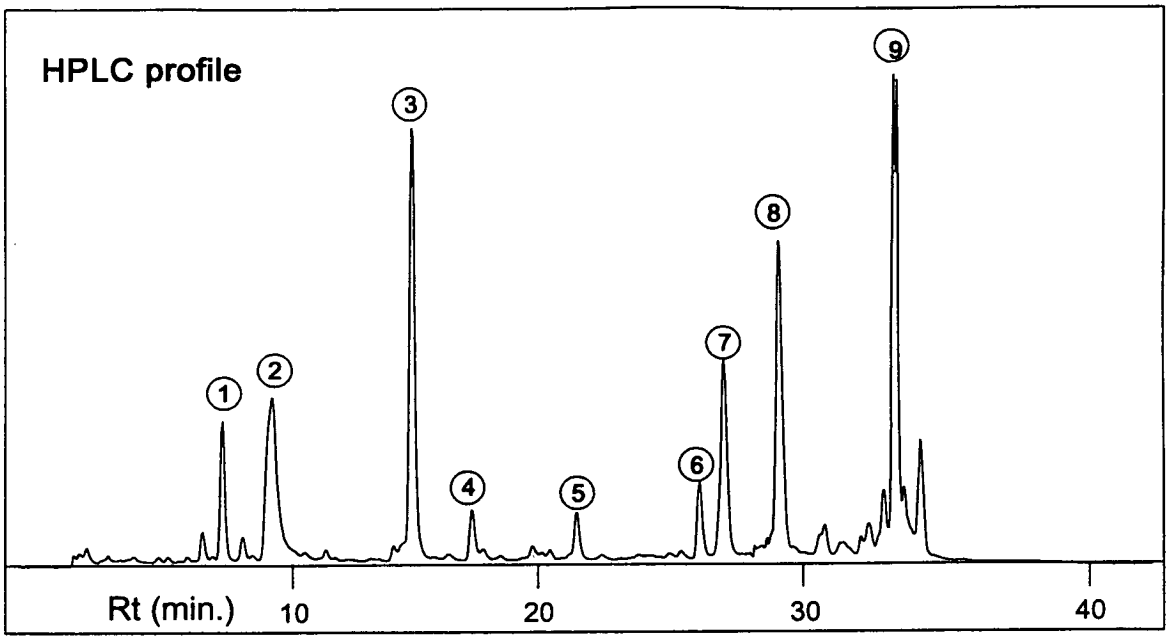
  - ex hort C. Craib (collected east of Escort)

Distribution



Aloe inconspicua is restricted to the area around Escourt in KwaZulu-Natal.

Aloe inermis Forsskål



Peak number	Retention time	Compound	Percentage
1	7.62	unidentified compound 1	4
2	8.76	unidentified compound 2	4
3	14.86	unidentified compound 3	17
4	17.15	unidentified compound 4	2
5	20.91	unidentified compound 5	2
6	25.79	unidentified compound 6	3
7	26.70	unidentified anthrone 1	9
8	28.55	unidentified anthrone 2	12
9	33.18	unidentified anthrones 3	19

The chromatogram is characterised by a series of unidentified compounds of which the UV absorbance spectra and retention times do not match any of the known compounds in *Aloe*. Peak 3 and 4 shows a similar UV spectra as the dihydroisocoumaringlucoside while the unidentified anthrones 1 and 2 shows an UV absorbance spectra correlating to the aloin-type anthrones. Peak 9 which is not completely separated shows a microdontin-type UV absorbance pattern.

- Taxonomic position:

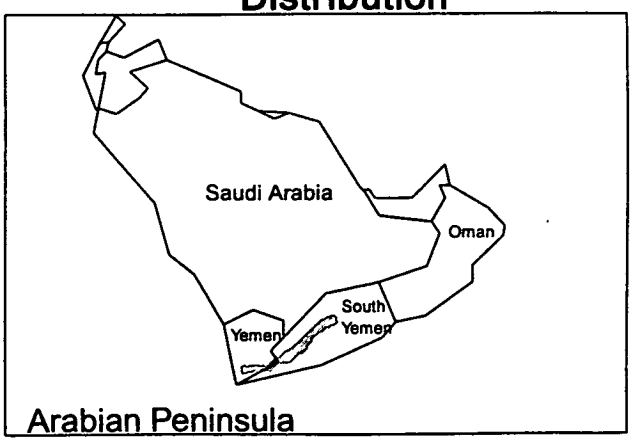
  Group 14 of the tropical aloes (Reynolds, 1966).

- Samples analysed:

  The leaf extract was investigated:

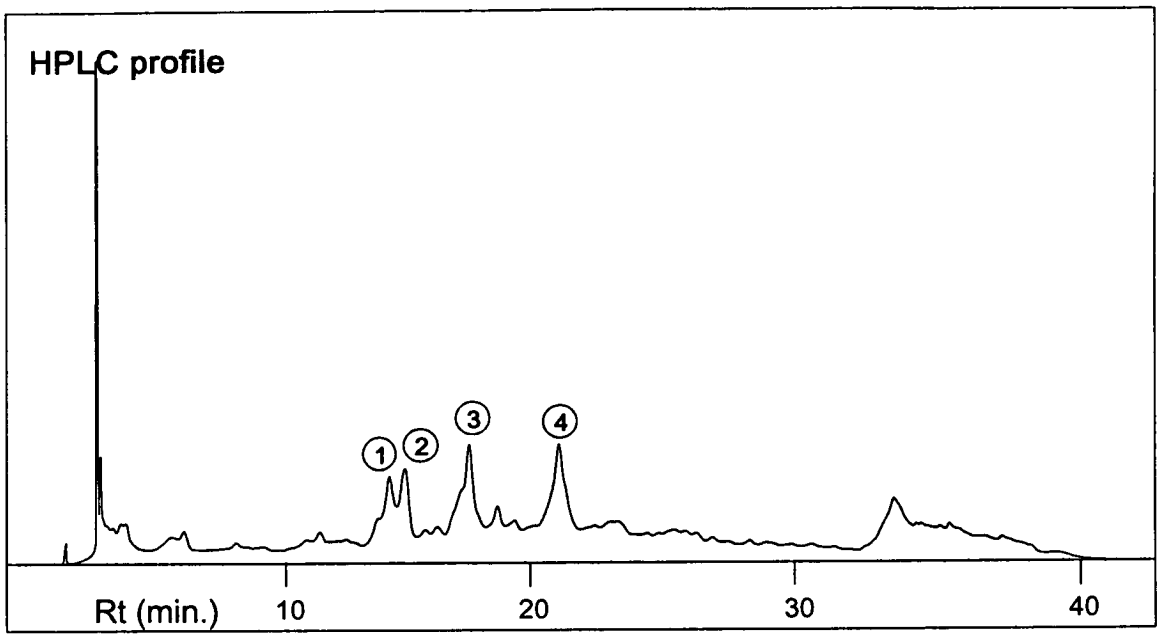
  - Lavranos 4338
  - NBI 10254

Distribution



Arabian Peninsula

This species is one of the earliest species of *Aloe* to be collected. It is abundant around Taizz in the Yemen and extends eastwards to the Hadhramaut in South Yemen.



Peak number	Retention time	Compound	Percentage
1	14.1	unidentified flavone 1	3
2	15.0	unidentified flavone 2	9
3	17.5	unidentified flavone 3	16
4	20.9	unidentified flavone 4	13

All the peaks noted on the chromatogram display the typical flavone-type UV absorbance spectrum.

- Taxonomic position:

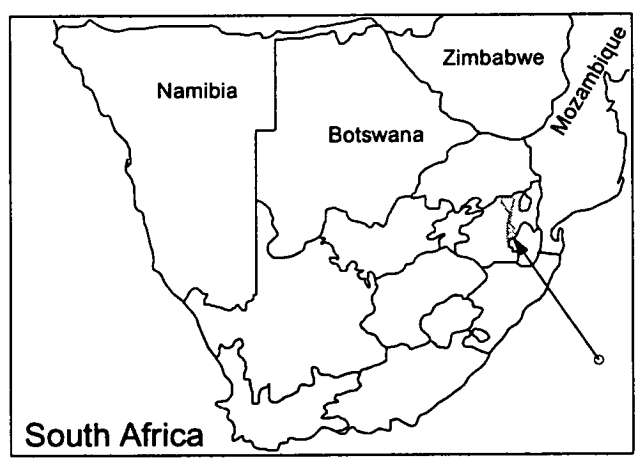
  Aloe section *Leptoaloe* (Reynolds, 1950).

- Samples analysed:

  The leaf extract was investigated:

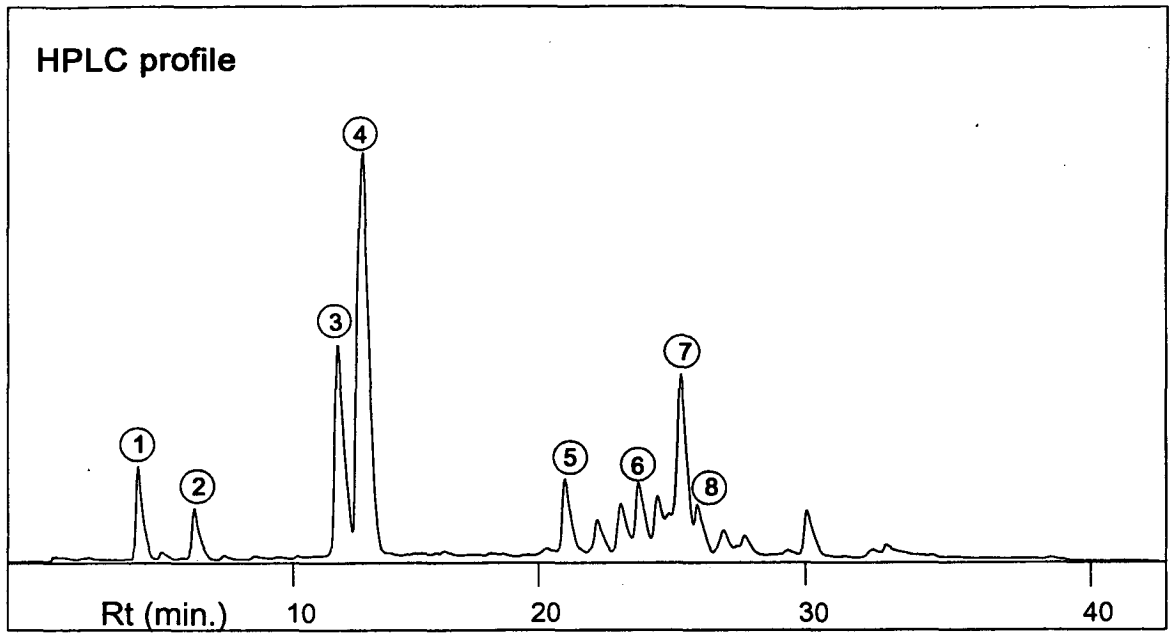
  - ex hort Craib (collected near Nelsburg)

Distribution



Aloe integra is distributed from Swaziland in the south, northwards to Pelgrim's Rest in Mpumalanga.

Aloe isaloensis H. Perrier



Peak number	Retention time	Compound	Percentage
1	4.84	aloesin	5
2	6.94	unidentified chromone 1	3
3	12.28	unidentified chromone 2	15
4	13.21	8-*O*-methyl-7-hydroxyaloin	36
5	20.84	unidentified chromone 3	4
6	22.94	homonataloin B	4
7	25.13	unidentified chromone 4	13
8	25.74	homonataloin A	3

All the unidentified chromones display UV absorbance spectra similar to the coumaroyl class of chromones.

- Taxonomic position:

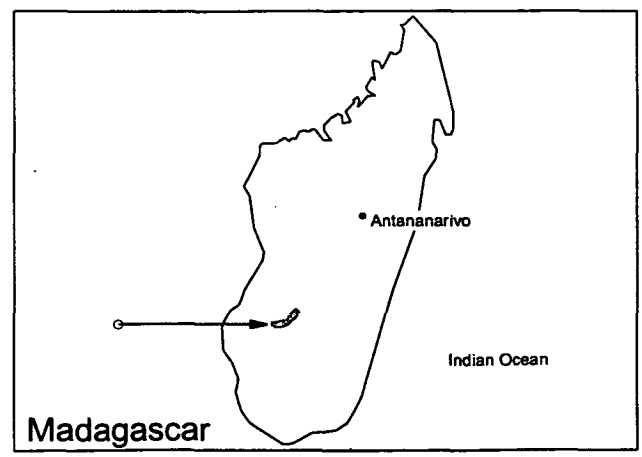
  Group 9 (Reynolds, 1966).

- Samples analysed:

  The leaf extract was investigated:

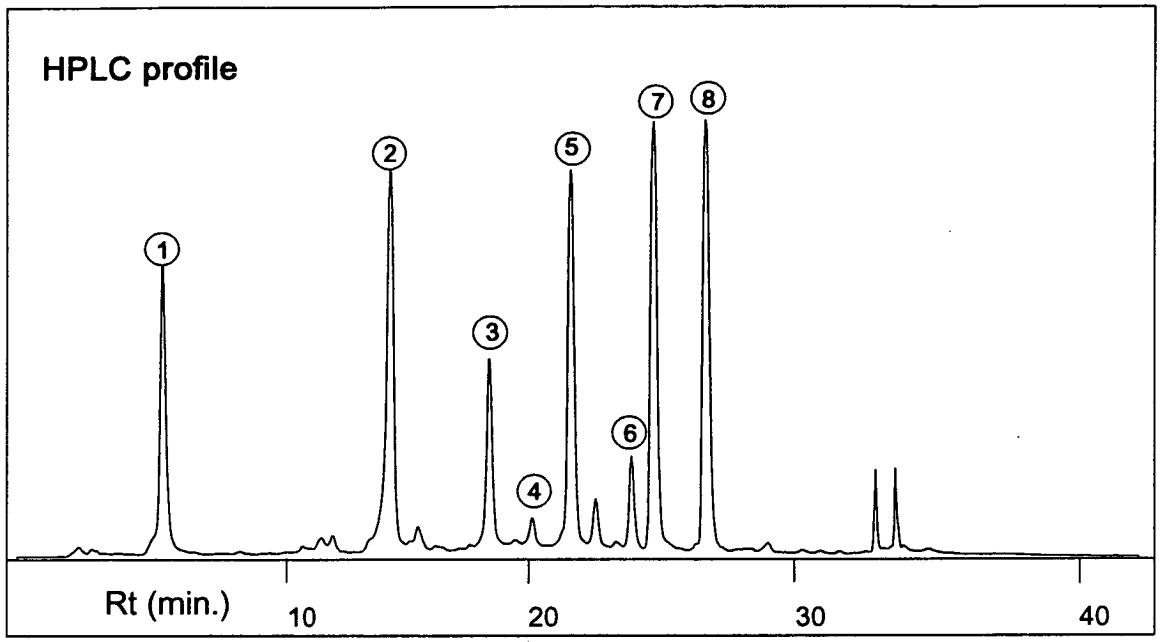
  - ex hort NBI

Distribution



Aloe isaloensis is associated with the sand stone slopes of the Isalo Range in the Fianarantso Province in Madagascar.

Aloe jacksonii Reynolds



Peak number	Retention time	Compound	Percentage
1	5.65	aloesin	11
2	14.45	unidentified chromone 1	19
3	18.28	unidentified anthrone 1	7
4	19.94	unidentified anthrone 2	1
5	21.11	unidentified anthrone 3	15
6	23.67	unidentified chromone 2	3
7	24.50	unidentified chromone 3	18
8	26.47	unidentified anthrone 4	18

The leaf exudate of *A. jacksonii* was very different to that of any other aloe analysed in this survey. The series of unidentified chromones all have an UV absorbance spectrum correlating the coumaric acid containing chromones. The series of unidentified anthrones all show a UV absorbance pattern correlating to homonataloin. All the exudate samples listed below were found to virtually identical.

- Taxonomic position:

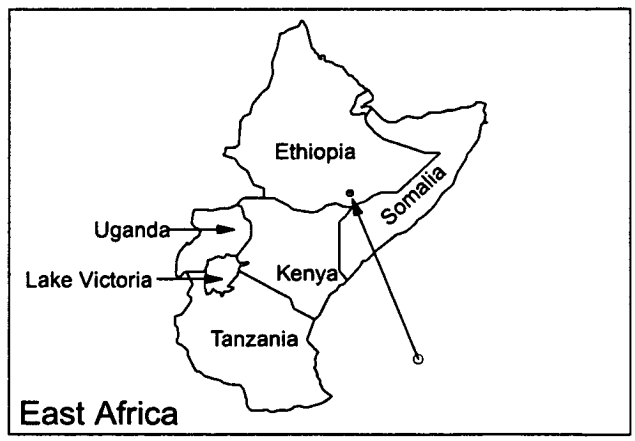
  Group 4 of the tropical aloes. (Reynolds, 1966).

- Samples analysed:

  The leaf exudate was investigated:

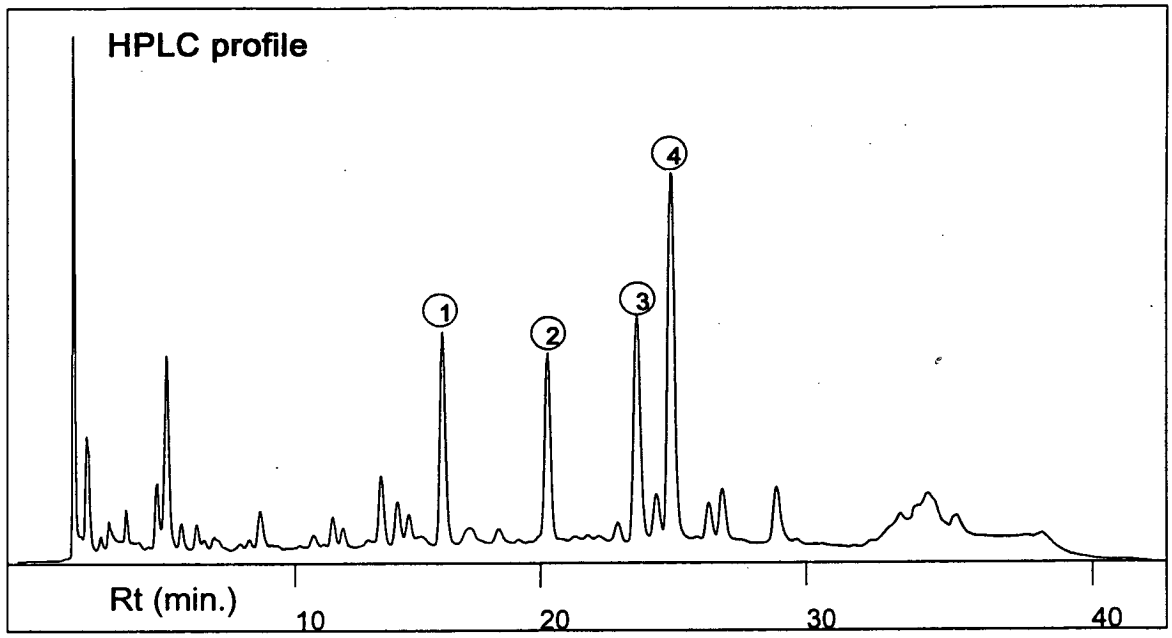
  - L. E. Newton 3956 (type material)
  - ex hort D. Hardy
  - NBI 5570

Distribution



Aloe jacksonii if found near El Carre in the southern parts of Ethiopia.

Aloe jucunda Reynolds



Peak number	Retention time	Compound	Percentage
1	16.10	unidentified compound 1	16
2	20.09	unidentified compound 2	15
3	23.51	aloin B	20
4	24.87	aloin A	31

The leaf phenolics in *A. jucunda* are present in extremely low quantities. No class of compound could be ascribed to the two unidentified compounds.

Distribution

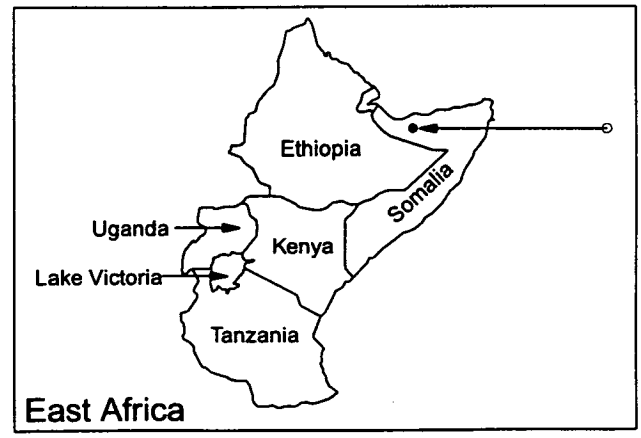
- Taxonomic position:

  Group 4 of the tropical aloes. (Reynolds, 1966).

- Samples analysed:

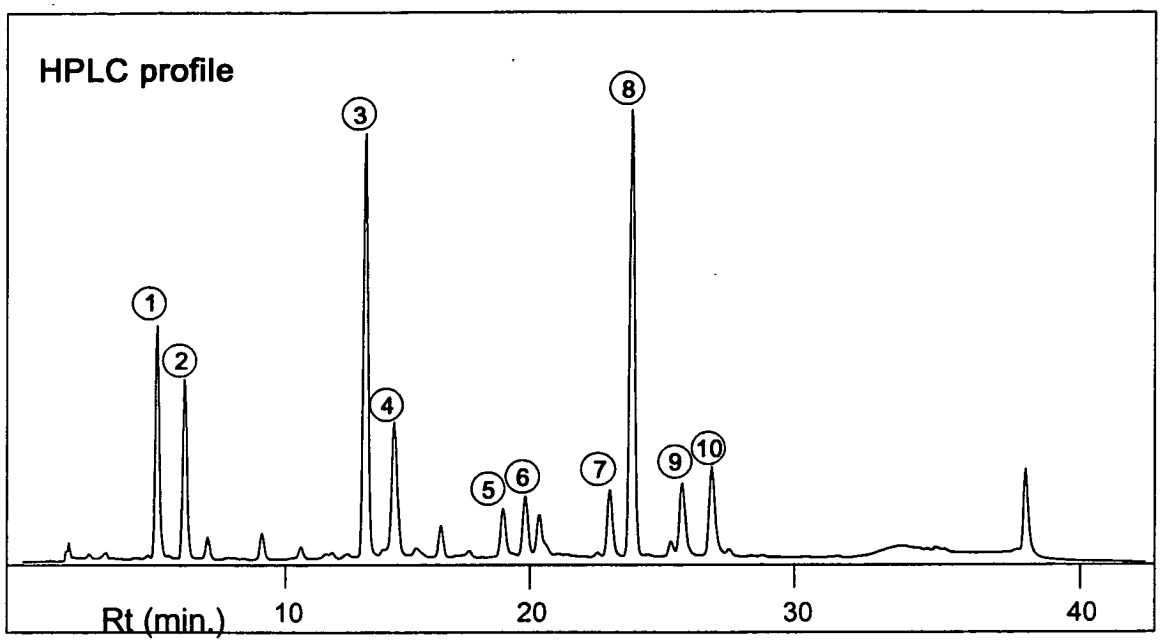
  The leaf exudate was investigated:

  - L. E. Newton 4082 (type locality)
  - NBI 5444



Aloe jucunda grows north of Ghor at Gaan Libah in Somalia North.

Aloe kedongensis Reynolds



Peak number	Retention time	Compound	Percentage
1	5.21	aloesin	10
2	6.27	7-*O*-methylaloesin	8
3	13.28	aloenin	21
4	14.41	unidentified chromone	8
5	18.56	unidentified anthrone 1	3
6	19.41	unidentified anthrone 2	3
7	22.66	unidentified compound 1	4
8	23.48	unidentified compound 2	23
9	25.41	nataloin B	5
10	26.55	nataloin A	6

The unidentified chromone probably relates to the coumaric acid containing group of chromones. The two unidentified anthrones display a UV absorbance spectrum identical to that of nataloin, while peak 7 and 8 both show UV spectra correlating to the unidentified compounds mentioned in *A. bussei* and *A mcloughlinii.*

- Taxonomic position:

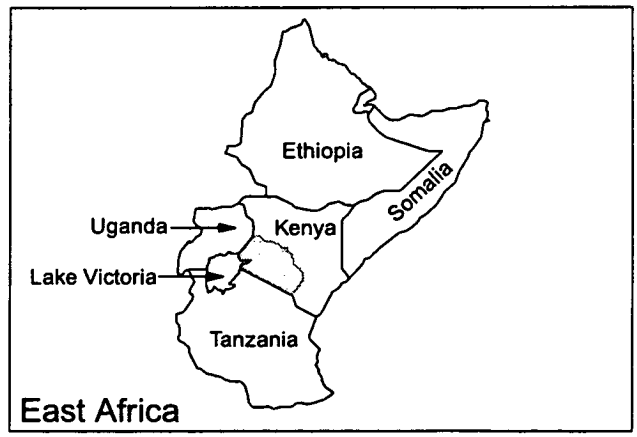
  Group 19 of the tropical aloes (Reynolds, 1966).

- Samples analysed:

  The leaf exudate was investigated:

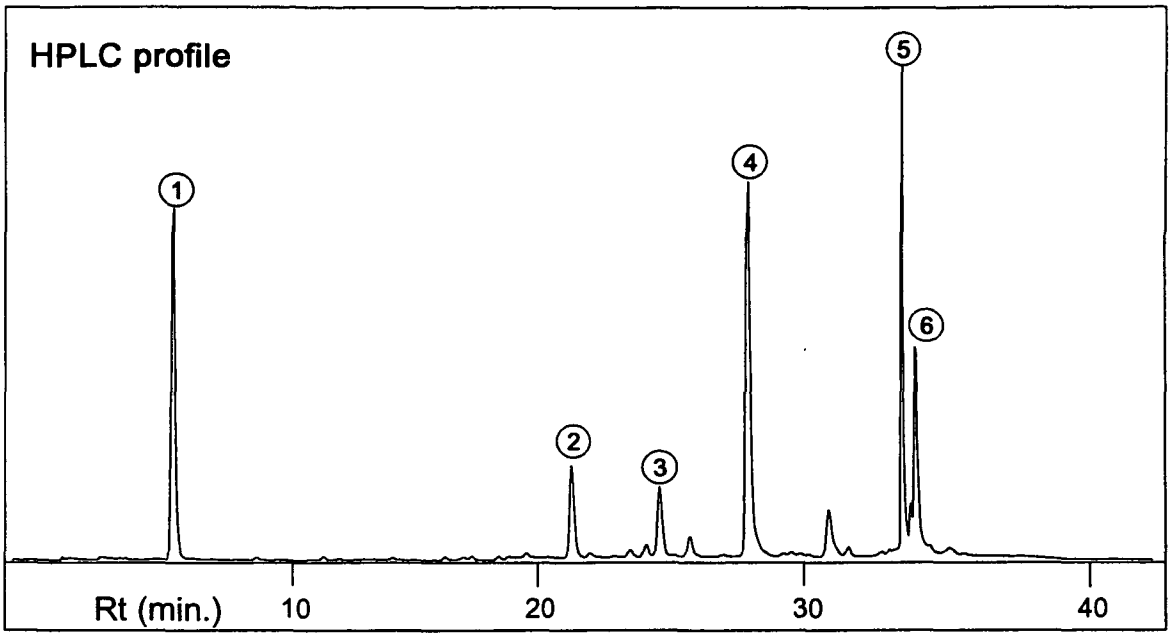
  - NBI 11210

Distribution



This species is found in open savannah woodland in the south western parts of Kenya.

Aloe khamiesensis Pillans



Peak number	Retention time	Compound	Percentage
1	5.99	aloesin	21
2	21.10	5-hydroxyaloin B	6
3	24.42	unidentified compound 1	5
4	27.71	microstigmin	28
5	33.56	unidentified compound 2	18
6	34.07	unidentified chromone	15

Judging by the UV absorbance characteristics, the unidentified compounds (peak 3 & 5) are probably anthrone derivatives, while the unidentified chromone (peak 6) probably relates to the cinnamoyl range of chromones.

- Taxonomic position:

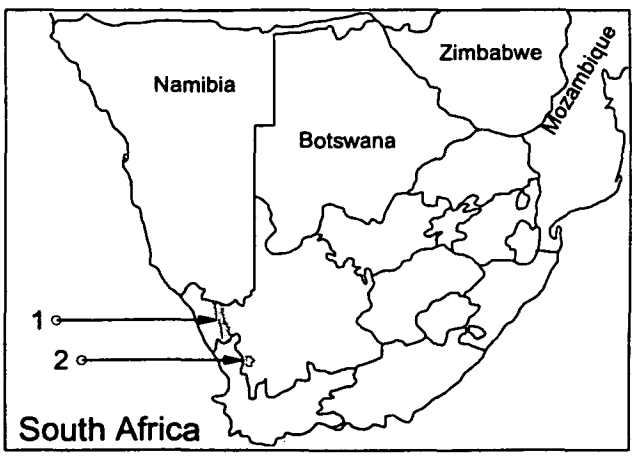
Aloe series *Purpurascentes* (Reynolds, 1950).

- Samples analysed:

The leaf exudate was investigated:

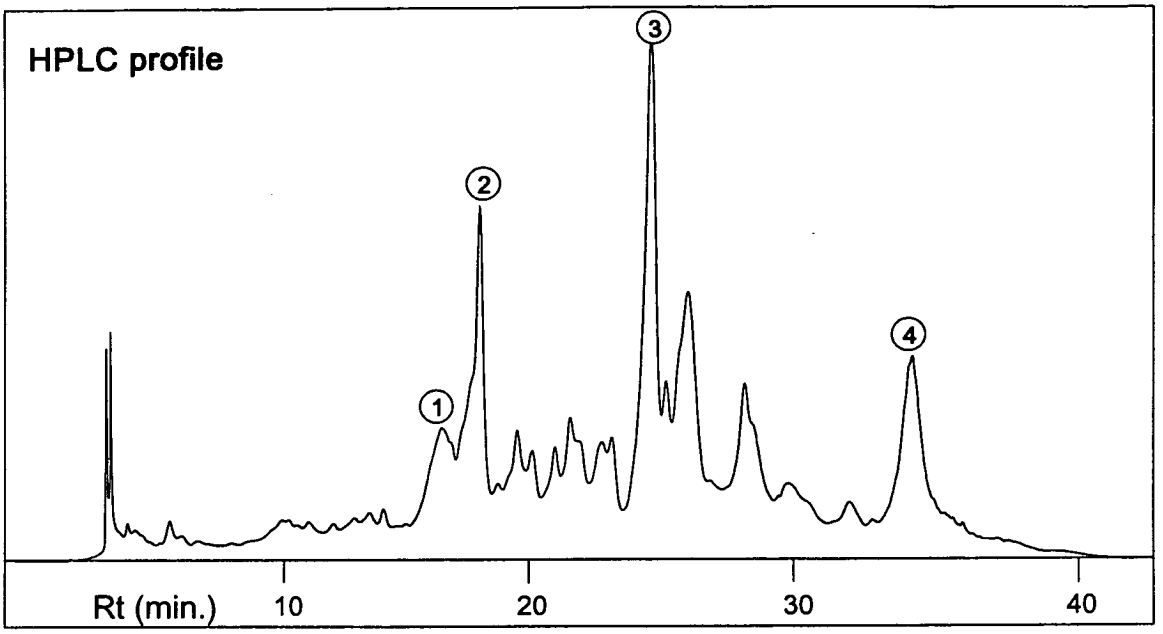
- Skuinshoogte
- ex hort JBG

Distribution



With a preference for a mountainous terrain, this species is found in parts of Namaqualand (1) and in the Calvinia district (2).

Aloe kniphofioides Baker



Peak number	Retention time	Compound	Percentage
1	16.5	unidentified flavone 1	7
2	17.9	unidentified flavone 2	12
3	24.5	unidentified flavone 3	18
4	36.0	unidentified flavone 4	14

Aloe kniphofioides follows the general pattern of the grass-like aloes, it contains various flavones.

- Taxonomic position:

  Aloe section *Leptoaloe* (Reynolds, 1950).

- Samples analysed:

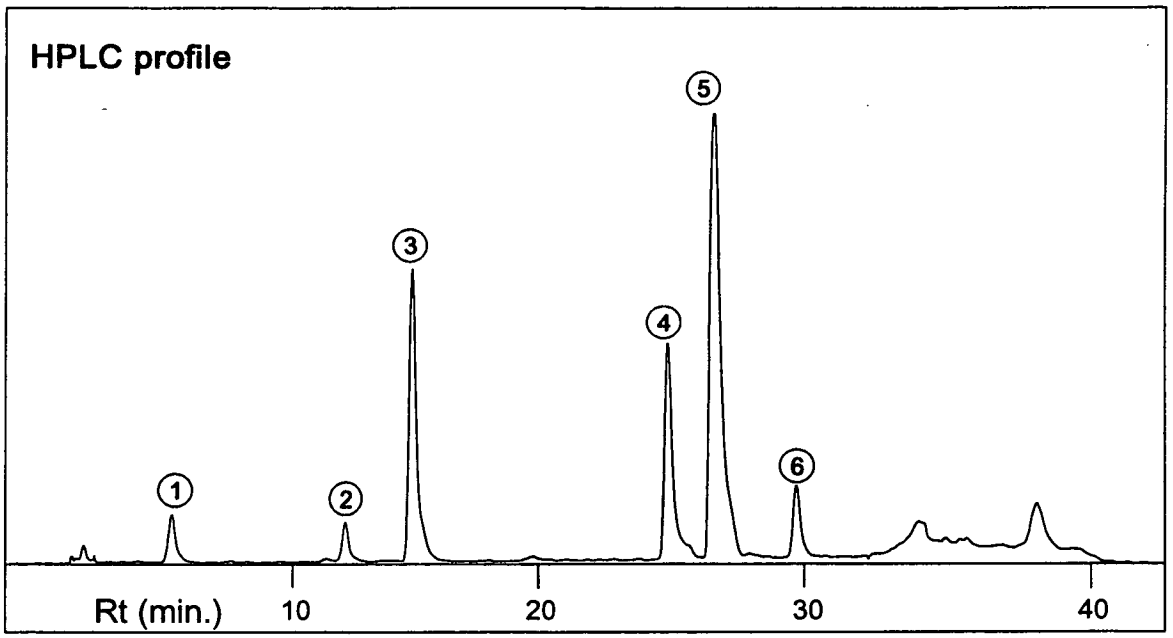
  The leaf extract was investigated:

  - ex hort Craib (collected near Piet Retief)

Distribution

This species has a disjunct distribution, occurring in the southern parts of KwaZulu-Natal (1) and in the Piet Retief and Barberton areas (2) in the north.

Aloe krapohliana Pole-Evans



Peak number	Retention time	Compound	Percentage
1	6.02	aloesin	3
2	12.52	homonataloside B	2
3	15.04	aloeresin A	18
4	24.65	homonataloin B	15
5	26.37	homonataloin A	40
6	29.47	unidentified chromone	5

This HPLC profile is almost identical to that recorded for species pertaining to *Aloe* series *Latebracteatae*. (see *A. cryptopoda* and *A. lutescens*).

- Taxonomic position:

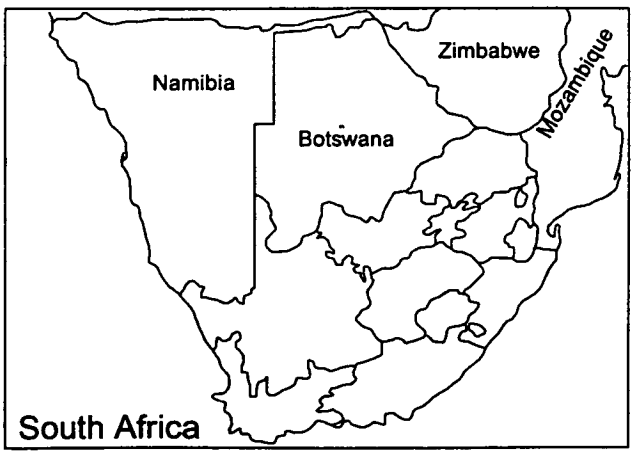
  Aloe series *Echinatae* (Reynolds, 1950).

- Samples analysed:

  The leaf exudate was investigated:

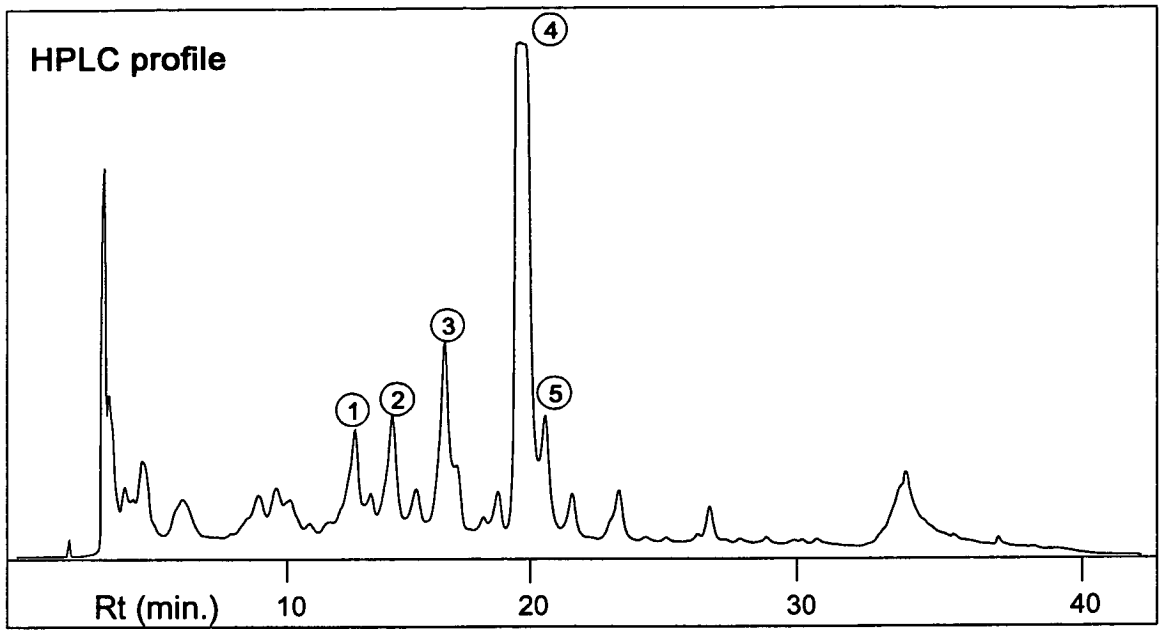
  - ex hort JBG
  - ex hort NBI

Distribution



Aloe krapohliana, with a preference for arid environemnts is restricted to the north-western Cape and extends into Namibia.

Aloe krausii Baker



Peak number	Retention time	Compound	Percentage
1	13.0	unidentified flavone 1	6
2	14.5	unidentified flavone 2	6
3	16.5	unidentified flavone 3	9
4	19.4	isovitexin	34
5	20.4	unidentified flavone 4	5

Various flavone-like compounds are present in the leaf extract of this species with the flavone, isovitexin being the major compound.

- Taxonomic position:

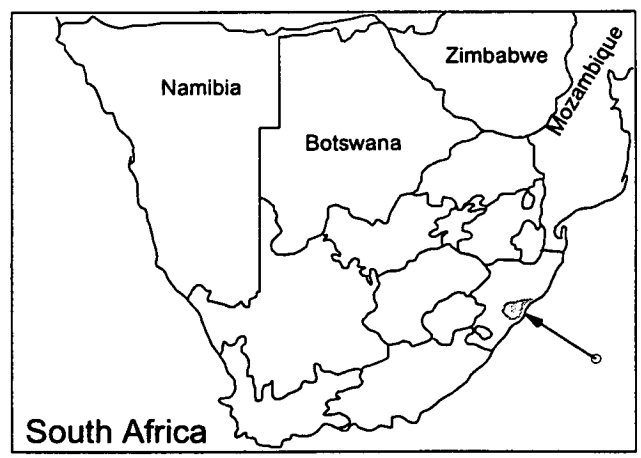
  Aloe section *Leptoaloe* (Reynolds, 1950).

- Samples analysed:

  The leaf extract was investigated:

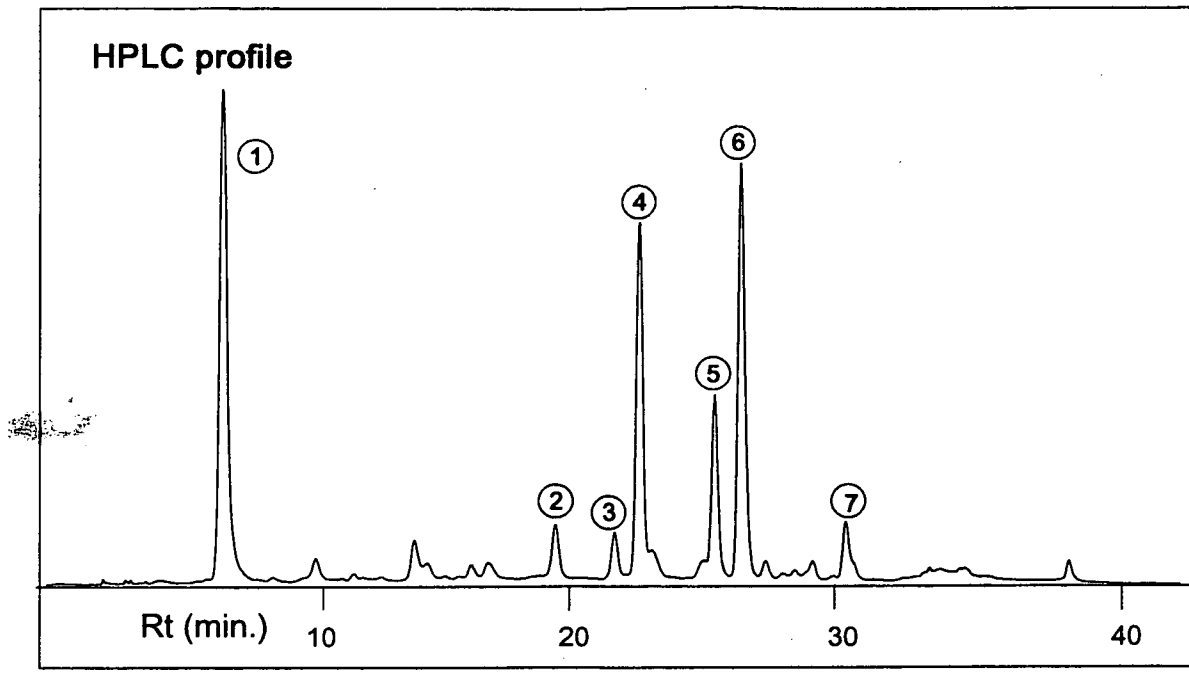
  - ex hort C. Craib (collected near Mooi River Falls)
  - NBI 29453

Distribution



Aloe krausii is restricted to the central grasslands of KwaZulu-Natal.

Aloe kulalensis L.E. Newton & Beentjie



Peak number	Retention time	Compound	Percentage
1	6.65	aloesin	29
2	19.31	unidentified chromone 1	3
3	21.54	unidentified chromone 2	2
4	22.49	aloeresin D	18
5	25.35	aloin B	9
6	26.34	aloin A	21
7	30.38	unidentified chromone 3	3

The unidentified chromones (2 & 3), show the same UV absorbance pattern and are identical to that of all the other coumaroyl chromones.

- Taxonomic position:

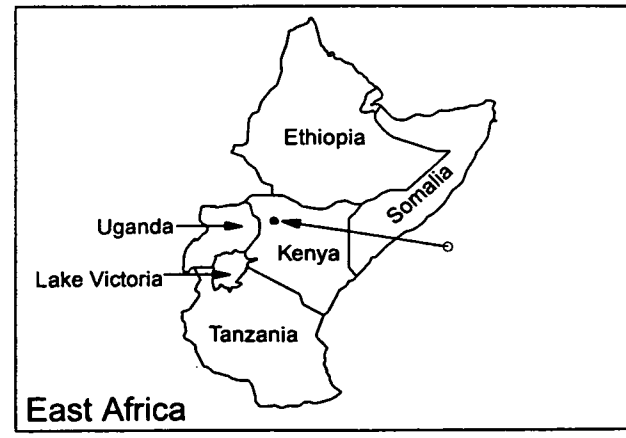
  Allied to *A. confusa* (Newton & Beentjie, 1990).

- Samples analysed:

  The leaf extract was investigated:

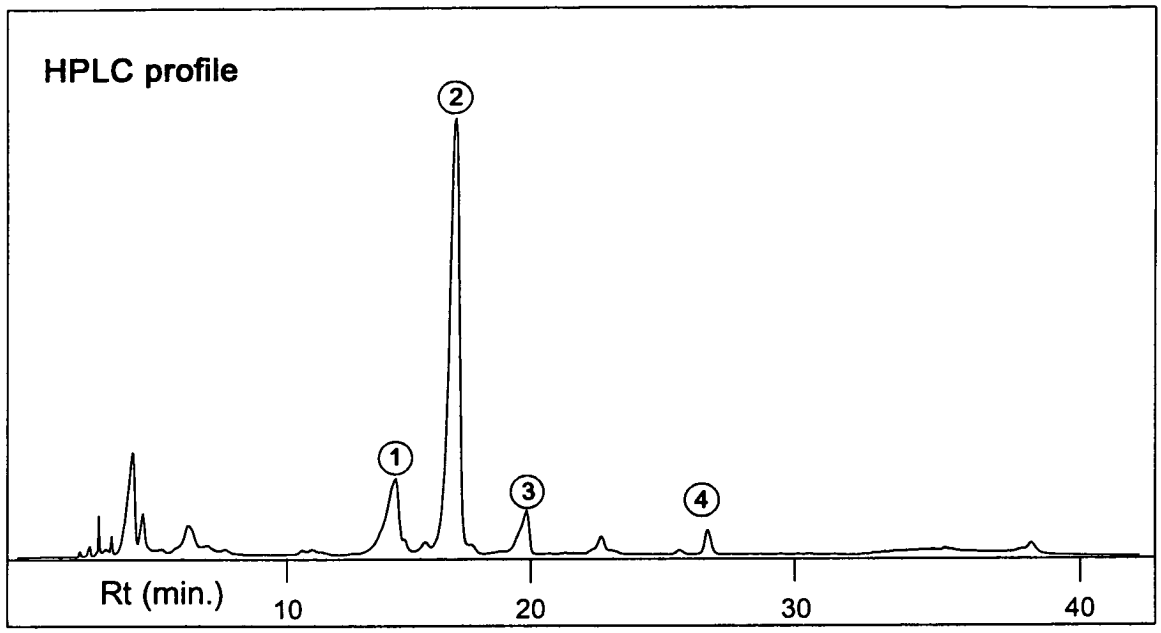
  - L. E. Newton 3219 (type plant)

Distribution



This species is only known from the slopes of Mount Kulal in the Marsabit District of Kenya.

Aloe labworana (Reynolds) S. Carter



Peak number	Retention time	Compound	Percentage
1	14.66	unidentified compound 1	14
2	16.99	plicataloside	58
3	19.66	unidentified compound 2	5
4	26.50	aloin A and B	tr

This is the only plicataloside-containing species to have trace amounts of aloin. No class of compound could be ascribed to peak 1.

- Taxonomic position:

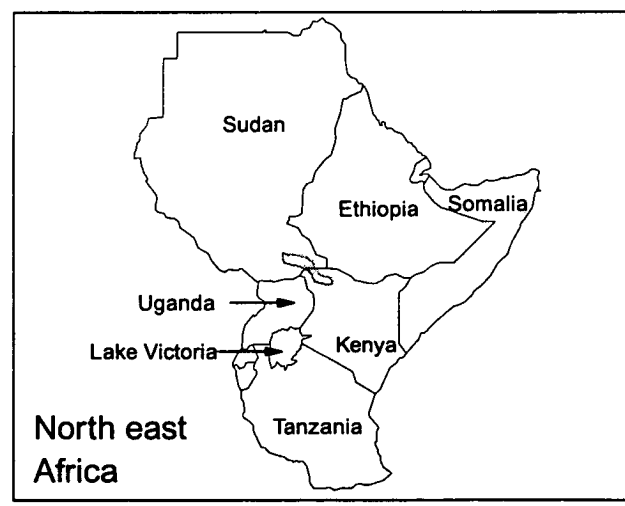
  Group 5 of the tropical aloes (Reynolds, 1966).

- Samples analysed:

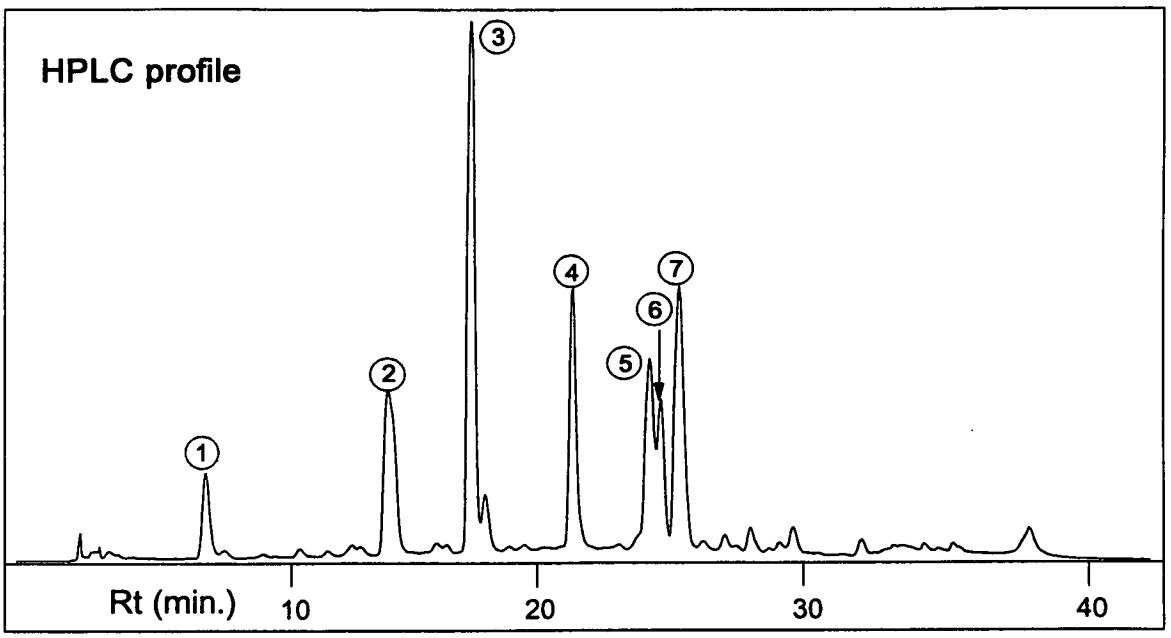
  The leaf extract and exudate was investigated:

  - NBI 17305
  - RBG, Kew 295-58-29212

Distribution



This species inhabits the Labwor Hills in Uganda from where it extends northwards to the Imatong Mts. in southern Sudan.



Peak number	Retention time	Compound	Percentage
1	7.11	aloesin	4
2	14.08	aloenin	12
3	17.24	unidentified compound 1	25
4	21.12	aloeresin D	12
5	24.05	aloin B	11
6	24.46	unidentified compund 2	7
7	25.13	aloin A	16

This profile is very similar to that of *A. cheranganiensis*. The UV absorbance of the two unidentified compounds are identical, yet they could not be ascribed to any group of compounds.

(See *A. cheranganiensis* and *A. leptosiphon*)

- Taxonomic position:

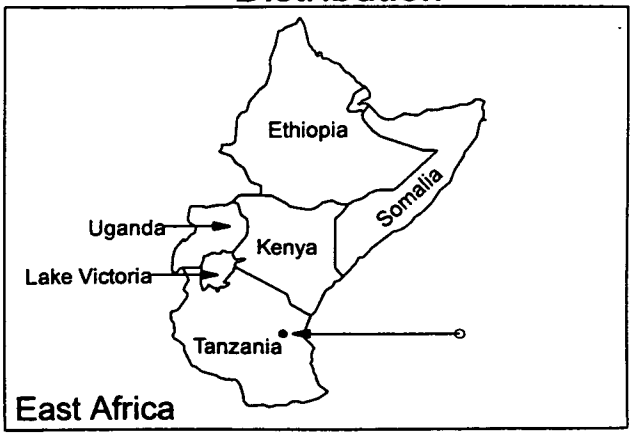
  Group 14 of the tropical aloes (Newton & Beentjie, 1990).

- Samples analysed:

  The leaf extract was investigated:

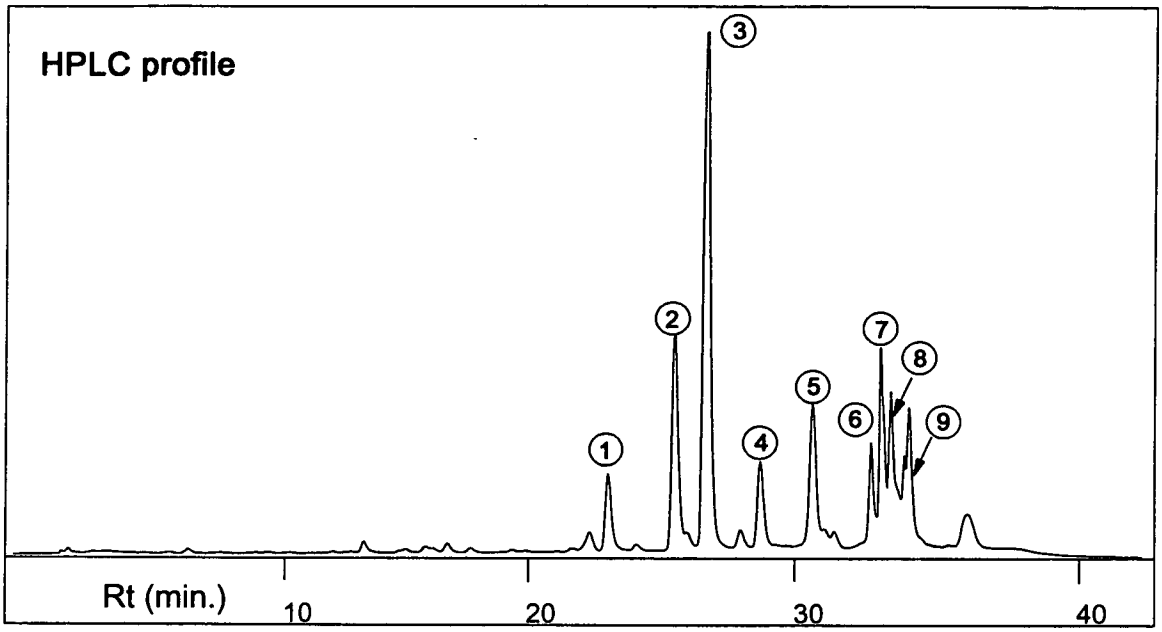
  - RBG, Kew 1990-1820

Distribution



Aloe leachii occurs in the Morogoro and Rufiji Districts of Tanzania.

Aloe lensayuensis Lavranos & L.E. Newton



Peak number	Retention time	Compound	Percentage
1	22.85	unidentified compound	1
2	25.37	aloin B	12
3	26.53	aloin A	32
4	28.60	aloinoside B	5
5	30.56	aloinoside A	8
6	32.81	microdontin B	5
7	33.15	microdontin A	7
8	33.57	unidentified anthrone 1	8
9	34.23	unidentified anthrone 2	7

The unidentified compound displays a UV spectrum correlating to that of dihydroisocoumaringlucoside. The unidentified anthrones display the same UV absorbance spectra as the microdontins.

- Taxonomic position:

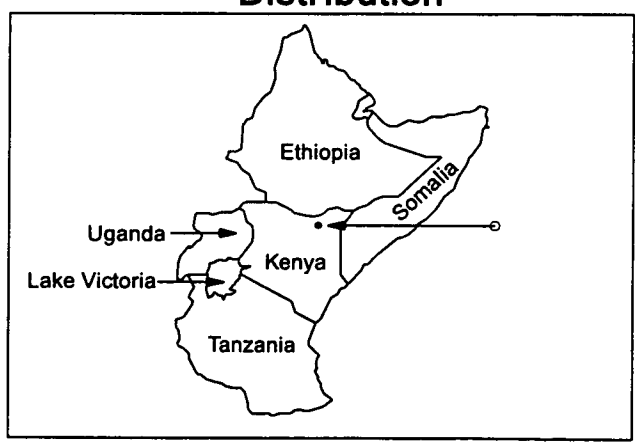
  Allied to *A. microdonta* (Lavranos & Newton, 1976).

- Samples analysed:

  The leaf exudate was investigated:

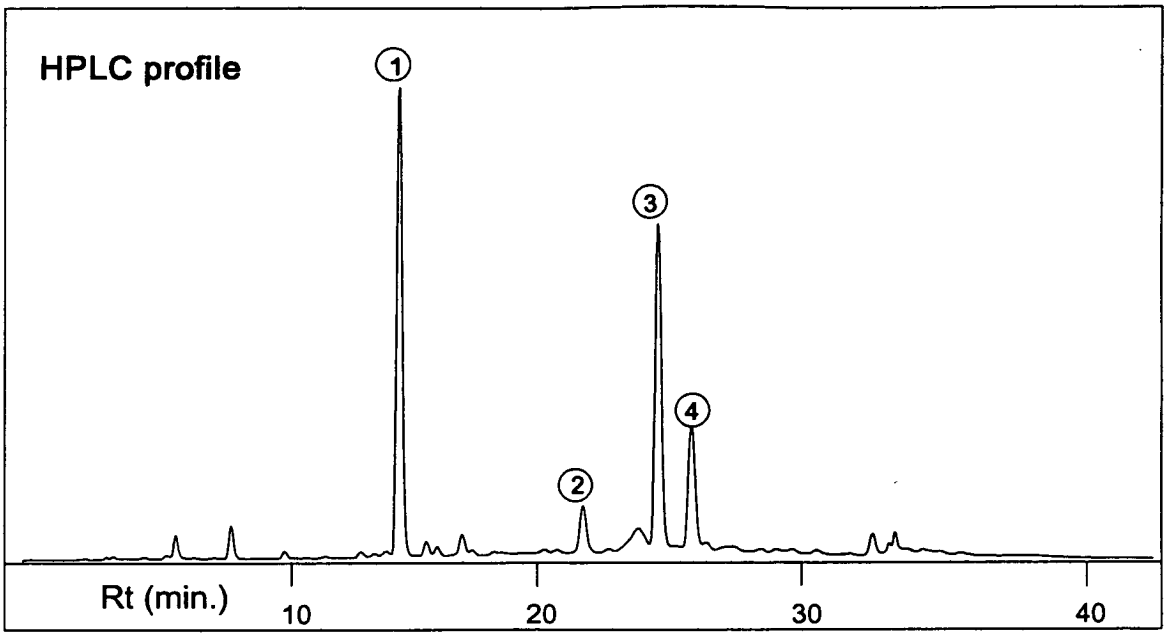
  - L. E. Newton 5571 (type locality)
  - RBG, Kew 242 63 24204

Distribution



This species in found near Buna at Lensayu Rocks in the northern Province of Kenya.

Aloe leptosiphon A. Berger



Peak number	Retention time	Compound	Percentage
1	14.28	aloenin	41
2	21.28	unidentified compound 1	5
3	24.18	aloin B and an unidentified compound 2	31
4	25.46	aloin A	12

The profile is very similar to that of *A. bussei* and *A. secudiflora* which is characterised by the presence of aloin and a compound co-eluting with aloin B. The unidentified compound (peak 2) could possibly be the same compound reported as unidentified in the two species mentioned above.

(See *A. bussei* and *A. secundiflora*)

- Taxonomic position:

  Group 5 of the tropical aloes (Reynolds, 1966).

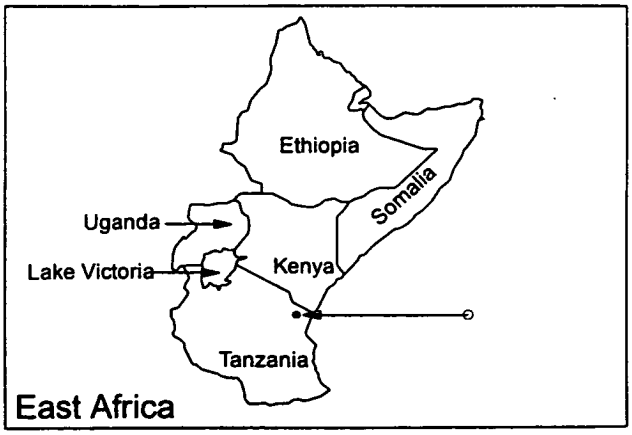
  Syn. *A. greenwayi* (Carter, 1994).

- Samples analysed:

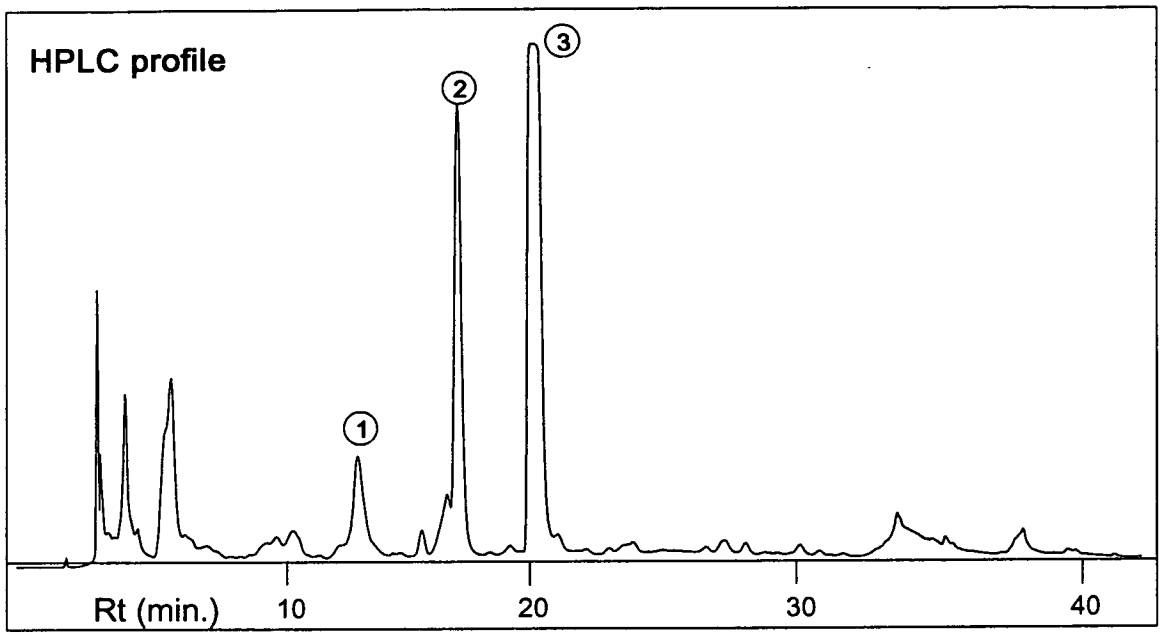
  The leaf extract was investigated:

  - RBG, Kew 1990-1812

Distribution



Aloe leptosiphon is distributed in the Tanga Province in Tanzania.



Peak number	Retention time	Compound	Percentage
1	13.2	unidentified flavone 1	7
2	17.0	unidentified flavone 2	19
3	19.8	isovitexin	34

The flavone, isovitexin in the major compound in the leaves of *A. linearifolia*.

- Taxonomic position:

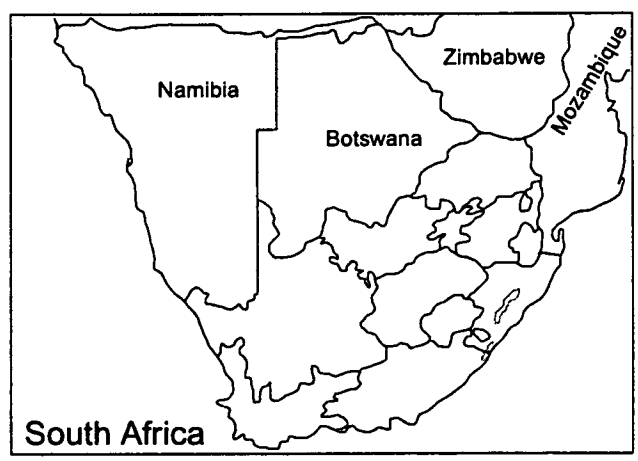
Aloe section *Leptoaloe* (Reynolds, 1950).

- Samples analysed:

The leaf extracts were investigated:

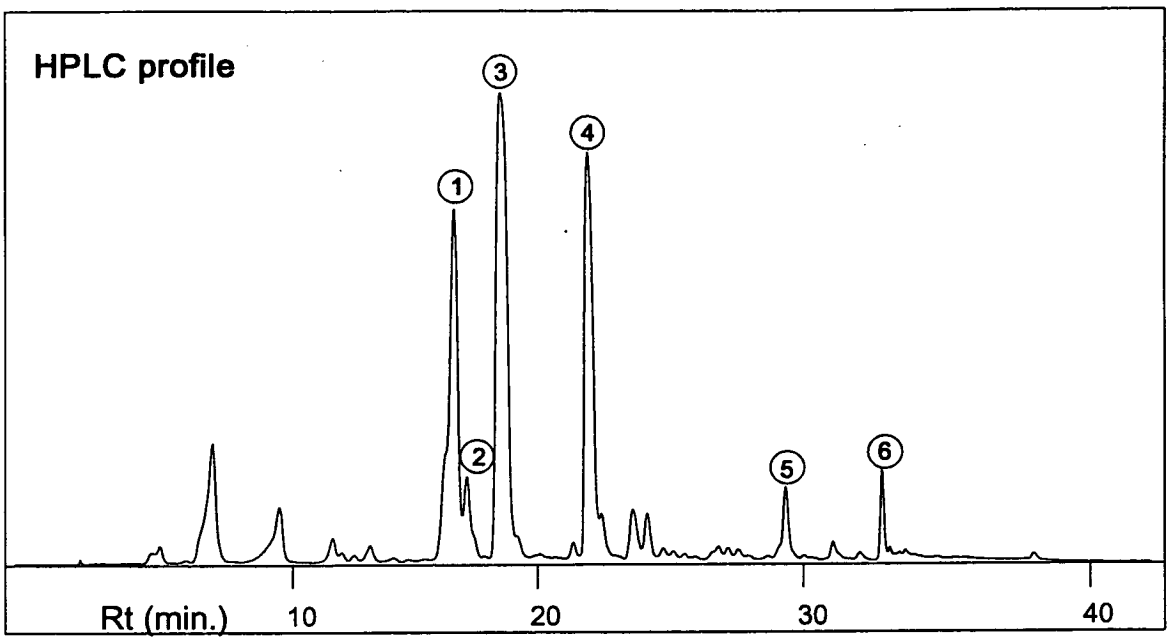
- ex hort C. Craib (collected near Margate)
- ex hort C. Craib (collected near Oribi Gorge)

Distribution



A more robust form is found near Bababango in northern KwaZula-Natal, while the 'typical' form grows along the coastal areas of south KwaZulu-Natal and extends to Lusikisiki in the Eastern Cape.

Aloe lineata (Aiton) Haworth



Peak number	Retention time	Compound	Percentage
1	16.63	unidentified flavonoid 1	19
2	17.11	unidentified flavonoid 2	4
3	18.37	unidentified flavonoid 3	30
4	21.68	unidentified flavonoid 4	20
5	29.19	unidentified flavonoid 5	3
6	32.86	unidentified flavonoid 6	2

This species is one of few species of *Aloe* which contain flavonoids in the leaf exudate rather than the characteristic chromones and anthrones.

(See *A. glauca* and *A. humilis*)

- Taxonomic position:

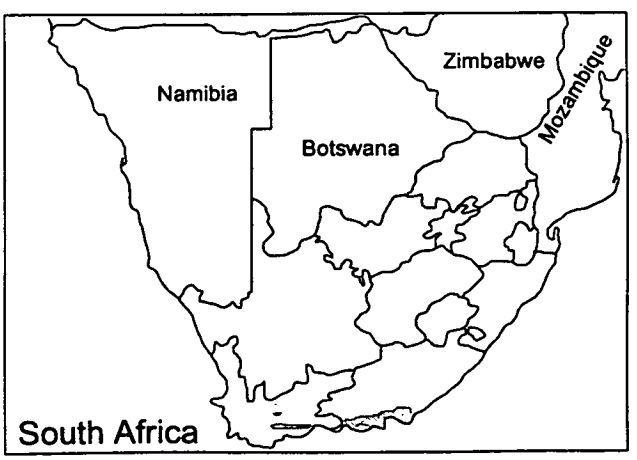
  Aloe series *Rhodacanthae* (Reynolds, 1950).

- Samples analysed:

  The leaf exudate was investigated:

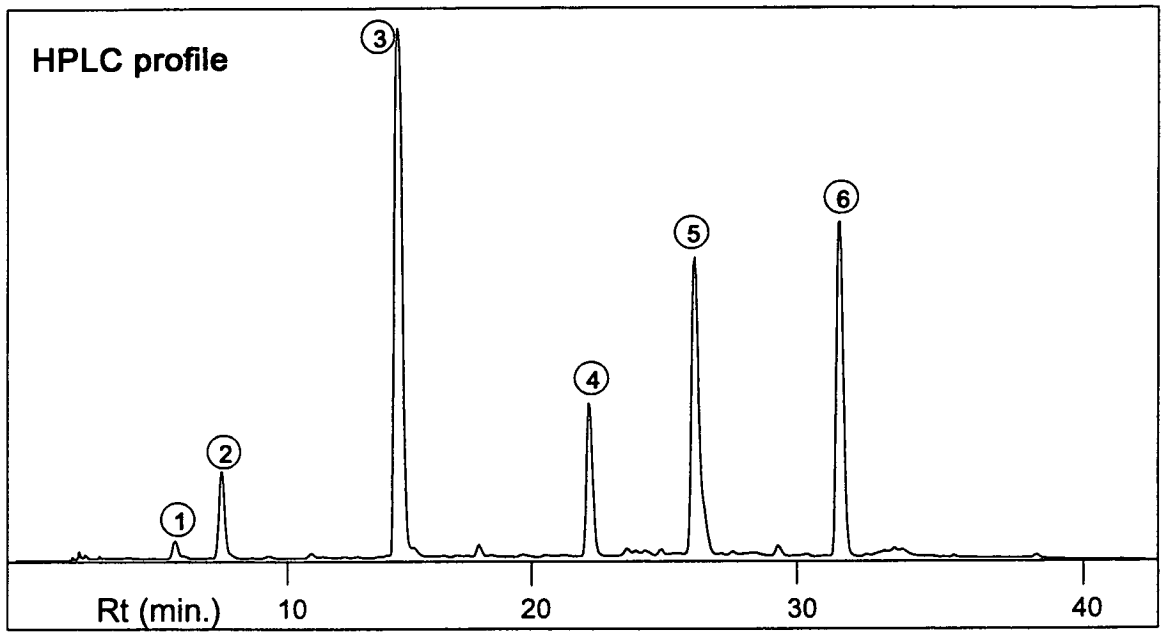
  - Tipper's Creek
  - Annsvilla
  - Vaalkranz

Distribution



This species is found between Riversdale in the west and Grahamstown in the east. It is especially common in the vicinity of Port Elizabeth.

Aloe littoralis Baker



Peak number	Retention time	Compound	Percentage
1	6.3	aloesin	1
2	8.1	7-O-methylaloesin	5
3	14.9	10-hydroxyaloin B	30
4	22.3	10-hydroxyaloin-6'-mono-acetate B	10
5	26.2	deacetyllittoraloin	23
6	31.6	littoraloin	25

Aloe littoralis is the species from which the novel compounds (peaks 3,5 and 6) have been isolated and characterised.

- Taxonomic position:

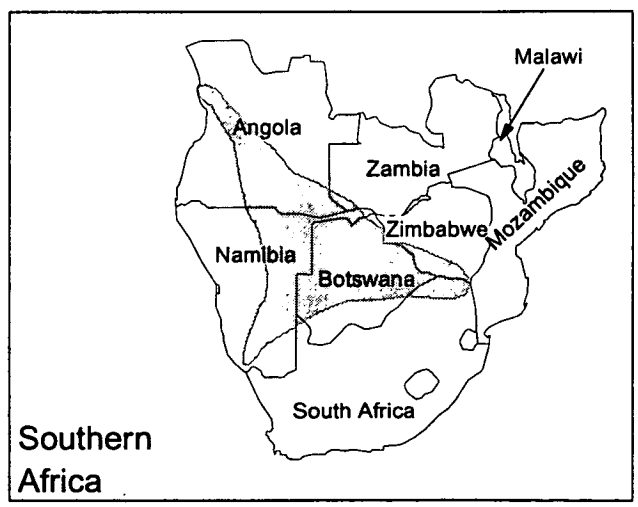
  Aloe series *Percrassae* (Reynolds, 1950).

- Samples analysed:

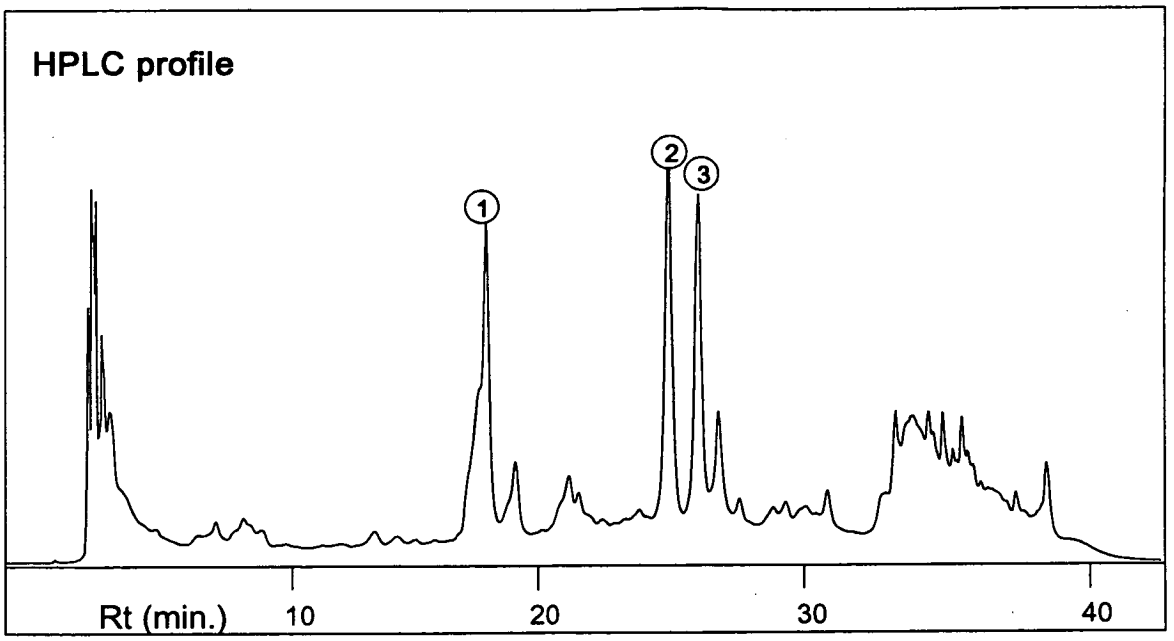
  The leaf exudate was investigated:

  - NBI (Etosha)
  - material collected at Vivo
  - NBI (Windhoek)

Distribution



Aloe littoralis is extensively distributed through southern Africa occurring in Angola, Namibia, Botswana, Mozambique and the most northern parts of South Africa.



Peak number	Retention time	Compound	Percentage
1	17.94	unidentified flavone	17
2	24.70	aloin B	12
3	25.96	aloin A	12

A. lomatophylloides displays the same chromatographic profile as all the other 'berried aloes' i.e. a combination of the anthrones aloin A and B with the characteristic flavone (most probably isovitexin).

- Taxonomic position:

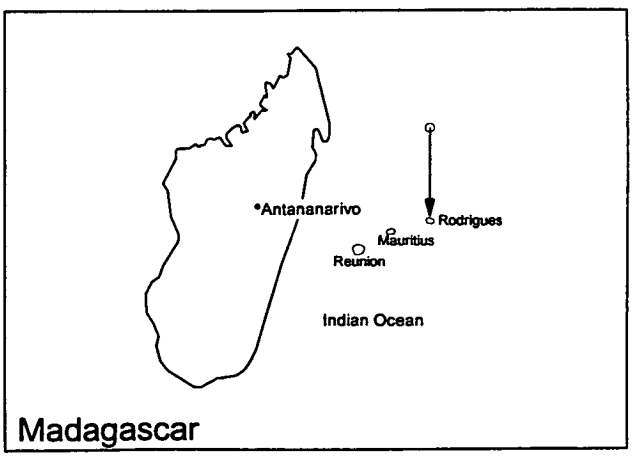
  Aloe section *Lomatophyllum* (Rowley, 1996).

- Samples analysed:

  The leaf exudate was investigated:

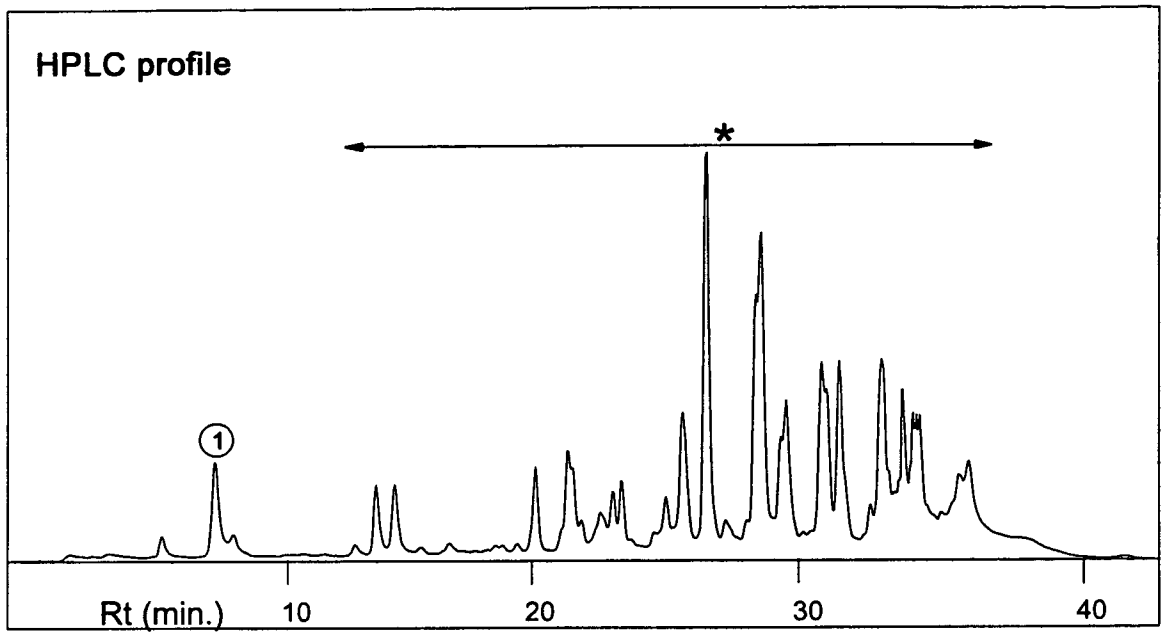
  - ex hort NBI

Distribution



Aloe lomatophylloides is restricted to the island of Rodrigues east of Madagascar.

Aloe longistyla Baker



Peak number	Retention time	Compound	Percentage
1	8.23	unidentified chromone	7

Concentration of leaf phenolics are very low. The UV spectra of the series of peaks denoted by * display a similar UV absorbance spectra to that of 5-hydroxyaloin. A similar pattern was found in *A. brevifolia*.

- Taxonomic position:

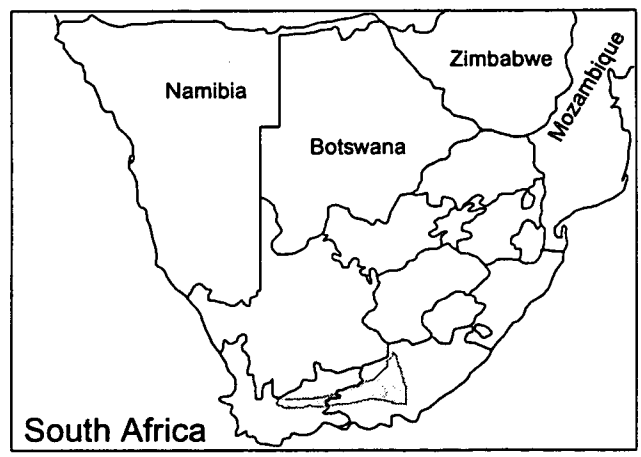
  Aloe series *Longistylae* (Reynolds, 1950).

- Samples analysed:

  The leaf exudate was investigated:

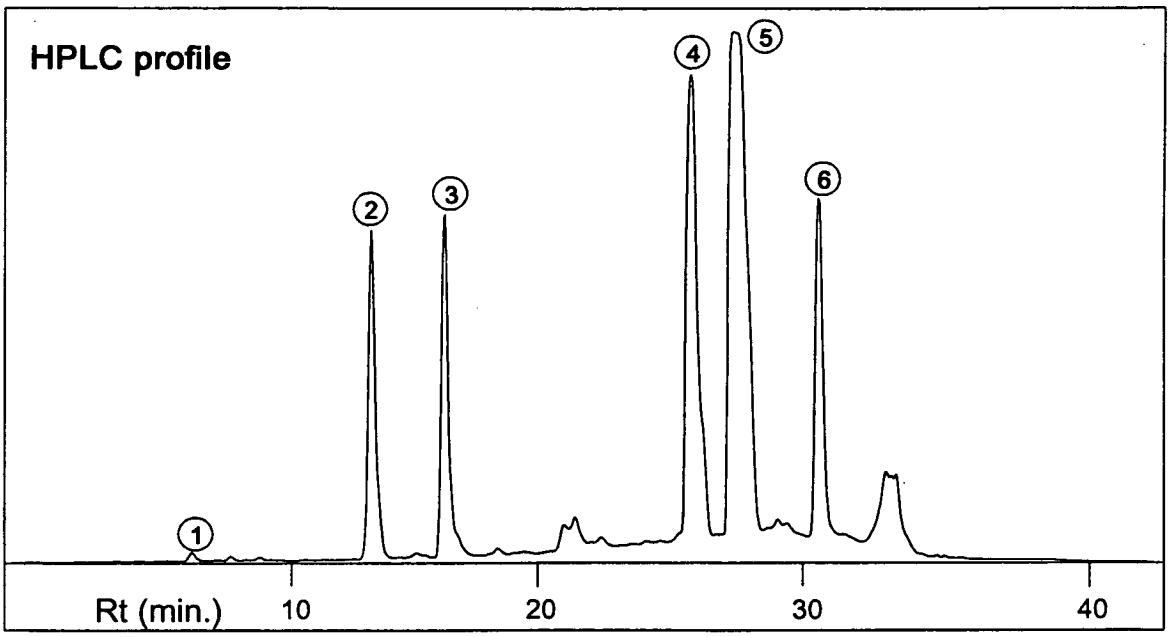
  - Calitzdorp
  - JBG 85-55-51

Distribution



With a preference for arid conditions this species is widely distributed in the Karoo. It is abundant near Calitzdorp, Graaff-Reinet, Cradock and Middelburg.

Aloe lutescens Groenewald



Peak number	Retention time	Compound	Percentage
1	6.68	aloesin	1
2	13.51	homonataloside B	9
3	16.28	3'-*O*-coumaroylaloesin	10
4	25.63	homonataloin B	22
5	27.30	homonataloin A	33
6	30.52	3',6'-di-*O*-coumaroylaloesin	11

This combination of compounds is unique to species pertaining to *Aloe* series *Latebracteatae*. (see *A. cryptopoda* and *A. wickensii*). Compounds represented by peak 2, 3 and 6 were isolated and characterised from this species (Van Heerden *et al.*, 1997).

- Taxonomic position:

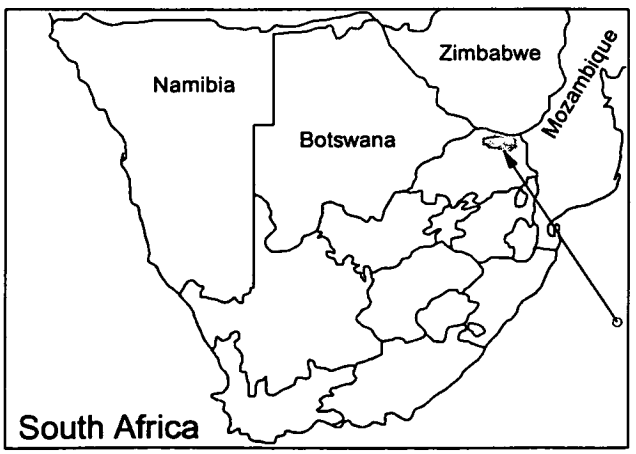
Aloe series *Latebracteatae* (Reynolds, 1950).

- Samples analysed:

The leaf exudate was investigated:

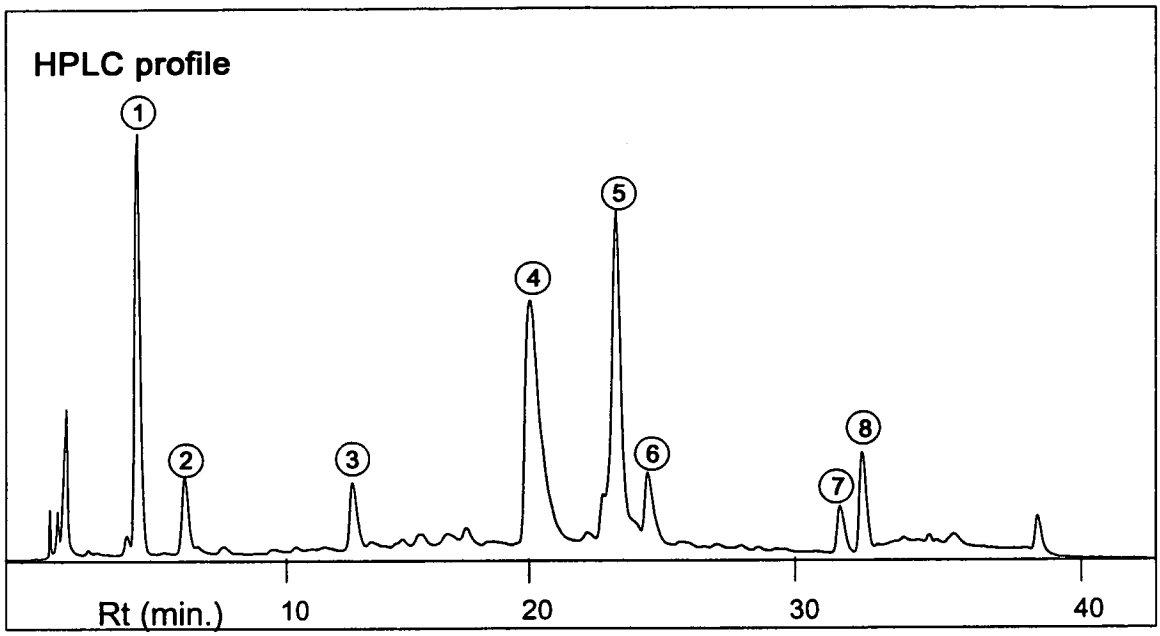
- JBG 85-5-332
- ex hort Nelspruit Botanical Garden
- Kingskloof

Distribution



Aloe lutescens is found in the vicinity of Messina and Chipese in the Northern Province of South Africa.

Aloe macroclada Baker



Peak number	Retention time	Compound	Percentage
1	4.95	aloesin	22
2	6.75	7-*O*-mehylaloesin	4
3	13.09	unidentified chromone 1	4
4	19.78	unidentified chromone 2	31
5	22.92	aloin B & unidentified compound	22
6	24.12	aloin A	5
7	31.31	unidentified anthrone 1	3
8	32.14	unidentified anthrone 2	6

The two unidentified anthrones show the same UV absorbance as aloin. Most anthrone-contianing Malagasy species have a series of aloin-like anthrones.

- Taxonomic position:

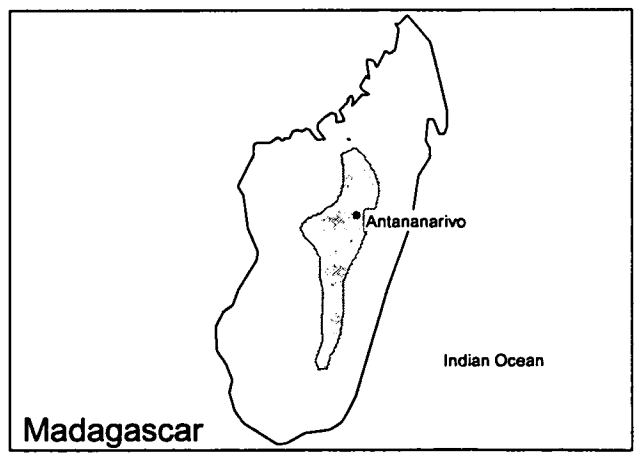
  Group 7 (Reynolds, 1966).

- Samples analysed:

  The leaf exudate was investigated:

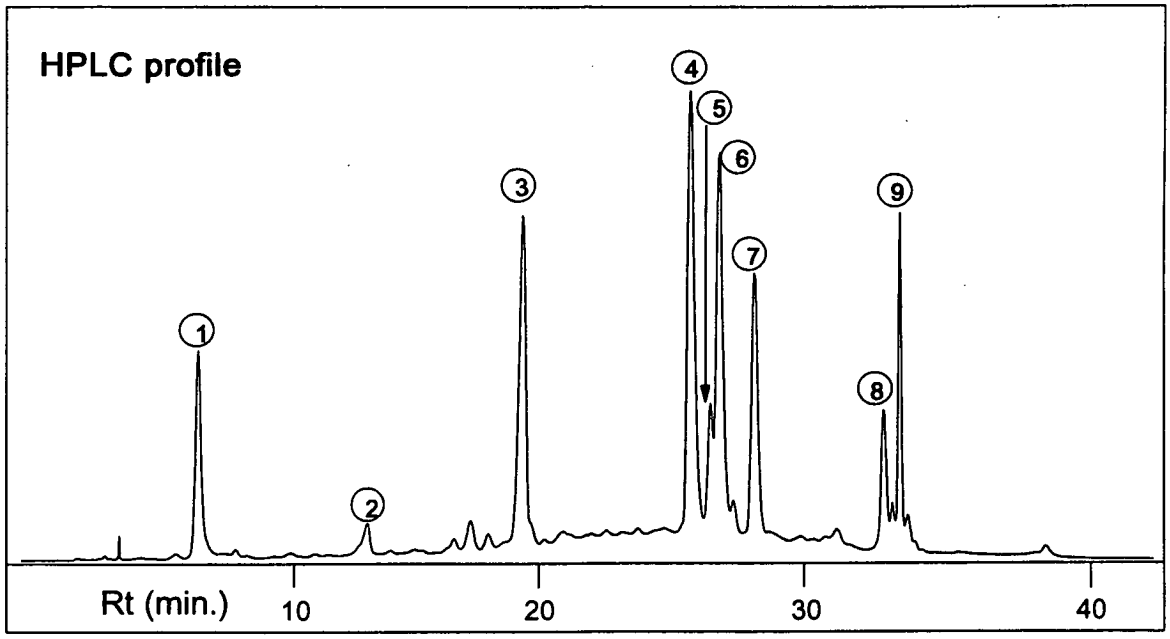
  - Lavranos *et al.* 30049

Distribution



Aloe macroclada is widely distributed throughout Madagascar. It extends from Antananarivo northwards to Tsaratanana and southwards to the Fort Dauphin area.

Aloe macrosiphon Baker



Peak number	Retention time	Compound	Percentage
1	6.63	aloesin	8
2	13.10	aloeresin C	2
3	19.06	unidentified chromone 1	16
4	25.39	aloin B	21
5	26.20	unidentified chromone 2	3
6	26.49	aloin A	19
7	27.87	unidentified chromone 3	11
8	32.88	unidentified chromone 4	5
9	33.60	unidentified chromone 5	8

Aloe macrosiphon is characterised by a series of unidentified chromones which all show the same UV absorbance spectra. These spectra correspond to the that of the coumaroyl chromones. The leaf exudate composition of *A. macrosiphon* and *A. compacta* were virtually identical.

- Taxonomic position:

  Group 11 of the tropical aloes (Reynolds, 1966).

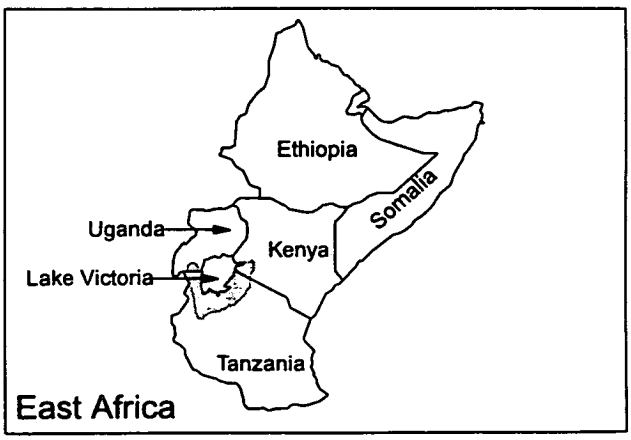
  Syn. *A. compacta* (Carter, 1994).

- Samples analysed:

  The leaf exudate was investigated:

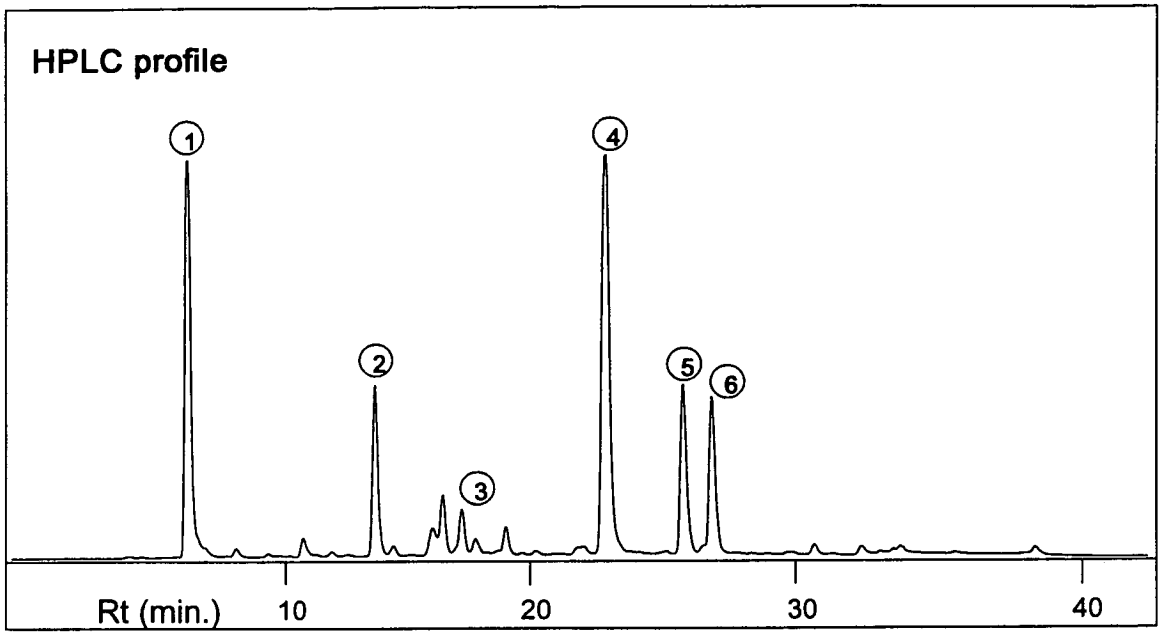
  - ex hort P. Favell (*A. macrosiphon*)
  - LEN 4250 (*A. macrosiphon*)
  - NBI 11157 (*A. compacta*)

Distribution



Aloe macrosiphon has a wide distribution in Uganda, Rwanda, Tanzania and Kenya.

Aloe marlothii A. Berger



Peak number	Retention time	Compound	Percentage
1	6.70	aloesin	24
2	13.91	aloeresin C	10
3	16.10	aloeresin A	2
4	22.62	aloeresin D	31
5	25.57	aloin B	11
6	26.33	aloin A	10

Aloe marlothii is one of the most chemically variable species of *Aloe*. For this reason 50 individuals in 28 population were sampled. The variation within and between populations were found to be extremely high with no geographical pattern. Most individuals contained the chromone content depicted above, but the occurrence of the anthrones homonataloin and aloin is erratic. (*Aloe spectabilis* shows the same pattern of variation and was considered to be conspecific with *A. marlothii*).

- Taxonomic position:

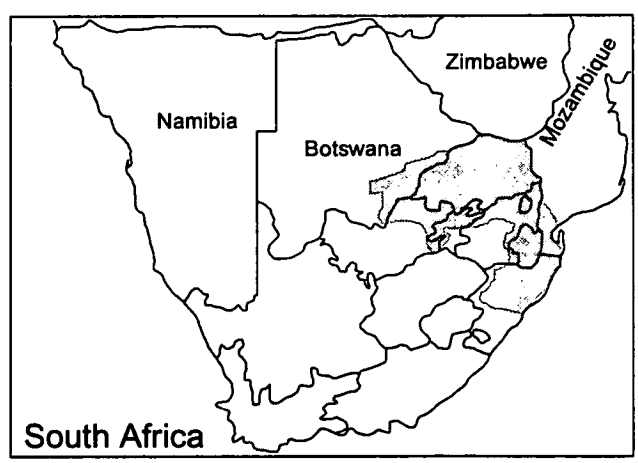
Aloe section *Pachydendron* (Reynolds, 1950).

- Samples analysed:

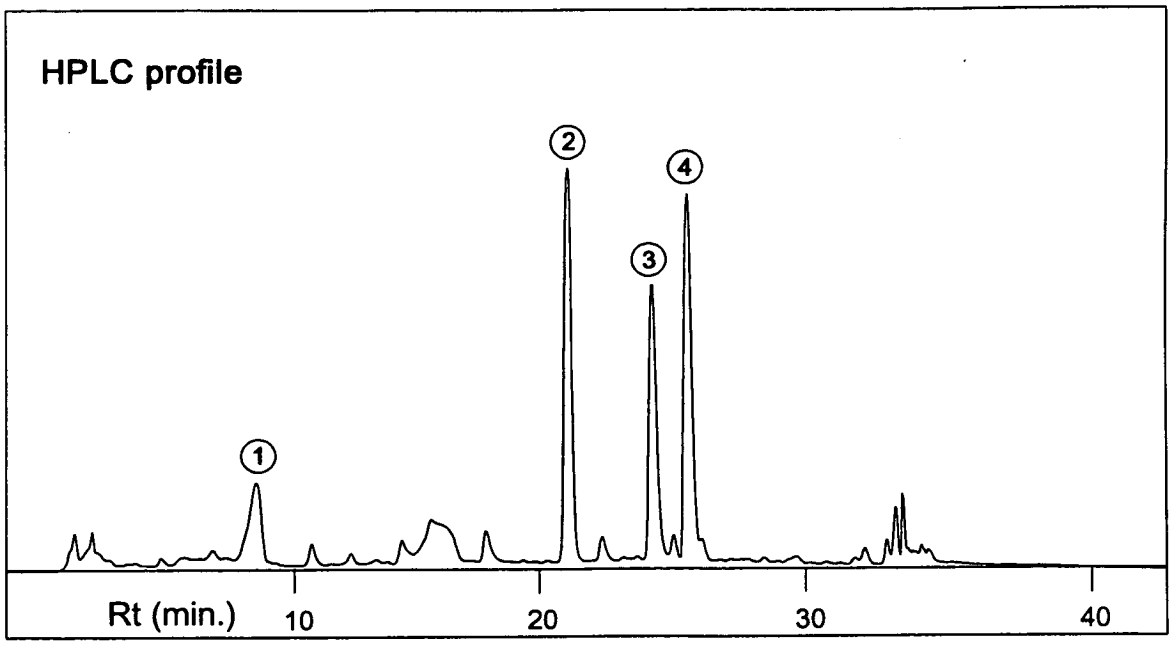
The leaf exudate was investigated:

- Vivo
- Potgietersrus
- De Loskop
- Witvlag
- Verwoerd Tunnels
- Boyne
- Kopermyn
- Chuniespoort
- Groblersdal
- Middelburg
- Zeerust
- Marico
- Klipriversberg
- Suikerbosrand
- Utrecht
- Goelela
- Pongola
- Nongoma
- Melmoth
- Dingaanstat
- Blood River
- Helpmekaar
- Dundee
- Muden
- Greyton
- Tugela Ferry
- Weenen
- Bergville

Distribution



This species is widely distributed throughout the north eastern parts of South Africa. It also occurs in the eastern parts of Botswana and in parts of Mozambique.



Peak number	Retention time	Compound	Percentage
1	9.14	unidentified compound	5
2	20.80	aloeresin D	27
3	23.95	aloin B	19
4	25.22	aloin A	26

Two samples of *A. massawana* were analysed. The LEN sample contained aloin and the chromone aloeresin D. The sample from Kew showed a complete different leaf exudate composition as it contained homonataloin and aloesin as major compounds. Personal communication with LEN confirmed the authenticity of his sample, while the origin of material at Kew could not be confirmed.

Distribution

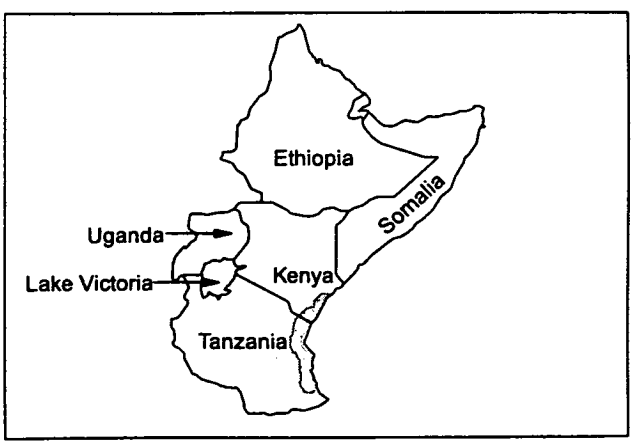
- Taxonomic position:

  Group 9 of the tropical aloes (Reynolds, 1966).

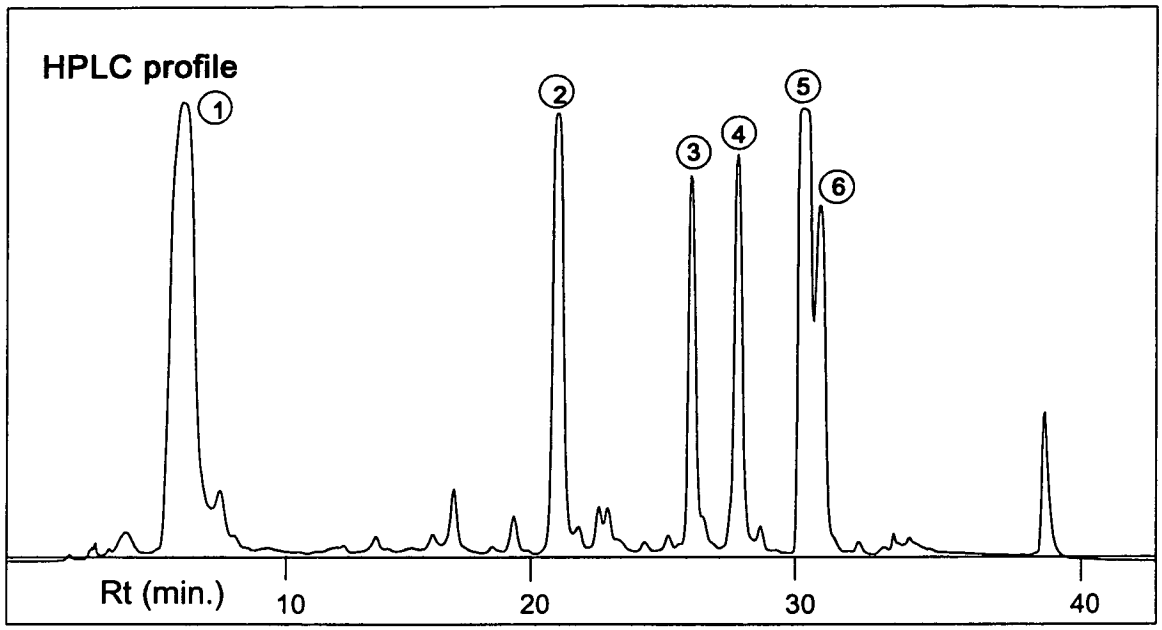
- Samples analysed:

  The leaf exudate was investigated:

  - L. E. Newton 4435
  - RBG, Kew 2287402104



This species has been reported along the coastal areas of Tanzania and Kenya. Unconfirmed reports on distribution include Eritrea and Mozambique.



Peak number	Retention time	Compound	Percentage
1	6.56	aloesin	30
2	20.71	unidentified chromone 1	13
3	25.73	homonataloin B	9
4	27.46	homonataloin A	9
5	29.93	unidentified chromone 1	16
6	30.52	unidentified chromone 2	10

The three unidentified chromones show an UV absorbance spectrum correlating to the cinnamoyl chromones isolated from *A. peglerae*. The retention time of peak 2 corresponds to that of aloeresin E, but as aloeresin E and F usually co-occur the identity of peak 2 has to be confirmed.

- Taxonomic position:

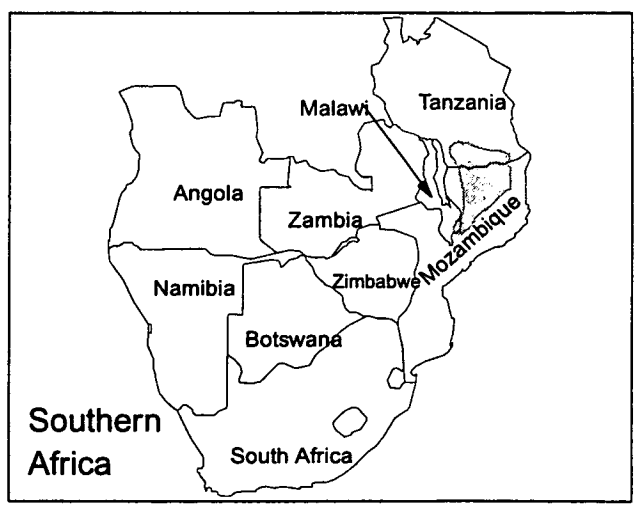
  Group 14 of the tropical aloes (Reynolds, 1966).

- Samples analysed:

  The leaf exudate was investigated:

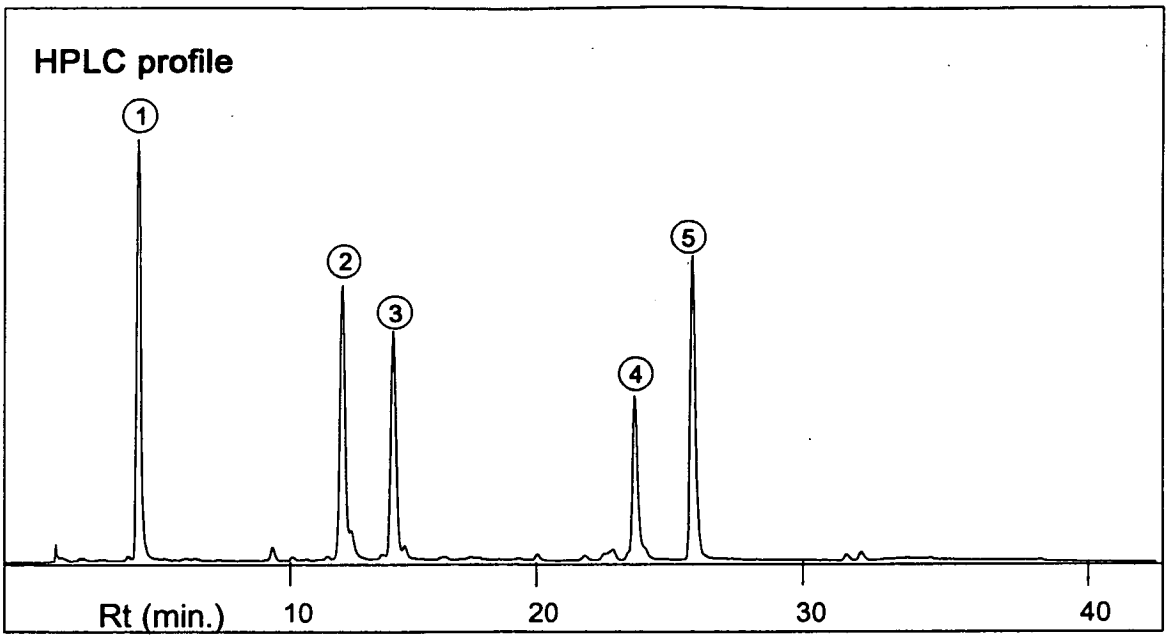
  - L.E. Newton 3836
  - NBI 31505I

Distribution



Aloe mawii is widely distributed in Tanzania, Malawi and Mozambique.

Aloe mayottensis A. Berger



Peak number	Retention time	Compound	Percentage
1	4.92	aloesin	24
2	12.58	unidentified chromone 1	19
3	14.48	unidentified chromone 2	15
4	23.56	homonataloin B	12
5	25.70	homonataloin A	22

The two unidentified chromones both show UV absorbance patterns characteristic of the coumaroyl chromones.

- Taxonomic position:

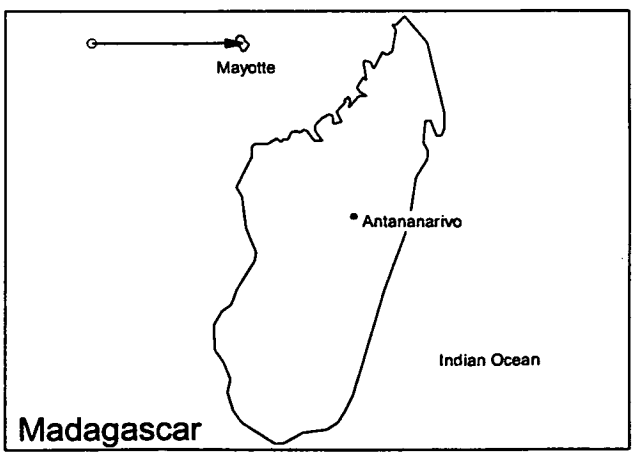
  Group *8* (Reynolds, 1966).

- Samples analysed:

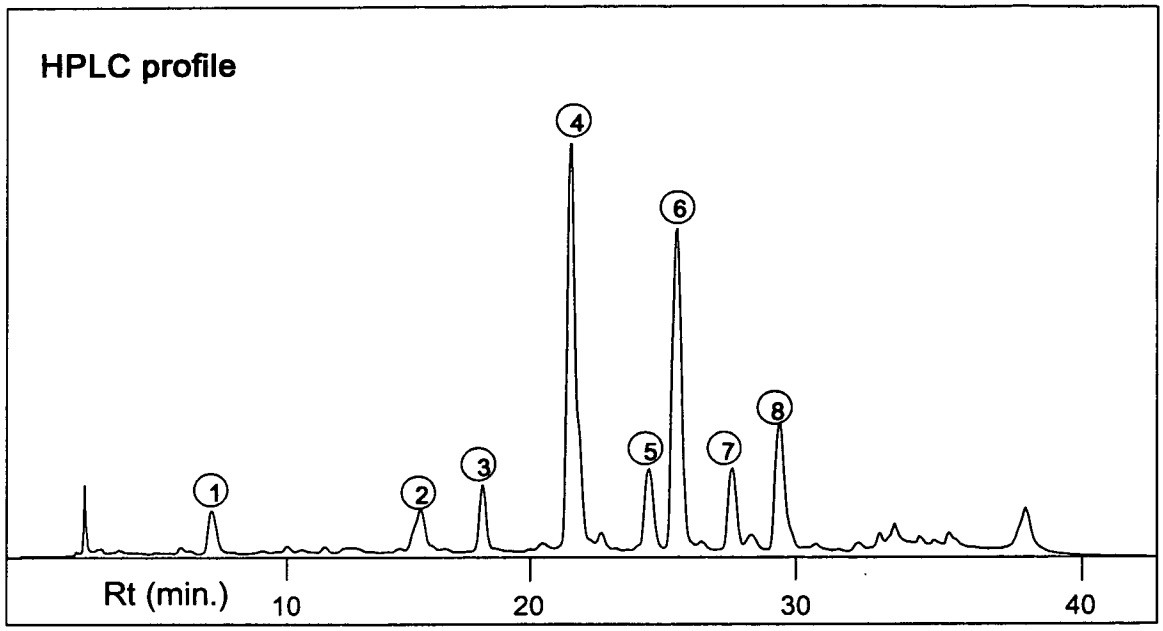
  The leaf exudate was investigated:

  - RBG, Kew 1976-451

Distribution



Aloe mayottensis is confined to Mayotte Island.



Peak number	Retention time	Compound	Percentage
1	7.33	aloesin	3
2	15.45	dihydroisocoumaringlucoside	4
3	17.84	unidentified chromone	4
4	21.15	aloeresin D	30
5	24.15	aloin B	6
6	25.20	aloin A	24
7	27.35	aloinoside B	6
8	29.15	aloinoside A	10

The chemical profile of this species is very similar to that reported for *A. aageodonta*. The microdontins may be present at level below the detection limits of the chromatograph.

- Taxonomic position:

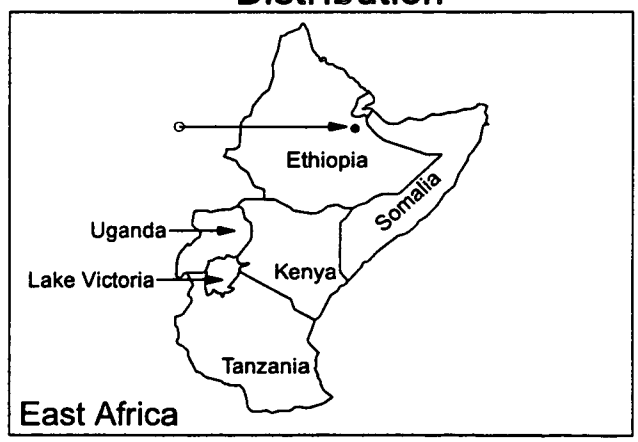
  Group 4 of the tropical aloes (Reynolds, 1966).

- Samples analysed:

  The leaf exudate was investigated:

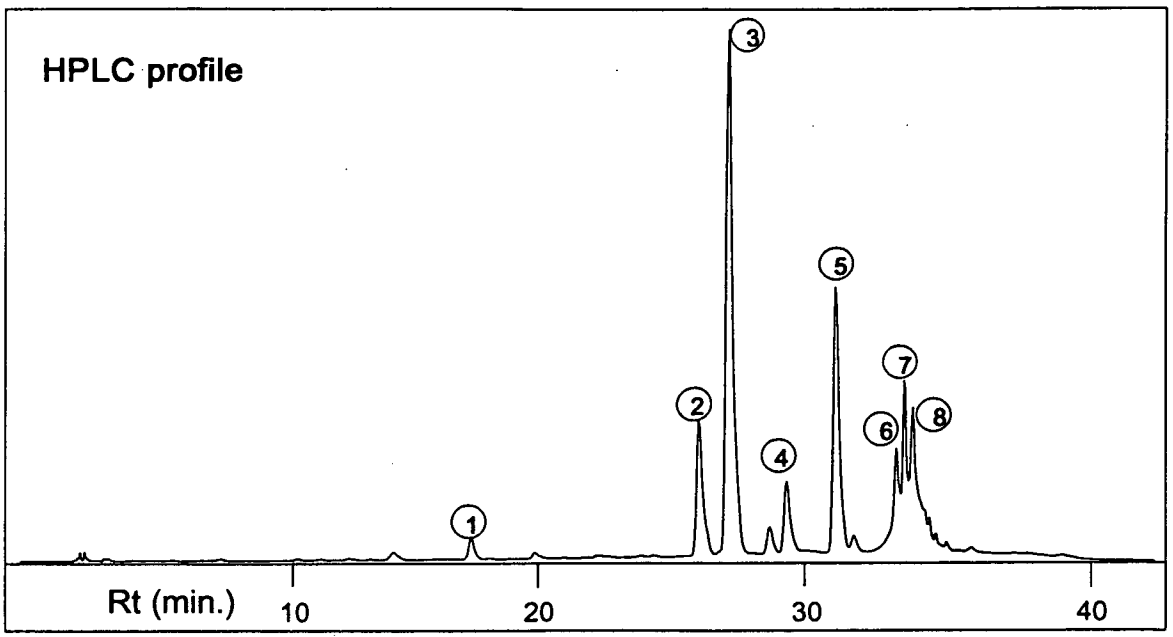
  - RBG, Kew 595-59-59502
  - RBG, Kew 485-84-04966

Distribution



Aloe mcloughlinii is found near Dire Dawa in the Harar Province of Ethiopia.

Aloe megalacantha Baker



Peak number	Retention time	Compound	Percentage
1	15.95	dihydroisocoumaringlucoside	1
2	24.21	aloin B	8
3	25.26	aloin A	28
4	27.39	aloinoside B	7
5	29.17	aloinoside A	24
6	32.50	microdontin B	2
7	32.97	microdontin A	6
8	33.52	unidentified anthrone	15

A chromatographic repetition of a general pattern detected in many species of tropical east Africa. The Demissew and Kew samples are identical.

- Taxonomic position:

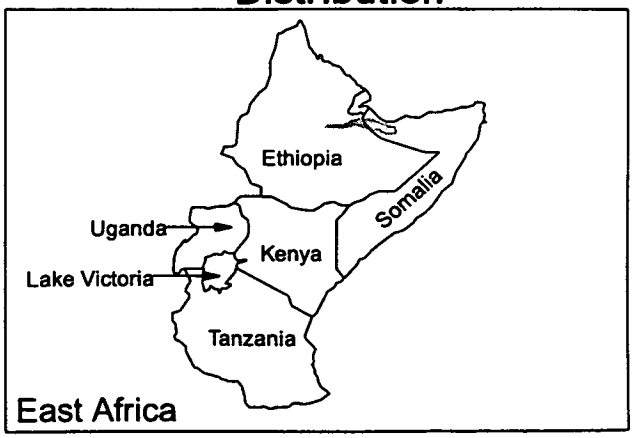
Group 17 of the tropical aloes (Reynolds, 1966).

- Samples analysed:

The leaf exudate was investigated:

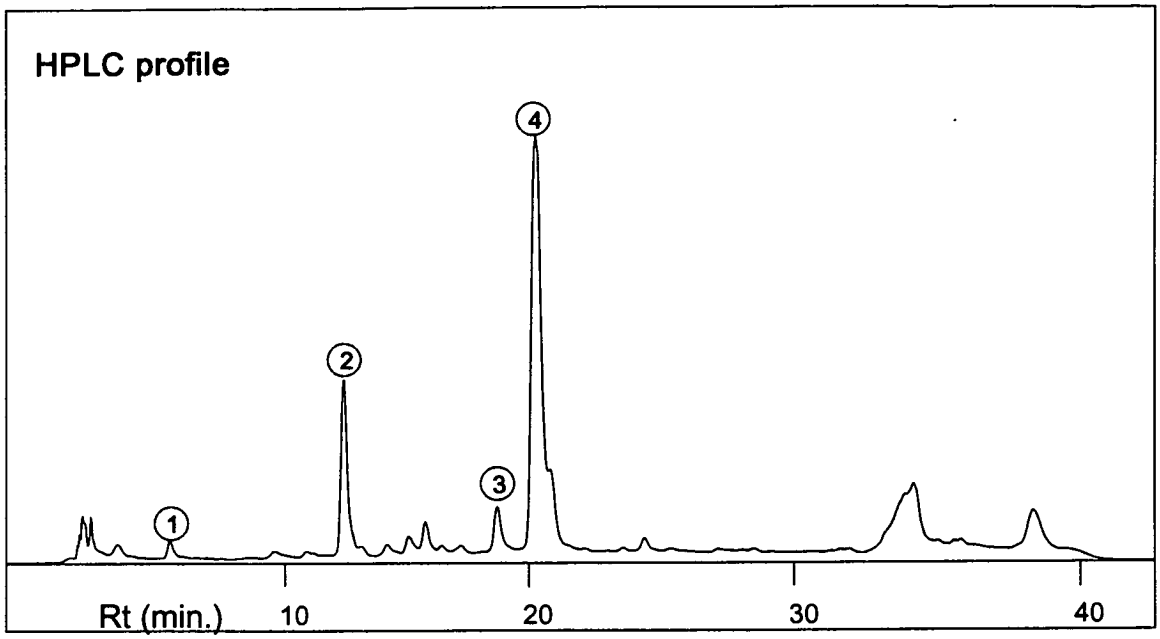
- Sebsebe 325
- RBG, Kew 144-93-01240

Distribution



Aloe megalacantha is widely distributed in Ethiopia and northern Somalia.

Aloe melanacantha A. Berger



Peak number	Retention time	Compound	Percentage
1	6.19	aloesin	1
2	12.79	unidentified chromone 1	11
3	18.55	unidentified chromone 2	3
4	19.99	aloeresin E	38

The unidentified chromone 2 displays the same UV absorbance spectrum as aloeresin E while the unidentified chromone 1 is probably a coumaroyl chromone derivative. This spectrum is similar to that recorded for *A. erinacea* with the exception that no aloeresin F or nataloin was detected in this species.

- Taxonomic position:

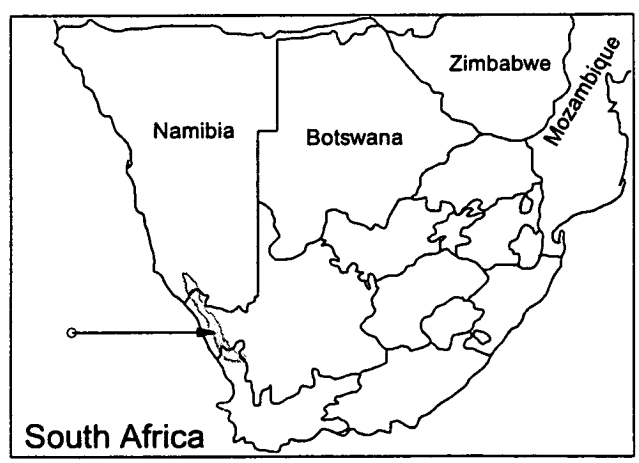
  Aloe series *Echinatae* (Reynolds, 1950)

- Samples analysed:

  The leaf exudate was investigated:

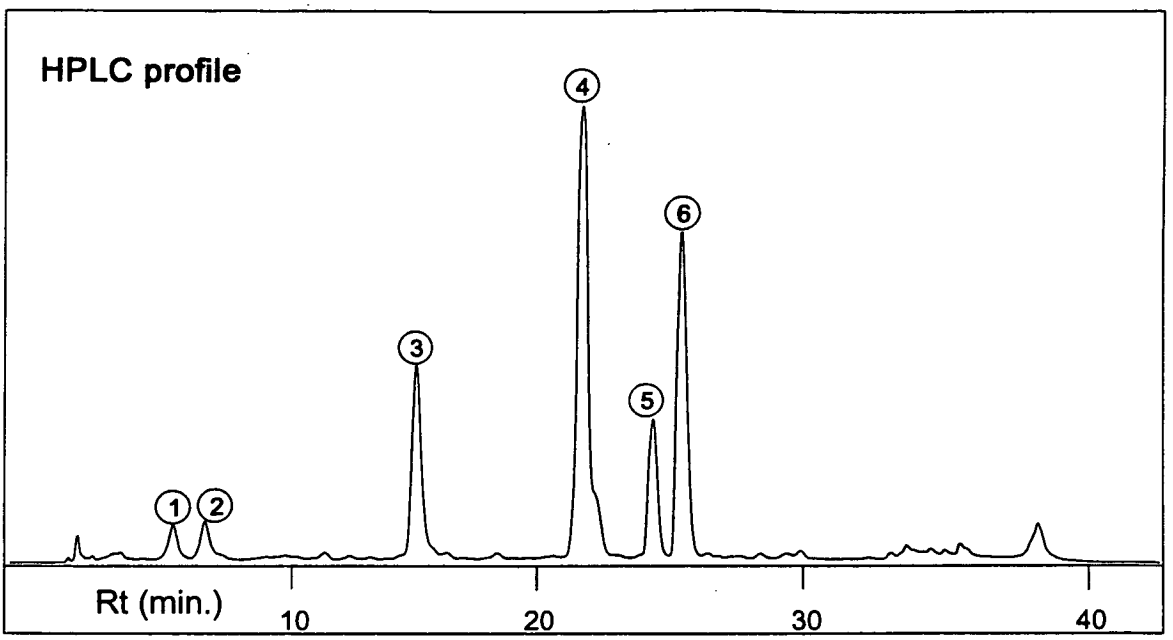
  - JBG 83-5-440

Distribution



This species extends form Nieuwoudtville in the south through to Witputs in Namibia.

Aloe menachensis (Schweinfurth) Blatter



Peak number	Retention time	Compound	Percentage
1	6.07	aloesin	3
2	7.24	7-*O*-methylaloesin	3
3	15.16	8-*O*-methyl-7-hydroxyaloin	15
4	21.41	aloeresin D	37
5	24.07	aloin B	24
6	25.11	aloin A	25

For the purpose of this study, the compound represented by peak 3, 8-*O*-methyl-7-hydroxyaloin was isolated and identified from *A. schelpei*. This profile is almost identical to that of *A. niebuhriana*.

- Taxonomic position:

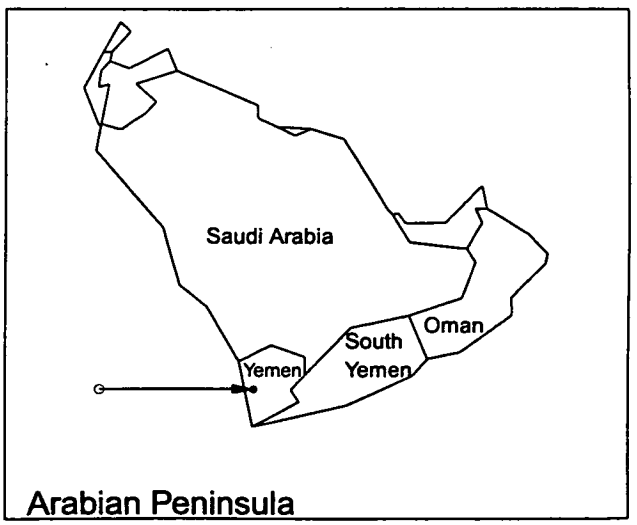
  Group 9 of the tropical aloes (Reynolds, 1966).

- Samples analysed:

  The leaf exudate was investigated:

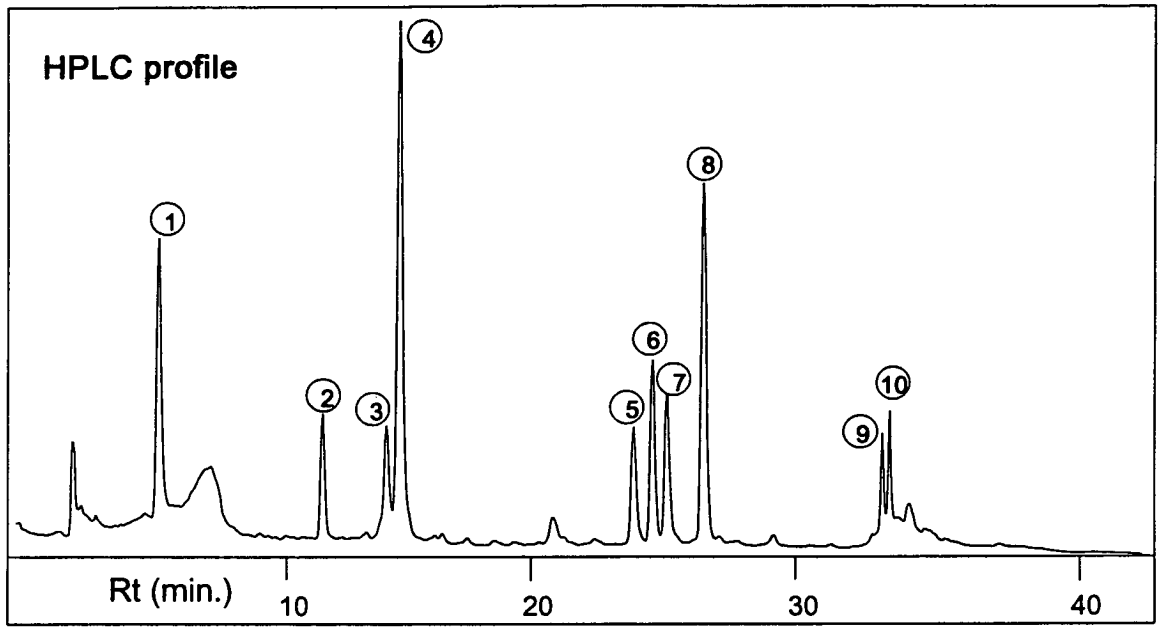
  - RBG, Kew 439-7504-505

Distribution



This high altitude species is only known from the Jabal Shibam in the Haraz mountains of Yemen.

Aloe mendesii Reynolds



Peak number	Retention time	Compound	Percentage
1	5.50	aloesin	13
2	11.83	homonataloside B	5
3	14.30	unidentified chromone 1	7
4	14.81	unidentified chromone 2	28
5	23.75	aloin B	6
6	24.47	homonataloin B	9
7	25.03	aloin A	7
8	26.44	homonataloin a	18
9	33.17	unidentified anthrone 1	3
10	33.45	unidentified anthrone 2	3

Aloe mendesii, like *A. mutabilis* is an exception where aloin co-occurs with homonataloin. Peak 9 and 10 have an UV absorbance spectra identical to that of aloin

- Taxonomic position:

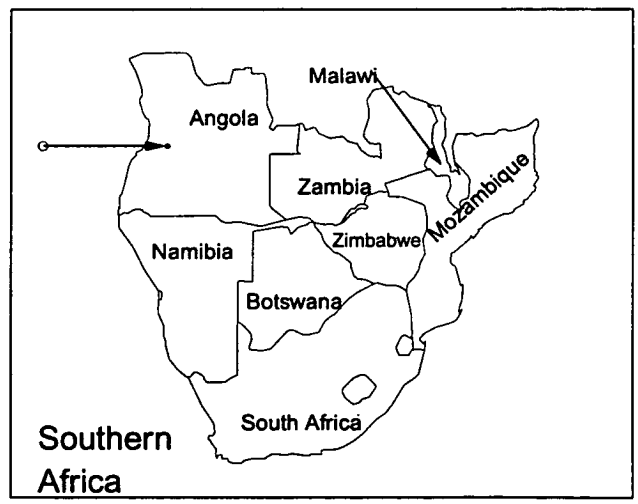
  Group 10 of the tropical aloes (Reynolds, 1966).

- Samples analysed:

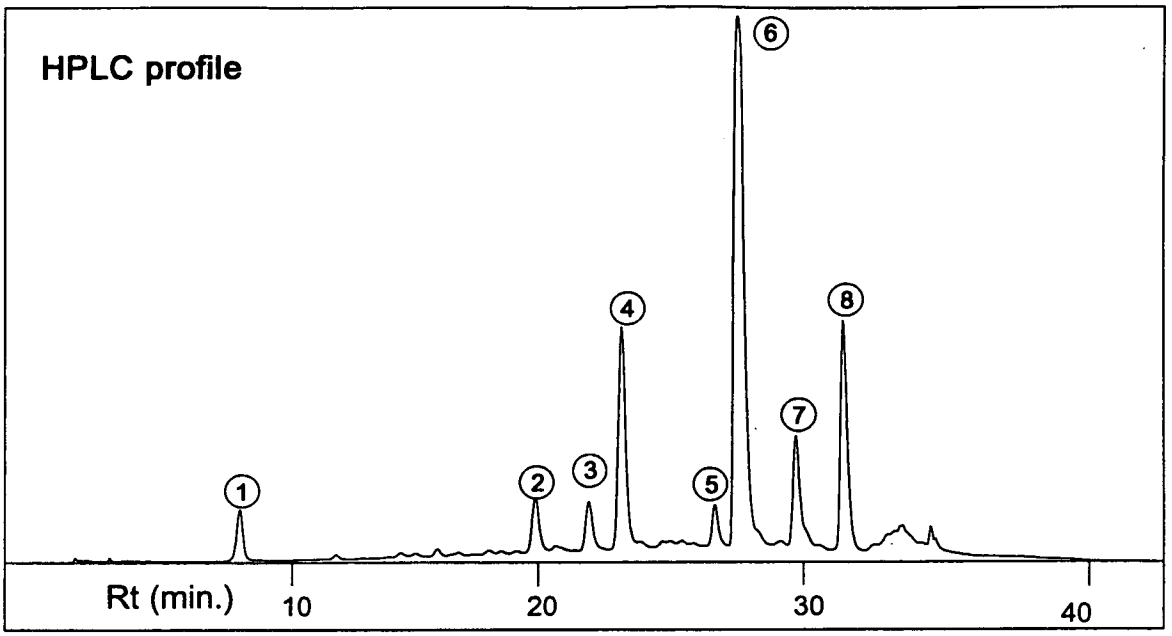
  The leaf exudate was investigated:

  - NBI 11992

Distribution



This high altitude aloe is known from the escarpment of the Humpata plateau in the Huila District of Angola.



Peak number	Retention time	Compound	Percentage
1	8.49	7-*O*-methylaloesin	3
2	19.74	unidentified chromone 1	3
3	21.79	unidentified chromone 2	3
4	23.05	aloeresin D	14
5	26.61	aloin B	2
6	27.42	aloin A	46
7	29.68	aloinoside B	7
8	31.44	aloinoside A	13

See comments mentioned under *A. mcloughlinii*.

- Taxonomic position:

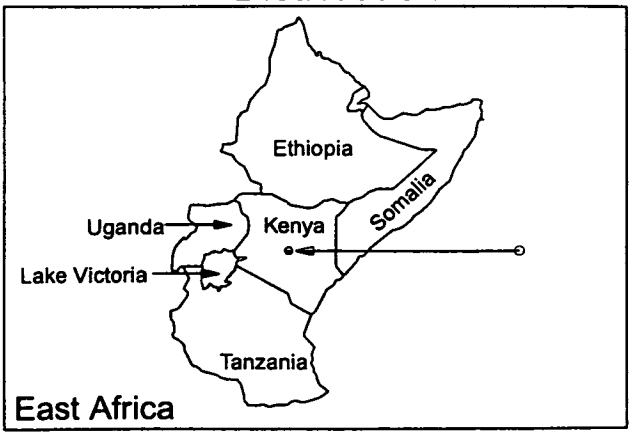
  Allied to *A. chrysostachys* (Lavranos, 1980).

- Samples analysed:

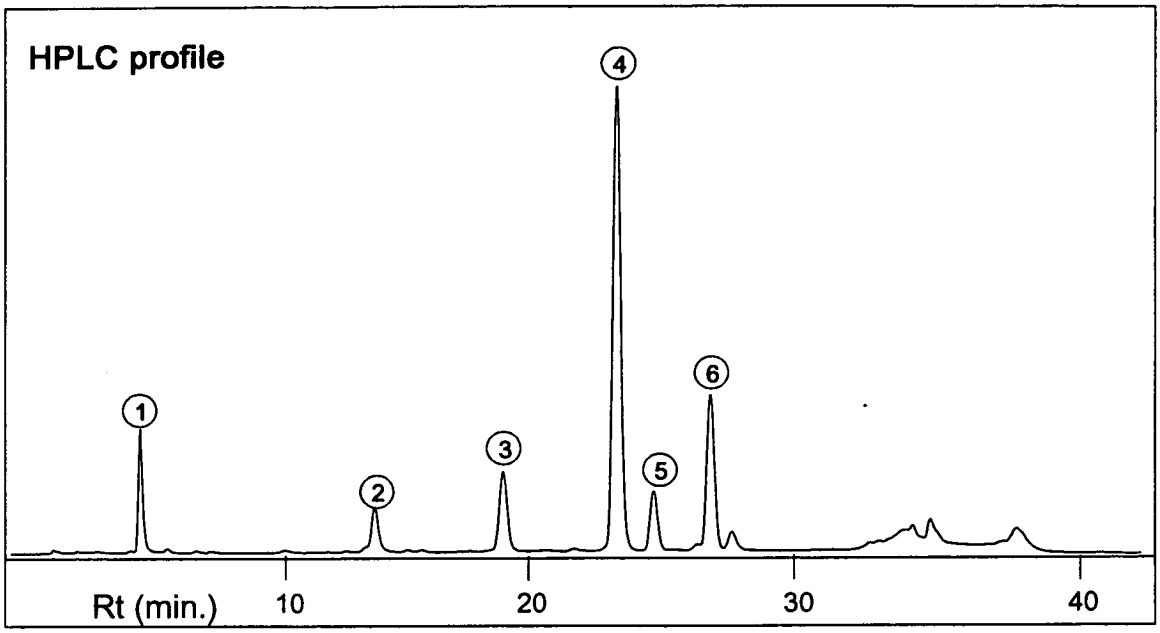
  The leaf exudate was investigated:

  - LEN 4246 (type locality)

Distribution



This aloe is only known from the type locality which is in the Meru Park in Kenya.



Peak number	Retention time	Compound	Percentage
1	4.99	aloesin	7
2	13.98	unidentified compound	5
3	18.92	aloeresin E	9
4	23.20	aloeresin F	52
5	24.60	homonataloin B	6
6	26.74	homonataloin A	16

The characteristic profile for species pertaining to series *Mitriformes*.

- Taxonomic position:

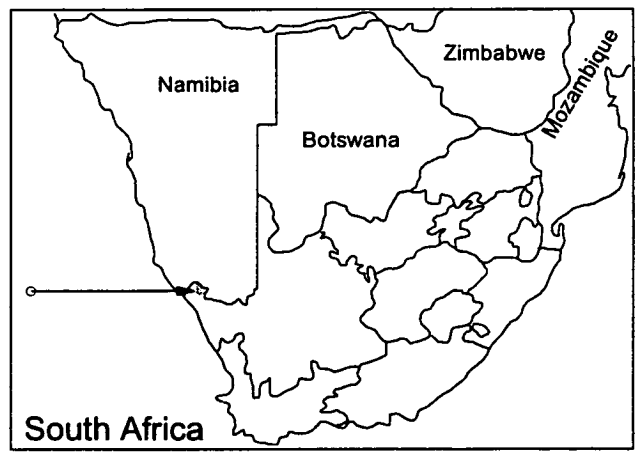
  Aloe series *Mitriformes* (Van jaarsveld, 1981).

- Samples analysed:

  The leaf exudate was investigated:

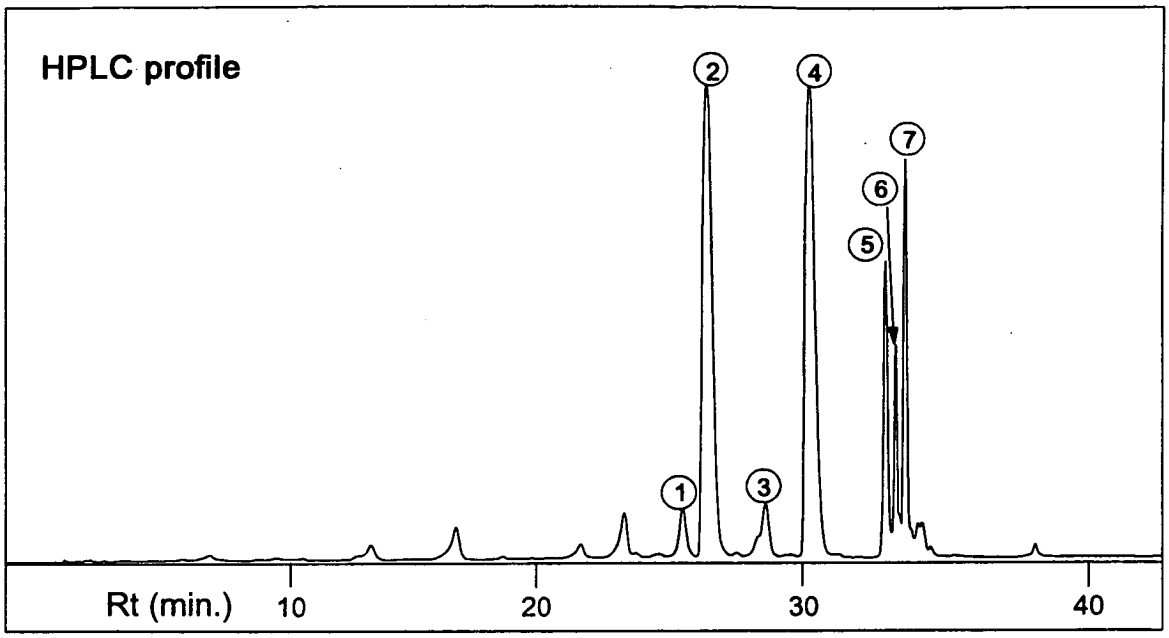
  - Rosyntjieberg (type material)

Distribution



Aloe meyeri is only known from the Rosyntjieberg mountain range which is the Richtersveld and extends marginally into Namibia.

Aloe microdonta Chiovenda



Peak number	Retention time	Compound	Percentage
1	25.36	aloin B	2
2	26.21	aloin A	31
3	28.51	aloinoside B	3
4	30.09	aloinoside A	31
5	33.04	microdontin B	7
6	33.41	microdontin A	5
7	33.76	unidentified anthrone	10

This HPLC profile represents one of the few examples where the two microdontins and the unidentified anthrone are virtually completely separated. All samples investigated were identical except for quantitative differences.

(See *A. boscawenii*)

- Taxonomic position:

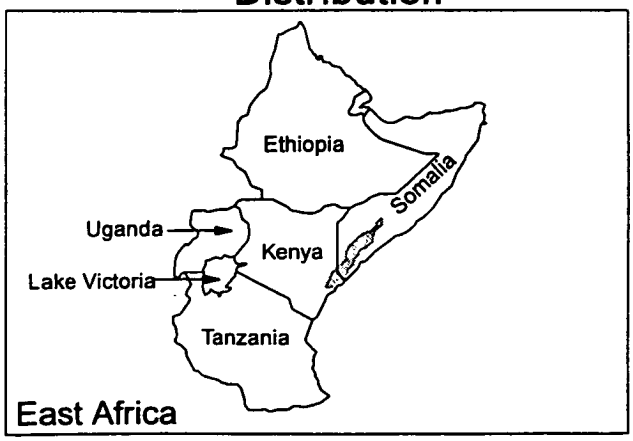
  Group 17 of the tropical aloes (Reynolds, 1966).

- Samples analysed:

  The leaf exudate was investigated:

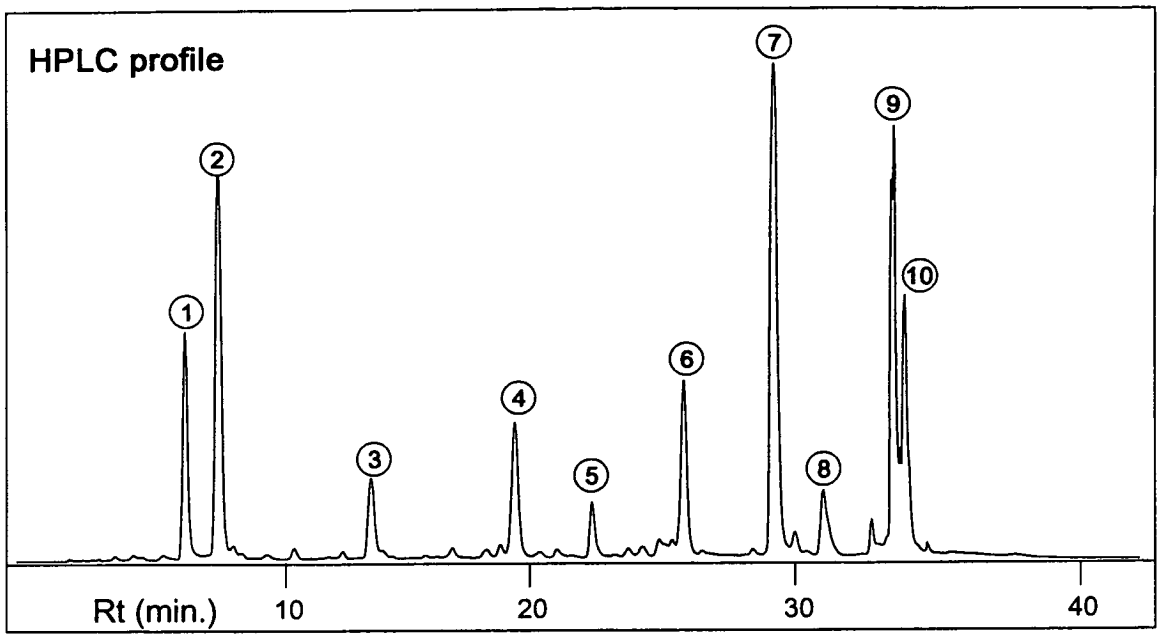
  - ex hort P. Favell
  - RBG, Kew 1966-12803
  - NBI 13501

Distribution



Aloe microdonta is common in the sandy soils of southern Somalia and the Tana River District in Kenya.

Aloe microstigma Salm-Dyck



Peak number	Retention time	Compound	Percentage
1	6.54	aloesin	8
2	7.82	7-*O*-methylaloesin	15
3	13.73	unidentified chromone 1	4
4	19.26	unidentified chromone 2	6
5	22.19	5-hydroxyaloin B	2
6	25.70	unidentified anthrone 1	7
7	29.09	microstigmin	22
8	31.00	unidentified chromone 3	3
9	33.68	unidentified anthrone 2	15
10	34.10	unidentified chromone 4	10

The unidentified anthrones display a UV absorbance spectra similar to that of microstigmin. Peaks 3, 4, and 8 all have the same UV spectra, while peak 10 compares well to the UV absorbance of the cinnamoyl chromones. This is the species from which microstigmin has been isolated.

- Taxonomic position:

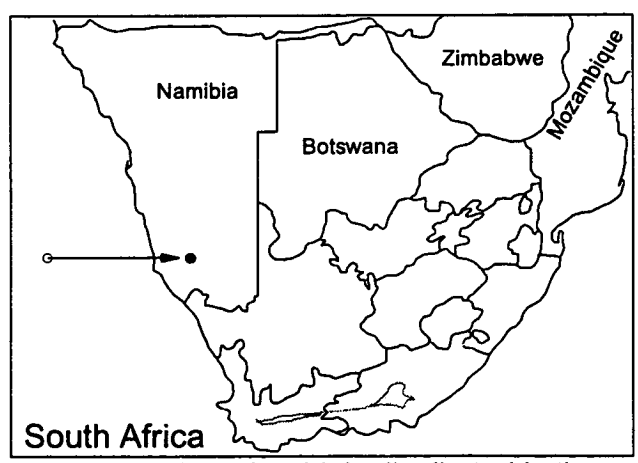
Aloe series *Purpurascentes* (Reynolds, 1950).

- Samples analysed:

The leaf exudate was investigated:

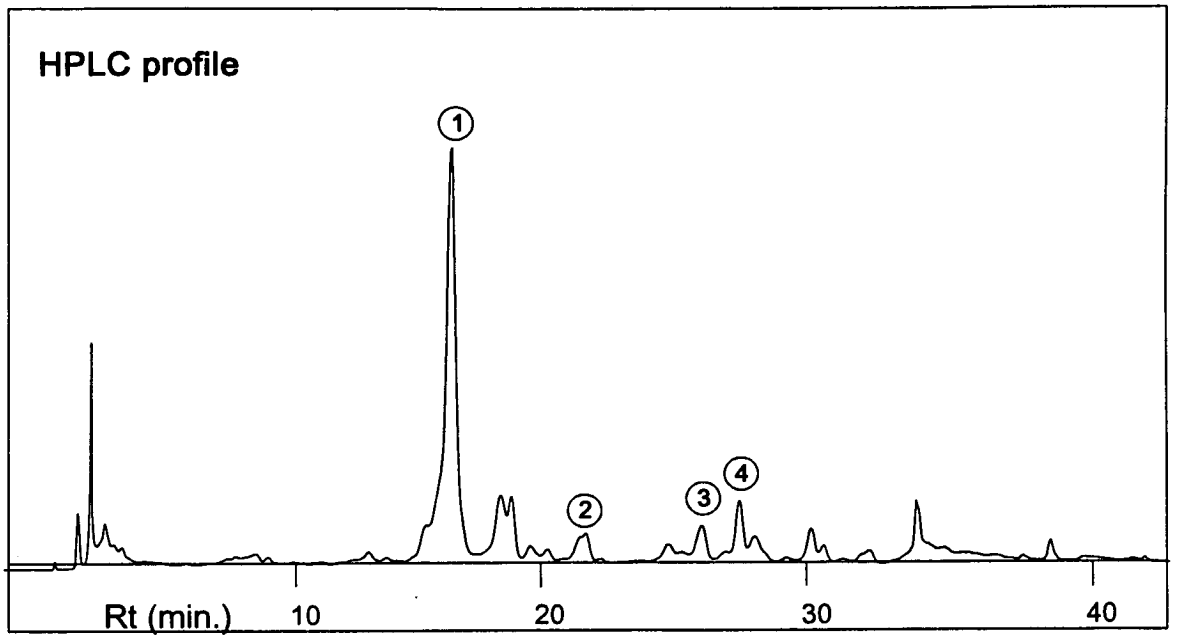
- material collected near Robertson
- Lavranos 29578
- 8 km south of Jansenville

Distribution



Aloe microstigma is widely distributed in the central interior of the Eastern and Western Cape. An isolated form occurs near Aus in Namibia.

Aloe millotii Reynolds



Peak number	Retention time	Compound	Percentage
1	16.49	8-*O*-methyl-7-hydroxyaloin	50
2	21.47	unidentified anthrone 1	4
3	25.75	unidentified anthrone 2	3
4	27.14	unidentified anthrone 3	6

The anthrone 8-*O*-methyl-7-hydroxyaloin which has a limited distribution in the aloes is the major compound. The two unidentified anthrones (peak 2 & 4) show UV spectra identical to that of nataloin and 7-hydroxyaloin. Peak 3 could possibly be homonataloin B.

- Taxonomic position:

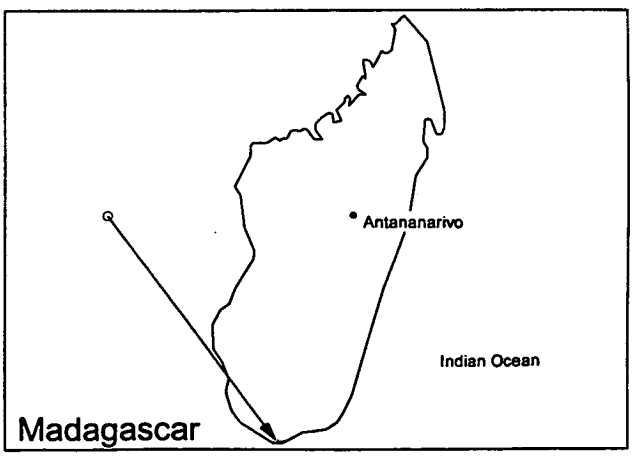
  Group 8 (Reynolds, 1966).

- Samples analysed:

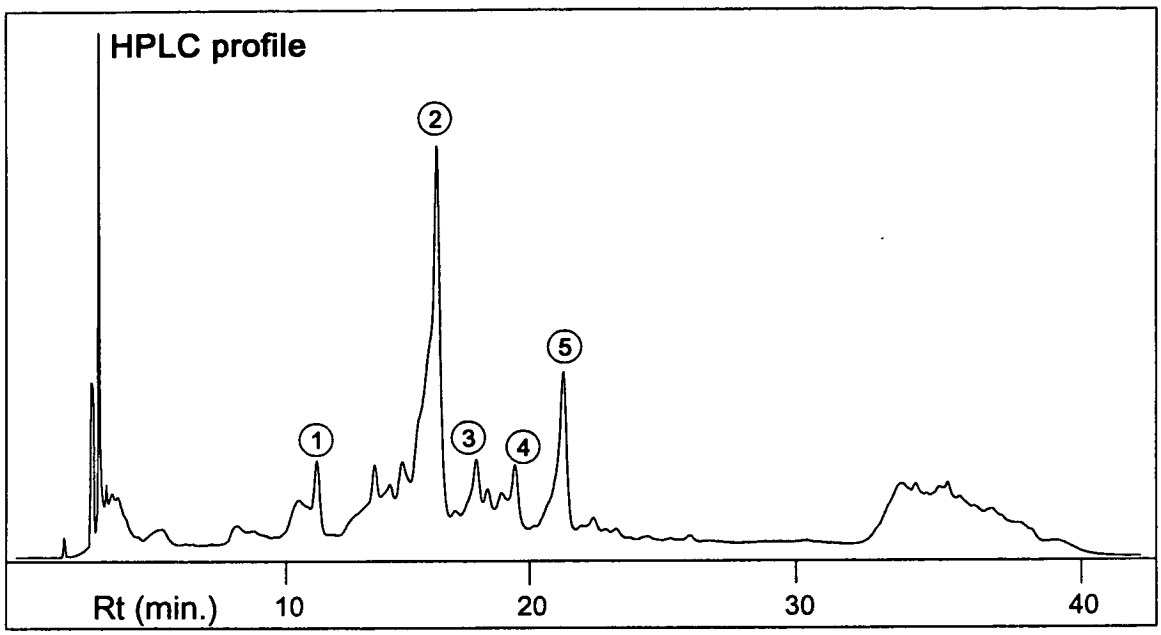
  The leaf extract was investigated:

  - Hardy 2829
  - NBI 14657

Distribution



Aloe millotii grows on limestone in the most southern part of Madagascar



Peak number	Retention time	Compound	Percentage
1	11.6	unidentified flavone 1	2
2	16.2	unidentified flavone 2	25
3	17.8	unidentified flavone 3	3
4	19.2	isovitexin	3
5	21.1	unidentified flavone 4	11

The five main compounds in the methanolic extract of the leaves are all possibly flavones (based on UV observations). The flavone, isovitexin has been positively identified.

- Taxonomic position:

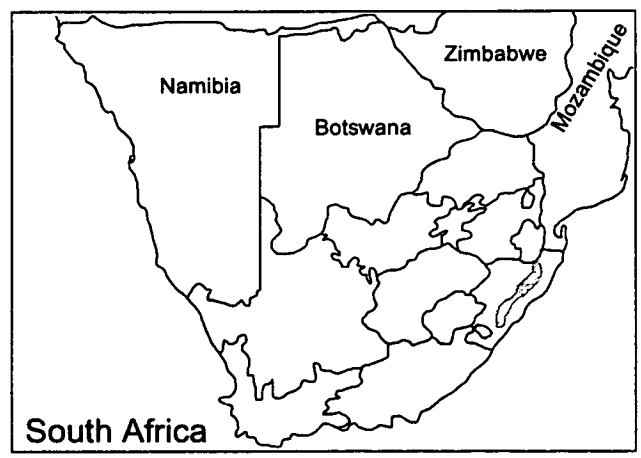
  Aloe section *Graminialoe* (Reynolds, 1950).

- Samples analysed:

  The leaf extract was investigated:

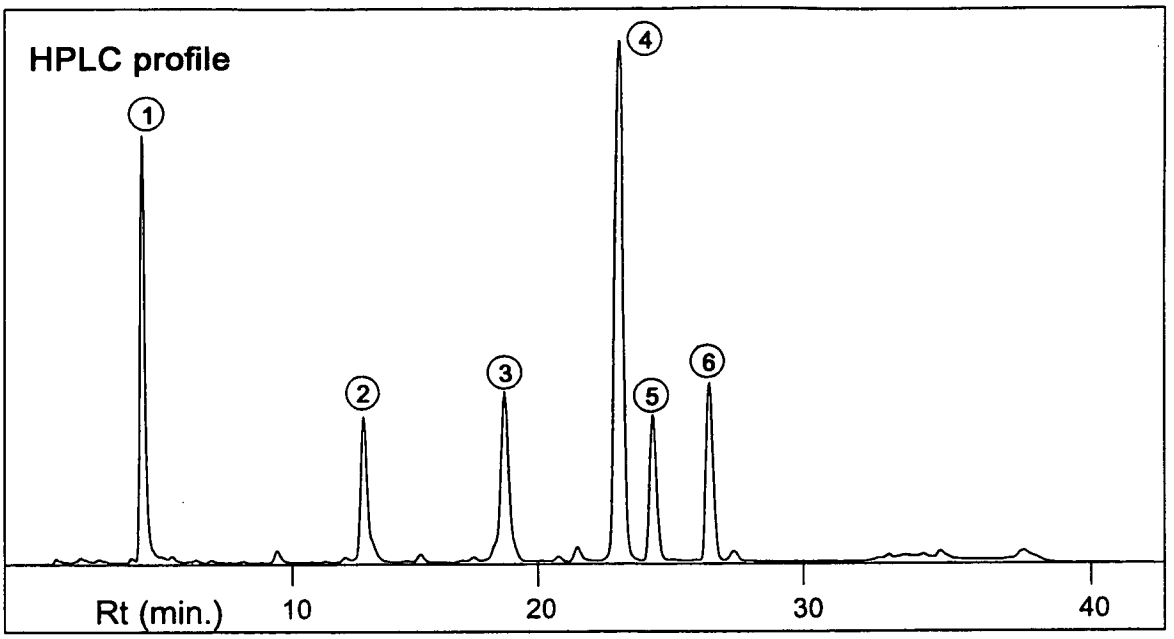
  - ex hort C. Craib (collected near The Brook)
  - NBI 31461
  - material collected near Carolina

Distribution



Aloe minima is widely distributed in the central areas of KwaZulu-Natal and extends northwards in Swaziland and Mpumalanga.

Aloe mitriformis Miller



Peak number	Retention time	Compound	Percentage
1	4.90	aloesin	18
2	13.31	aloeresin A	9
3	18.64	aloeresin E	13
4	22.94	aloeresin F	37
5	24.23	homonataloin B	9
6	26.37	homonataloin A	11

All the samples investigated were identical. The sample collected near Nieuwoudtville did not contain aloeresin E.

- Taxonomic position:

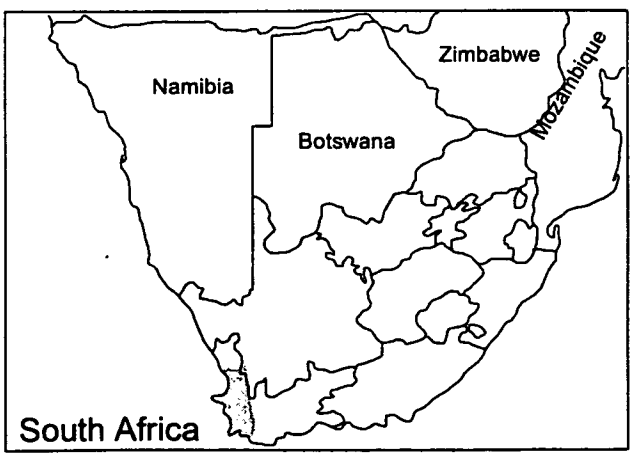
Aloe series *Latebracteatae* (Reynolds, 1950).

- Samples analysed:

The leaf exudate was investigated:

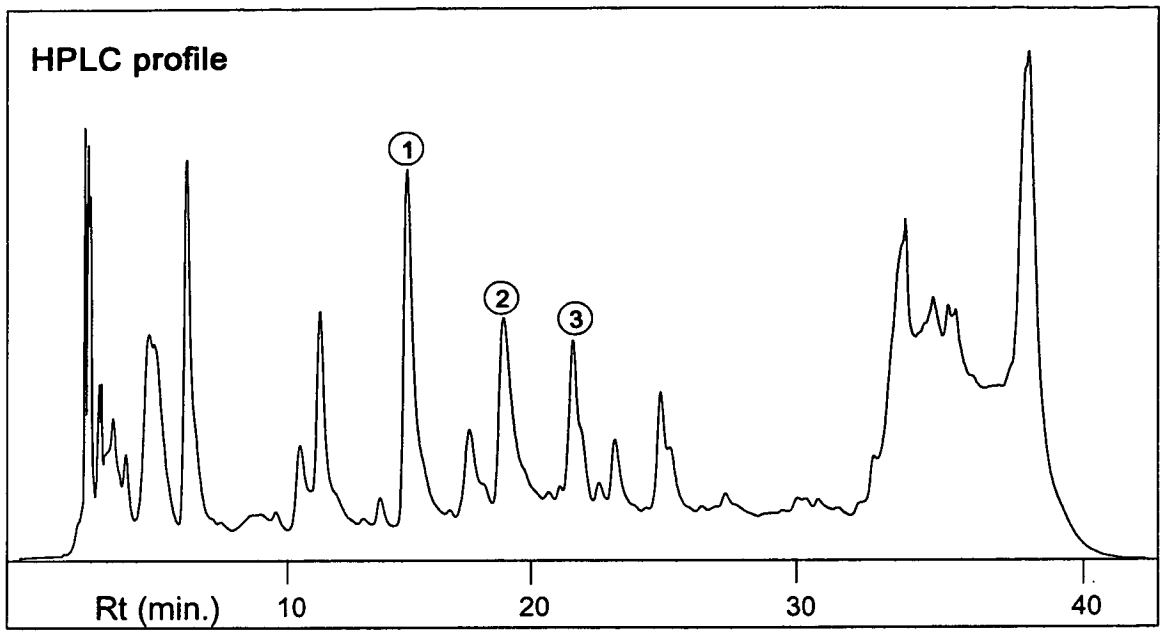
- Du Toitskloof
- Kogman's Kloof
- Slanghoek
- NBI 28570 (Touws river)
- Gifberg
- Nieuwoudtville

Distribution



Aloe mitriformis is common on rocky places in the south-western Cape.

Aloe modesta Reynolds



Peak number	Retention time	Compound	Percentage
1	15.0	unidentified flavone 1	11
2	18.6	unidentified flavone 2	7
3	21.3	unidentified flavone 3	6

Only trace amounts of what seem to be flavones were detected in *A. modesta*.

- Taxonomic position:

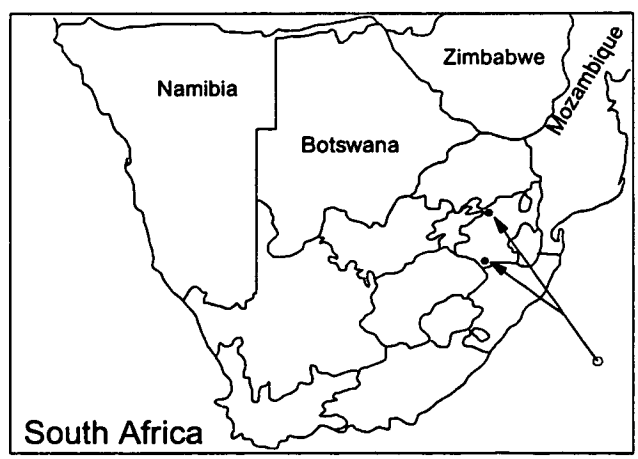
  Aloe section *Leptoaloe* (Reynolds, 1950).

- Samples analysed:

  The leaf extract was investigated:

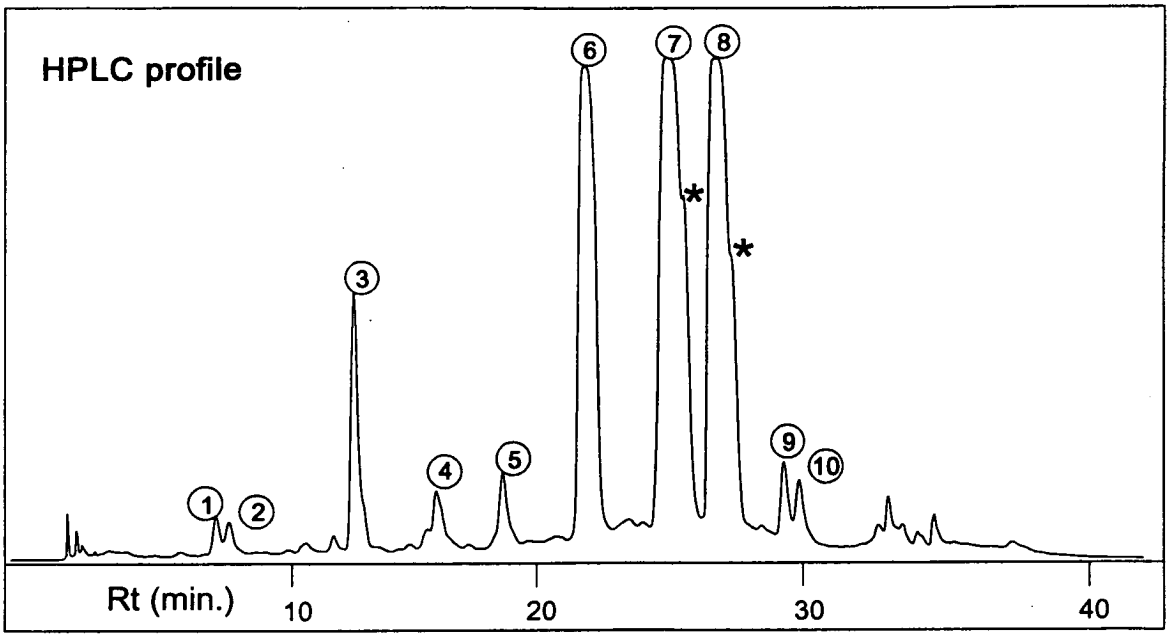
  - ex hort NBI

Distribution



Only two localities are known for *A. modesta;* near Dullstroom and near Wakkerstroom, both localities are in Mpumalanga.

Aloe molederana Lavranos & Glen



Peak number	Retention time	Compound	Percentage
1	7.75	aloesin	1
2	8.23	7-*O*-methylalaoesin	1
3	13.01	homonataloside B	5
4	15.88	dihyroisocoumaringlucoside	tr
5	18.72	unidentified chromone 1	2
6	21.79	aloeresin D	21
7	24.90	aloin B	24
8	26.68	aloin A	24
9	29.37	unidentified chromone 1	2
10	29.97	unidentified chromone 2	2

The presence of homonataloside B hints on a taxonomic affinity with various other tropical species (e.g. *A. abyssicola*). It is interesting to note that aloeresin A is absent with aloeresin D present. The shoulder on the homonataloin peaks (*), is an unidentified compound co-eluting with homonataloin.

- Taxonomic position:

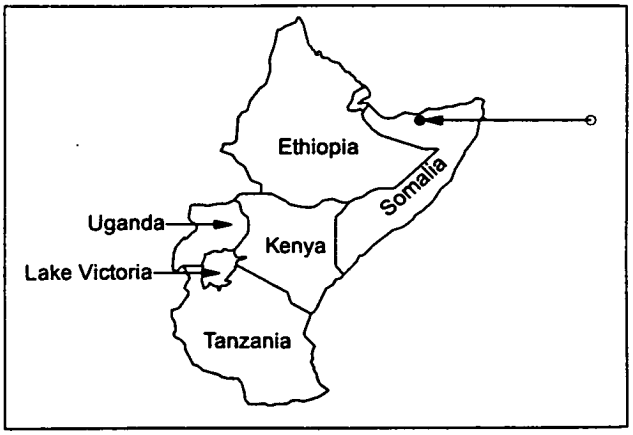
  Possibly related to *A. pubescens, A. massawana, A. vacillans* and others (Lavranos & Glen, 1989).

- Samples analysed:

  The leaf exudate was investigated:

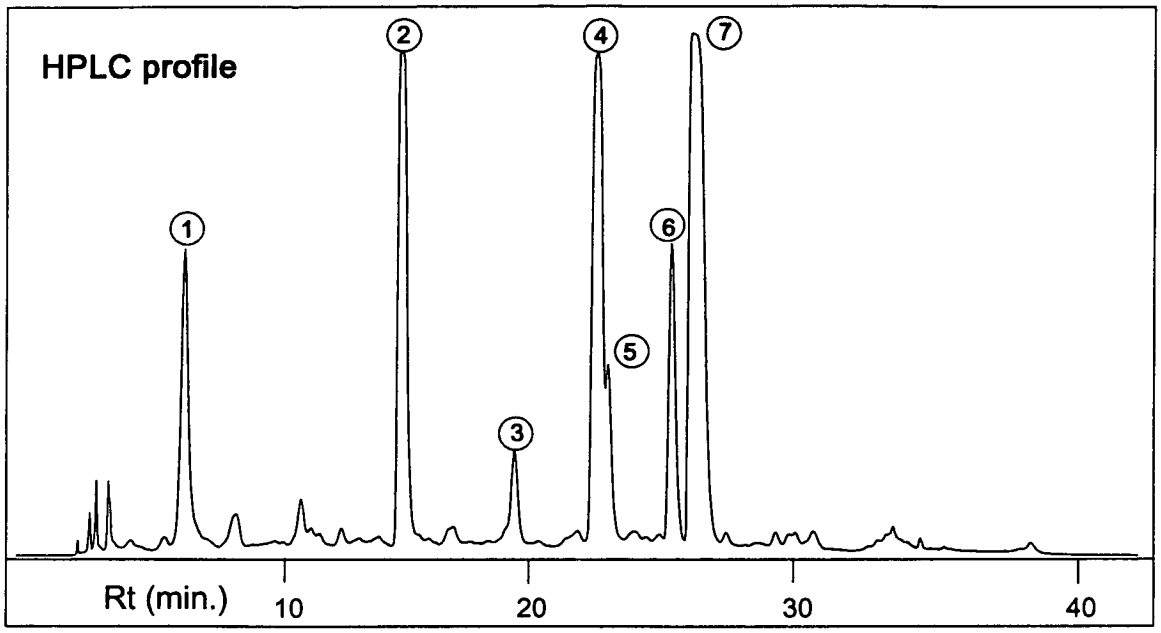
  - NBI 11194

Distribution



Aloe molederana is restricted to the hills southwest of Erigavo in northern Somalia.

Aloe monticola Reynolds



Peak number	Retention time	Compound	Percentage
1	6.54	aloesin	9
2	14.93	aloenin	17
3	19.27	unidentified chromone 1	3
4	22.41	aloeresin D	19
5	22.74	unidentified compound 2	4
6	25.27	aloin B	8
7	26.06	aloin A	29

The unidentified compound (peak 5) displays the same UV spectrum characteristic of the dihydroisocoumaringlucoside.

- Taxonomic position:

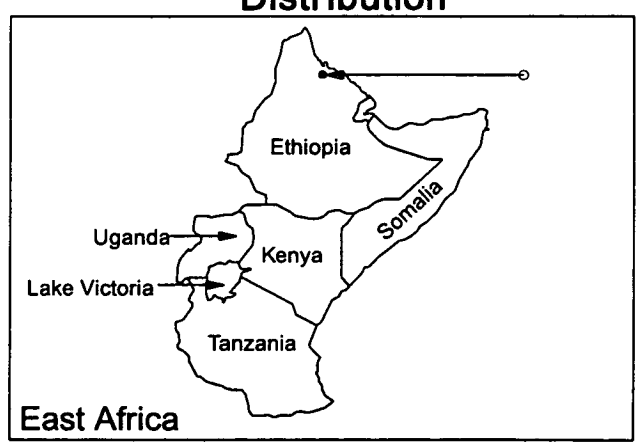
  Group 16 of the tropical aloes (Reynolds, 1966).

- Samples analysed:

  The leaf exudate was investigated:

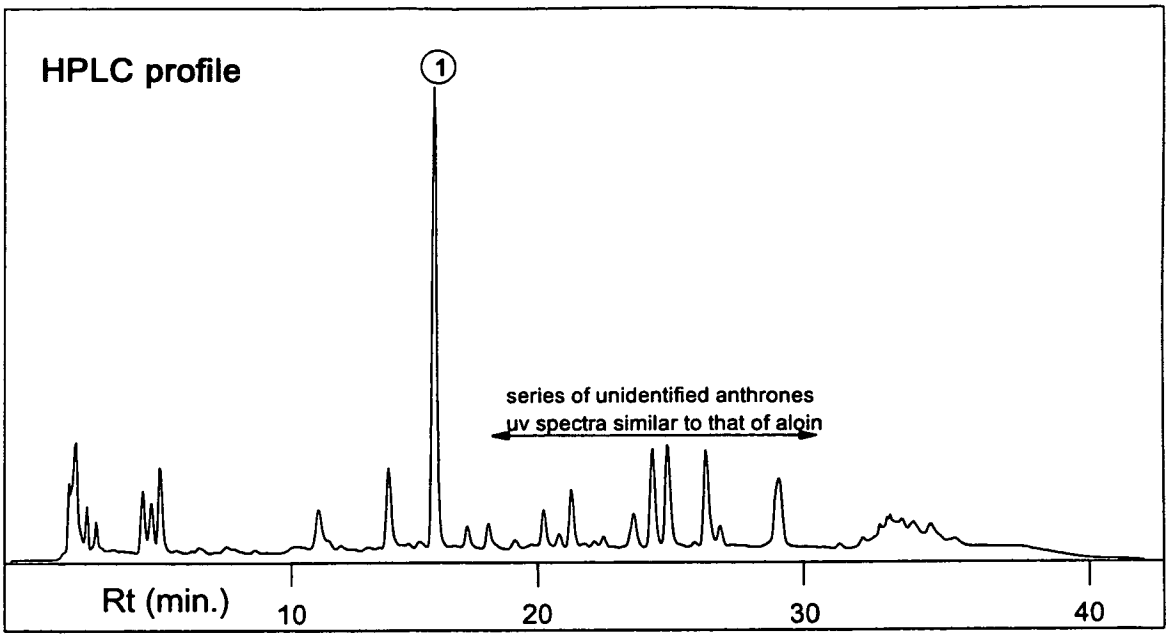
  - ex hort P. Favell

Distribution



This high altitude species inhabits the mountainous areas in northern Ethiopia.

Aloe morijensis S. Carter & Brandham



Peak number	Retention time	Compound	Percentage
1	16.06	plicataloside	34

Aloe morijensis is one of the few chemical exceptions in *Aloe*. Plicataloside is seen here to co-occur with low concentrations of anthrones, and not in isolation as depicted in the other plicataloside-containing representatives.

- Taxonomic position:

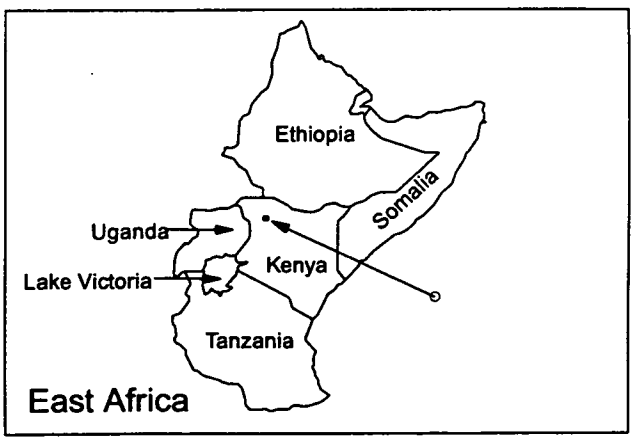
  Allied to *A. gilberti* (Newton, 1994).

- Samples analysed:

  The leaf exudate was investigated:

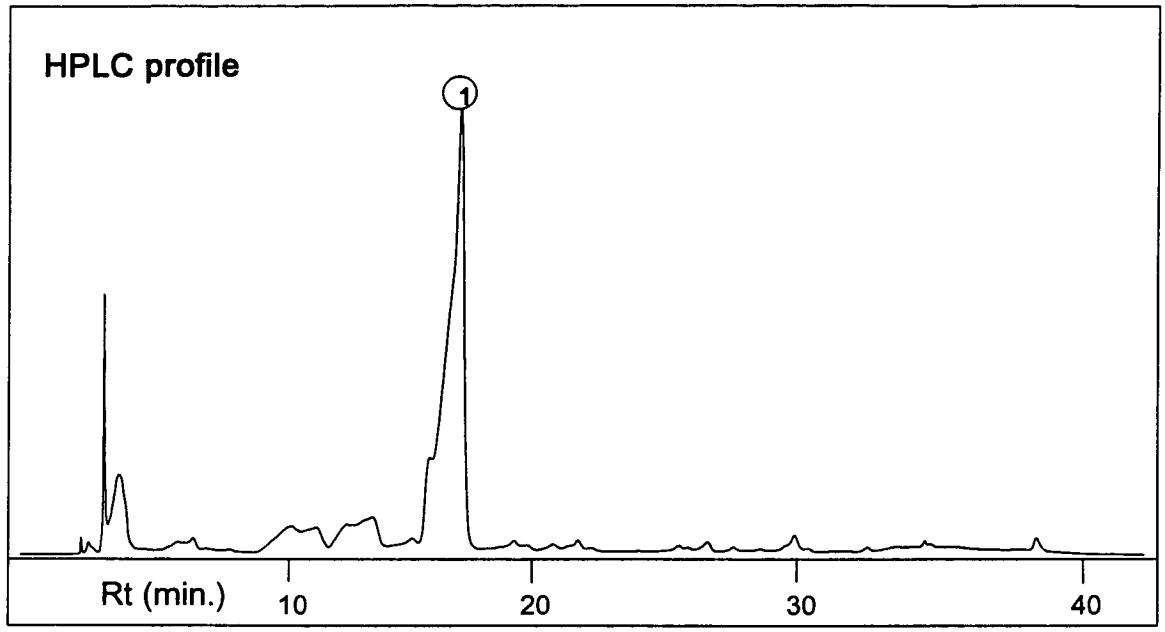
  - L. E. Newton 3661

Distribution



Aloe morijensis is found in the Loita Hills south of Morijo in Kenya.

Aloe multicolor L.E. Newton



Peak number	Retention time	Compound	Percentage
1	16.90	plicataloside	73

A repetition of the chemical profile for a large number of species in tropical east Africa.

- Taxonomic position:

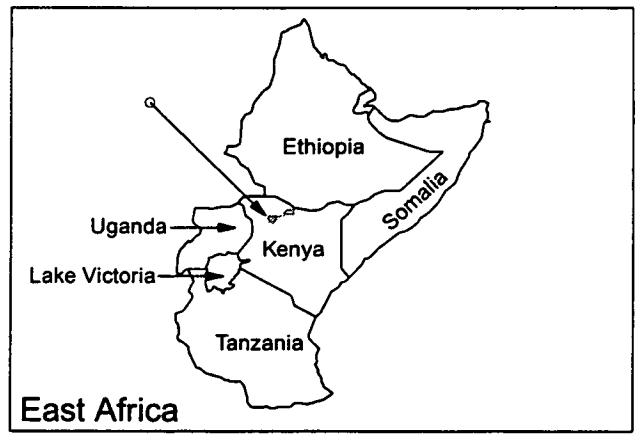
  Possibly allied to *A. gilberti* (Newton, 1994).

- Samples analysed:

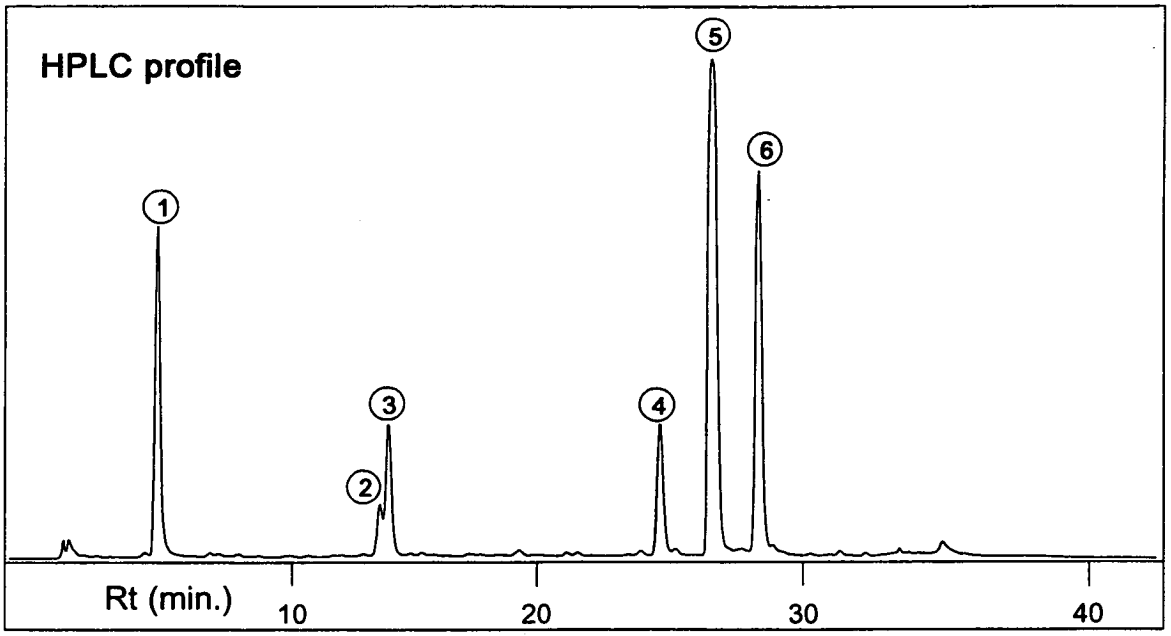
  The leaf exudate was investigated:

  - L.E. Newton 4133 (type plant)

Distribution



Aloe multicolor inhabits the southern parts of Mount Kulal in the Marsabit District of Kenya.



Peak number	Retention time	Compound	Percentage
1	5.50	aloesin	16
2	13.88	unidentified chromone 1	3
3	14.19	unidentified chromone 2	7
4	24.40	homonataloin B	7
5	26.28	homonataloin A	42
6	28.09	unidentified chromone 3	23

All three the unidentified chromones display the UV spectrum typical of the chromone compounds containing a coumaroyl ester group. Various samples of *A. munchii* were injected and showed no variation within a population in terms of leaf exudate composition.

Distribution

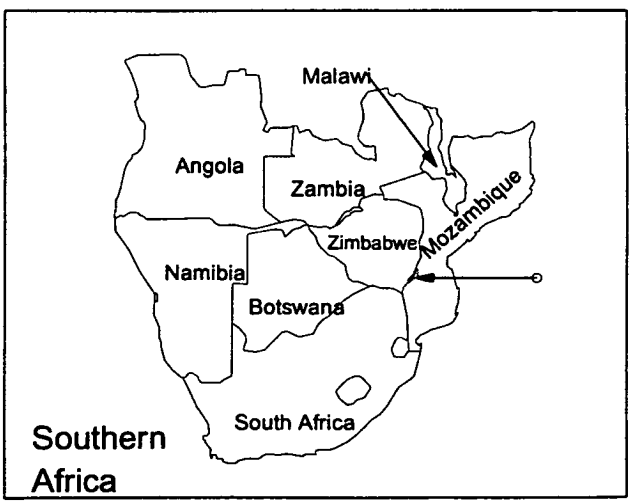
- Taxonomic position:

  Group 18 of the tropical aloes (Reynolds, 1966).

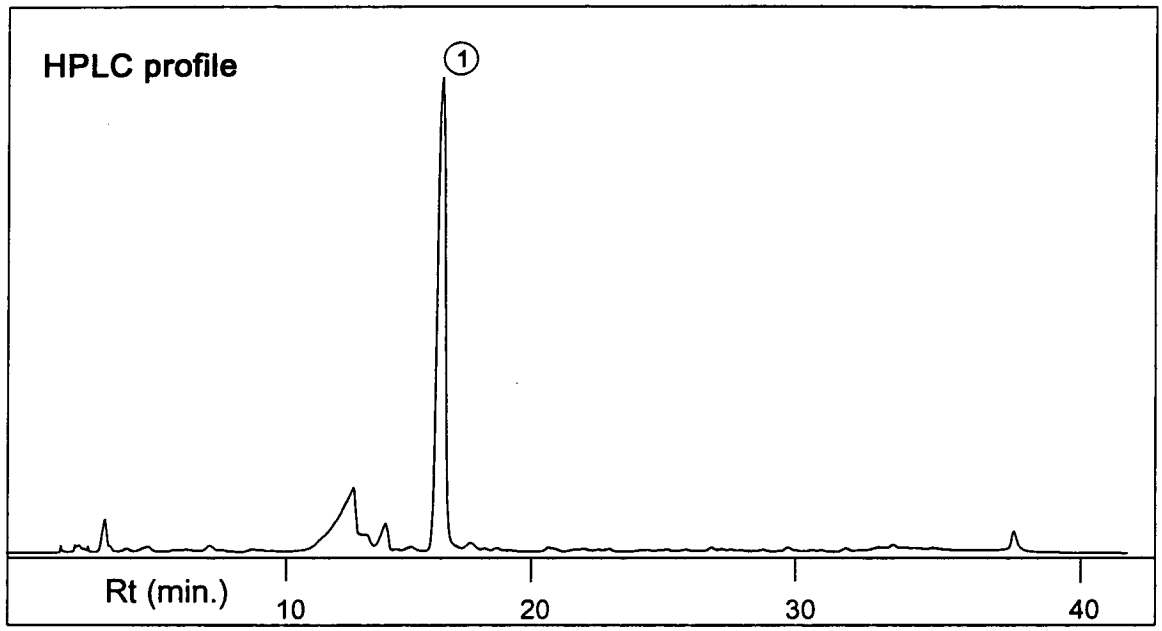
- Samples analysed:

  The leaf exudate was investigated:

  - De Castro 144



Aloe munchii is abundant in the Chimanimani area on the border between Zimbabwe and Mozambique.



Peak number	Retention time	Compound	Percentage
1	16.83	plicataloside	68

A repetition of the chemical profile for a large number of species in tropical east Africa.

Distribution

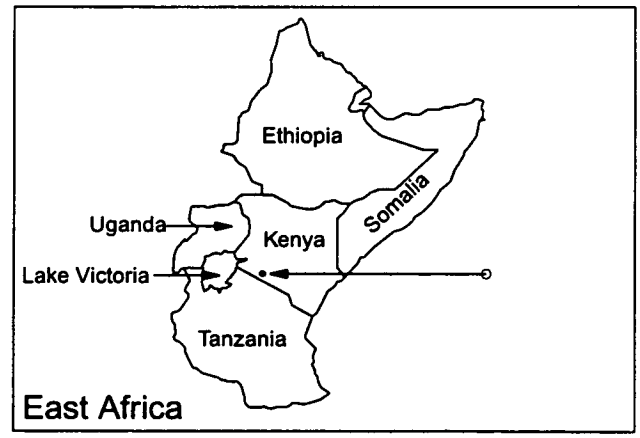
- Taxonomic position:

  Allied to *A. guerrae* (Newton, 1992).

- Samples analysed:

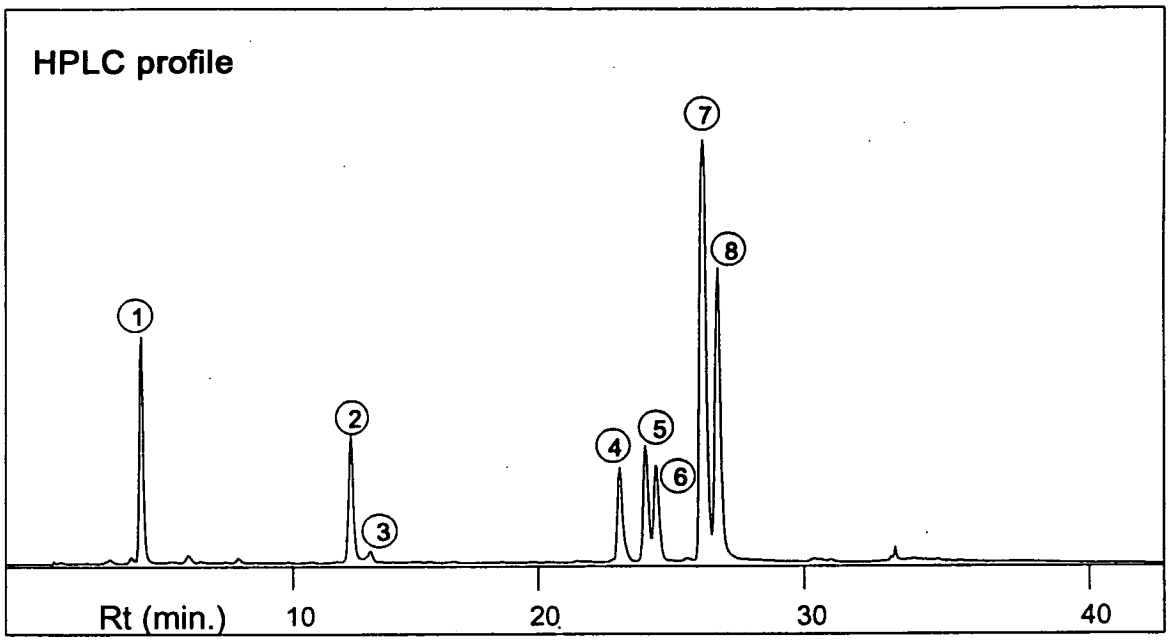
  The leaf exudate was investigated:

  - L. E. Newton 2497 (type plant)



Aloe murina is found on the Nguruman Escarpment in the Masai District of Kenya.

Aloe mutabilis Pillans



Peak number	Retention time	Compound	Percentage
1	4.99	aloesin	11
2	12.76	unidentified chromone	8
3	13.51	8-*O*-methyl-7-hydroxyaloin	1
4	22.80	aloin B	7
5	23.77	homonataloin B	7
6	24.15	aloin A	7
7	25.85	homonataloin B	36
8	26.42	unidentified chromone	22

Aloe mutabilis is a chemical exception as the two anthrone isomers which usually are mutually exclusive (aloin and homonataloin) co-occur in *A. mutabilis*. This is the only South African species which contains 8-*O*-methyl-7-hydroxyaloin. The Ellert sample was identical to the NBI (Blouberg) sample. The sample collected at Chuniespoort did not contain aloin, only homonataloin.

- Taxonomic position:

  Aloe series *Arborescentes* (Reynolds, 1950).

- Samples analysed:

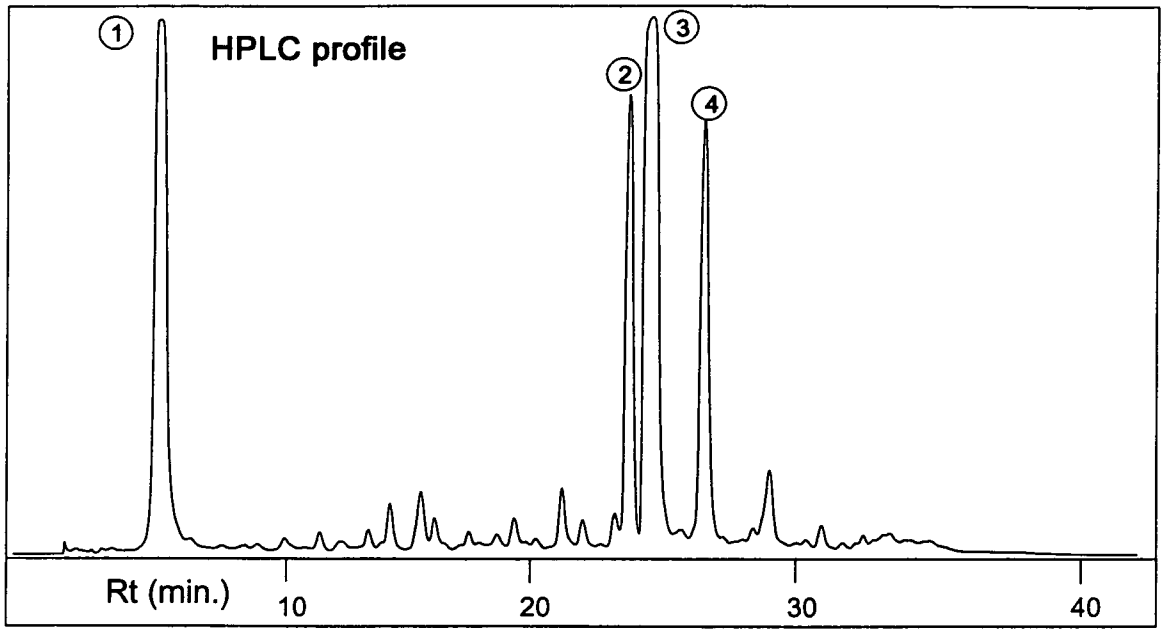
  The leaf exudate was investigated:

  - A. Ellert 25
  - ex hort NBI (Blouberg)
  - Chuniespoort

Distribution

Aloe mutabilis is found in the Magaliesberg on the highveld and in the Pietersburg vicinity of South Africa.

Aloe mzimbana Christian



Peak number	Retention time	Compound	Percentage
1	5.62	aloesin	15
2	23.68	unidentified chromone 1	10
3	24.56	homonataloin B and unidentified chromone 2	41
4	26.55	homonataloin A	18

The unidentified chromones both have a UV spectrum correlating to the coumaroyl chromones.

- Taxonomic position:

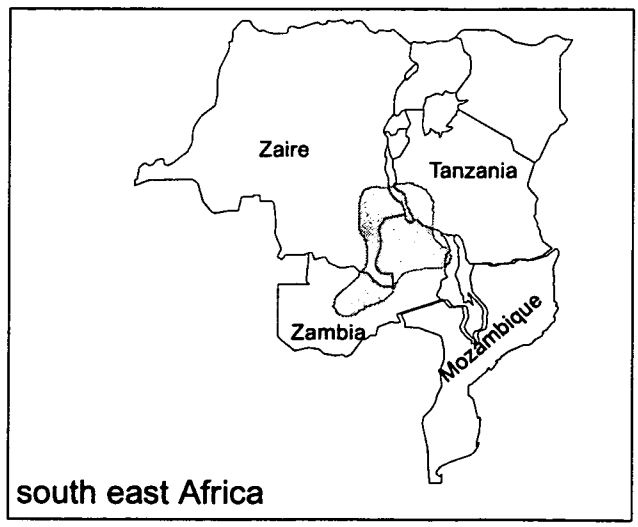
  Group 8 of the tropical aloes (Reynolds, 1966).

- Samples analysed:

  The leaf exudate was investigated:

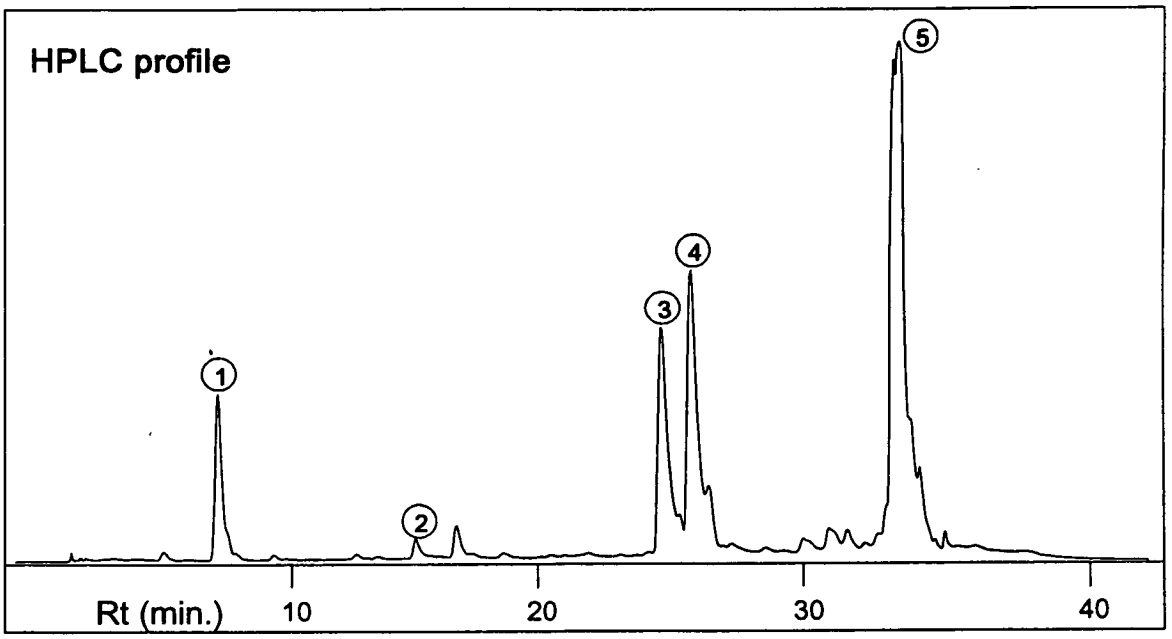
  - RBG, Kew 364 85038/2

Distribution



Aloe mzimbana is widely distributed in south east Africa; Tanzania, Zaire, Zambia and Malawi.

Aloe namibensis Giess



Peak number	Retention time	Compound	Percentage
1	7.6	7-*O*-methylaloesin	7
2	15.1	10-hydroxyaloin B	1
3	24.5	aloin B	14
4	25.6	aloin A	17
5	33.1	unidentified aloin derivatives	44

Aloe namibensis displays a high degree of chromatographic similarity with *A. corallina* and *A. dewinteri*. Peak 5 is probably two or more compounds which have not separated.

- Taxonomic position:

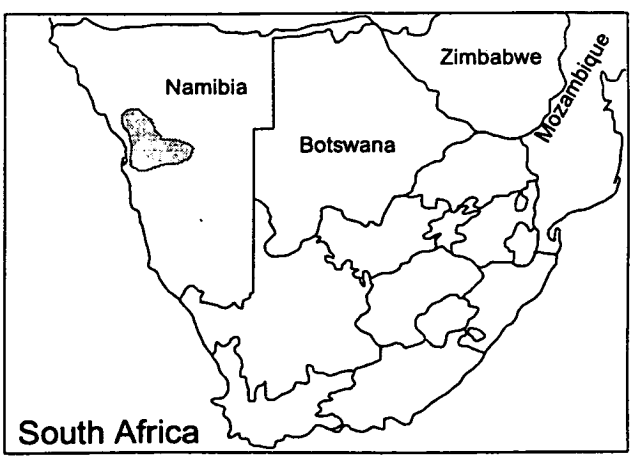
  Aloe series *Asperifoliae* (Giess, 1970).

- Samples analysed:

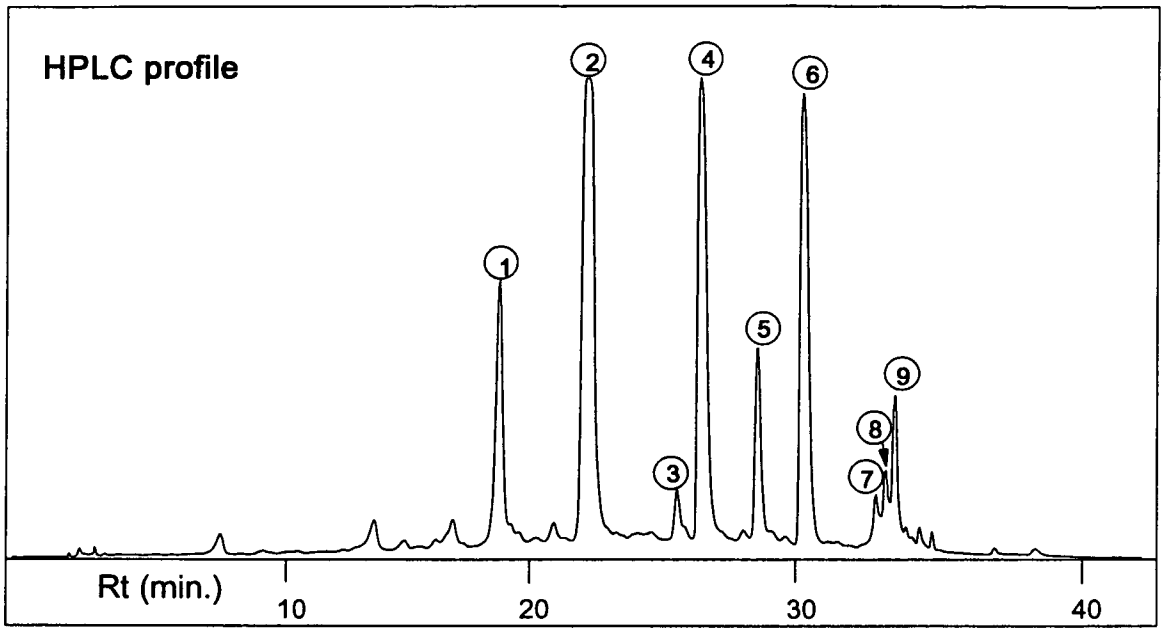
  The leaf exudate was investigated:

  - NBI 28193

Distribution



Aloe namibensis has a sympatric distribution with *A. asperifolia* in the Swakopmund area of Namibia.



Peak number	Retention time	Compound	Percentage
1	18.75	unidentified chromone 1	10
2	22.03	aloeresin D	27
3	25.45	aloin B	2
4	26.30	aloin A	21
5	28.01	aloinoside B	6
6	30.22	aloinoside A	18
7	33.04	microdontin B	2
8	33.42	microdontin A	2
9	33.76	unidentified anthrone	5

This species represents one of the few examples where chromones were found to co-occur with the anthrones aloin, aloinoside and microdontin.

Distribution

- Taxonomic position:

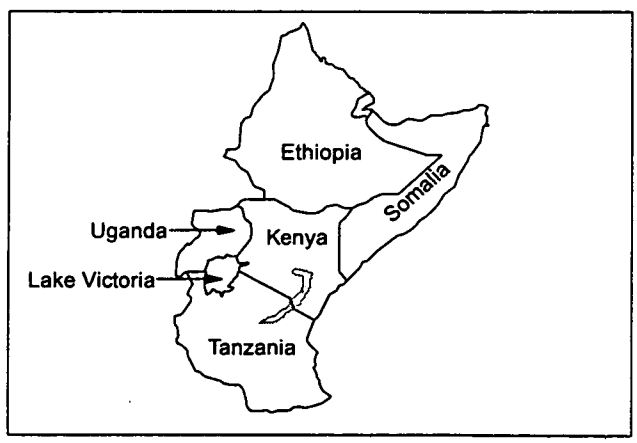
  Group 19 of the tropical aloes (Reynolds, 1966).

  Syn. *A. rabaiensis* sensu Reynolds (Carter, 1994).

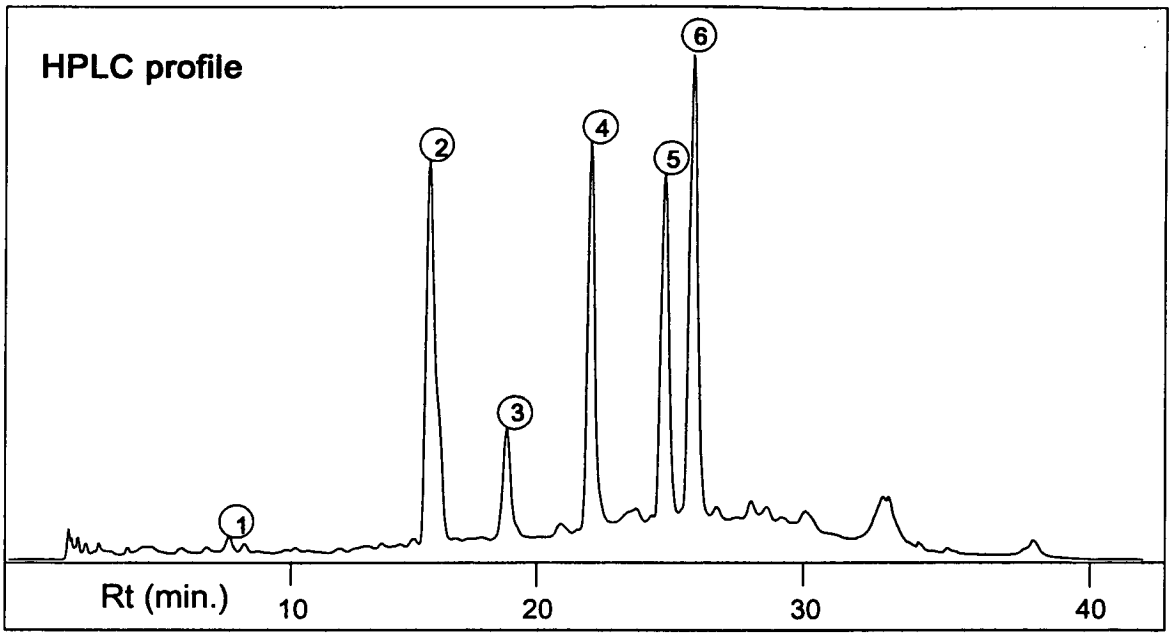
- Samples analysed:

  The leaf exudate was investigated:

  - L. E. Newton 3531 (near type locality)



Aloe ngongensis occupies various habitats in Kenya and Tanzania.



Peak number	Retention time	Compound	Percentage
1	8.27	7-*O*-methylaloesin	1
2	15.96	8-*O*-methyl-7-hydroxyaloin	22
3	18.93	unidentified chromone	6
4	22.10	aloeresin D	17
5	24.87	aloin B	17
6	25.94	aloin A	24

Both samples analysed were virtually identical, the NBI sample did however contains trace amounts of aloesin.

- Taxonomic position:

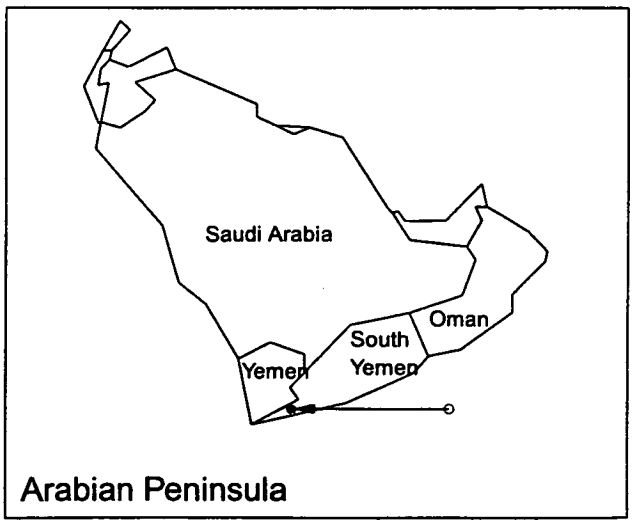
  Group 9 of the tropical aloes (Reynolds, 1966).

- Samples analysed:

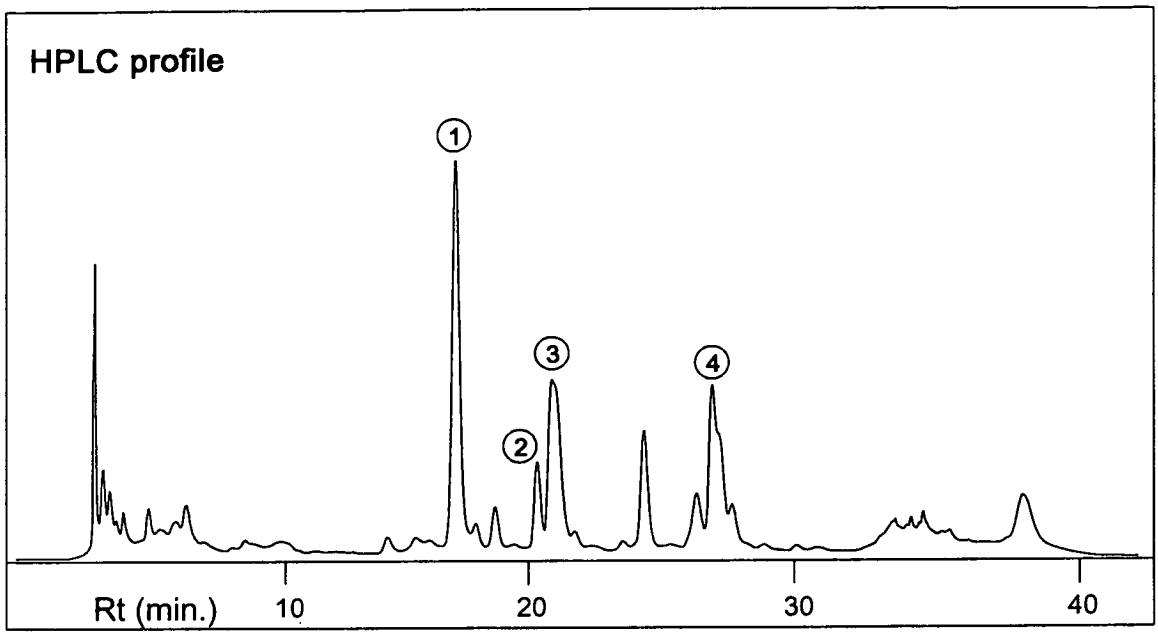
  The leaf exudate was investigated:

  - RBG, Kew 1975-4506
  - NBI 10221

Distribution



Aloe niebuhriana is found in the south-western corner of the Arabian Peninsula.



Peak number	Retention time	Compound	Percentage
1	17.0	unidentified flavone 1	23
2	20.1	unidentified flavone 2	4
3	21.4	unidentified flavone 3	12
4	26.2	unidentified flavone 4	10

Peak 1 displays an UV absorbance spectrum identical to that of isovitexin. Like all the other representatives of the *Leptoaloe* and *Graminialoe* this species only contains flavones.

- Taxonomic position:

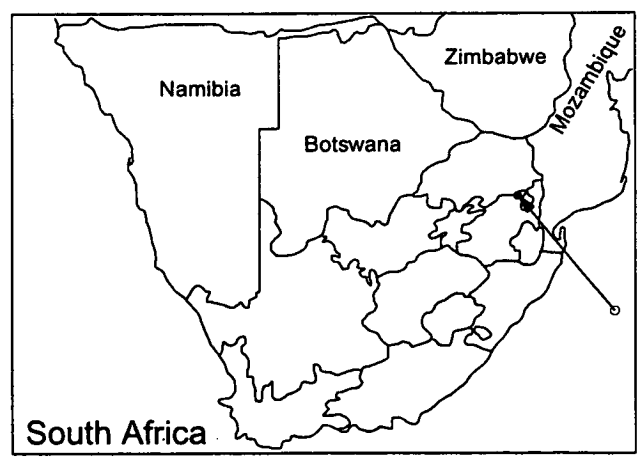
  Aloe section *Leptoaloe* (Reynolds, 1950).

- Samples analysed:

  The leaf extract was investigated:

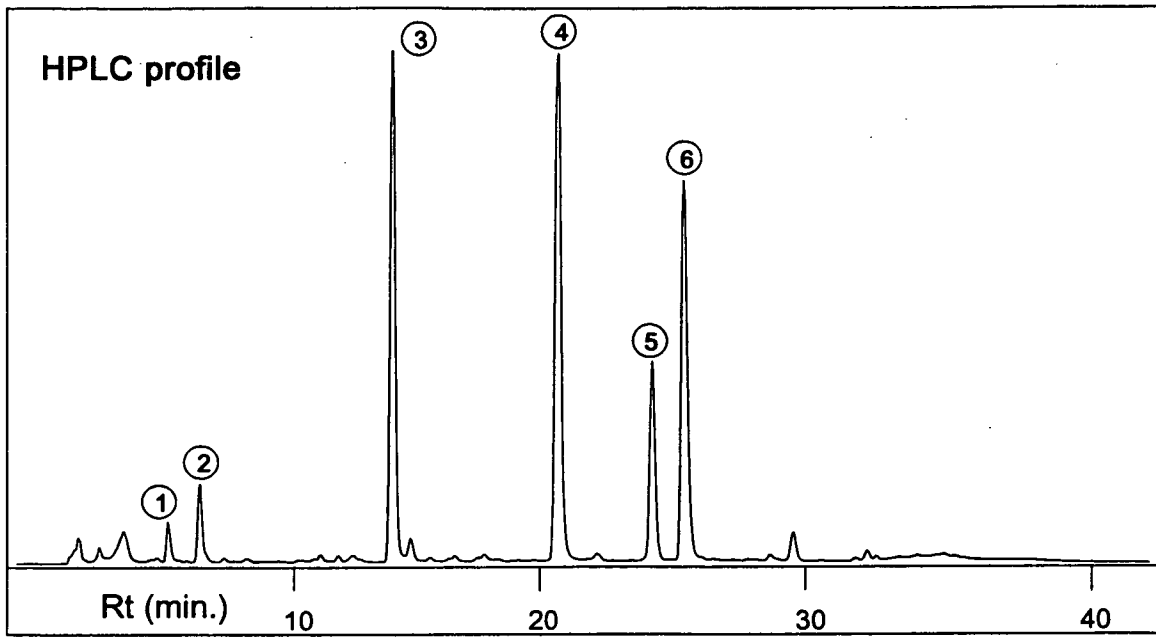
  - sample collected at God's Window (Mpumalanga)

Distribution



Aloe nubigena is restricted to the eastern precipe faces of the Drakensberg. It is abundant in and around Graskop (Mpumalanga).

Aloe nyeriensis Christian ex I. Verdoorn



Peak number	Retention time	Compound	Percentage
1	5.72	aloesin	2
2	6.91	7-*O*-methylaloesin	4
3	14.22	aloenin	25
4	20.53	aloeresin D	31
5	24.14	aloin B and unidentified chromone	11
6	25.31	aloin A	22

An unidentified chromone, probably relates to the coumaric acid esters of aloesin co-elutes with aloin B. Various populations of this species was sampled in Kenya and little variation in leaf exudate composition was found between and with populations.

- Taxonomic position:

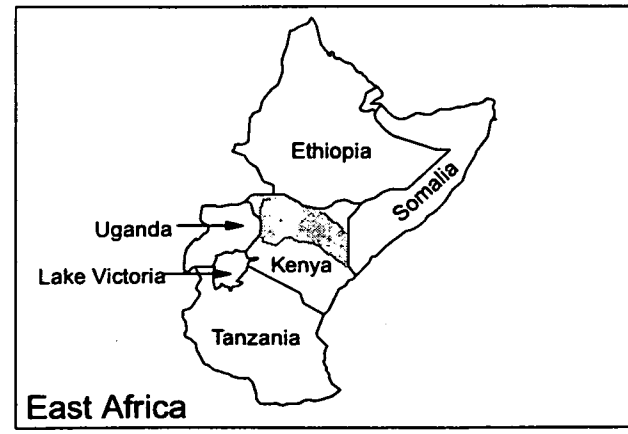
Group 19 of the tropical aloes (Reynolds, 1966).

- Samples analysed:

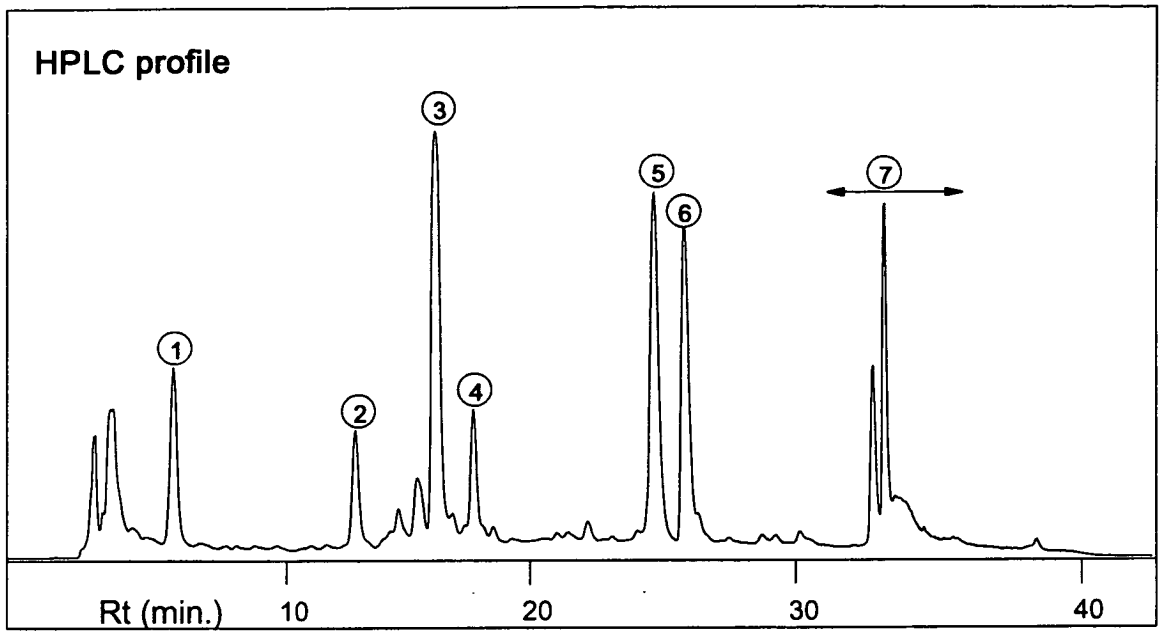
The leaf exudate was investigated:

- material collected near Nanyuki (Kenya)
- material collected near Rhumuruti (Kenya)
- ex hort RBG, Kew

Distribution



This species is widely distributed in the northern parts of Kenya where it is usually found in open bushland.



Peak number	Retention time	Compound	Percentage
1	6.35	aloesin	6
2	13.24	unidentified compound	4
3	16.25	aloeresin A	20
4	17.72	unidentified flavone	5
5	24.44	aloin B	16
6	25.59	aloin A	13
7	33.00	unidentified anthrones	18

This species shows the general pattern for the 'berried aloes' and for most members of series *Macrifoliae*. The series of peaks (7) all show UV spectra resembling that of aloin.

- Taxonomic position:

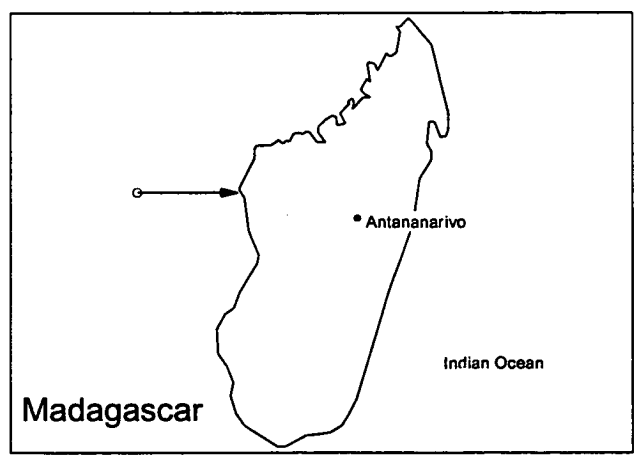
  Aloe section *Lomatophyllum* (Rowley, 1996).

- Samples analysed:

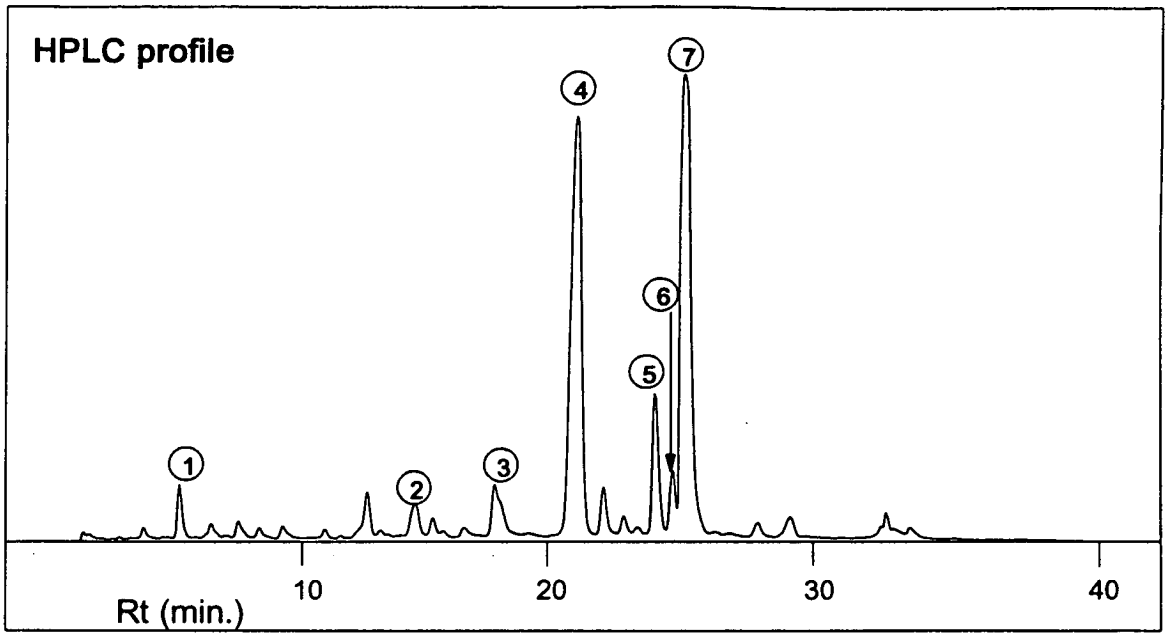
  The leaf exudate was investigated:

  - NBI 10853

Distribution



Aloe occidentale grows along the western coast of Madagascar.



Peak number	Retention time	Compound	Percentage
1	5.81	aloesin	2
2	15.00	8-*O*-methyl-7-hydroxyaloin	2
3	18.09	unidentified compound 1	3
4	21.26	aloeresin D	28
5	24.26	aloin B	6
6	24.94	unidentified compound 2	3
7	25.35	aloin A	36

The unidentified compound (peak 3), displays a UV absorbance spectrum resembling that of the dihydroisocoumaringlucoside.

- Taxonomic position:

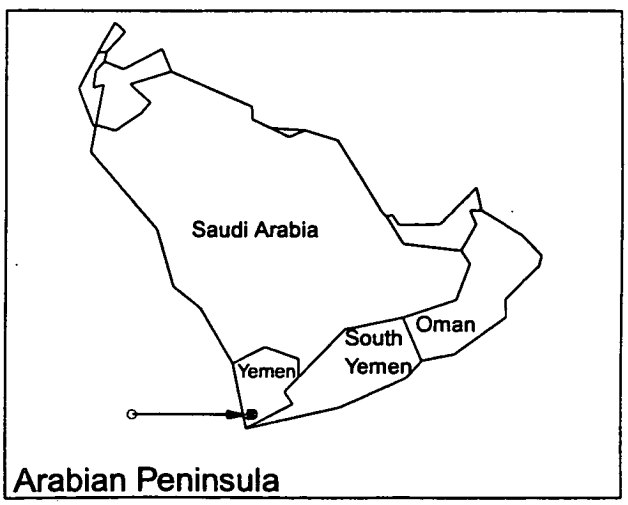
  Group 9 of the tropical aloes (Reynolds, 1966).

- Samples analysed:

  The leaf exudate was investigated:

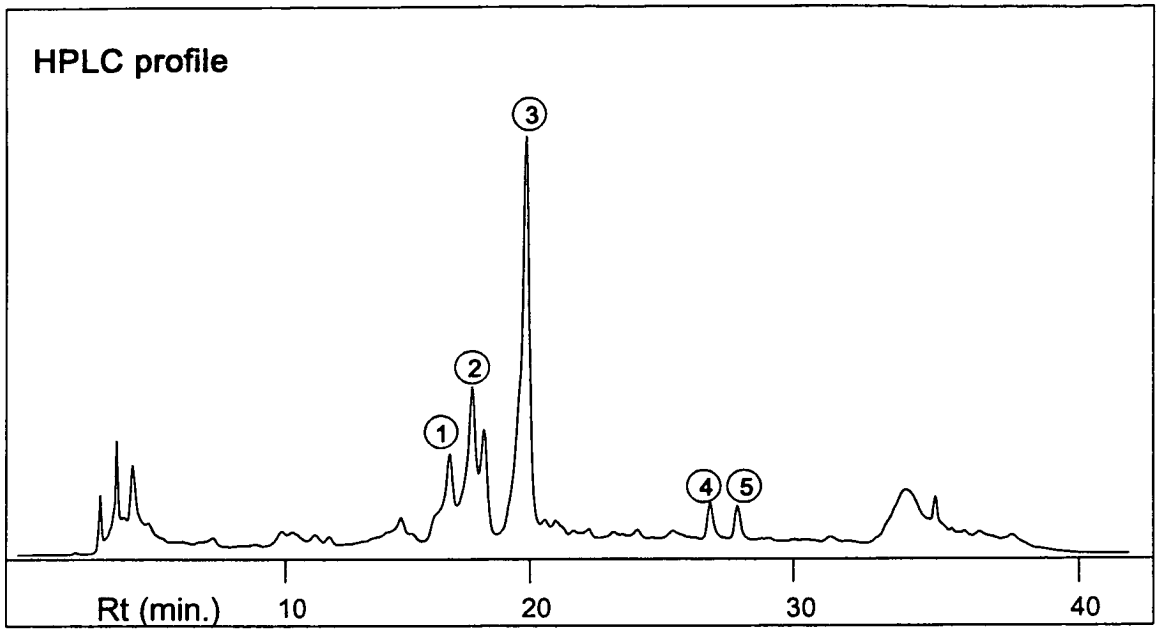
  - RBG, Kew 206-84-01590

Distribution



This species is known from the foot hills of Badjil and Jebel Buru in the Yemen.

Aloe orientalis (H. Perrier) L. E. Newton & G. D. Rowley



Peak number	Retention time	Compound	Percentage
1	16.51	unidentified compound 1	2
2	17.73	unidentified compound 2	8
3	19.80	unidentified flavone	33
4	26.95	aloin B	2
5	28.00	aloin A	2

(See *A. aldabrensis* & *A. occidentalis*).

- Taxonomic position:

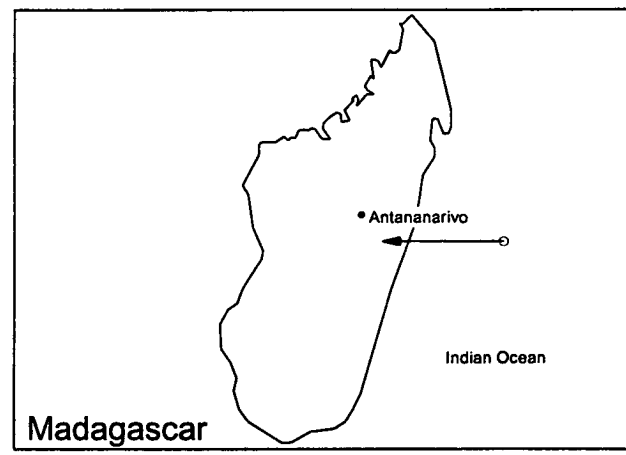
  Aloe section *Lomatophyllum* (Rowley, 1996).

- Samples analysed:

  The leaf exudate was investigated:

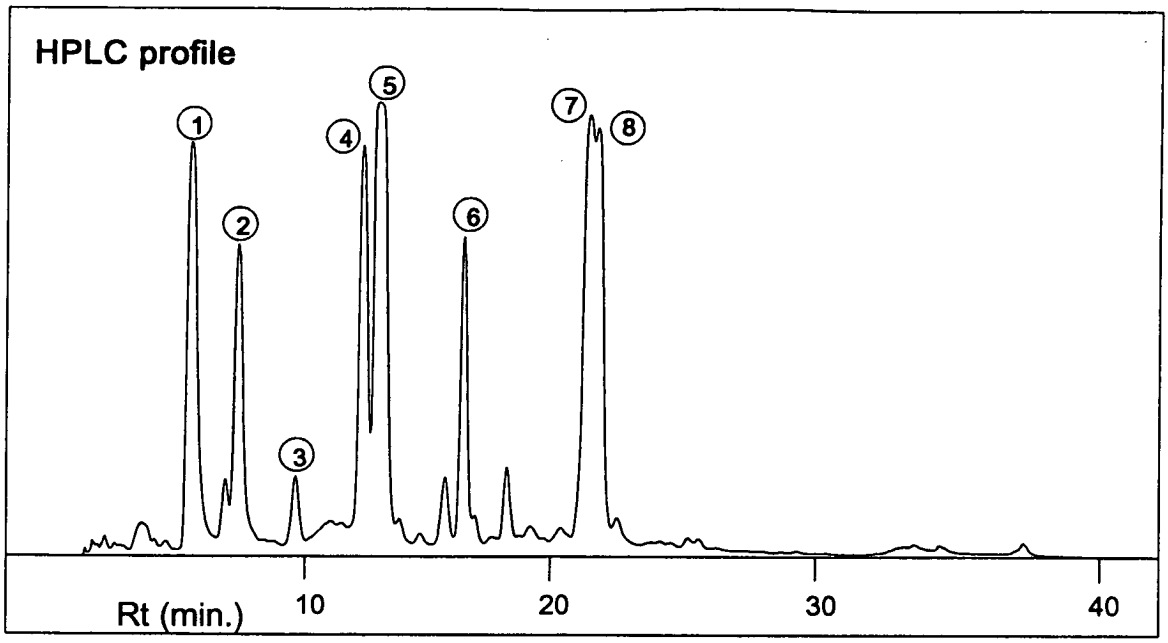
  - NBI 19481

Distribution



Aloe orientalis is distributed on the eastern part or Madagascar.

Aloe orthlopha Christian & Milne-Redhead



Peak number	Retention time	Compound	Percentage
1	6.22	aloesin	14
2	8.04	7-*O*-methylaloesin	9
3	10.26	unidentified chromone 1	2
4	12.89	unidentified chromone 2	11
5	13.53	unidentified chromone 3	19
6	17.34	unidentified chromone 4	7
7	21.71	unidentified chromone 5	15
8	21.90	unidentified chromone 6	12

The leaf exudate of *Aloe orthlopha* is characterised by a series of unidentified chromones and the total absence of anthrones. Judging by UV absorbance these chromones are coumaric acid esters of aloesin. The sample from BSM differed in chromone composition, but was also devoid of any anthrones.

- Taxonomic position:

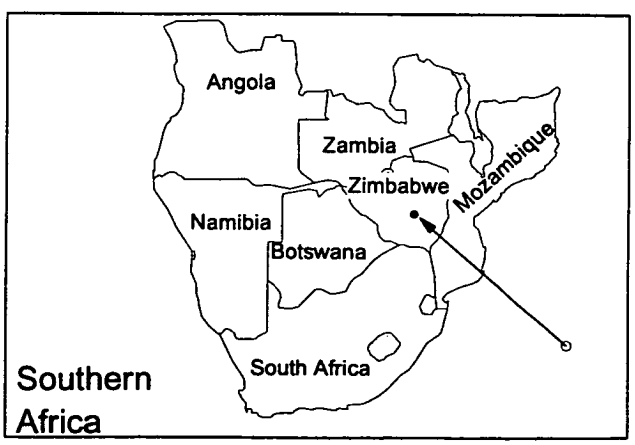
  Group 14 of the tropical aloes (Reynolds, 1966).

- Samples analysed:

  The leaf exudate was investigated:

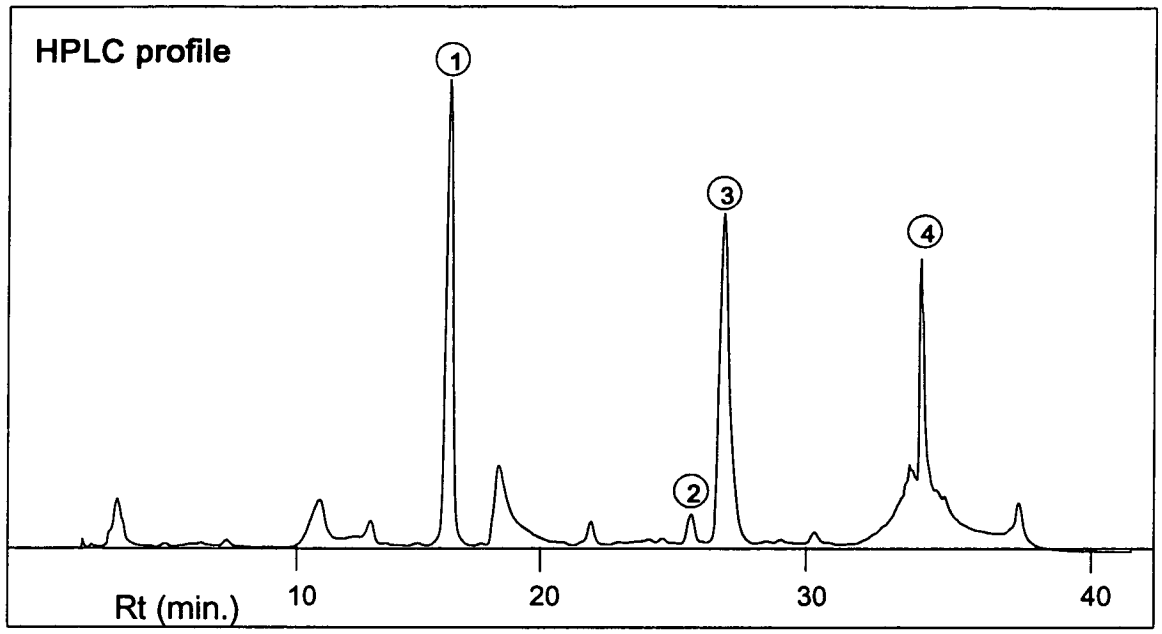
  - A. Ellert 45
  - ex hort BSM

Distribution



Aloe orthlopha is common along the Mtoroshanga Pass NW of Harare in Zimbabwe.

Aloe otallensis Baker



Peak number	Retention time	Compound	Percentage
1	16.56	plicataloside	25
2	25.95	unidentified anthrone	2
3	27.22	unidentified compound 2	26
4	34.43	unidentified compound 3	10

The unidentified compound (peak 2), displays an UV absorbance spectrum identical to aloin A and B. When present, plicataloside usually occurs as the only compound. The unidentified compounds do not relate to any of the known classes of compounds screened for in this survey.

- Taxonomic position:

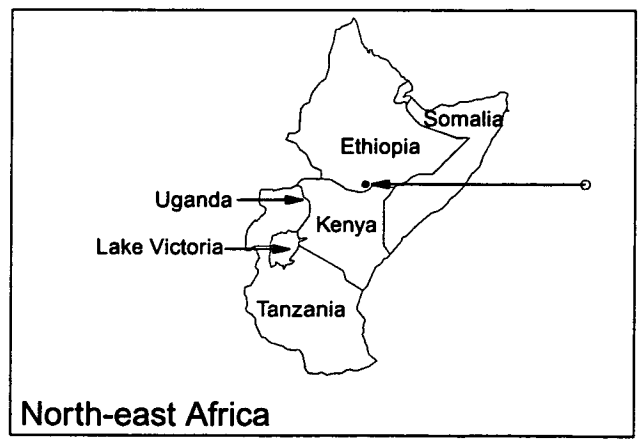
  Group 9 of the tropical aloes (Reynolds, 1966).

- Samples analysed:

  The leaf exudate was investigated:

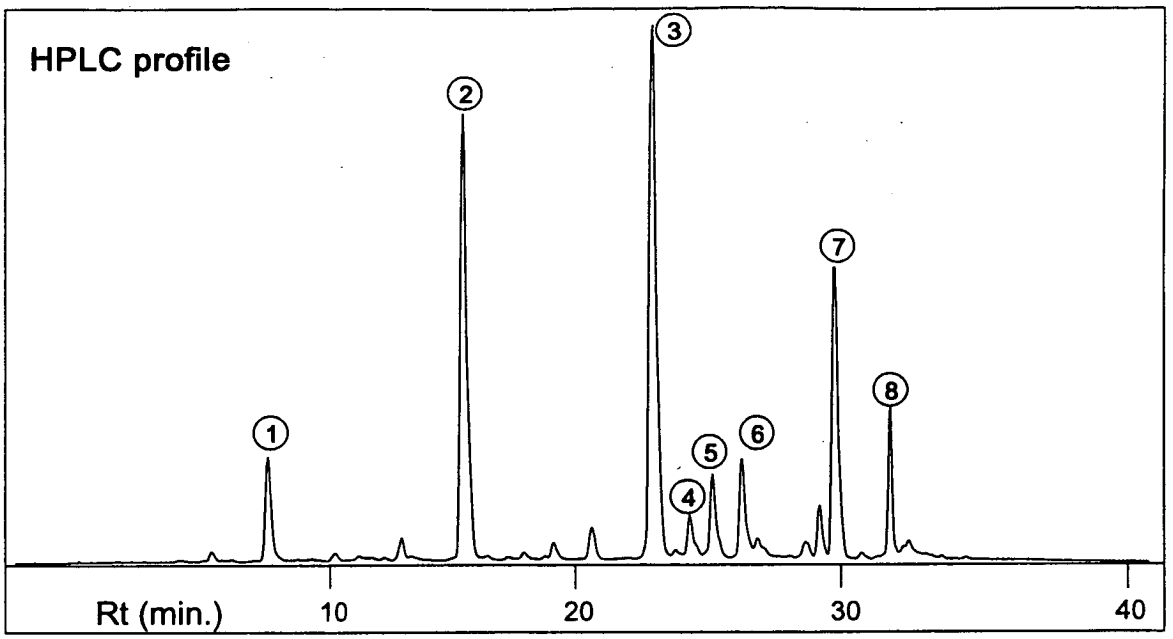
  - RBG, Kew 194-09-01294l

Distribution



This species is only known from its type locality which is Ahele Bekaka in the southern part of Ethiopia.

Aloe pachygaster Dinter



Peak number	Retention time	Compound	Percentage
1	7.6	7-*O*-methylaloesin	5
2	15.1	10-hydroxyaloin B	23
3	22.4	10-hydroxyaloin-6'-mono-acetate B	31
4	24.5	aloin B	2
5	25.6	aloin A	4
6	26.1	unidentified anthrone 1	4
7	29.1	unidentified anthrone 2	14
8	31.2	littoraloin	5

Aloe pachygaster contains the characteristic compounds of species in *Aloe* sect. *Asperifoliae*; 10-hydroxyaloin B together with a various other anthrones. (see *A. claviflora*)

- Taxonomic position:

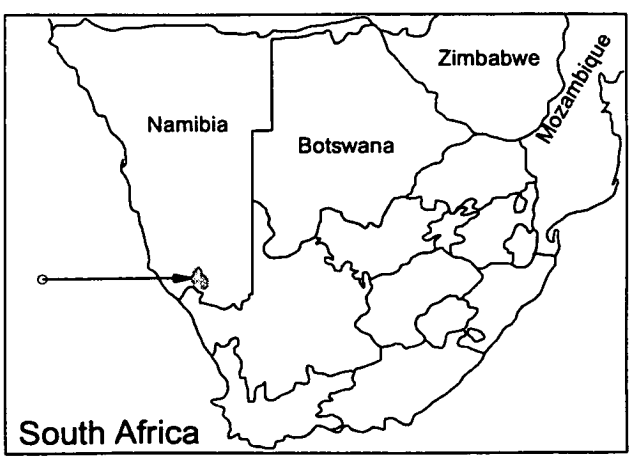
  Aloe series *Asperifoliae* (Giess, 1974).

- Samples analysed:

  The leaf exudate was investigated:

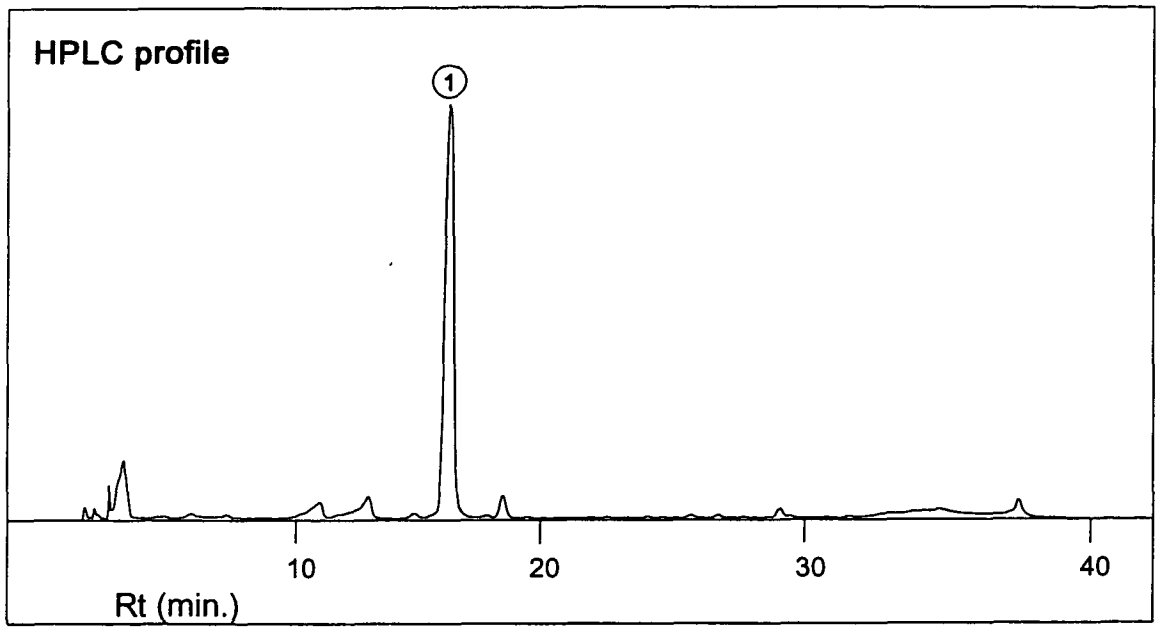
  - ex hort JBG
  - NBI 1120/70

Distribution



Aloe pachygaster is usually associated with dolomite and lime stone soils and is restricted to the Luderitz and Bethanian Districts of Namibia.

Aloe palmiformis Baker



Peak number	Retention time	Compound	Percentage
1	16.60	plicataloside	82

- Taxonomic position:

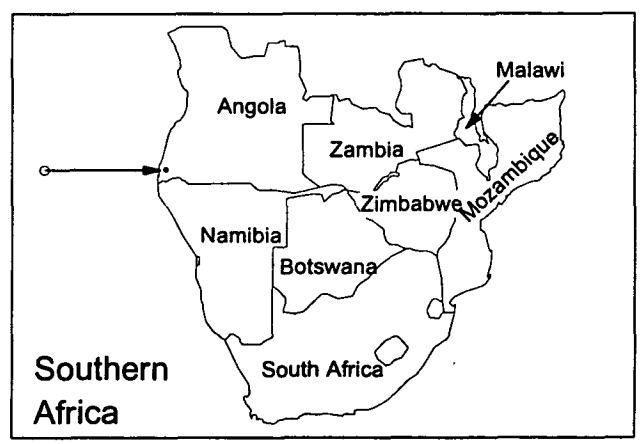
  Group 19 of the tropical aloes (Reynolds, 1966).

- Samples analysed:

  The leaf exudate was investigated:

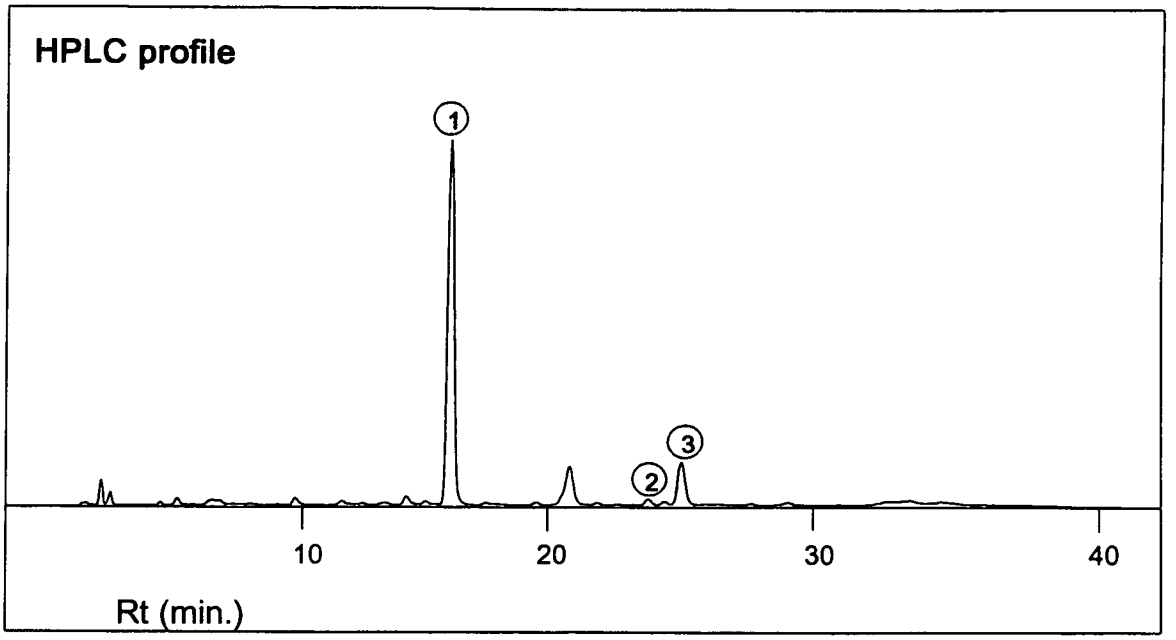
  - RBG, Kew 224-94-020-95

Distribution



Aloe palmiformis is common in the Huila District of Angola.

Aloe parvidens M. G. Gilbert & Sebsebe



Peak number	Retention time	Compound	Percentage
1	16.34	plicataloside	76
2	24.23	aloin B	11
3	25.31	aloin A	10

Two samples of *A. parvidens* were investigated. The sample obtained from the RBG (Kew), also contained plicataloside as the major compound, but high levels of aloesin and unidentified chromones co-occured. It is interesting to note that the LEN sample also had a chemical peculiarity, as the occurence of aloin with plicataloside is an exception rather than the rule.

- Taxonomic position:

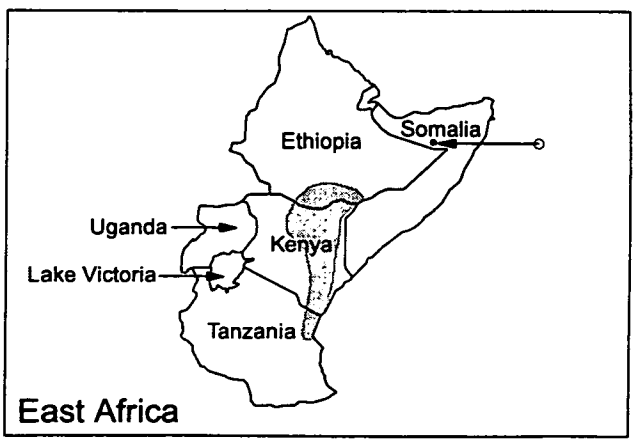
  Unknown (Gilbert & Sebsebe, 1992).

- Samples analysed:

  The leaf exudate was investigated:

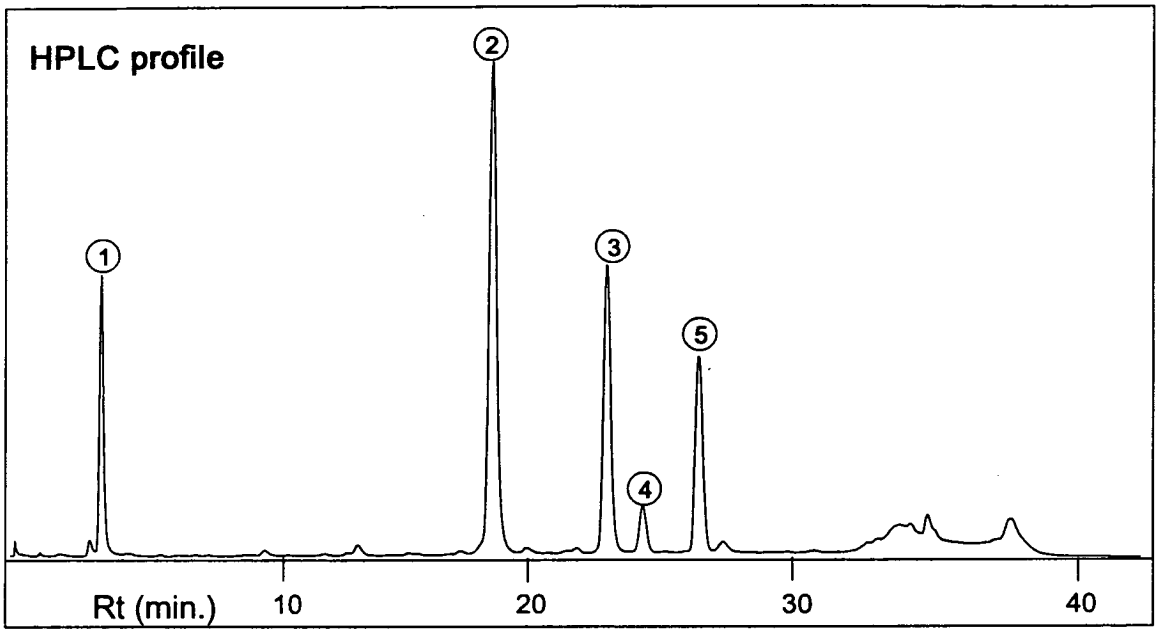
  - L. E. Newton 4384
  - RBG, Kew 1985-4219

Distribution



Aloe parvidens is widely distributed in east Africa where it is usually found on sandy soils. Its distrubution includes parts of Somalia, Kenya, Tanzania and Ethiopia.

Aloe pearsonii Schönland



Peak number	Retention time	Compound	Percentage
1	4.89	aloesin	20
2	18.56	aloeresin E	42
3	22.90	aloeresin F	20
4	24.27	homonataloin B	8
5	26.40	homonataloin A	15

Aloe pearsonii was clearly misplaced in series *Macrifoliae* as it displays the characteristic exudate profile of species in series *Mitriformes*.

- Taxonomic position:

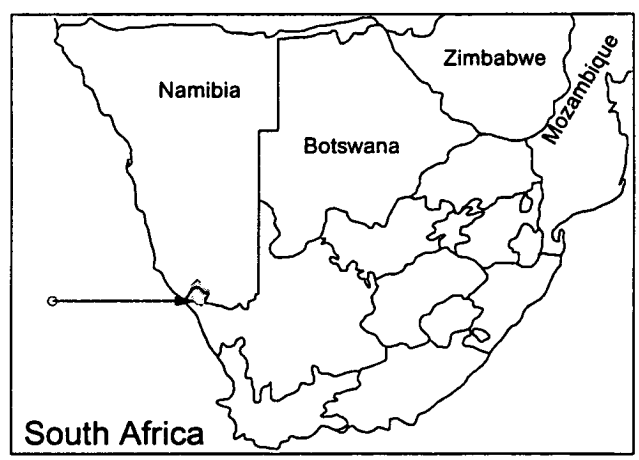
  Aloe series *Macrifoliae* (Reynolds, 1950).

- Samples analysed:

  The leaf exudate was investigated:

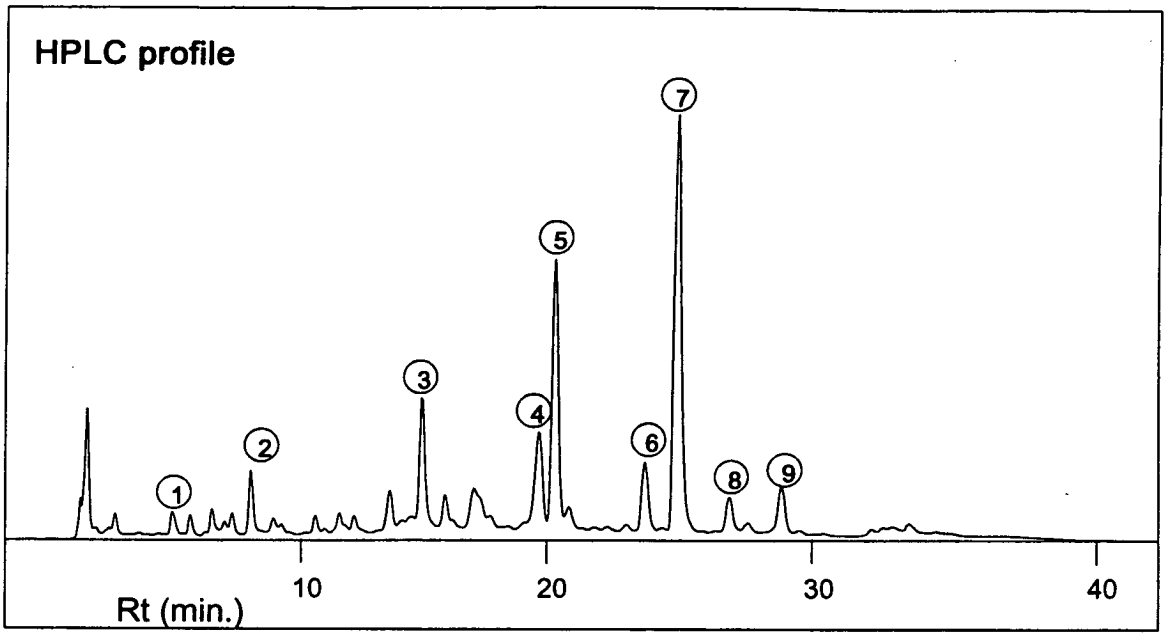
  - Helskloof
  - NBI 29382

Distribution



This species tolerates the most arid conditions in Southern Africa. It is found in the 'great bulge' of the Orange River and extends northwards to Witputs.

Aloe peckii P.R.O. Bally & I. Verdoorn



Peak number	Retention time	Compound	Percentage
1	5.58	aloesin	tr
2	8.59	unidentified compound 1	3
3	15.20	dihydroisocoumaringlucoside	8
4	19.81	unidentified compound 2	8
5	20.43	aloeresin D	19
6	23.95	aloin B	5
7	25.20	aloin A	35
8	27.25	aloinoside B	3
9	29.25	aloinoside A	4

- Taxonomic position:

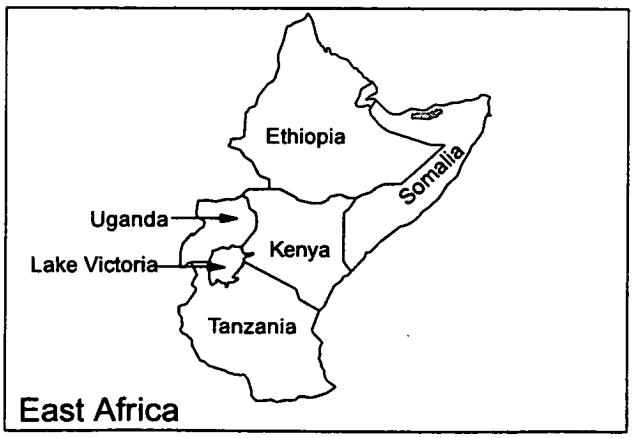
Group 4 of the tropical aloes (Reynolds, 1966).

- Samples analysed:

The leaf exudate was investigated:

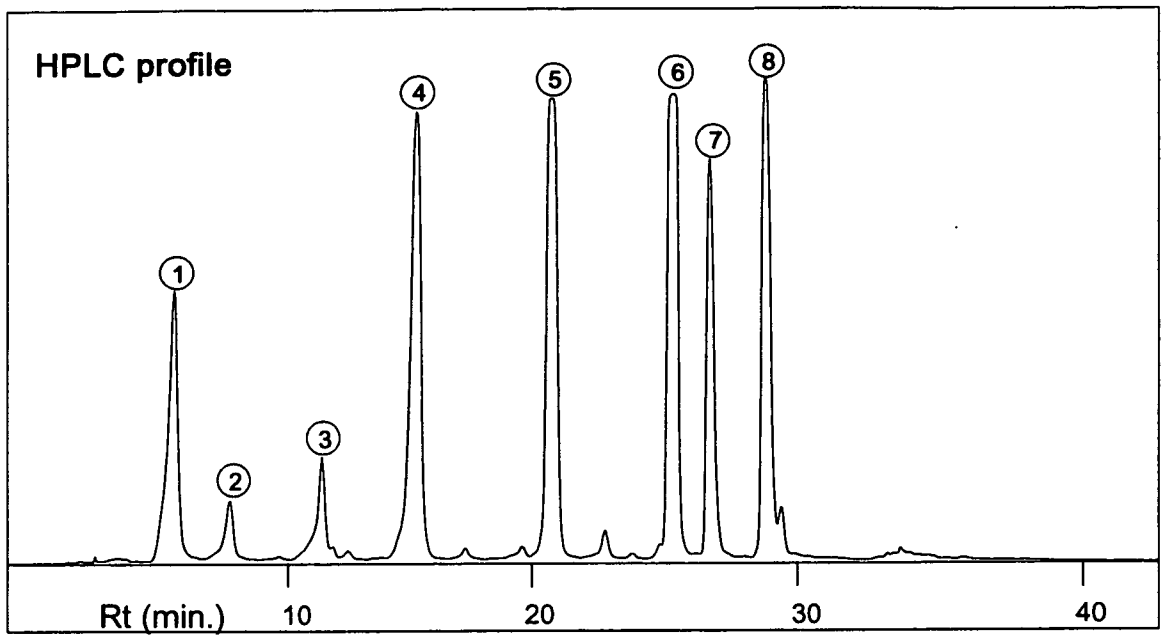
- RBG, Kew 084-81-011-40
- ex hort JBG
- ex hort D. Hardy

Distribution



Aloe peckii is distributed in the northern parts of Somalia especially in the Ahl Mountains.

Aloe peglerae Schönland



Peak number	Retention time	Compound	Percentage
1	6.72	aloesin	10
2	8.36	7-*O*-methylaloesin	2
3	11.85	unidentified chromone	4
4	15.44	aloeresin A	17
5	20.53	aloeresin E	18
6	25.06	aloeresin F	19
7	26.38	homonataloin B	11
8	28.46	homonataloin A	15

Aloe peglerae is the species from which aloeresin E and F was isolated and characterised. The chromatographic pattern displayed above is characteristic of all the species in the *Mitriformes*-group.
(See *A. mitriformis*, *A. angelica*, *A. yavellana*)

- Taxonomic position:

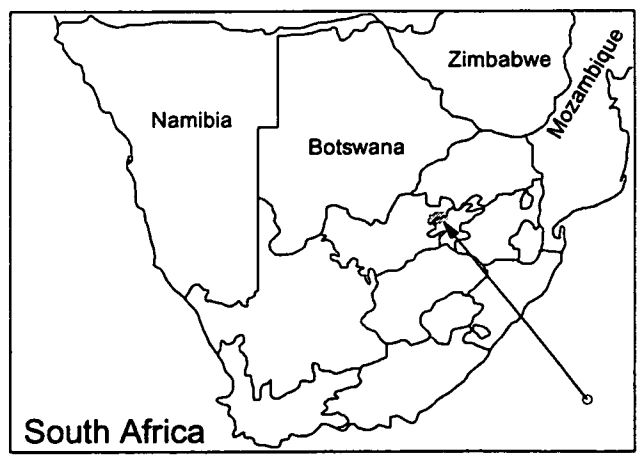
  Aloe series *Longistylae* (Reynolds, 1950).

- Samples analysed:

  The leaf exudate was investigated:

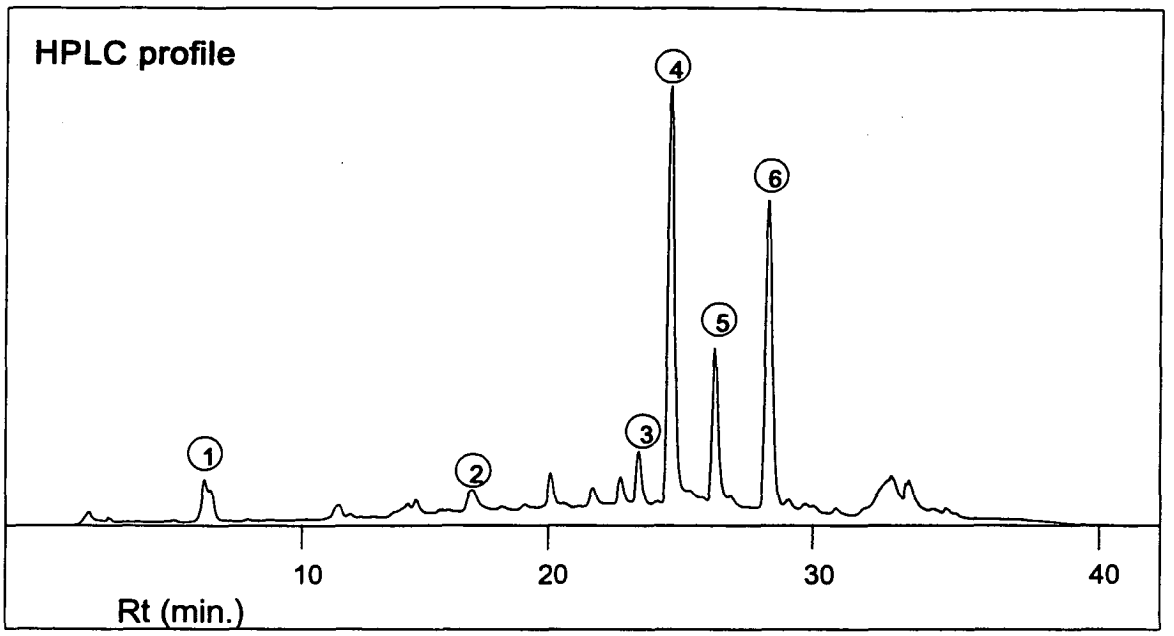
  - Kingskloof
  - Scheerpoort (3 samples)

Distribution



Aloe peglerae is localised in the Magaliesberg in the Gauteng and North West Provinces of South Africa.

Aloe penduliflora Baker



Peak number	Retention time	Compound	Percentage
1	6.79	7-*O*-methylaloesin	1
2	15.53	dihyroisocoumaringlucoside	tr
3	23.67	aloin B	4
4	24.87	aloin A	35
5	26.60	aloinoside B	12
6	28.65	aloinoside A	29

The sample collected at RBG Kew contained aloeresin D in addition to the compounds above.

- Taxonomic position:

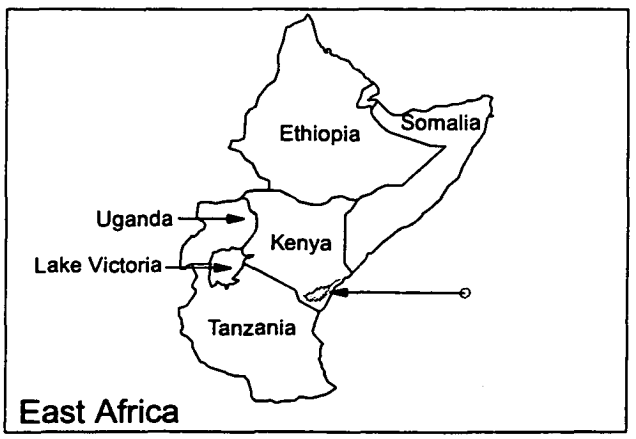
Group 19 of the tropical aloes (Newton, 1991).

- Samples analysed:

The leaf exudate was investigated:

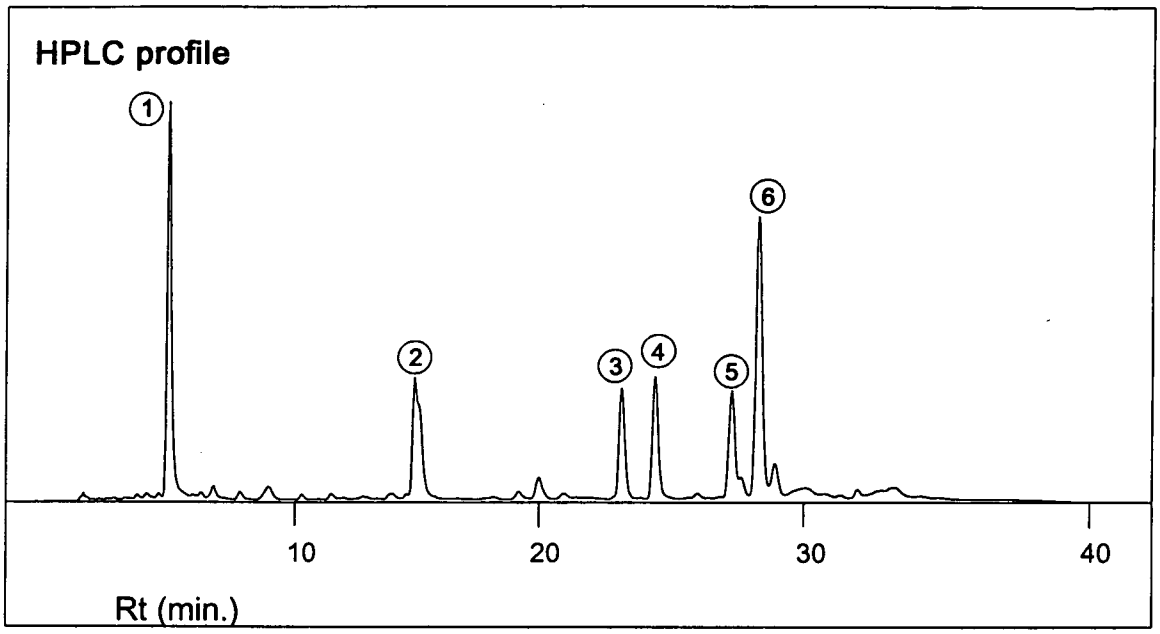
- L. E. Newton 3543
- RBG, Kew 349-63-34907

Distribution



Aloe penduliflora is found on rocky clearings in the forest at Mount Kasigau in the Taita District of Kenya.

Aloe percrassa Todaro



Peak number	Retention time	Compound	Percentage
1	5.54	aloesin	24
2	15.25	7-hydroxyaloin	9
3	23.31	aloin B	9
4	24.63	aloin A	10
5	27.59	unidentified chromone 1	9
6	28.64	unidentified chromone 2	29

Several samples of *A. percrassa* were investigated. The anthrone 7-hydroxyaloin occurred in all the species investigated. The first two samples contained the late eluting unidentified chromones which are probably cinnamoyl chromones.
Aloe debrana which has been placed under synonymy with *A. percrassa* contained the same compounds in the leaf exudate.

- Taxonomic position:

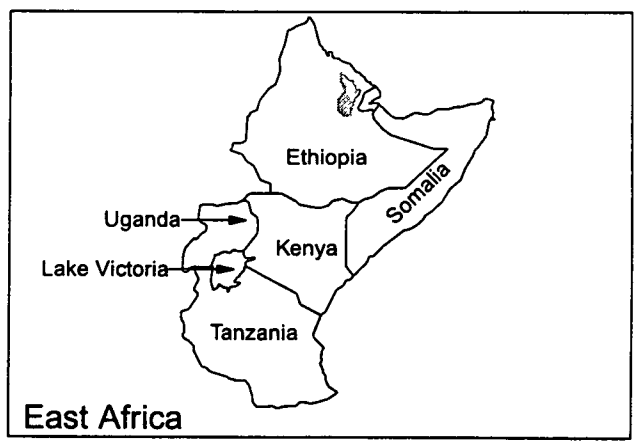
Group 4 of the tropical aloes (Reynolds, 1966).

- Samples analysed:

The leaf exudate was investigated:

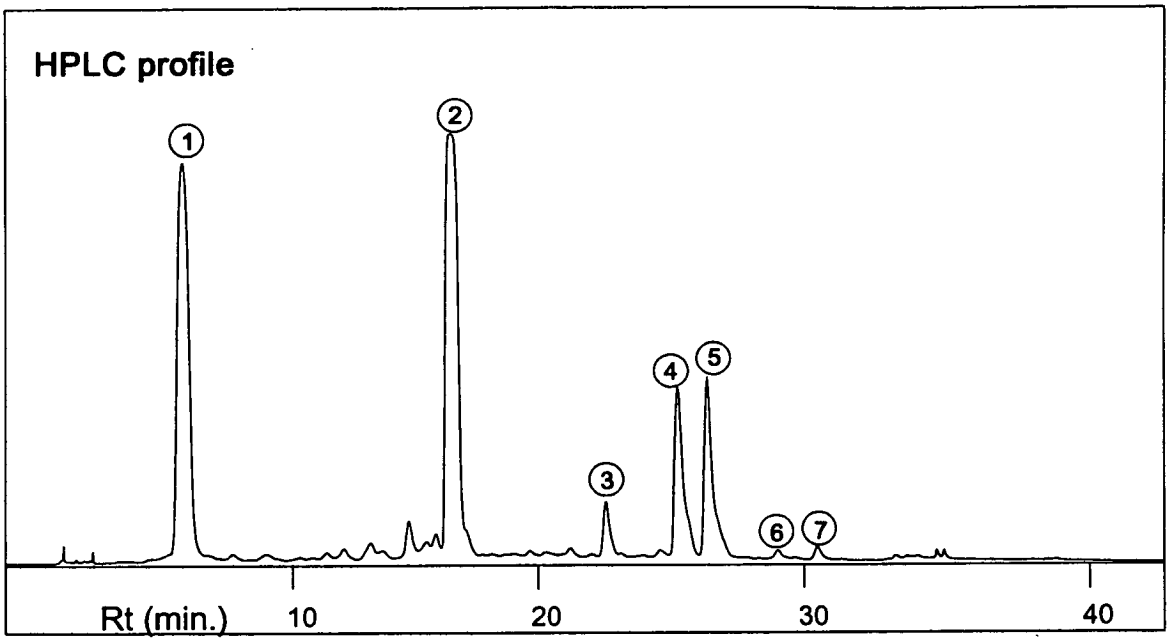
- Sebsebe 4616
- RBG, Kew 368-70-03585
- ex hort JBG
- Sebsebe 206

Distribution



Aloe percrassa is common in the north-eastern parts of Ethiopia.

Aloe petricola Pole-Evans



Peak number	Retention time	Compound	Percentage
1	6.49	aloesin	32
2	16.49	aloeresin A	35
3	22.28	unidentified compound	3
4	24.92	aloin B	10
5	26.01	aloin A	11
6	28.65	unidentified anthrone 1	tr
7	30.14	unidentified anthrone 2	1

The two late eluting anthrones (peaks 6 & 7) were also found to be present in equally low concentrations in *A. aculeata* and in *A. gerstneri*.

- Taxonomic position:

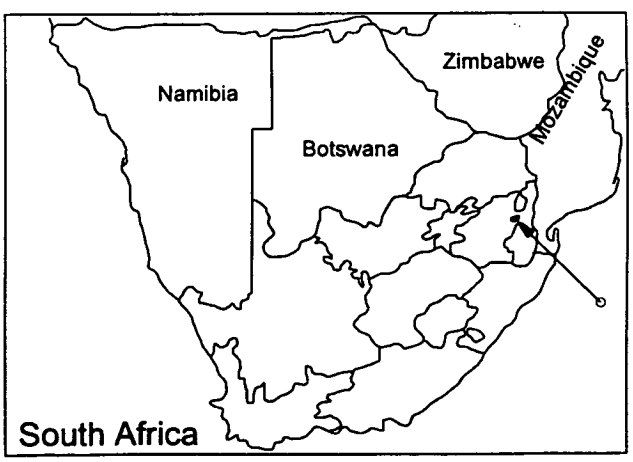
  Aloe section *Pachydendron* (Reynolds, 1950)

- Samples analysed:

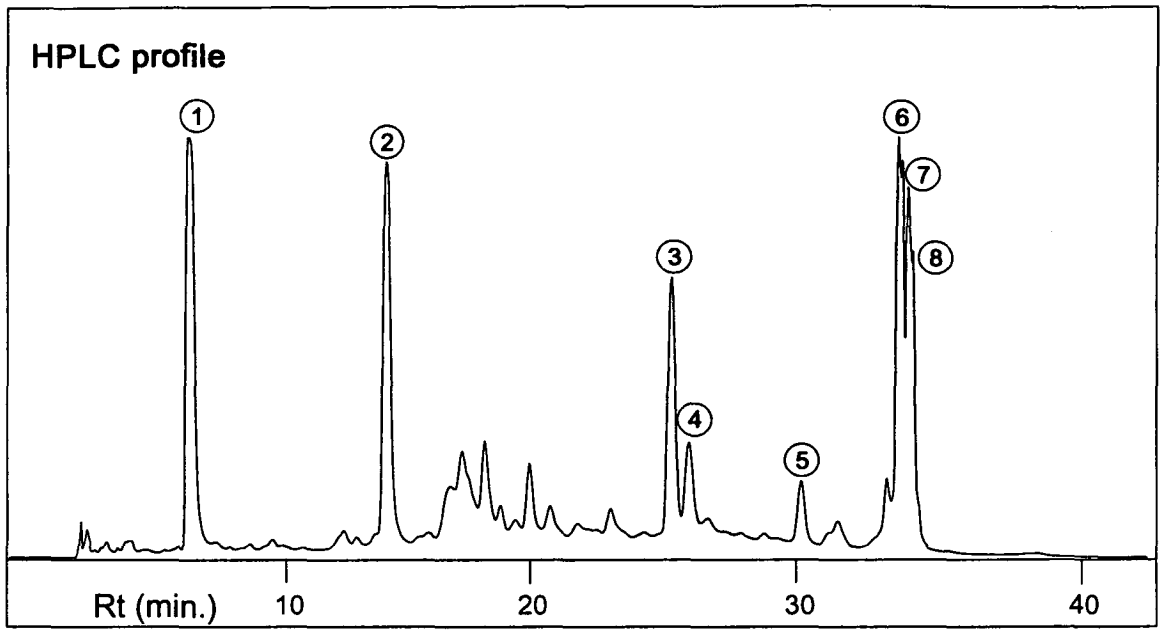
  The leaf exudate was investigated:

  - NBI 26458

Distribution



Aloe petricola is found near Nelspruit in the Mpumalanga Province of South Africa.



Peak number	Retention time	Compound	Percentage
1	6.87	aloesin	17
2	14.4	unidentified chromone 1	15
3	25.21	unidentified chromone 2	9
4	26.56	unidentified chromone 3	1
5	30.06	microstigmin	2
6 & 7	33.70	unidentified compound 1 & 2	14
8	34.06	unidentified compound 3	13

The leaf exudate of *A. pictifolia* is characterised by a series of unidentified chromones. Peak 3 and 8 display an UV absorbance spectrum typical of the cinnamoyl chromones, while the UV spectrum of peak 3 compares well to that of the coumaroyl chromones.

- Taxonomic position:

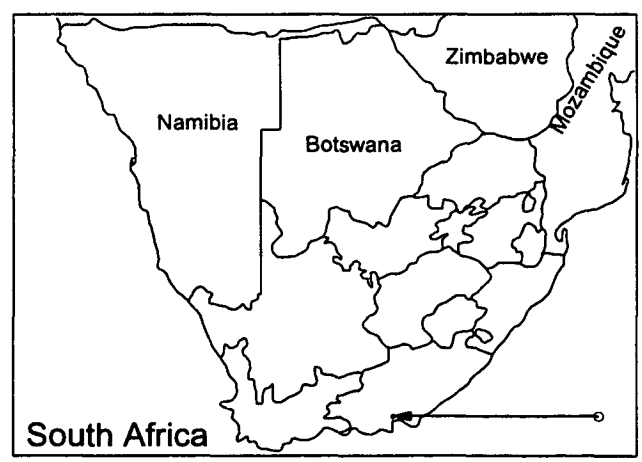
Aloe series *Humiles* (Hardy, 1976), series *Purpurascentes* (Laubscher & Swart, 1977 and van Jaarsveld, 1993).

- Samples analysed:

The leaf exudate was investigated:

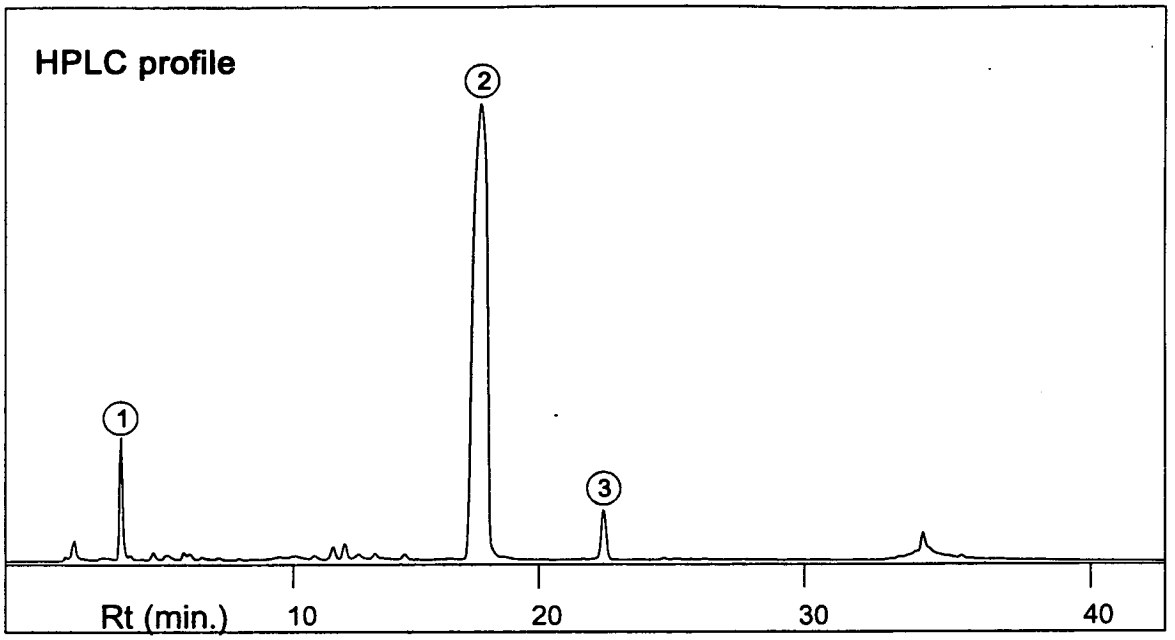
- NBI 3559
- ex hort Hardy (type material)
- ex hort JBG

Distribution



Aloe pictifolia is only known from the type locality which is on steep rocky cliffs north of Humansdorp.

Aloe plicatilis (L.) Miller



Peak number	Retention time	Compound	Percentage
1	4.21	unidentified compound 1	7
2	17.61	plicataloside	82
3	22.15	unidentified compound 2	4

Aloe plicatilis is the species from which the naphthalene compound plicataloside was isolated. This compound is mostly found in species distributed in east Africa. The chromones and anthrones usually associated with aloes are not present in the plicataloside containing species.

- Taxonomic position:

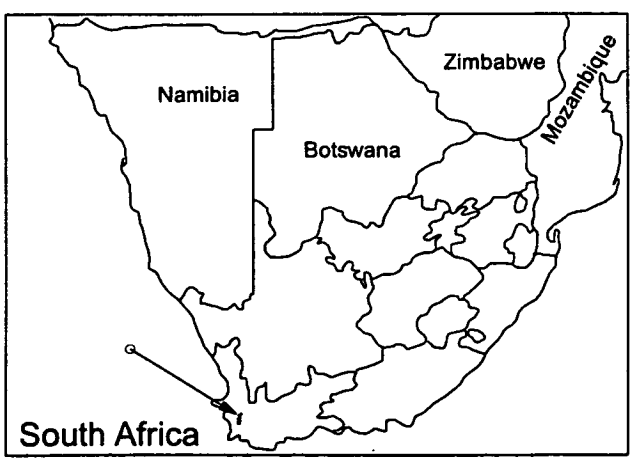
  Aloe section *Kumara* (Reynolds, 1950)

- Samples analysed:

  The leaf exudate was investigated:

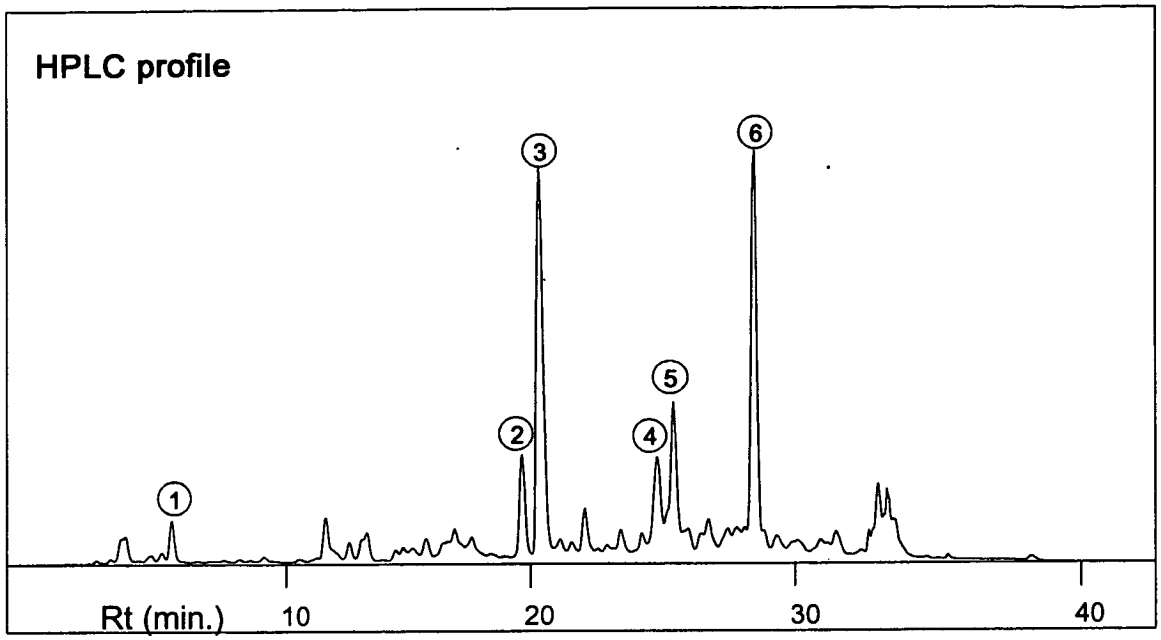
  - NBG 19503

Distribution



This species has a preference for the high rainfall areas of the western Cape mountains. It is distributed from Franschhoek in the south to Elandskloof in the north.

Aloe polyphylla Schönland & Pillans



Peak number	Retention time	Compound	Percentage
1	5.61	aloesin	tr
2	19.49	unidentified anthrone 1	5
3	20.14	unidentified anthrone 2	23
4	24.69	unidentified anthrone 3	6
5	25.29	unidentified anthrone 4	9
6	28.33	unidentified anthrone 5	20

The species is characterised by a series of unidentified anthrones which all show the same UV absorbance spectra typical of nataloin and the 7-hydroxy analoque. The only other species to have a range of these compounds with identical UV absorbance spectra is *Aloe succotrina.*

- Taxonomic position:

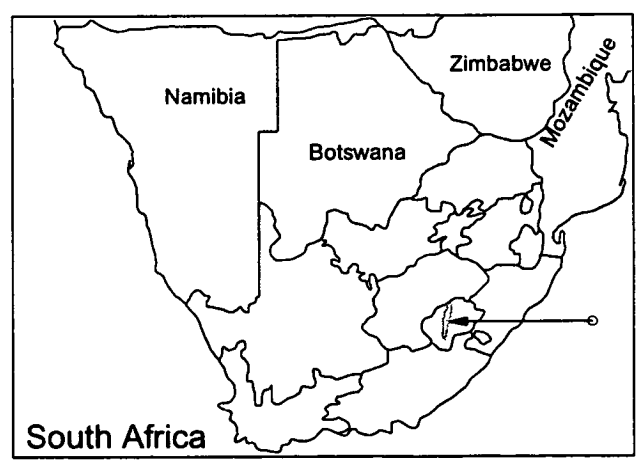
Aloe series *Rhodacanthae* (Reynolds, 1950).

- Samples analysed:

The leaf exudate was investigated:

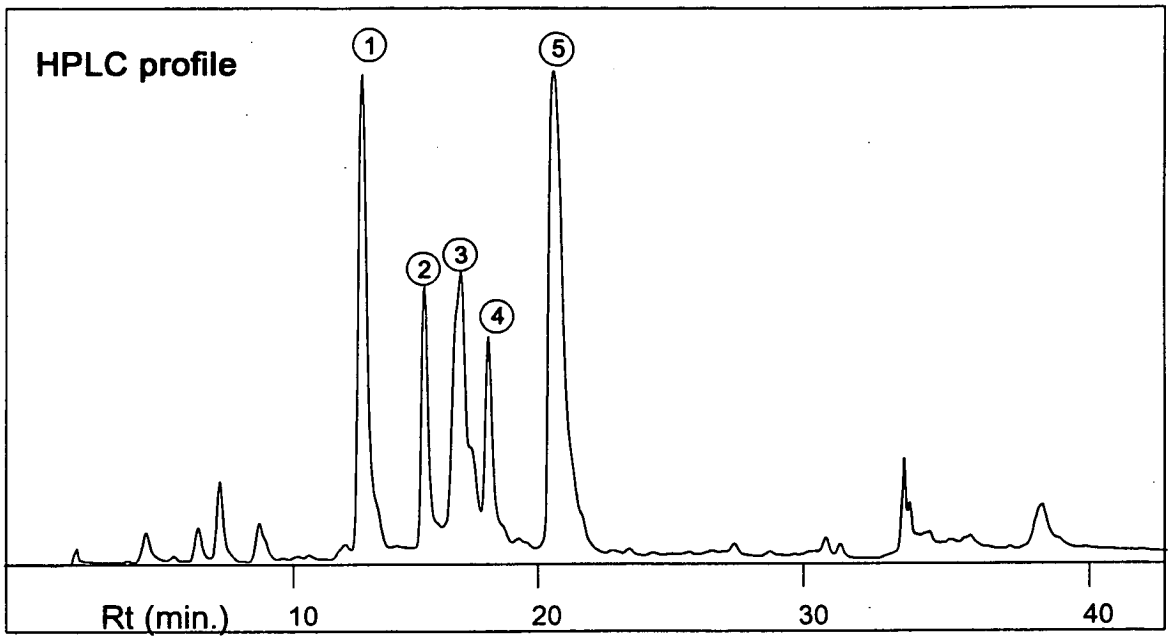
- Likalaneng (Lesotho)
- Molomo (Lesotho)

Distribution



This high altitude species is distributed in a band from the northern to southern parts of Lesotho.

Aloe pratensis Baker



Peak number	Retention time	Compound	Percentage
1	13.17	unidentified flavonoid 1	19
2	15.49	unidentified flavonoid 2	8
3	16.85	unidentified flavonoid 3	15
4	17.87	unidentified flavonoid 4	7
5	20.28	unidentified flavonoid 5	30

Aloe pratensis is one of few flavonoid containing species. This species (see *A. glauca*, *A. lineata*, *A. humilis*) only contains flavanones / dihydroflavonols in the leaf exudate and no anthrones or chromones have been detected.

- Taxonomic position:

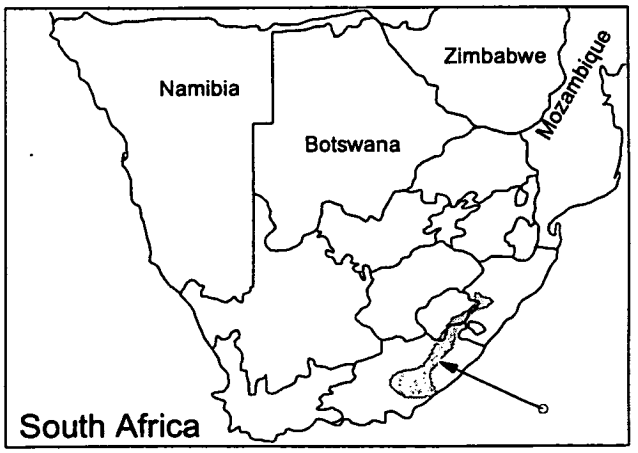
  Aloe series *Rhodacanthae* (Reynolds, 1950).

- Samples analysed:

  The leaf exudate was investigated:

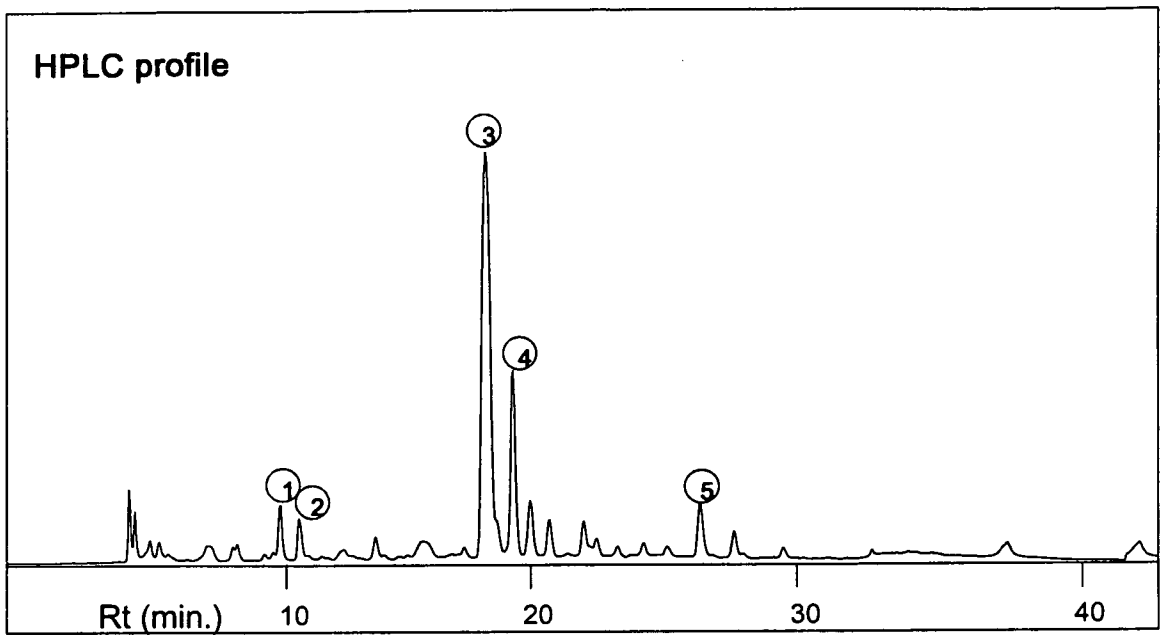
  - ex hort JBG

Distribution



Aloe pratensis occupies various habitats which stretches from Grahamstown in the south to the high altitudes of the Drakensberg in the north.

Aloe pretoriensis Pole-Evans



Peak number	Retention time	Compound	Percentage
1	10.62	unidentified flavonoid 1	3
2	11.35	unidentified flavonoid 2	3
3	18.56	unidentified flavonoid 3	44
4	19.62	unidentified flavonoid 4	12
5	26.82	unidentified flavonoid 5	4

Aloe pretoriensis is one of few aloes which produce complex mixtures of flavonoids (flavanones / dihydroflavanoles) and not the commonly detected anthrones and chromones.

- Taxonomic position:

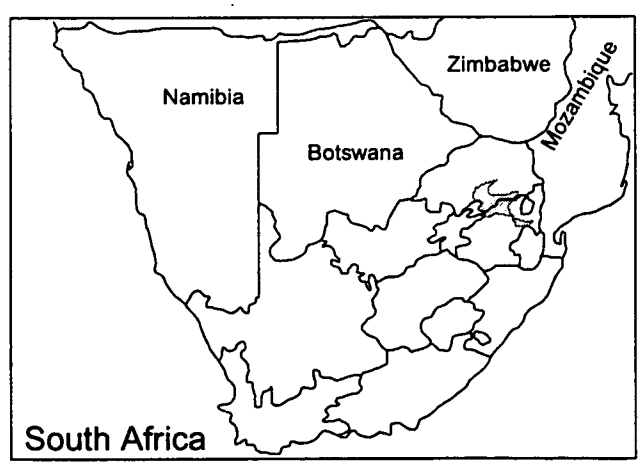
  Aloe series *Superpositae* (Reynolds, 1950).

- Samples analysed:

  The leaf exudate was investigated:

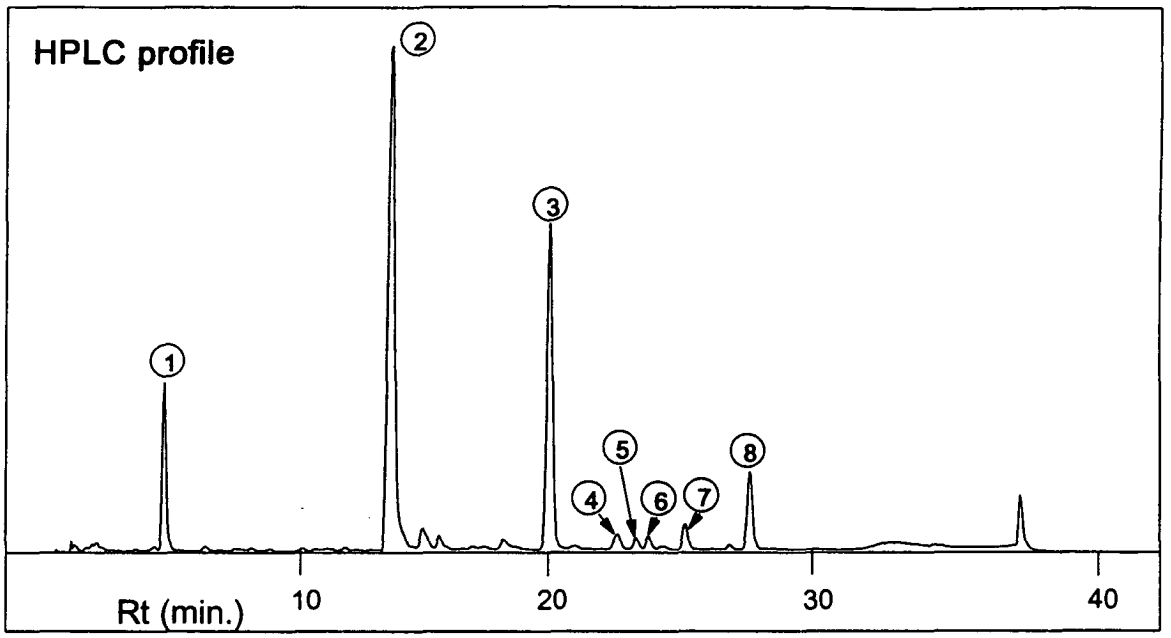
  - Soutpan, Pretoria
  - NBI 2483
  - ex hort NBI (ex Waterberg)

Distribution



Aloe pretoriensis is found in the grasslands in the northern part of South Africa.

Aloe pubescens Reynolds



Peak number	Retention time	Compound	Percentage
1	5.21	aloesin	10
2	14.07	8-*O*-methyl-7-hydroxyaloin	47
3	20.18	aloeresin D	26
4	22.87	aloin B	1
5	23.58	homonataloin B	1
6	24.07	aloin A	1
7	25.49	homonataloin A	2
8	28.02	unidentified chromone	6

This is one of the few aloe species where aloin co-occurs with homonataloin. Both samples showed the same leaf exudate composition. The unidentified chromone (peak 8) has a UV spectrum correlating to the cinnamoyl chromones.

- Taxonomic position:

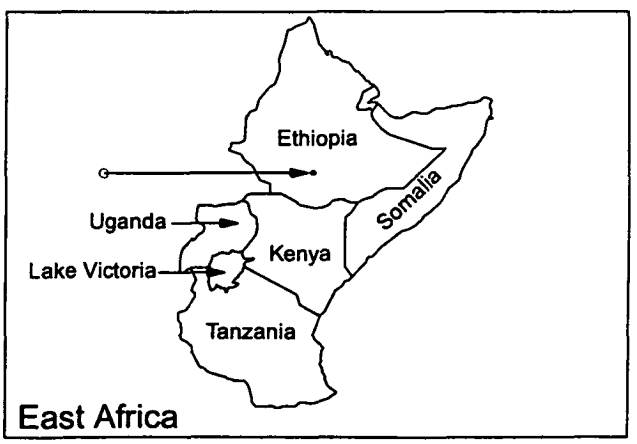
  Group 9 of the tropical aloes (Reynolds, 1966).

- Samples analysed:

  The leaf exudate was investigated:

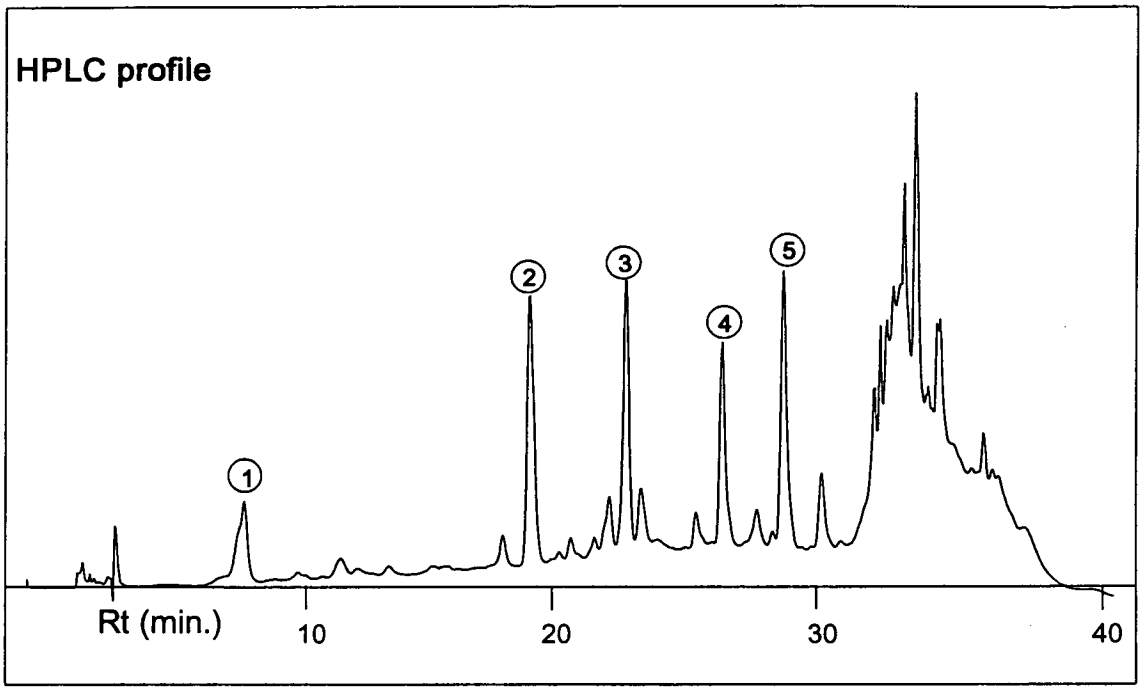
  - Sebsebe 316
  - Kew 439 75 04512

Distribution



Aloe pubescens is found near Shashamanna south of Addis Ababa in Ethiopia.

Aloe pulcherrima M. G. Gilbert & Sebsebe



Peak number	Retention time	Compound	Percentage
1	6.7	tr	tr
2	18.06	7-hydroxyaloin B	14
3	22.13	unidentified compound	16
4	27.81	nataloin B	13
5	29.56	nataloin A	14

This is the species from which nataloin A / B has been isolated (sample from E. Dagne) and has been used as a standard in this study. The phenolics are present at very low concentrations.

- Taxonomic position:

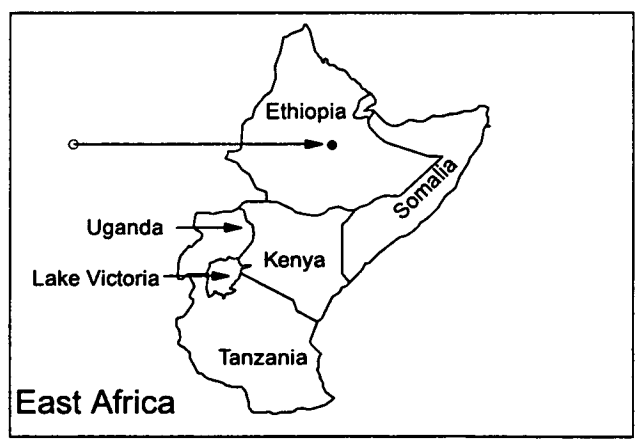
  Allied to *A. steudneri* and *A. ankoberensis* (Gilbert & Sebsebe, 1997).

- Samples analysed:

  The leaf exudate was investigated:

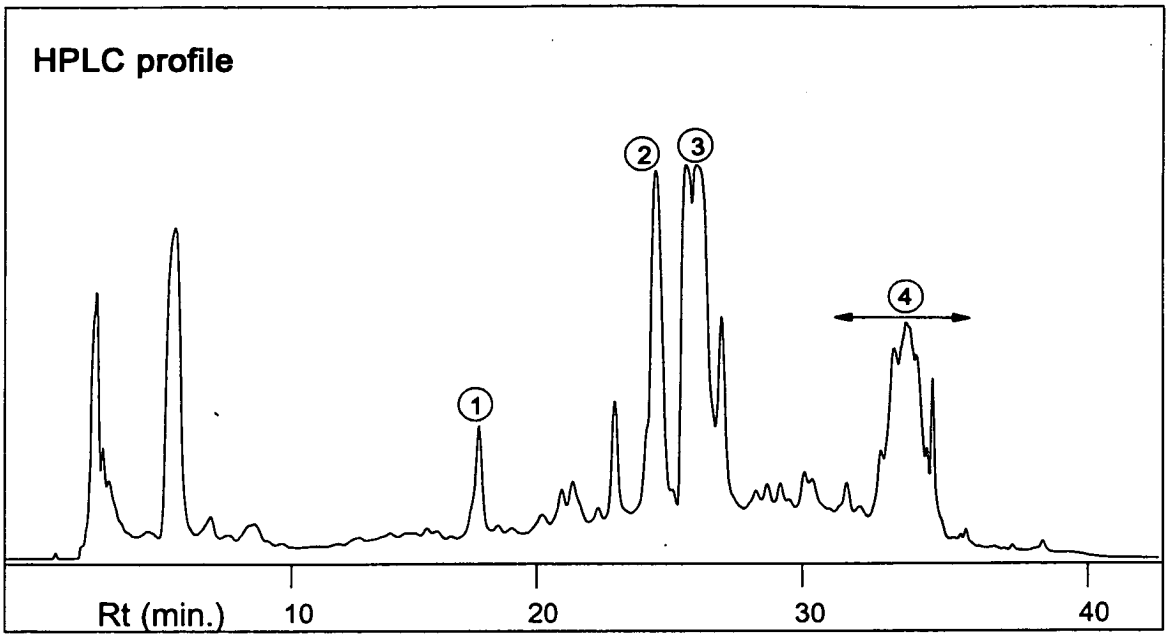
  - Sebsebe 171

Distribution



This species is found on basalt slopes in the Shewa Region of Ethiopia.

Aloe purpurea Lamarck



Peak number	Retention time	Compound	Percentage
1	17.70	unidentified flavone	2
2	24.28	aloin B	13
3	25.80	aloin A	14
4	33.00	unidentified comounds	15

A. purpurea contains high levels of the anthrones aloin A and B. Various compounds were found to co-elute with the two anthrones.

- Taxonomic position:

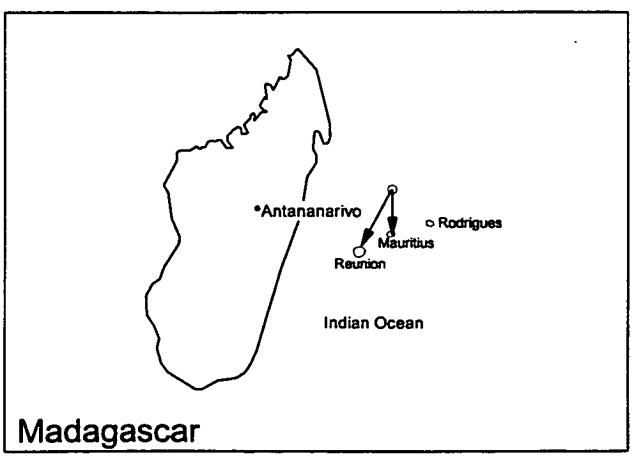
  Aloe section *Lomatophyllum* (Rowley, 1996).

- Samples analysed:

  The leaf extract was investigated:

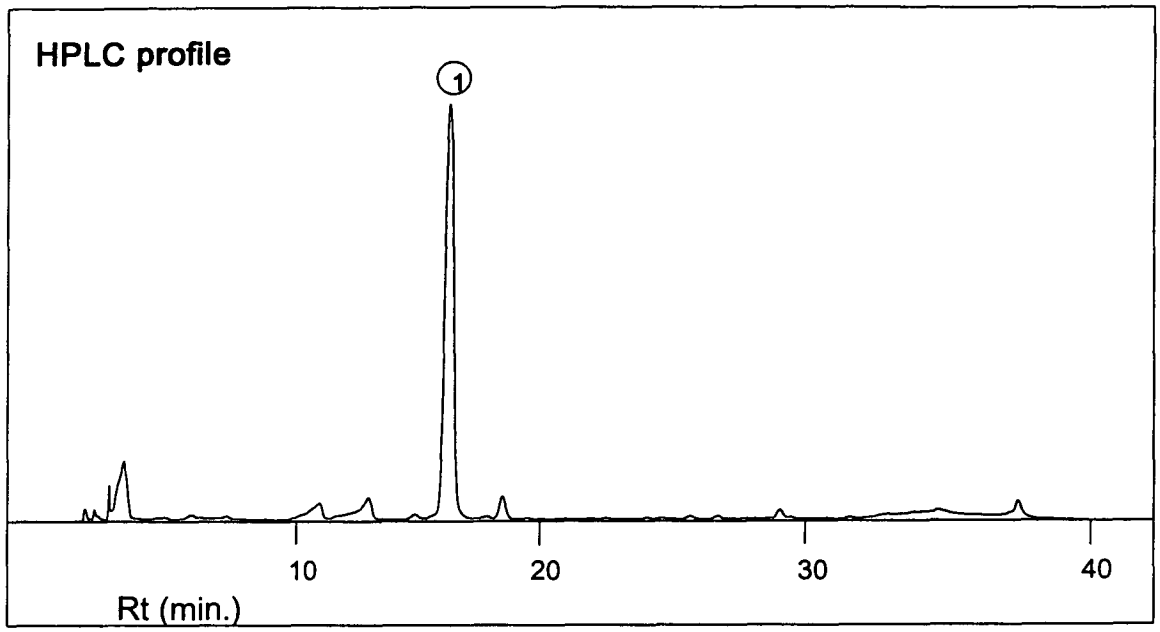
  - NBI 31155

Distribution



Aloe purpurea has been recorded on both the islands of Mauritius and Reunion.

Aloe pustuligemma L.E. Newton



Peak number	Retention time	Compound	Percentage
1	16.60	plicataloside	78

- Taxonomic position:

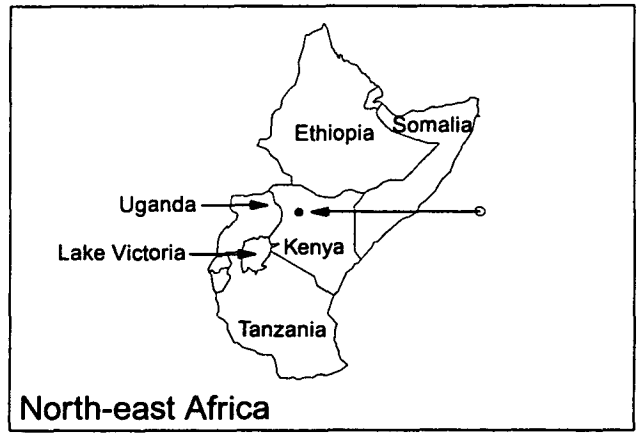
  Allied to *A. tugenensis* and *A. otallensis* (Newton, 1994).

- Samples analysed:

  The leaf exudate was investigated:

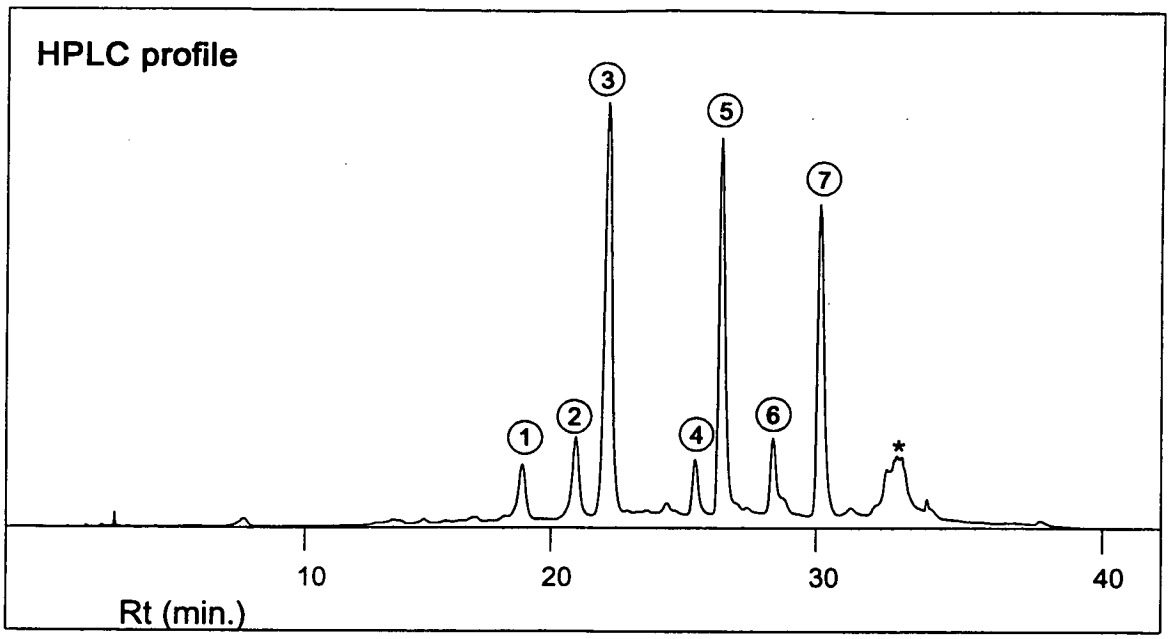
  - L.E. Newton 3739 (type plant)

Distribution



Aloe pustuligemma is only known from the type locality which is the Emurua Akirim Plateau in the Northern Frontier Province of Kenya.

Aloe rabaiensis Rendle



Peak number	Retention time	Compound	Percentage
1	19.11	unidentified chromone 1	4
2	21.18	unidentified chromone 2	6
3	22.40	aloeresin D	28
4	25.82	aloin B	3
5	26.80	aloin A	21
6	28.84	aloinoside B	5
7	30.64	aloinoside A	18

The morphological similarity between *A. rabaiensis* and *A. ngongensis* is supported on the chemical level. The only difference between the two profiles is the quantitative difference in the microdontin fraction. These compounds seem to be present in *A. rabaiensis* but in concentrations below the detection parameters of the HPLC system (*).

Distribution

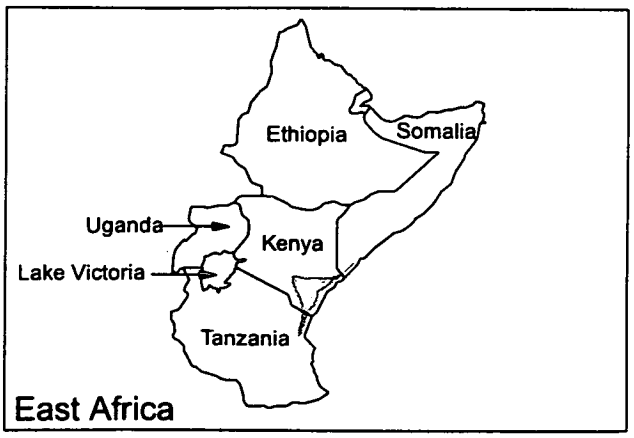
- Taxonomic position:

  Group 19 of the tropical aloes (Reynolds, 1966).

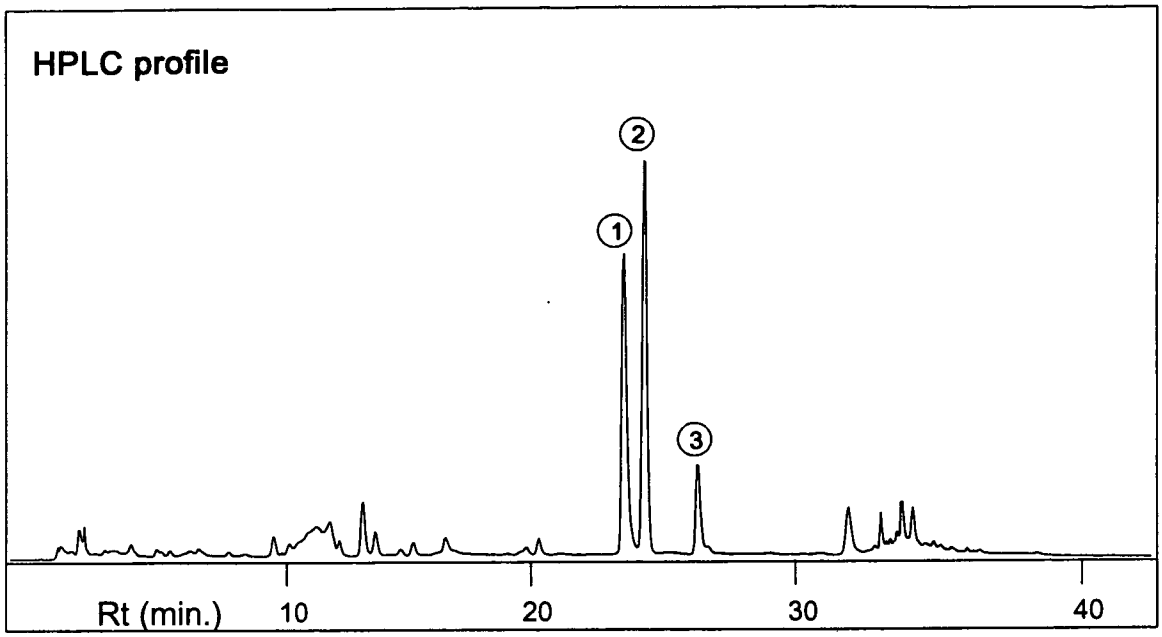
- Samples analysed:

  The leaf exudate was investigated:

  - RBG, Kew 1975-903



Aloe rabaiensis is widely distributed in the open bushveld of Kenya, Tanzania and southern Somalia.



Peak number	Retention time	Compound	Percentage
1	23.29	unidentified compound 1	27
2	24.07	unidentified compound 2	32
3	26.07	unidentified compound 3	7

No class of compound could be assigned to any of the three unidentified exudate phenolics.

- Taxonomic position:

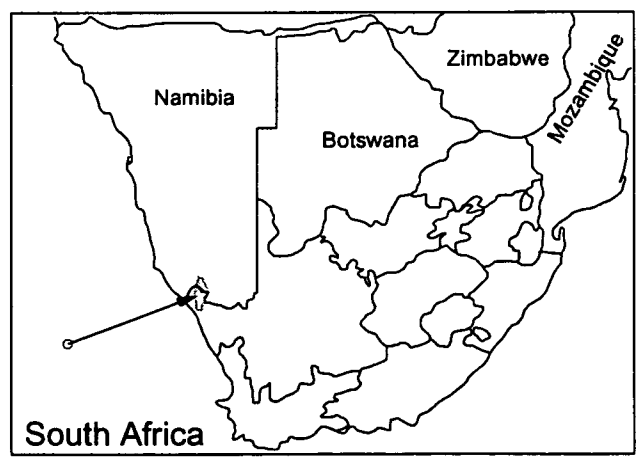
  Aloe section *Dracoaloe* (Reynolds, 1950).

- Samples analysed:

  The leaf exudate and extract was investigated:

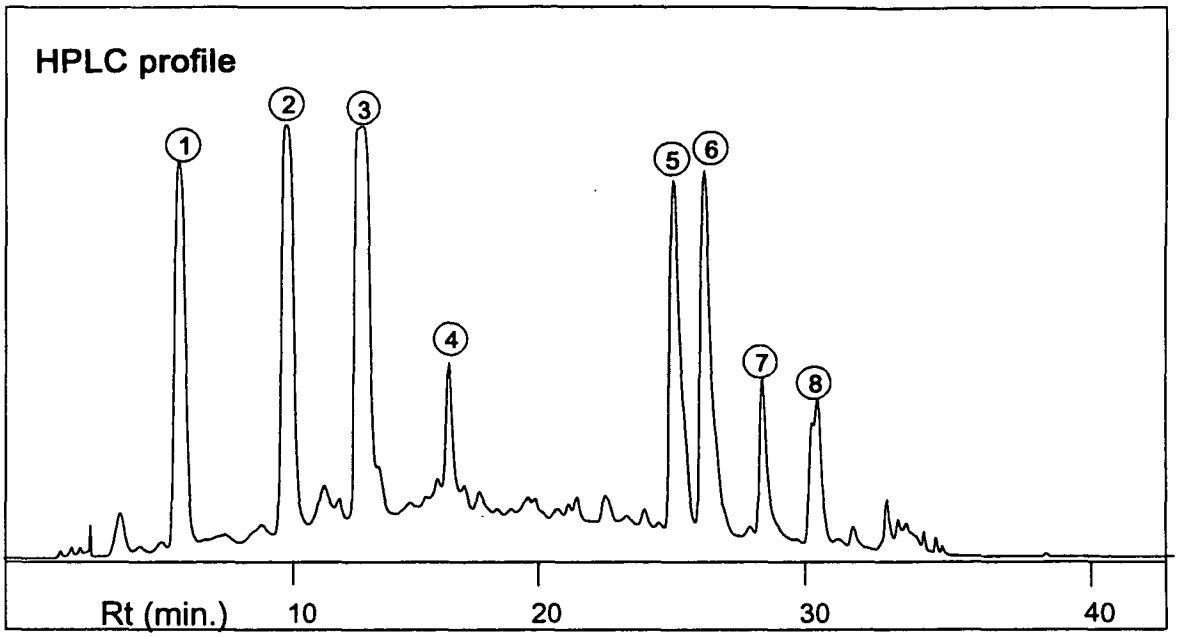
  - NBI 29276
  - ex hort NBG 1121/70

Distribution



Aloe ramosissima is found in the Richtersveld and marginally extends across the border into Namibia.

Aloe reitzii Reynolds



Peak number	Retention time	Compound	Percentage
1	6.44	aloesin	9
2	10.38	unidentified chromone 1	12
3	13.26	unidentified chromone 2	17
4	16.15	aloeresin A	4
5	24.81	aloin B	10
6	25.92	aloin A	11
7	28.12	unidentified anthrone 1	4
8	30.17	unidentified anthrone 2	4

The two unidentified anthrones have an UV spectra resembling that of aloin and the aloinosides. A similar chromatographic profile has been recorded for *A. aculeata*, *A. gerstneri* and *A. petricola.*

- Taxonomic position:

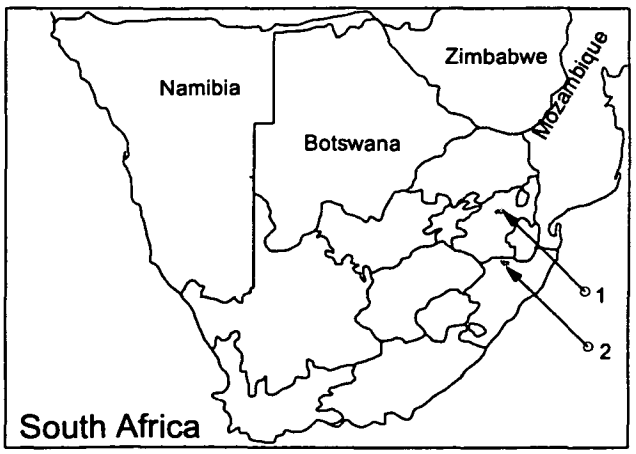
  Aloe section *Pachydendron* (Reynolds, 1950).

- Samples analysed:

  The leaf exudate was investigated:

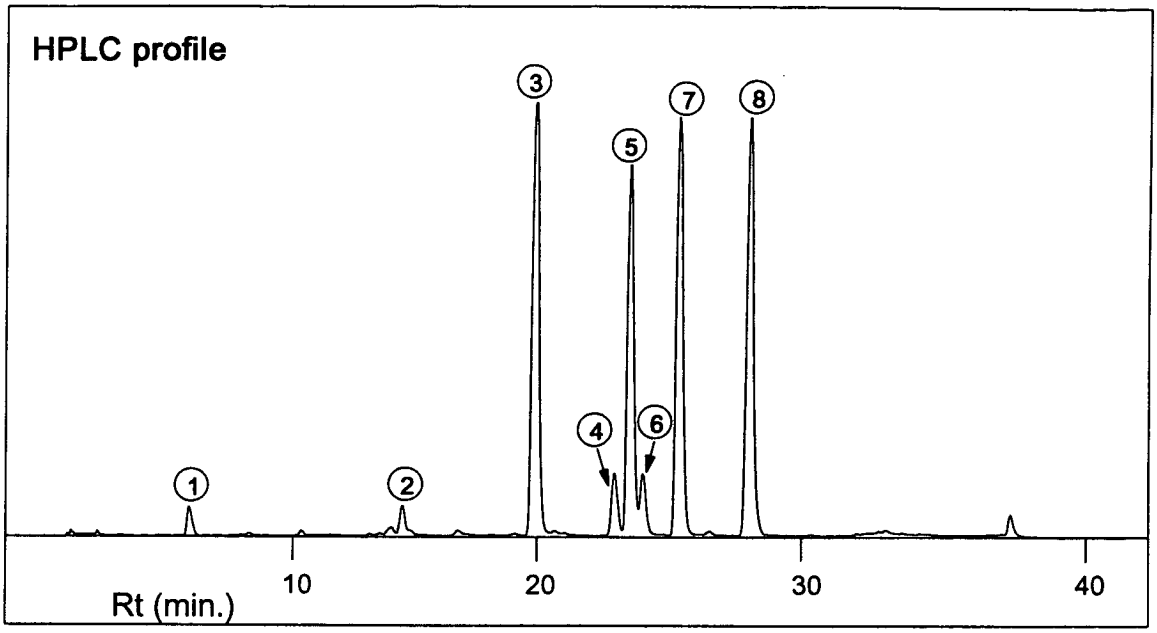
  - NBG 503/61

Distribution



Aloe reitzii is found near Belfast (1) in Mpumalanga and in the grasslands of KwaZulu-Natal (2).

Aloe retrospiciens Reynolds & P.R.O. Bally



Peak number	Retention time	Compound	Percentage
1	6.44	7-*O*-methylaloesin	1
2	14.41	8-*O*-methyl-7-hydroxyaloin	tr
3	20.03	aloeresin D	25
4	23.15	aloin B	3
5	23.74	homonataloin B	20
6	24.27	aloin A	3
7	25.65	homonataloin A	23
8	28.40	unidentified chromone	23

The HPLC profile of this species closely resembles that of *A. pubescens*. The co-occurence of aloin and homonataloin was found to be exceptional in this survey. The unidentified chromone is probably a cinnamoyl chromone.

- Taxonomic position:

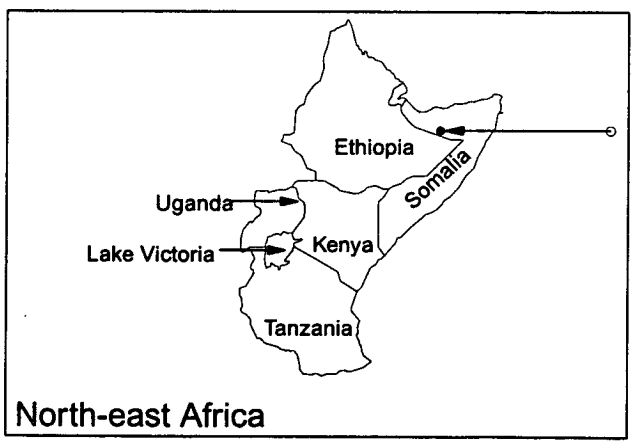
  Group 19 of the tropical aloes (Reynolds, 1966).

- Samples analysed:

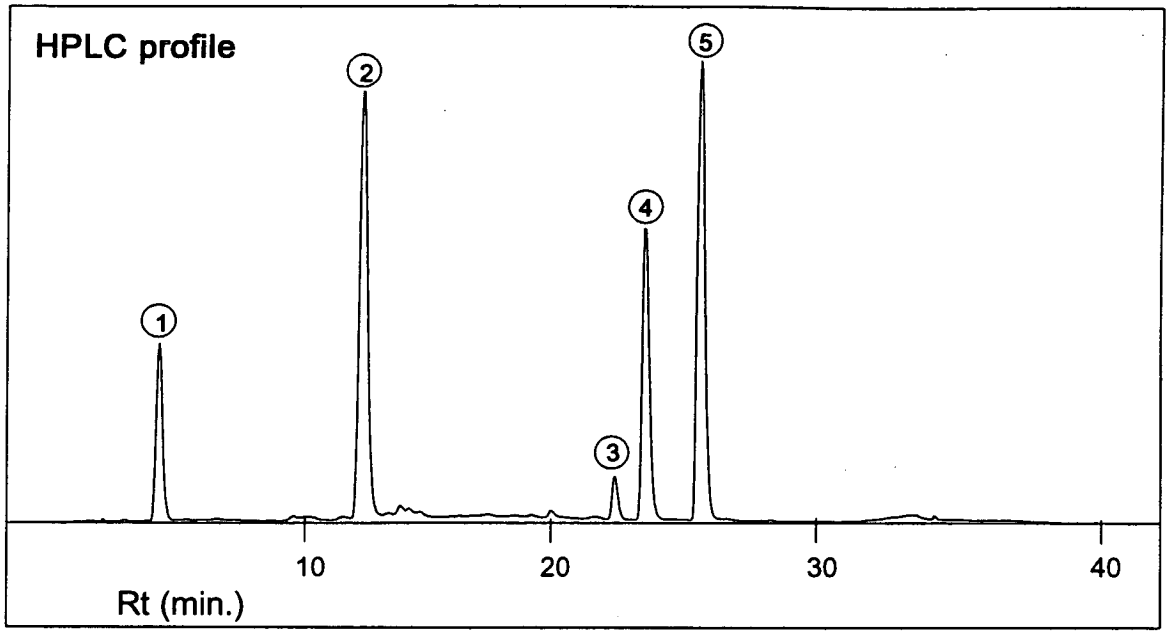
  The leaf exudate was investigated:

  - RBG, Kew 630 54 63008

Distribution



This species is found near the Darburruk Village NE of Hargeisa in Somalia.



Peak number	Retention time	Compound	Percentage
1	5.00	aloesin	11
2	12.90	aloeresin A	34
3	22.69	unidentified chromone	2
4	23.86	homonataloin B	19
5	25.97	homonataloin A	33

The sample taken from a plant at the NBI showed the presence of homonatalin A and B together with aloeresin D.

- Taxonomic position:

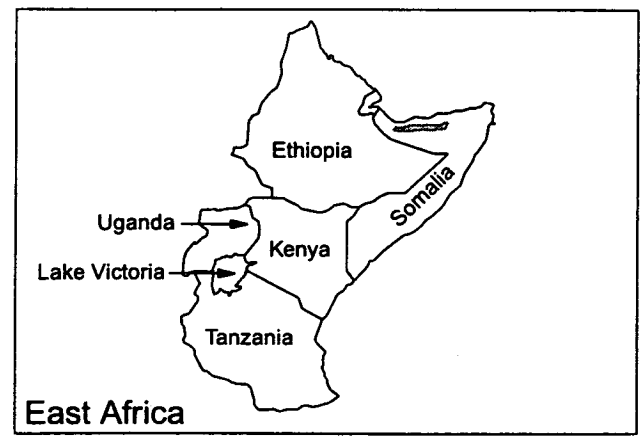
  Group 9 of the tropical aloes (Reynolds, 1966).

- Samples analysed:

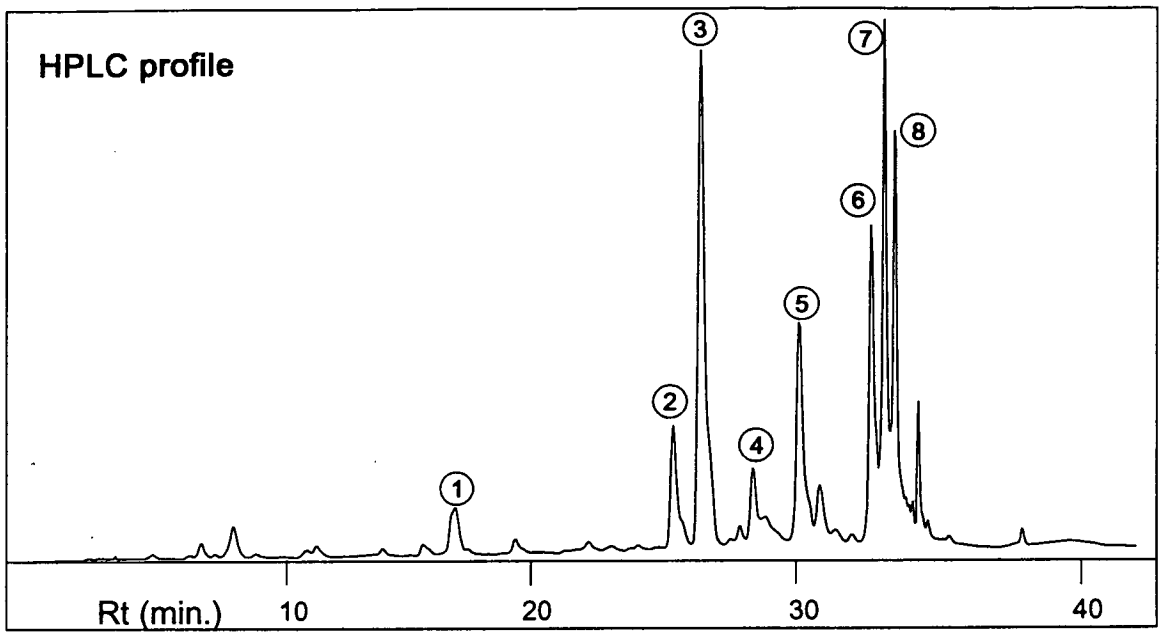
  The leaf exudate was investigated:

  - RBG, Kew 1973-1245
  - NBI, Reynolds 7618

Distribution



Aloe rigens is found near Darburruk and Bawn in Somalia North.



Peak number	Retention time	Compound	Percentage
1	16.64	dihydroisocoumaringlucoside	3
2	25.09	aloin B	6
3	26.14	aloin A	25
4	28.19	aloinoside B	4
5	29.98	aloinoside A	11
6	32.77	microdontin B	12
7	33.27	microdontin A	16
8	33.68	unidentified anthrone	16

- Taxonomic position:

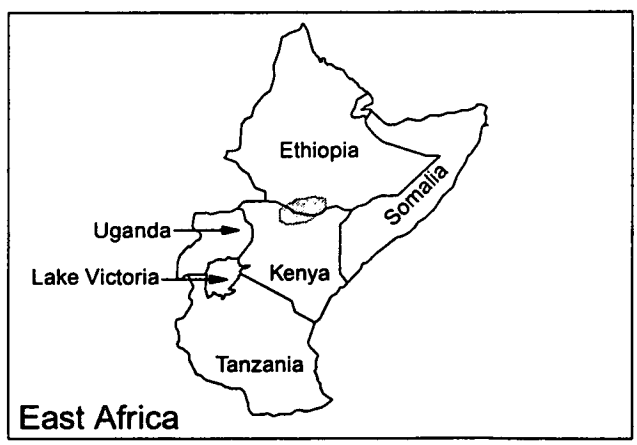
  Group 8 of the tropical aloes (Reynolds, 1966).

- Samples analysed:

  The leaf exudate was investigated:

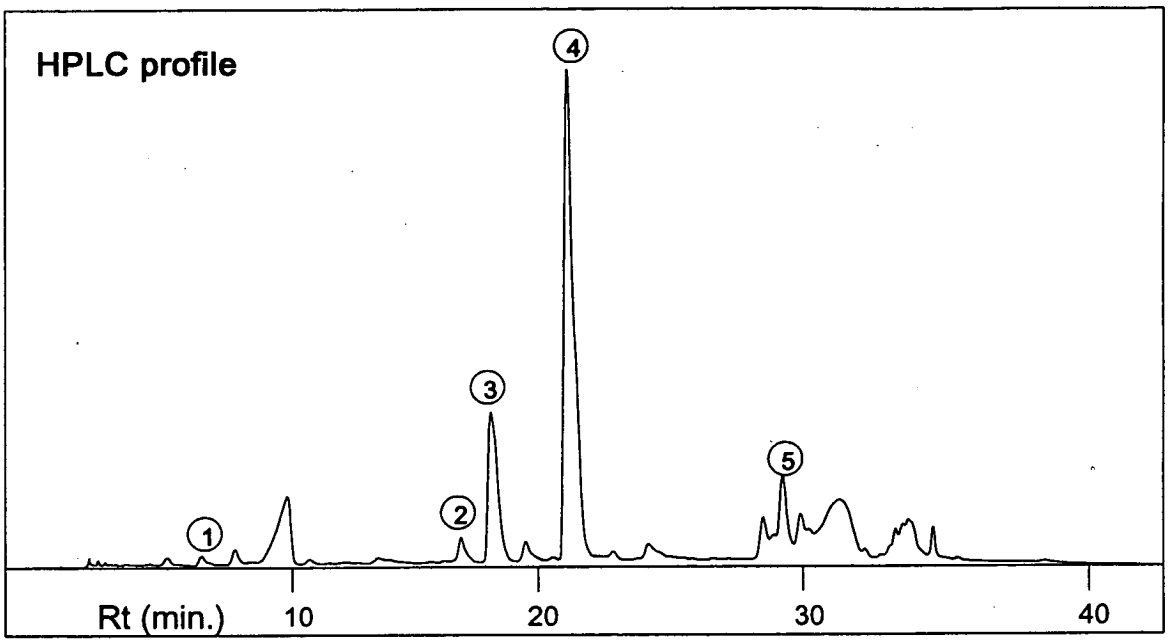
  - Sebsebe 321

Distribution



Aloe rivae is found on rock slopes in the Northern Frontier Province of Kenya and in the southern parts of Ethiopia.

Aloe rubroviolacea Schweinfurth



Peak number	Retention time	Compound	Percentage
1	6.47	aloesin	tr
2	16.59	dihydroisocoumaringlucoside	2
3	17.73	unidentified anthrone 1	12
4	20.64	unidentified anthrone 2	40
5	29.07	unidentified chromone	5

The unidentified anthrones 1 & 2, (peak 2 & 3), both have a UV absorbance spectra resembling that of 7-hydroxyaloin and nataloin A and B. The unidentified chromone could possibly be a cinnamic acid derivative of aloesin.
Three samples were analysed; all three contained aloesin and the dihydro-isocoumaringlucoside. The sample from RBG (Kew), contained an anthrone (Rt 29.23) of which the UV spectrum is not comparable to any compound detected in this study. The D. Hardy sample showed a major unidentified peak (Rt 21.13).

- Taxonomic position:

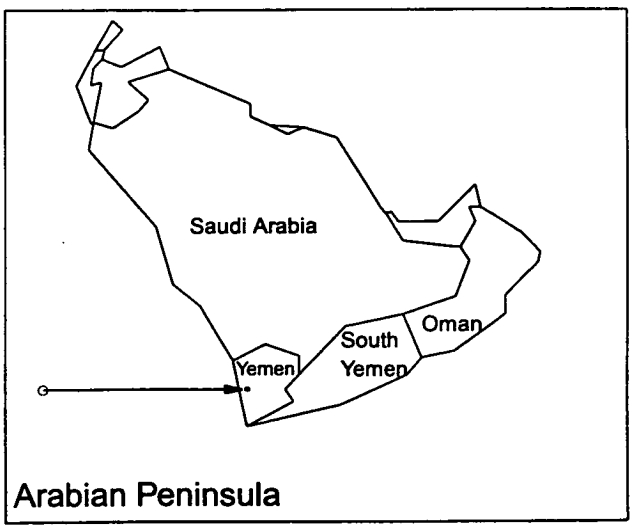
  Group 15 of the tropical aloes (Reynolds, 1966).

- Samples analysed:

  The leaf exudate was investigated:

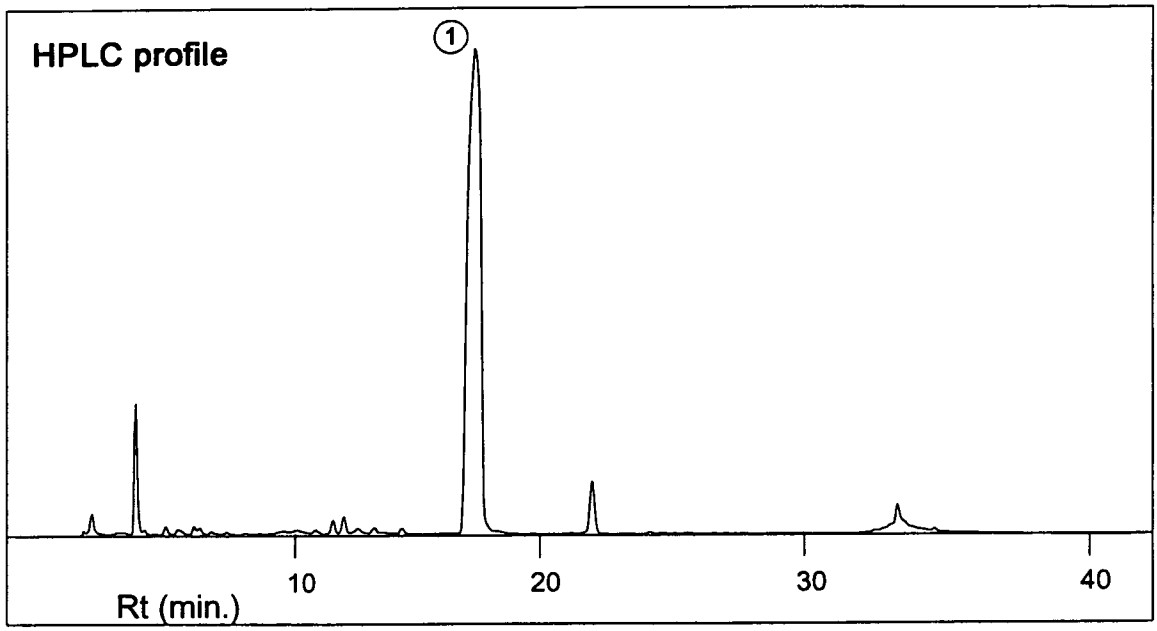
  - NBI 15816
  - RBG, Kew 1977-1247
  - ex hort D. Hardy

Distribution



Aloe rubroviolacea is found in the Haraz mountains in the Yemen, Southern Arabia.

Aloe rugosifolia M. G. Gilbert & Sebsebe



Peak number	Retention time	Compound	Percentage
1	16.63	plicataloside	95

- Taxonomic position:

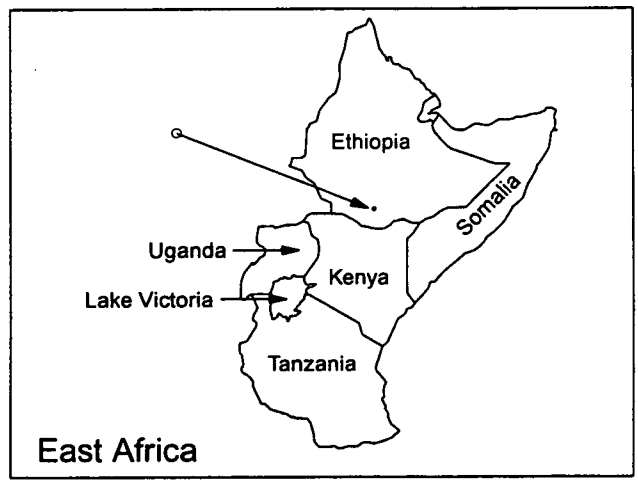
  Allied to species pertaining to group 4 of the tropical aloes (Gilbert & Demissew, 1992).

- Samples analysed:

  The leaf exudate was investigated:

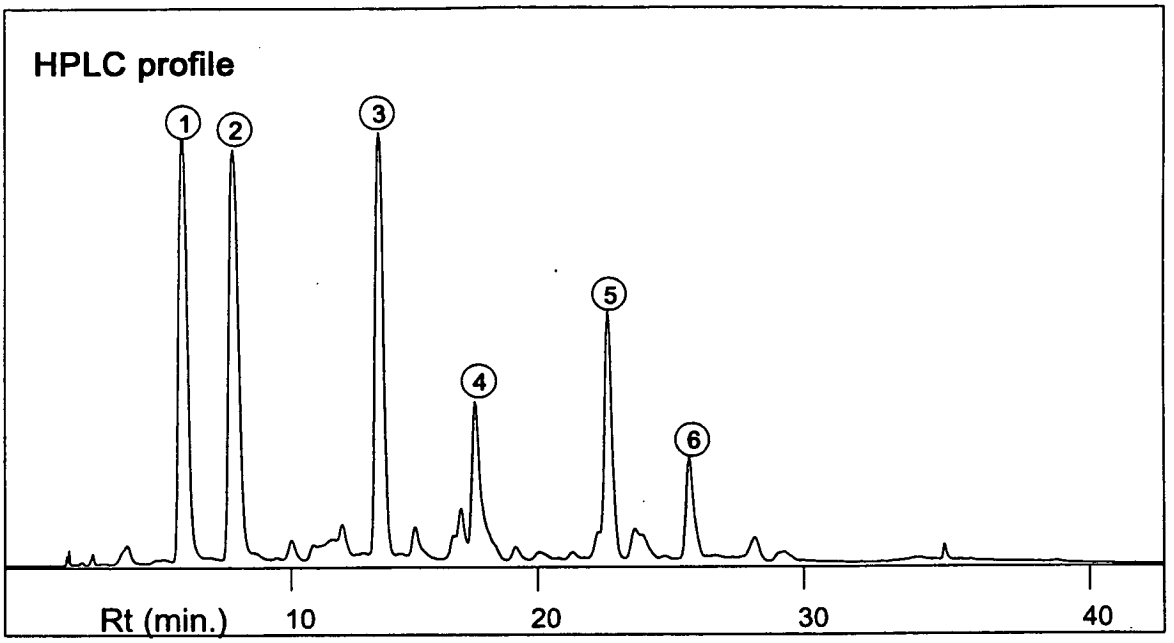
  - Sebsebe 22

Distribution



This species is found near Yavello in the Sadamo region of Ethiopia.

Aloe rupestris Baker



Peak number	Retention time	Compound	Percentage
1	6.48	aloesin	20
2	8.34	7-*O*-methylaloesin	22
3	13.84	unidentified chromone 1	18
4	17.43	unidentified chromone 2	8
5	22.39	unidentified chromone 3	11
6	25.43	unidentified chromone 4	4

Aloe rupestris is the species from which 7-*O*-methylaloesin has been isolated. *Aloe rupestris* is chemically peculiar as it only produces various chromones and no anthrones. *Aloe thraskii* produces the same range of unidentified chromones with the co-occurence of the anthrone homonataloin.

- Taxonomic position:

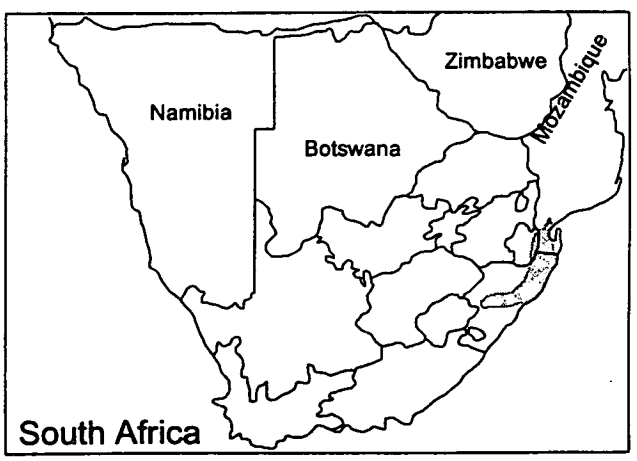
  Aloe section *Pachydendron* (Reynolds, 1950).

- Samples analysed:

  The leaf exudate was investigated:

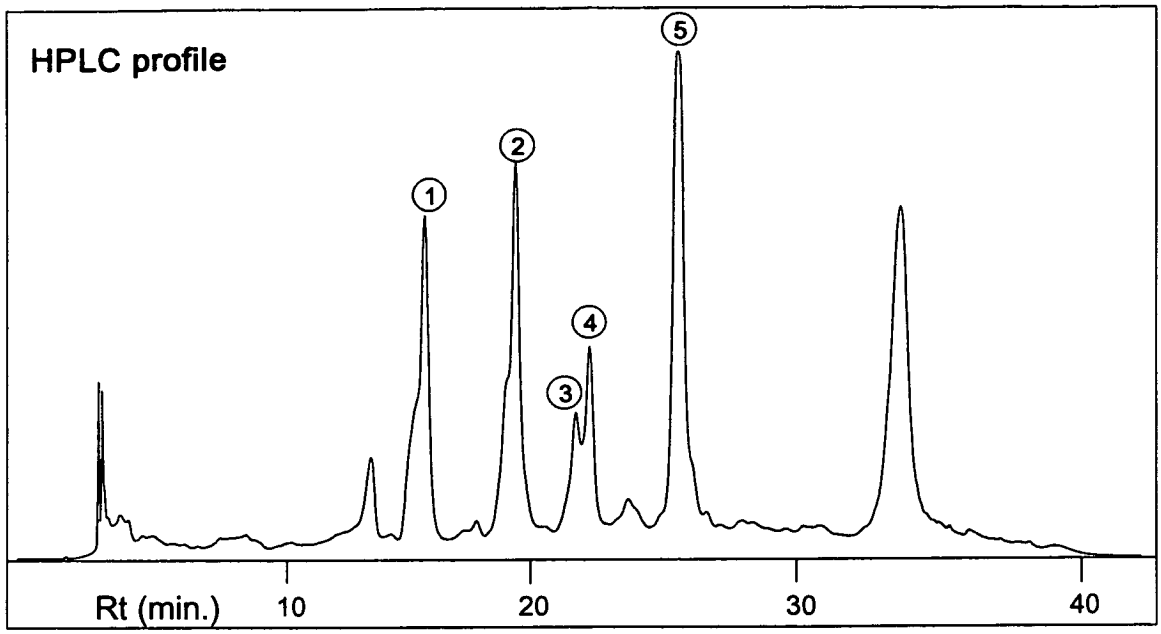
  - ex hort NBG
  - NBI 8284 (Swaziland)
  - Muden
  - ex hort Nelspruit Botanical Garden

Distribution



Aloe rupestris is distributed along the northern coast of KwaZulu-Natal, in Swaziland and the southern parts of Mozambique.

Aloe saundersiae Reynolds



Peak number	Retention time	Compound	Percentage
1	15.8	unidentified flavone 1	11
2	19.2	unidentified flavone 2	14
3	21.5	unidentified flavone 3	5
4	22.0	unidentified compound 1	5
5	25.4	unidentified compound 2	22

Besides the three flavones, two unknown compounds (peak 4 and 5) are detected in *A. saundersiae*. These two compounds display the same UV absorbance spectrum and are also reported in *A. thompsoniae*.

- Taxonomic position:

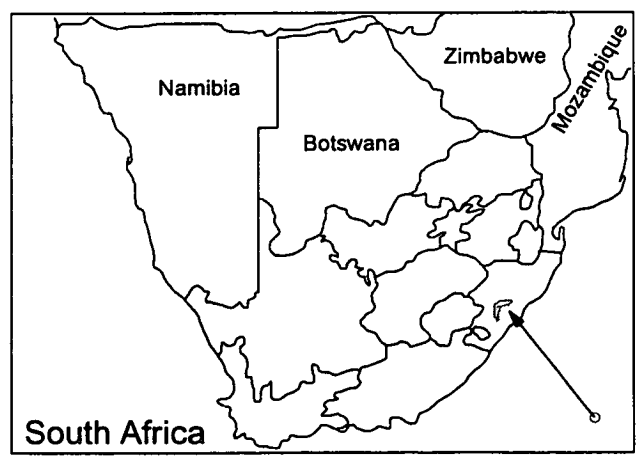
  Aloe section *Graminialoe* (Reynolds, 1950).

- Samples analysed:

  The leaf extract was investigated:

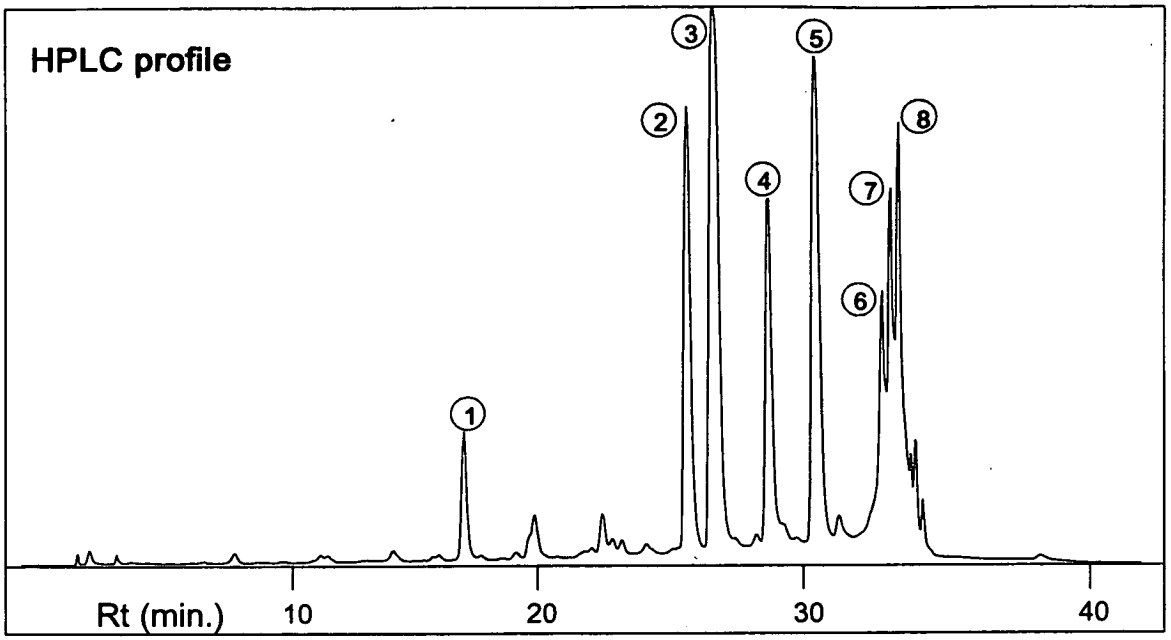
  - ex hort C. Craib (collected near Melmoth)

Distribution



Aloe saudersiae has only been recorded in and around the Greytown area in KwaZulu-Natal.

Aloe scabrifolia L. E. Newton & Lavranos



Peak number	Retention time	Compound	Percentage
1	17.00	dihydroisocoumaringlucoside	3
2	25.55	aloin B	12
3	26.53	aloin A	22
4	28.74	aloinoside B	10
5	30.49	aloinoside A	16
6	33.12	microdontin B	9
7	33.45	microdontin A	8
8	33.75	unidentified anthrone	12

- Taxonomic position:

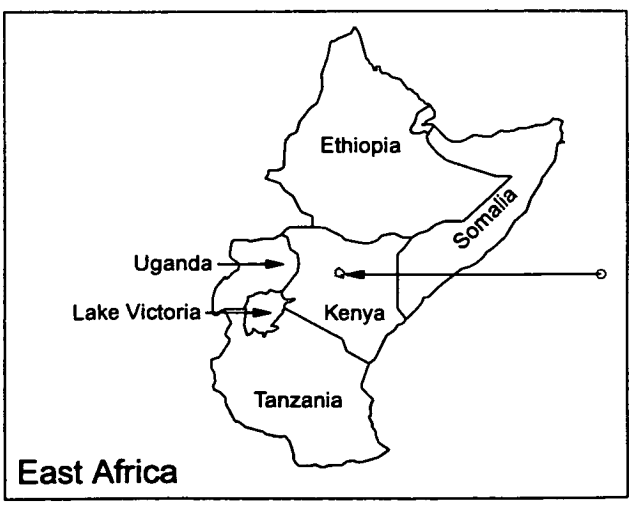
  Group 14 of the tropical aloes (Newton & Lavranos, 1990).

- Samples analysed:

  The leaf exudate was investigated:

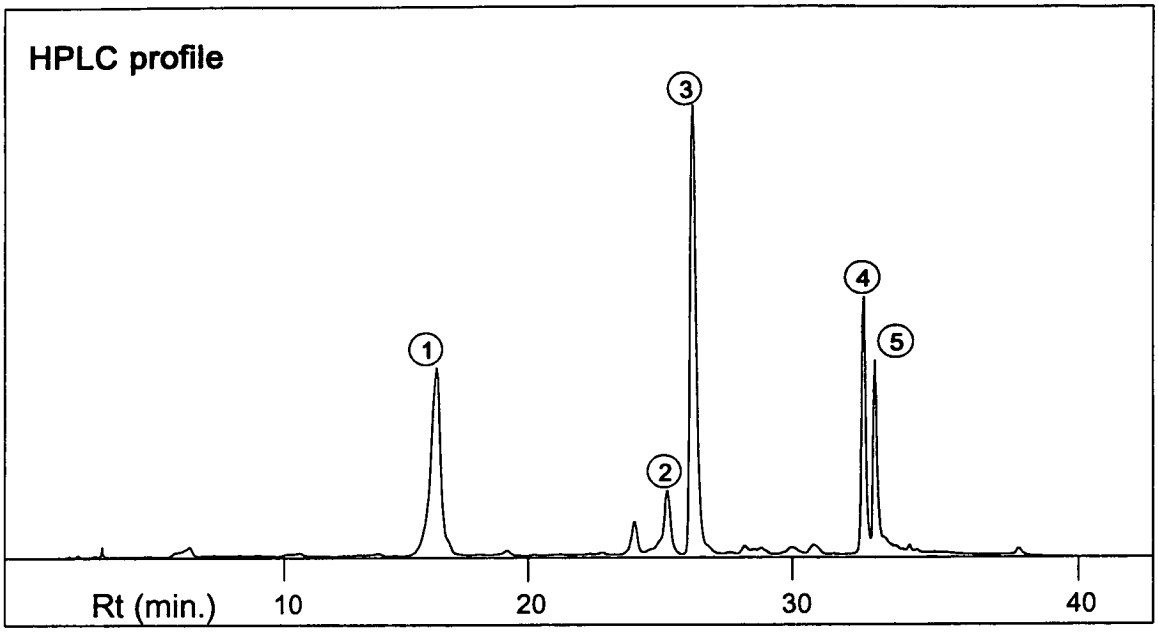
  - L. E. Newton 3272

Distribution



Aloe scabrifolia is widespread in the Laikipia, Meru and Samburu Districts of Kenya.

Aloe schelpei Reynolds



Peak number	Retention time	Compound	Percentage
1	16.39	8-*O*-methyl-7-hydroxyaloin	26
2	25.32	aloin B	7
3	26.30	aloin A	37
4	32.91	microdontin B	13
5	33.34	microdontin A	12

Aloe schelpei is the species from which 8-*O*-methyl-7-hydroxyaloin has been isolated and used as a reference compound in this study.

- Taxonomic position:

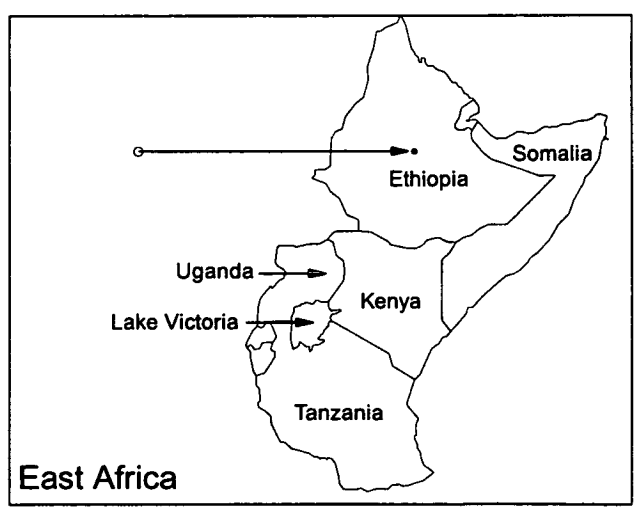
  Group 17 of the tropical aloes (Reynolds, 1966).

- Samples analysed:

  The leaf exudate was investigated:

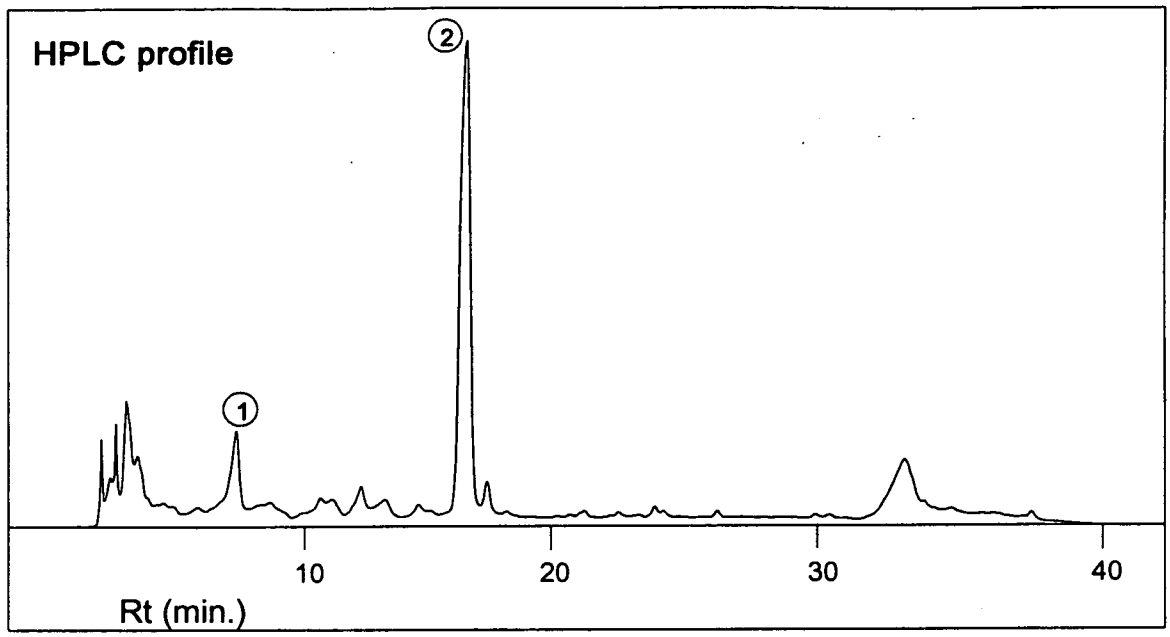
  - ex hort NBI
  - RBG, Kew 427 64 42705

Distribution



Aloe schelpei grows on steep grass land slopes of the Boli Gorge north of Addis Ababa.

Aloe schweinfurthii Baker



Peak number	Retention time	Compound	Percentage
1	7.91	unidentified compound	9
2	16.87	plicataloside	59

- Taxonomic position:

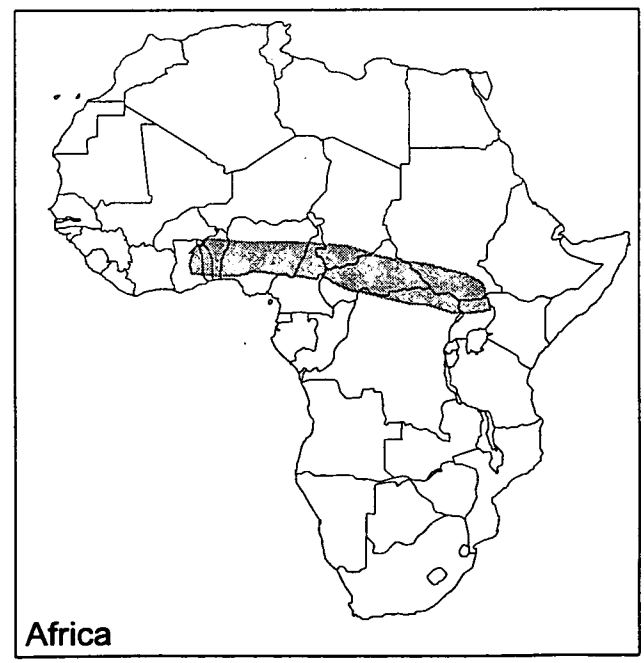
  Group 17 of the tropical aloes (Reynolds, 1966).

- Samples analysed:

  The leaf exudate was investigated:

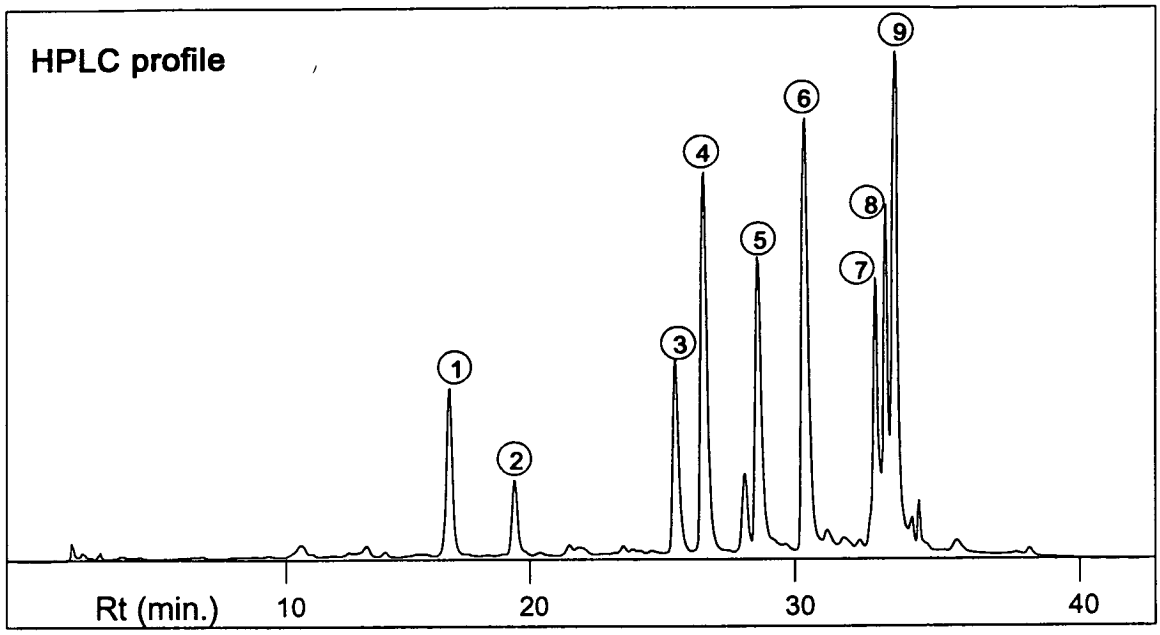
  - ex hort NBI

Distribution



Aloe schweinfurthii is one of the most widely distributed aloes. Its western limit lies in Ghana from where it extends eastwards to Sudan, northern Zaire and Uganda.

Aloe scobinifolia Reynolds & P. R. O. Bally



Peak number	Retention time	Compound	Percentage
1	16.74	dihydroisocoumaringlucoside	6
2	19.23	unidentified chromone	3
3	25.41	aloin B	6
4	26.45	aloin A	14
5	28.52	aloinoside B	11
6	30.29	aloinoside A	17
7	33.02	microdontin B	8
8	33.42	microdontin A	9
9	33.77	unidentified anthrone	17

- Taxonomic position:

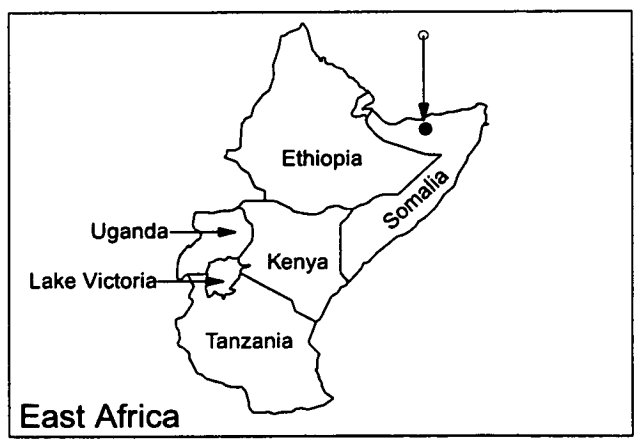
  Group 13 of the tropical aloes (Reynolds, 1966).

- Samples analysed:

  The leaf exudate was investigated:

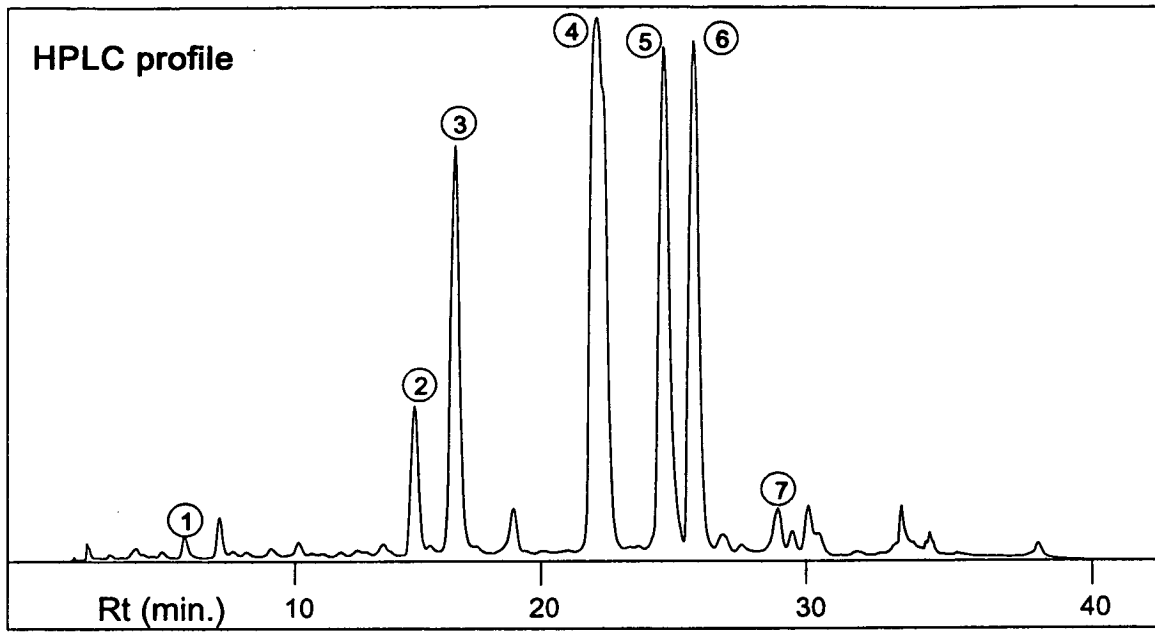
  - ex hort BSM
  - RBG, Kew 084-81-01110

Distribution



A. scobinifolia is densely distributed around Erigavo in northern Somalia.

Aloe scorpioides L. C. Leach



Peak number	Retention time	Compound	Percentage
1	6.33	aloesin	1
2	15.06	10-hydroxyaloin B	4
3	16.59	unidentified anthrone 1	14
4	21.91	unidentified anthrone 2	32
5	24.44	aloin B	20
6	25.56	aloin A	19
7	28.83	unidentified anthrone 3	1

This Angolan endemic contains the chemotaxonomic marker of *Aloe* series *Asperifoliae*, 10-hydroxyaloin B (peak 2). Peaks 3 and 4 are derivatives of 10-hydroxyaloin B (see *A. littoralis*). The NBI and Kew sample displayed the same HPLC profile.

(See *A. gossweileri*, *A. littoralis* and *A. claviflora*)

- Taxonomic position:

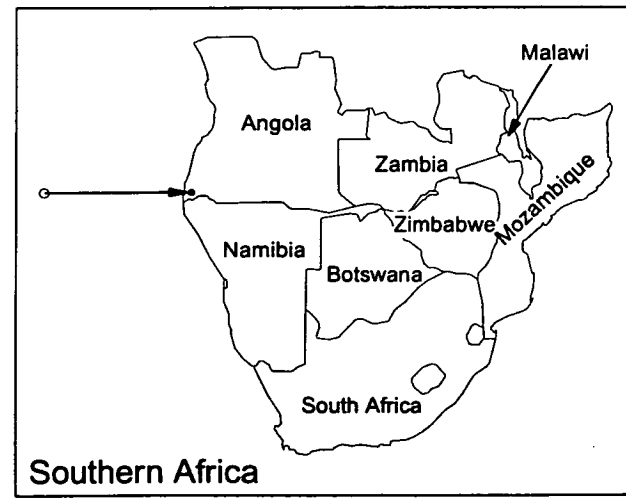
Allied to *A. palmiformis* (Leach, 1974).

- Samples analysed:

The leaf exudate and extract was investigated:

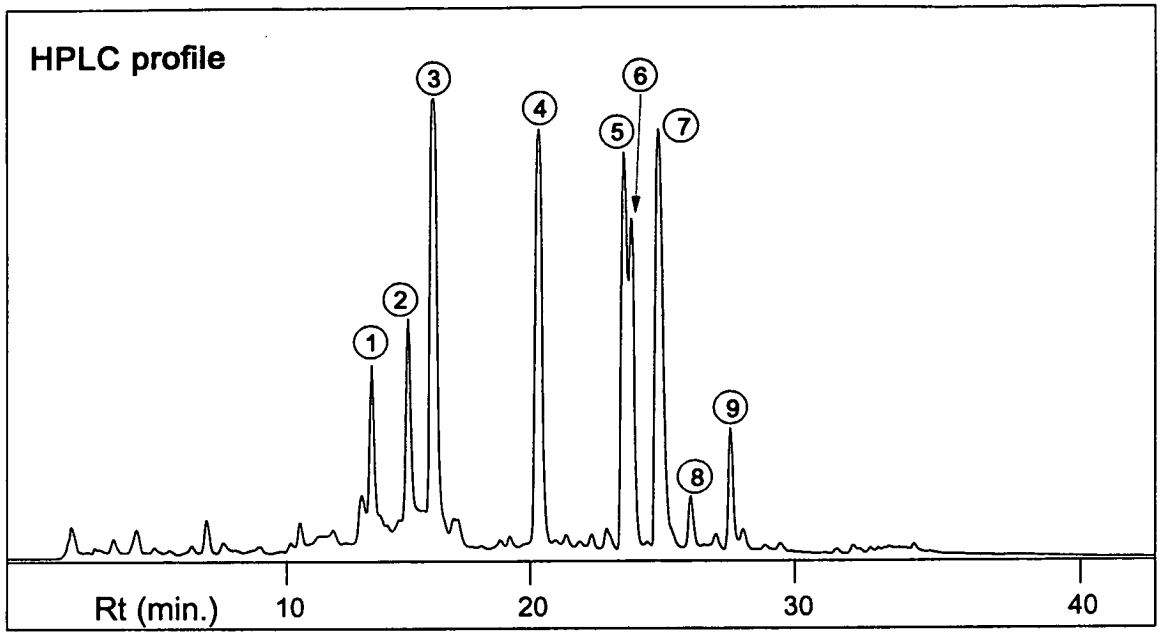
- RBG, Kew 224-74-0209-0
- ex hort NBI (leaf extract)

Distribution



A. scorpioides occupies the lower slopes of Serra da Chela in the Namibe area of Angola.

Aloe secundiflora Engler var. *secundiflora*



Peak number	Retention time	Compound	Percentage
1	13.80	aloenin	5
2	15.18	unidentified compound 1	5
3	16.09	unidentified compound 2	17
4	20.05	aloeresin D	16
5	23.23	aloin B	13
6	23.53	unidentified compound 3	10
7	24.52	aloin A	18
8	25.75	unidentified compound 4	2
9	27.23	unidentified compound 5	3

This characteristic combination of compounds have been detected in a number of *Aloe* species. All the unidentified compounds display similar UV absorbing spectra and correlate to those reported in *A. dorotheae*, *A. bussei* and others.

- Taxonomic position:

  Group 14 of the tropical aloes (Reynolds, 1966).

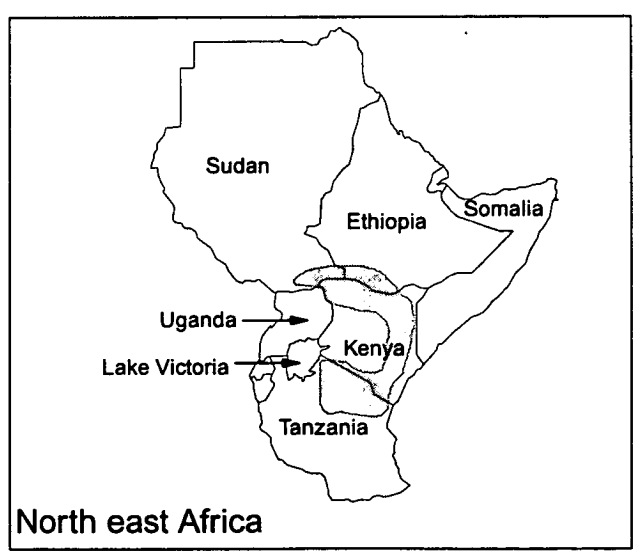
- Samples analysed:

  The leaf exudate was investigated:

  - L. E. Newton 4016 (type locality)
  - Sebsebe 219

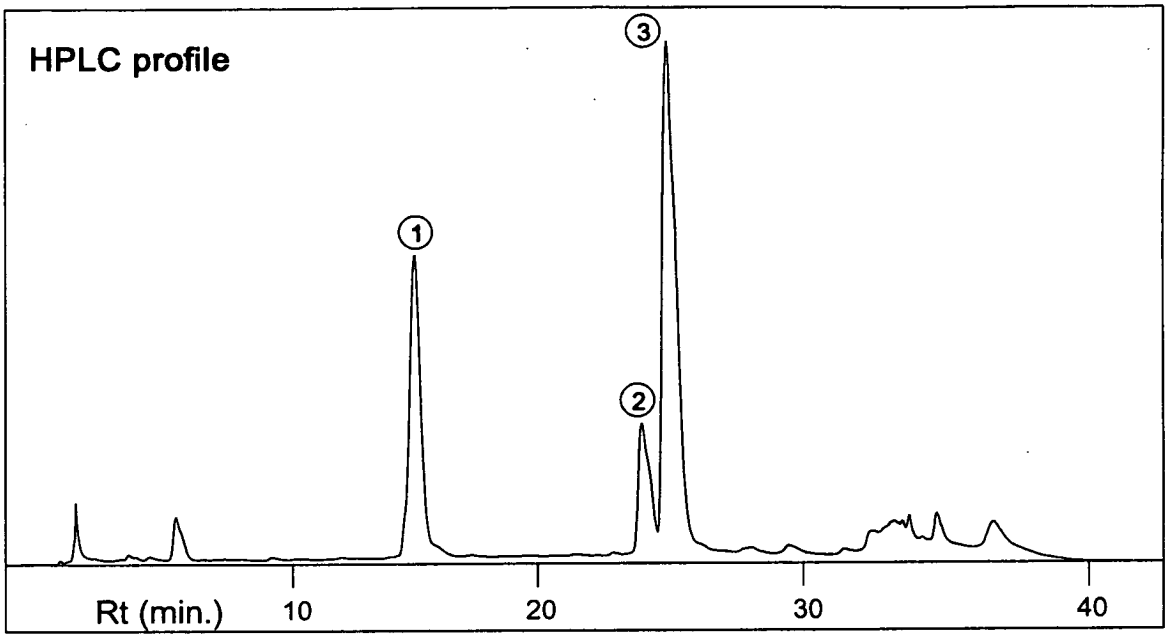
*The LEN sample was collected under the name of *A. marsabitensis* but has since been placed under synonymy with *A. secundiflora* var. *secundiflora*.

Distribution



This species is widely distributed in parts of Kenya, Tanzania, Ethiopia and southern Sudan.

Aloe sinana Reynolds



Peak number	Retention time	Compound	Percentage
1	15.61	8-*O*-methyl-7-hydroxyaloin	25
2	23.94	aloin B	11
3	24.87	aloin A	49

As is the case in *A. sinkatana*, 8-*O*-methyl-7-hydroxyaloin co-occurs with the anthrones, aloin A and B.

- Taxonomic position:

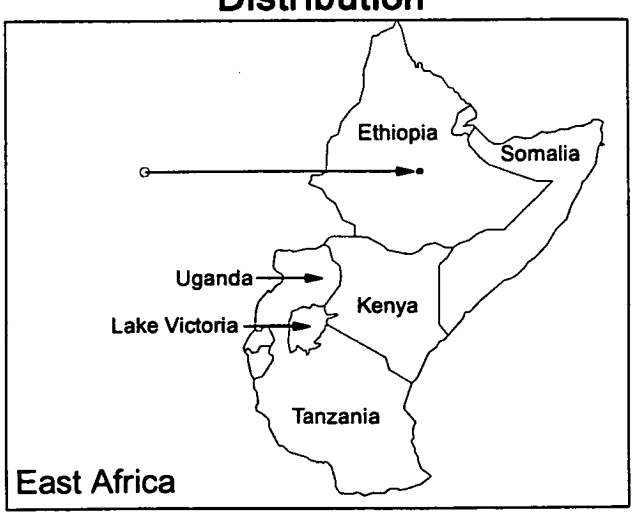
  Group 13 of the tropical aloes (Reynolds, 1966).

- Samples analysed:

  The leaf exudate was investigated:

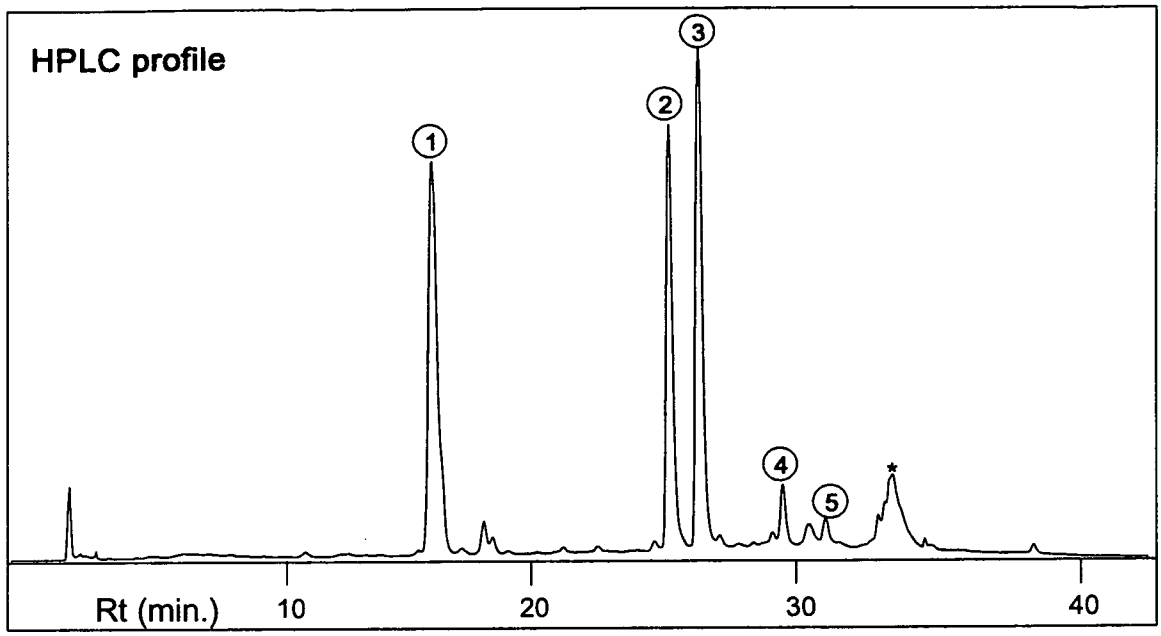
  - Sebsebe 4659

Distribution



Aloe sinana co-occurs with *A. camperi* north-east of Debre Sina in the Shoa Province of Ethiopia.

Aloe sinkatana Reynolds



Peak number	Retention time	Compound	Percentage
1	16.03	8-*O*-methyl-7-hydroxyaloin	29
2	25.04	aloin B	22
3	26.13	aloin A	27
4	28.94	aloinoside B	3
5	30.90	aloinoside A	2

An unusual combination of anthrones are represented in *A. sinkatana*. It is the only example where the compound denoted as peak 1 co-occurs with the aloinosides. The "base-line hump" in the region marked * could be the microdontins present in very low concentration.

- Taxonomic position:

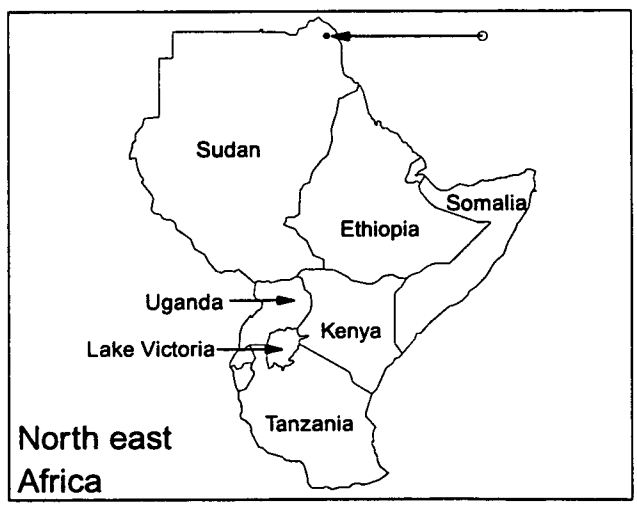
  Group 13 of the tropical aloes (Reynolds, 1966).

- Samples analysed:

  The leaf exudate was investigated:

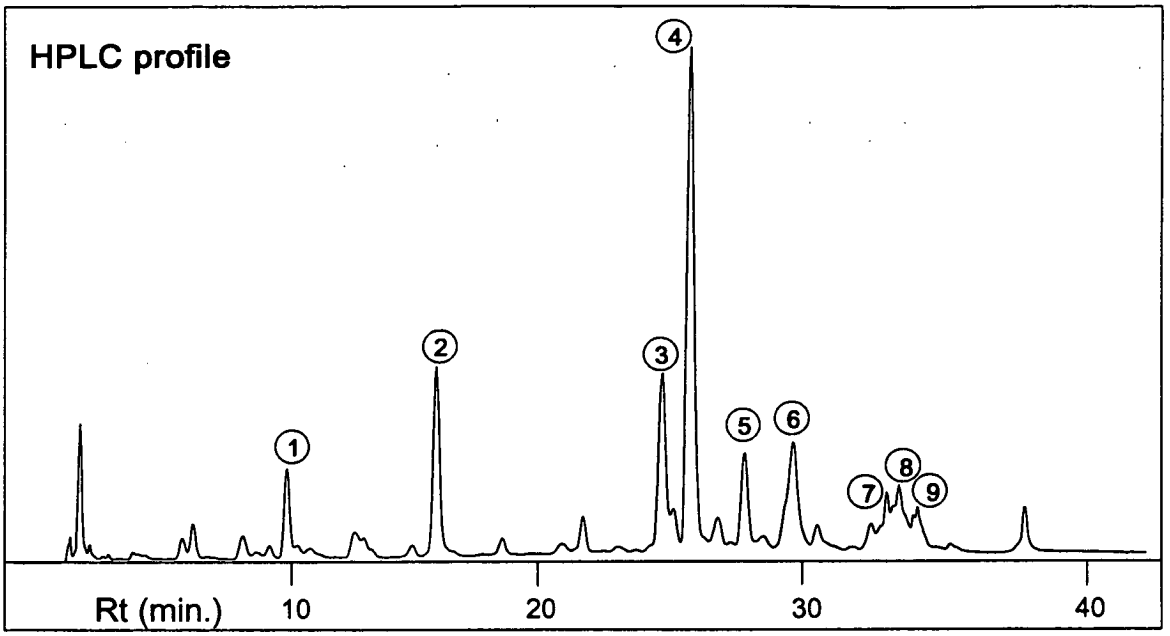
  - ex hort BSM

Distribution



As suggested by the name, this species is abundant around Sinkat in the northern region of Sudan.

Aloe somaliensis W. Watson



Peak number	Retention time	Compound	Percentage
1	10.24	unidentified compound	3
2	16.00	dihydroisocoumaringlucoside	10
3	24.62	aloin B	11
4	25.67	aloin A	31
5	27.78	aloinoside B	5
6	29.61	aloinoside A	9
7	32.55	microdontin B	6
8	33.15	microdontin A	3
9	33.55	unidentified anthrone	4

The UV absorbance spectra of the unidentified compound (peak 1), is identical to that of dihydroisocoumaringlucoside. The microdontins are present in low quantities, but the UV spectra confirmed their presence in the leaf exudate.

- Taxonomic position:

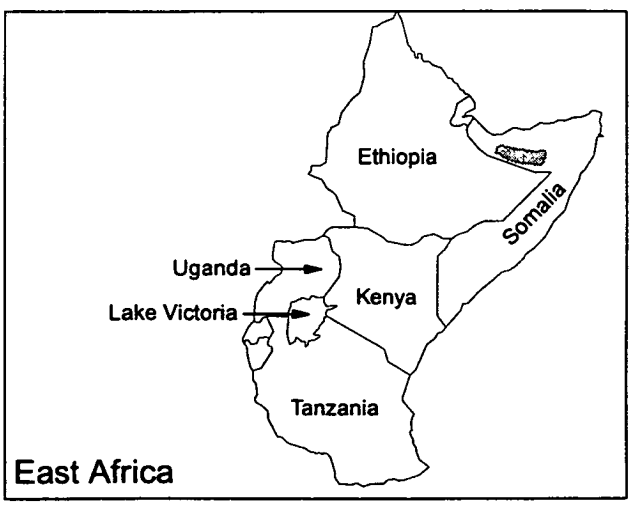
  Group 4 of the tropical aloes (Reynolds, 1966).

- Samples analysed:

  The leaf exudate was investigated:

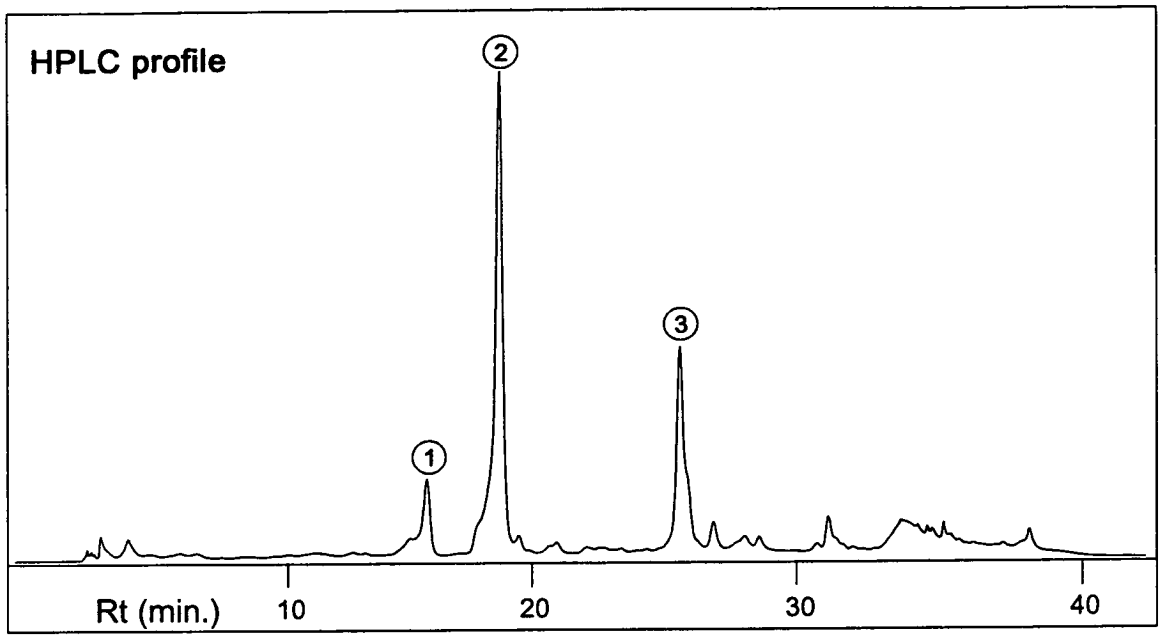
  - RBG, Kew 084-81-01055
  - NBI 11169

Distribution



A. somaliensis has a distribution in the northern parts of Somalia round Borama and Hargeisa.

Aloe soutpansbergensis I. Verdoorn



Peak number	Retention time	Compound	Percentage
1	15.8	unidentified flavone 1	9
2	18.5	isovitexin	44
3	25.4	unidentified flavone 3	21

- Taxonomic position:

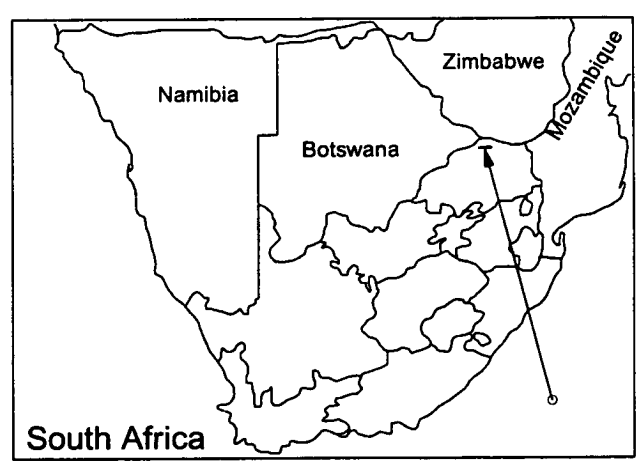
  Aloe section *Leptoaloe* (Verdoorn, 1962).

- Samples analysed:

  The leaf extract was investigated:

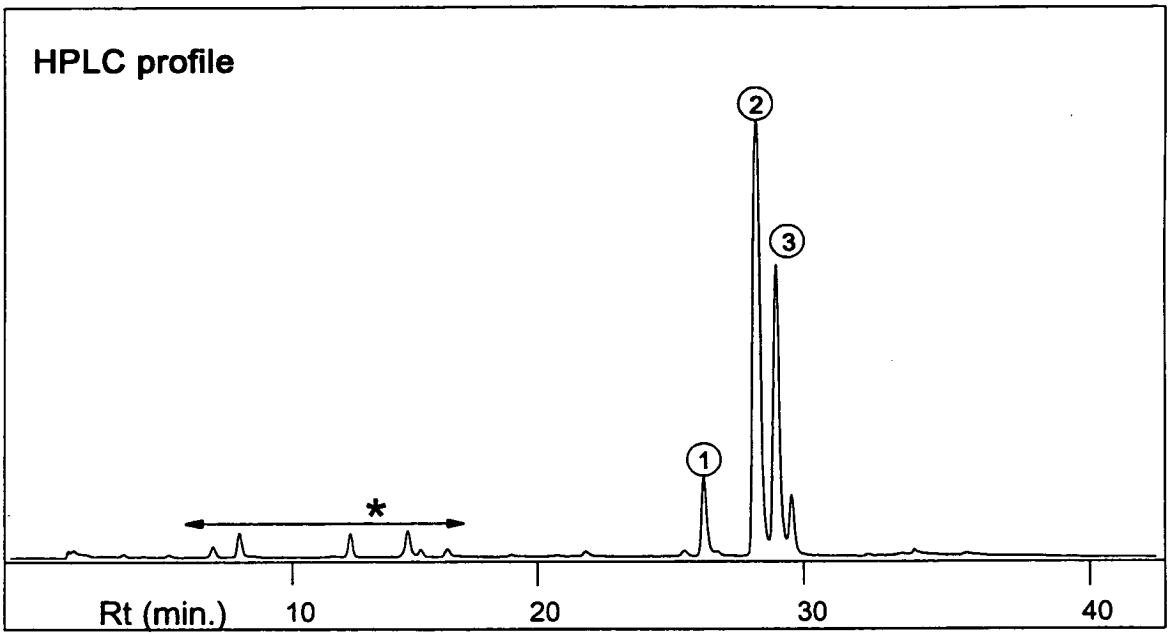
  - ex hort C. Craib (collected near Letjume)
  - ex hort D. Hardy

Distribution



Aloe soutpansbergensis is restricted to the Soutpansberg in the Northern Province.

Aloe speciosa Baker



Peak number	Retention time	Compound	Percentage
1	26.03	homonataloin B	7.0
2	27.98	homonataloin A	50
3	28.75	speciosa chromone	28

The area donated by * represents a series of coumaroyl chromones in low concentrations. The speciosa chromone has recently been isolated from this species. ((E)-2-acetonyl-8-(2'-6'-di-*O*-coumaroyl-β-D-glucopyranosyl-7-methoxy-5-methyl-chromone).

- Taxonomic position:

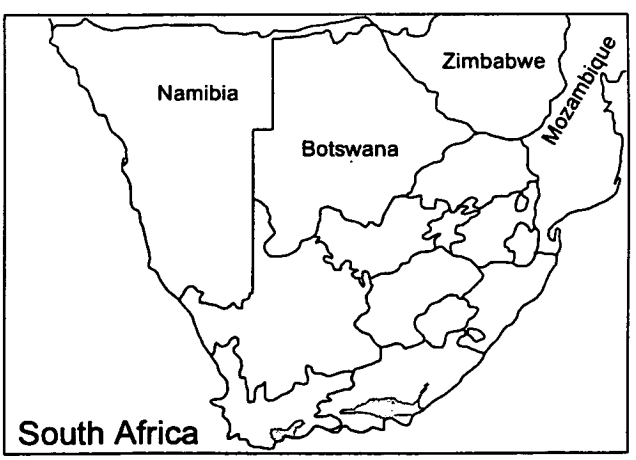
  Aloe series *Principales* (Reynolds, 1950)

- Samples analysed:

  The leaf exudate was investigated:

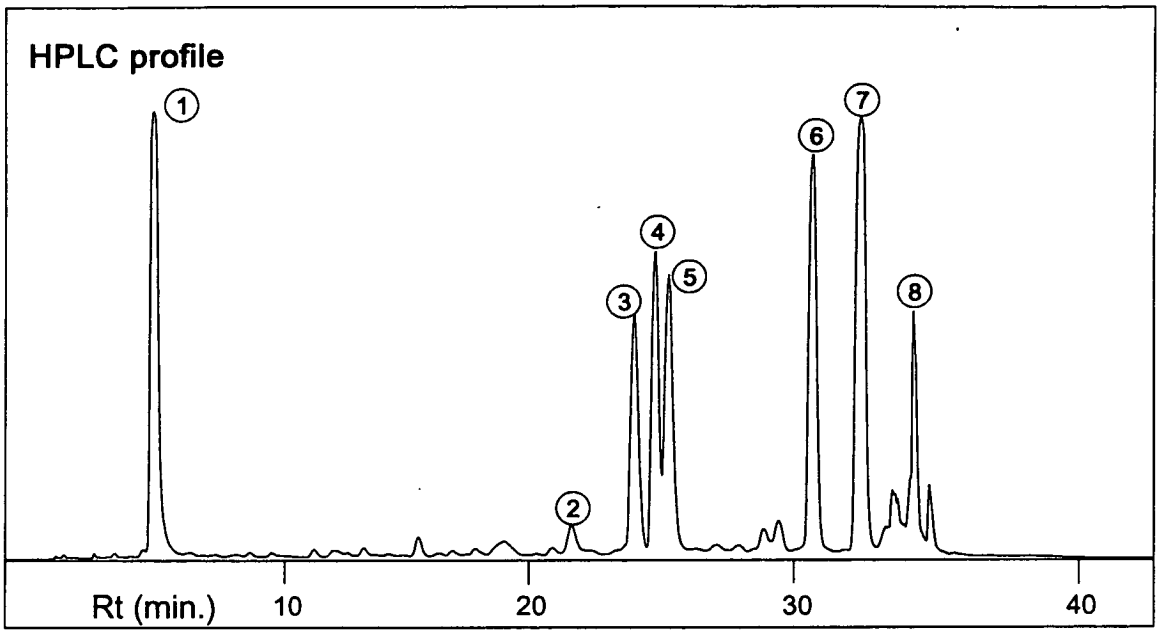
  - Fort Brown

Distribution



Aloe speciosa is found near Swellendam in the west and extends to the Kei River in the east.

Aloe spicata Linné (*fil.*)



Peak number	Retention time	Compound	Percentage
1	5.58	aloesin	17
2	21.36	unidentified chromone 1	1
3	23.71	aloin B	9
4	24.49	6'-*O*-coumaroylaloesin	10
5	25.00	aloin A	11
6	30.37	unidentified chromone 2	15
7	32.12	unidentified chromone 3	20
8	34.08	unidentified compound	6

The two late eluting chromones (peaks 6 & 7) are probably cinnamoyl chromones . (See *A. alooides*)

- Taxonomic position:

Aloe section *Anguialoe* (Reynolds, 1950).

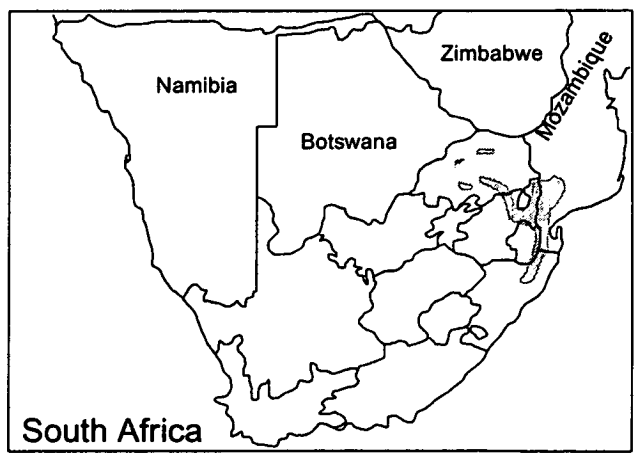
This species was previously known as *Aloe sessiliflora* (Pole-Evans).

- Samples analysed:

The leaf exudate was investigated:

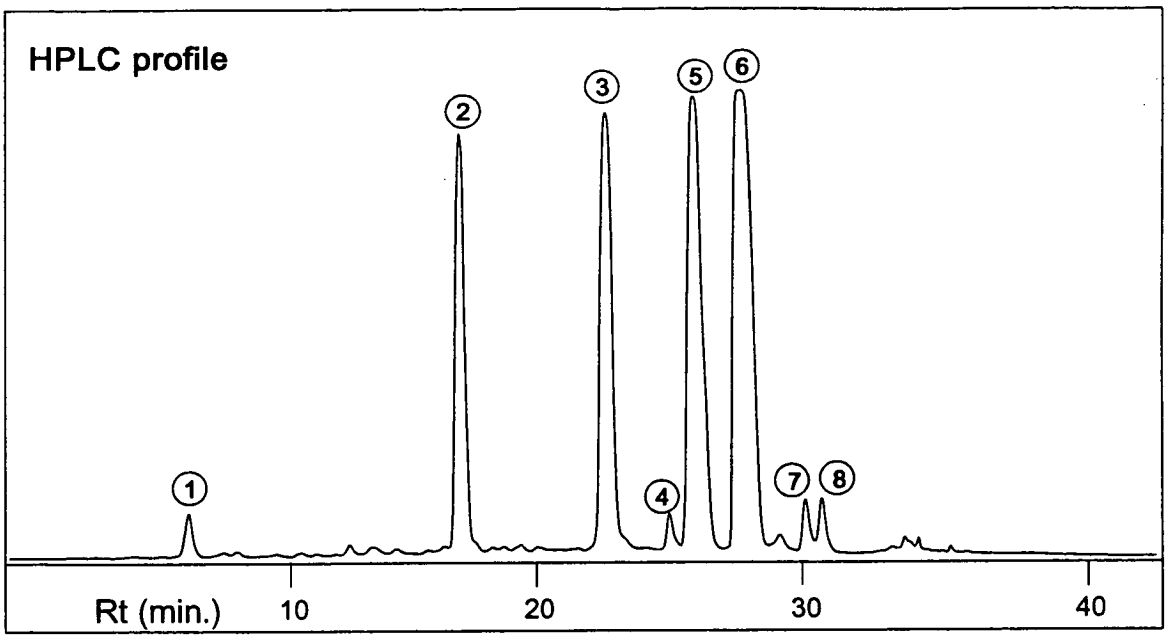
- Bourke's Luck
- NBI 24959

Distribution



Aloe spicata is widely distributed occurring in Mpumalanga, Swaziland, Northern Province, KwaZulu-Natal and Mozambique.

Aloe splendens Lavranos



Peak number	Retention time	Compound	Percentage
1	6.67	aloesin	1
2	16.85	aloeresin A	15
3	22.35	aloeresin D	20
4	24.79	unidentified chromone 1	1
5	25.64	homonataloin B	26
6	27.45	homonataloin A	33
7	29.88	unidentified chromone 2	2
8	31.37	unidentified chromone 3	2

The unidentified chromones (peak 4 and 7) show the UV absorbing spectra typical of the cinnamoyl chromones while the unidentified chromone 3 is probably related to the coumaroyl group of chromones.

Distribution

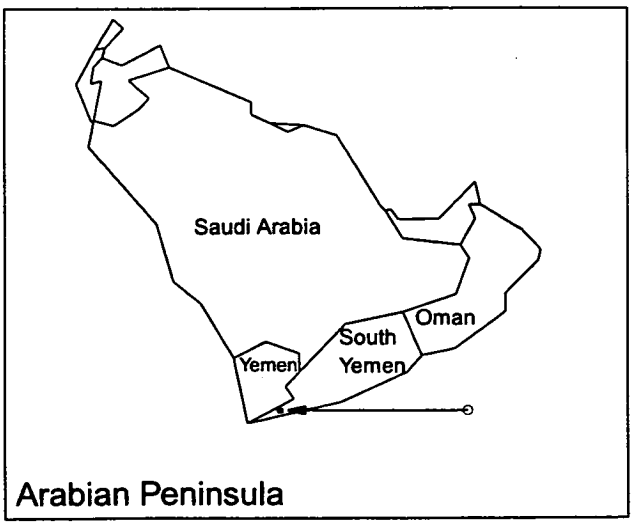
- Taxonomic position:

  Group 9 of the tropical aloes (Reynolds, 1966).

- Samples analysed:

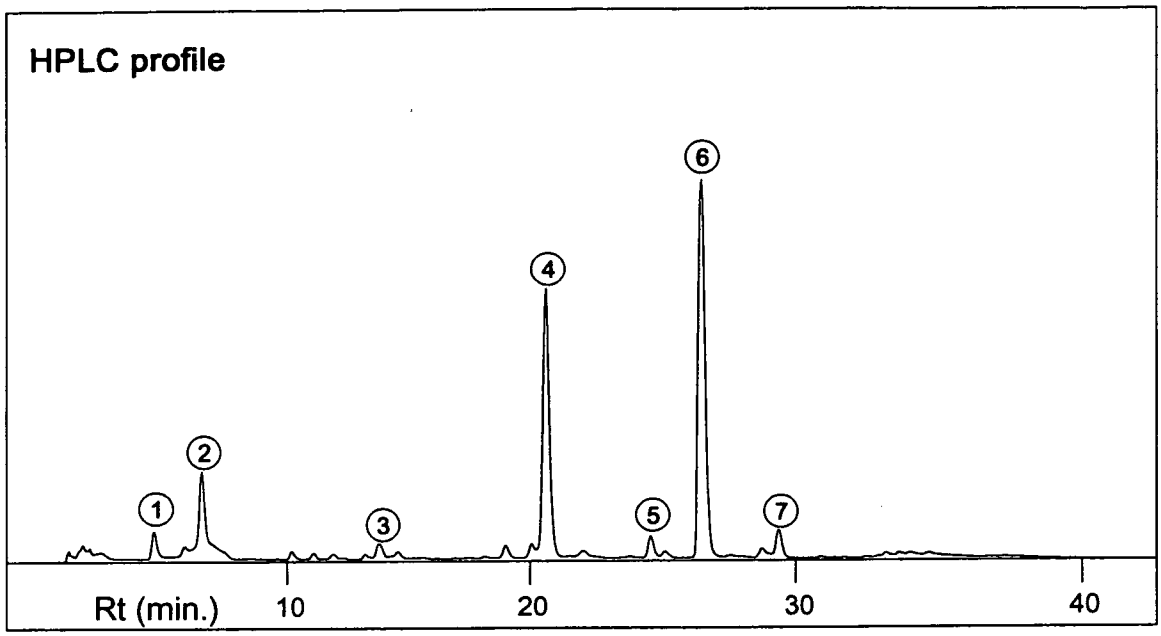
  The leaf exudate was investigated:

  - NBI 10214



Aloe splendens is found of the Dathina Plain near Mudiyaib South Yemen.

Aloe squarrosa Baker



Peak number	Retention time	Compound	Percentage
1	5.49	aloesin	2
2	7.29	7-*O*-methylaloesin	9
3	13.58	homonataloside B	tr
4	20.42	aloeresin D	30
5	24.32	homonataloin B	2
6	26.26	homonataloin A	45
7	29.17	unidentified chromone	3

The unidentified chromone displays the UV absorbance spectra typical of the cinnamoyl chromones. Research on *A. lutescens* (with a similar HPLC profile) indicated that peak four could possibly be a derivative of aloeresin D.

- Taxonomic position:

  Group 19 of the tropical aloes (Reynolds, 1966).

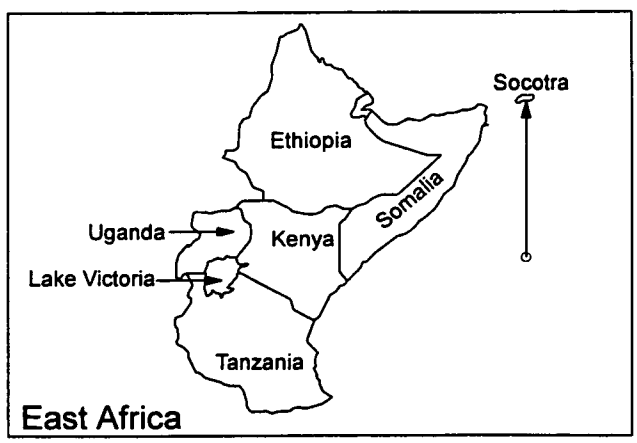
  Syn. *A. zanzibarica* (Lavranos, 1969).

- Samples analysed:

  The leaf exudate was investigated:

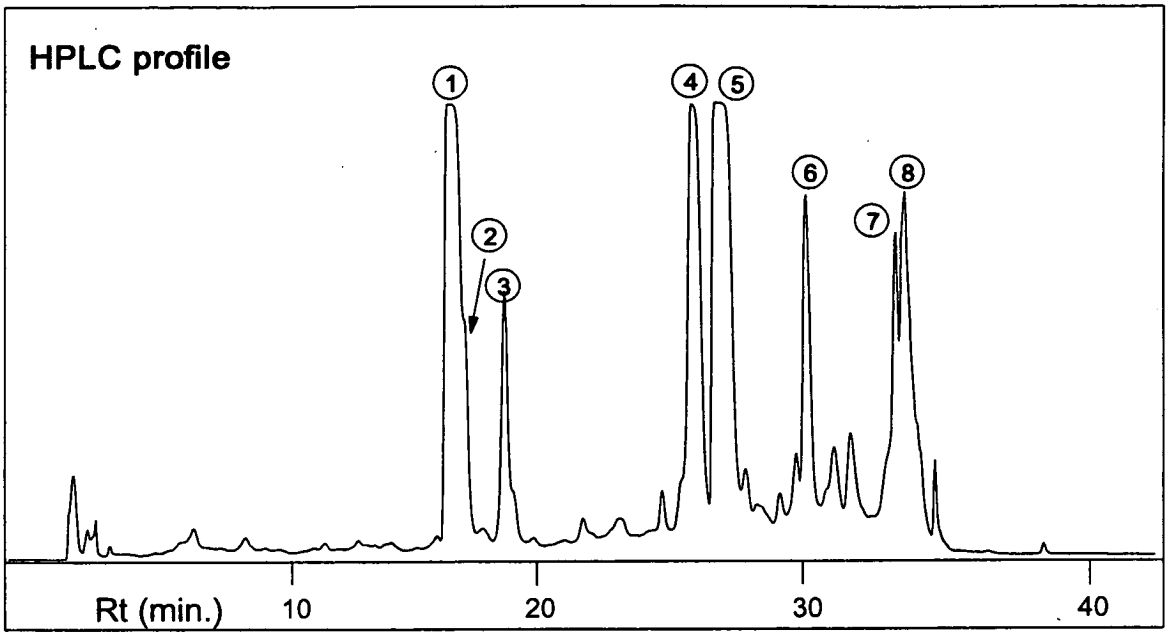
  - ex hort NBI

Distribution



Aloe squarrosa is confined to the limestone cliffs of Jabal in the west of Socotra.

Aloe steudneri Schweinfurth



Peak number	Retention time	Compound	Percentage
1	16.49	8-*O*-methyl-7-hydroxyaloin	18
2	17.12	dihydroisocoumaringlucoside	2
3	18.60	unidentified anthrone 1	5
4	25.56	aloin B	15
5	26.53	aloin A	20
6	29.90	unidentified anthrone 2	7
7	33.37	microdontin B	6
8	33.63	microdontin A	10

The unidentified anthrone 1 is probably a derivative of 8-*O*-methyl-7-hydroxyaloin (identical UV spectra). Dihydroisocoumaringlucoside co-elutes with peak 1. Peak 6 displays the UV absorbance maxima characteristic for aloin A and B.

- Taxonomic position:

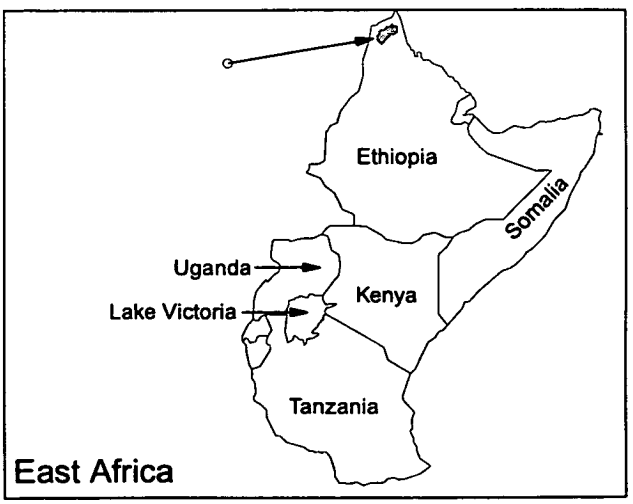
  Group 16 of the tropical aloes (Reynolds, 1966).

- Samples analysed:

  The leaf exudate was investigated:

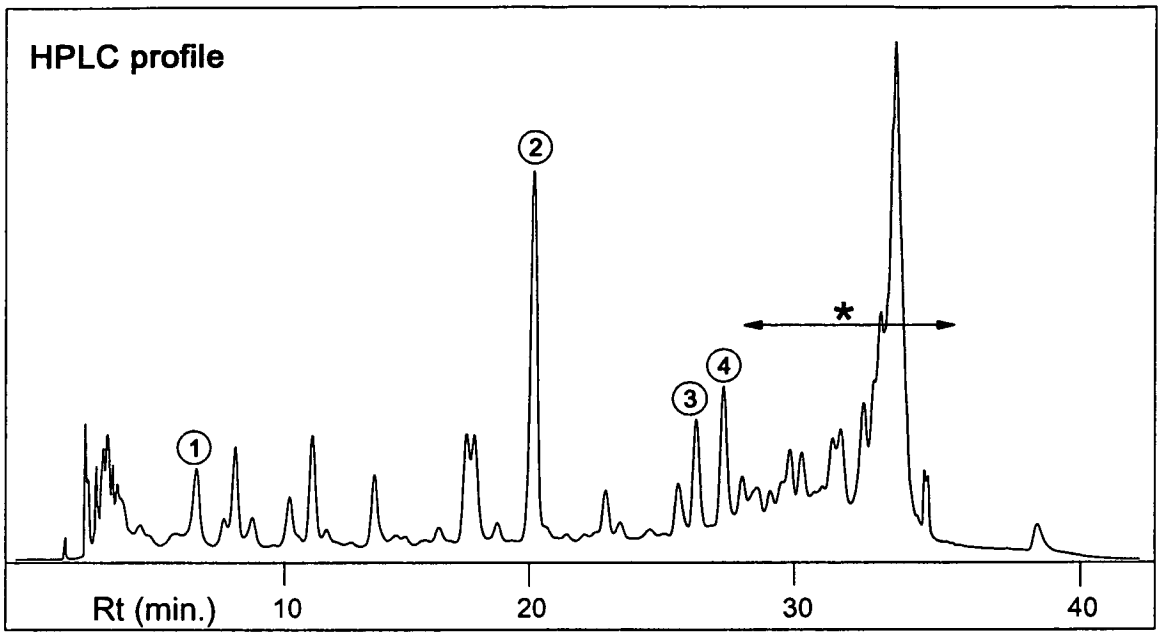
  - RBG, Kew 1987-4090
  - ex hort BSM

Distribution



Aloe steudneri is a high altitude species which is distributed in the Tigre Province of Ethiopia.

Aloe striatula Haworth



Peak number	Retention time	Compound	Percentage
1	7.0	aloesin	2
2	20.0	unidentified flavone	13
3	26.2	aloin A	3
4	27.2	aloin B	4

Very much the same pattern as reported for *A. gracilis* is repeated in *A. striatula*. All peaks in the area denoted by * display an UV absorbance pattern identical to the anthrone, aloin.

- Taxonomic position:

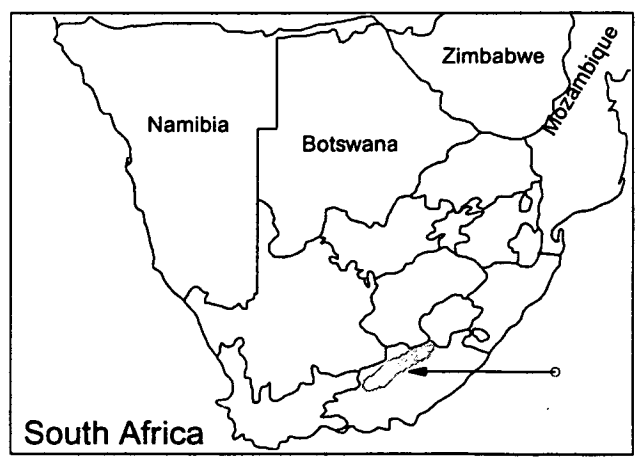
  Aloe series *Macrifoliae* (Reynolds, 1950).

- Samples analysed:

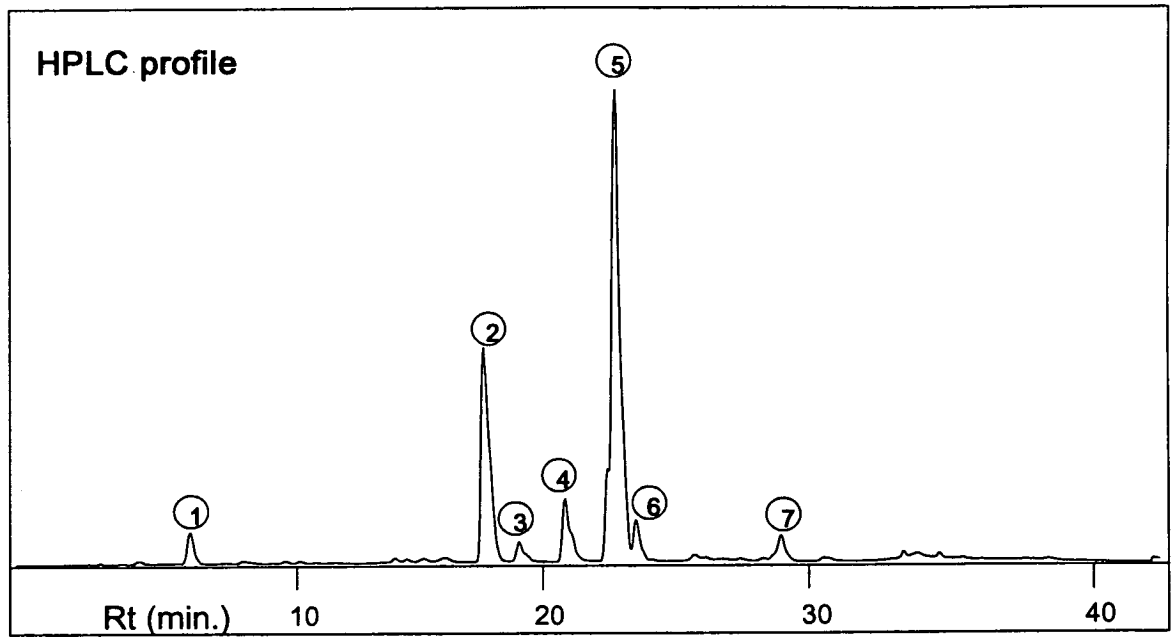
  The leaf extract was investigated:

  - ex hort NBG
  - ex hort JBG

Distribution



Aloe striatula inhabits the mountainous area around Graaff-Reinet and extends eastwards through Somerset East to Cathcart.



Peak number	Retention time	Compound	Percentage
1	6.56	aloesin	3
2	17.71	7-hydroxyaloin B	24
3	19.05	7-hydroxyaloin A	2
4	20.79	unidentified anthrone 1	7
5	22.72	unidentified anthrone 2	56
6	23.51	unidentified anthrone 3	4
7	28.98	unidentified anthrone 4	3

Rauwald *et al. (1986)* isolated three anthrone isomer pairs. The 7-hydroxyaloin pairs have been matched with a reference sample. The other four anthrones show the same UV absorbance spectra as that displayed for 7-hydroxyaloin and most probably represent the mono- and di-acetate analogues of 7-hydroxyaloin.

Distribution

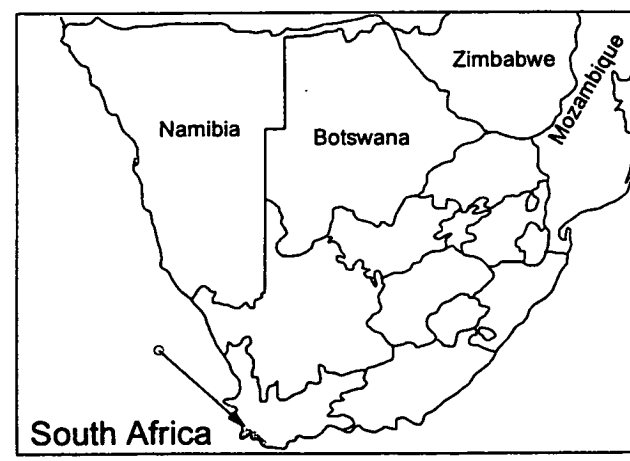
- Taxonomic position:

  Aloe series *Purpurascentes* (Reynolds, 1950).

- Samples analysed:

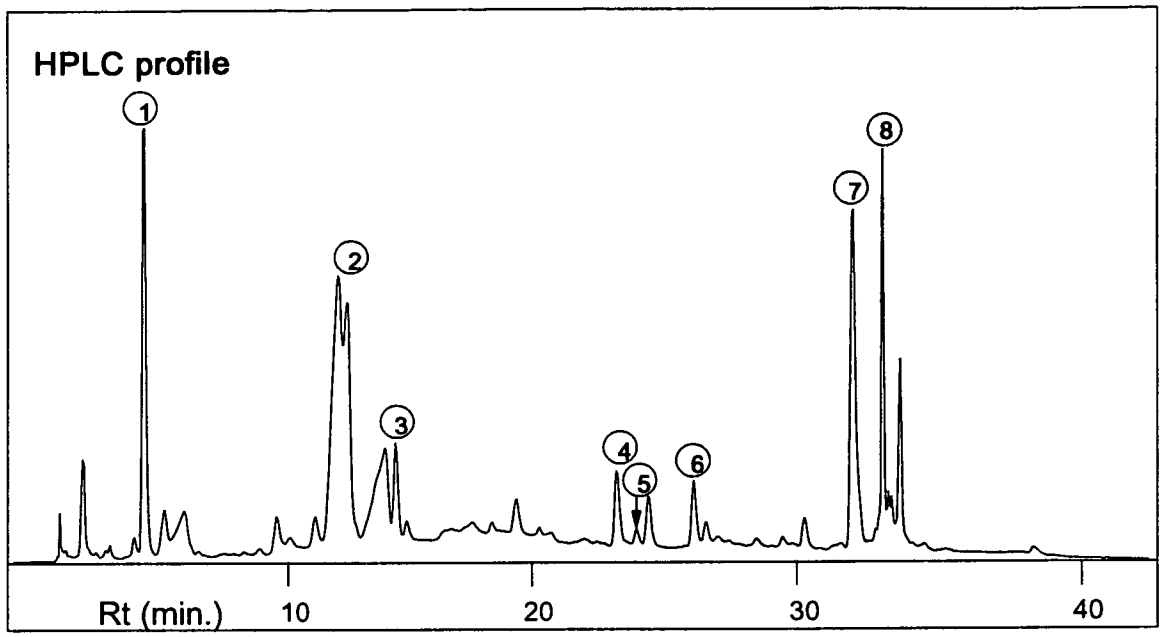
  The leaf exudate was investigated:

  - Hermanus
  - Table Mountain



Aloe succotrina is restricted to the mountain slopes of the SW Cape, South Africa.

Aloe suffulta Reynolds



Peak number	Retention time	Compound	Percentage
1	4.99	aloesin	12
2	12.44	unidentified chromones 1	20
3	14.22	unidentified anthrone	9
4	23.02	unidentified compound	3
5	23.77	homonataloin B	1
6	25.99	homonataloin A	2
7	31.91	unidentified chromone 2	14
8	33.04	unidentified chromone 3	7

This chemically anomalous species produces a series of unidentified coumaroyl chromones. Various samples were analysed but no 'perfect separation' of the compounds could be achieved.

- Taxonomic position:

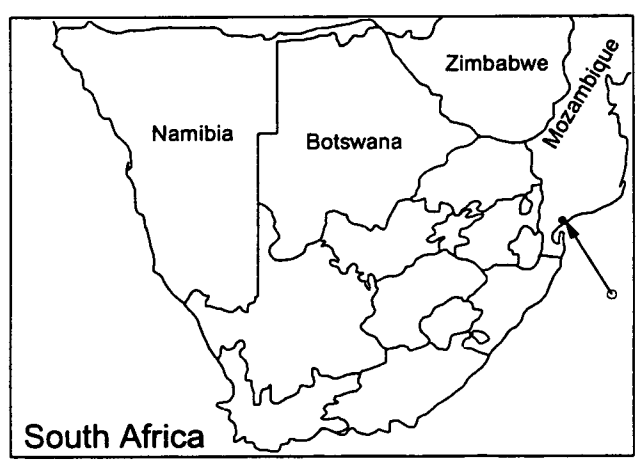
  Aloe series *Aethiopicae* (Reynolds, 1950).

- Samples analysed:

  The leaf exudate was investigated:

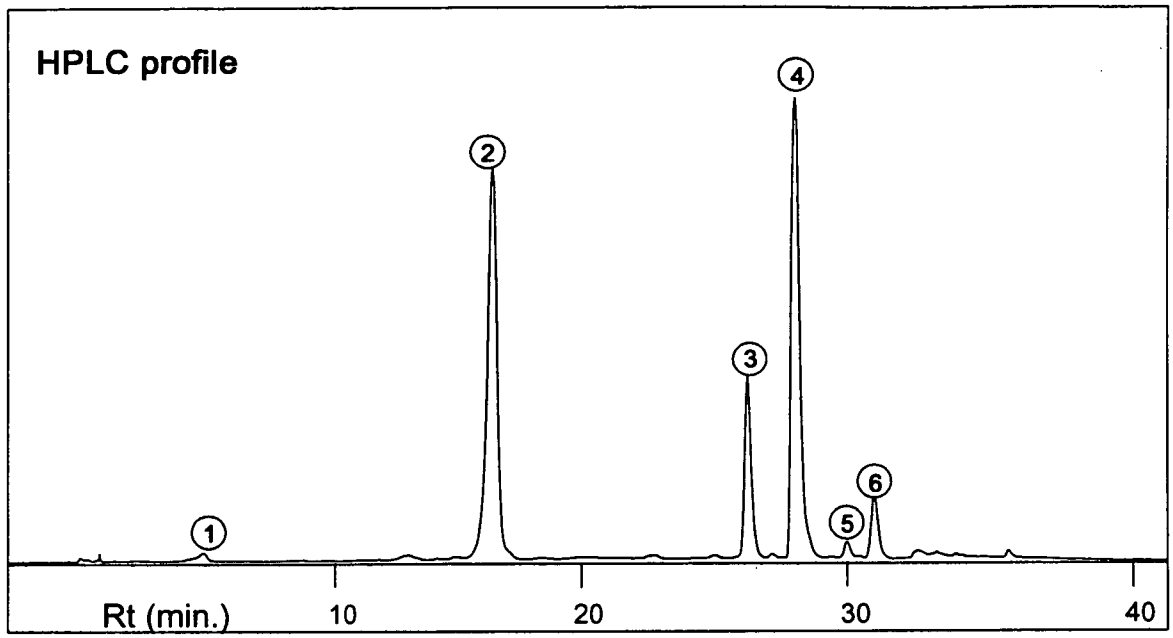
  - Mahatini Flats
  - ex hort JBG

Distribution



Aloe suffulta is only known from a single locality just north of Maputo in Mozambique.

Aloe suprafoliata Pole-Evans



Peak number	Retention time	Compound	Percentage
1	6.17	aloesin	1
2	16.92	aloeresin A	39
3	26.45	homonataloin B	12
4	28.17	homonataloin B	40
5	30.13	unidentified anthrone	1
6	31.15	unidentified chromone	5

The late eluting chromone (peak 6) shows the same UV absorbing characteristics as aloesin and aloeresin A while the unidentified anthrone is most probably a derivative of homonataloin.

- Taxonomic position:

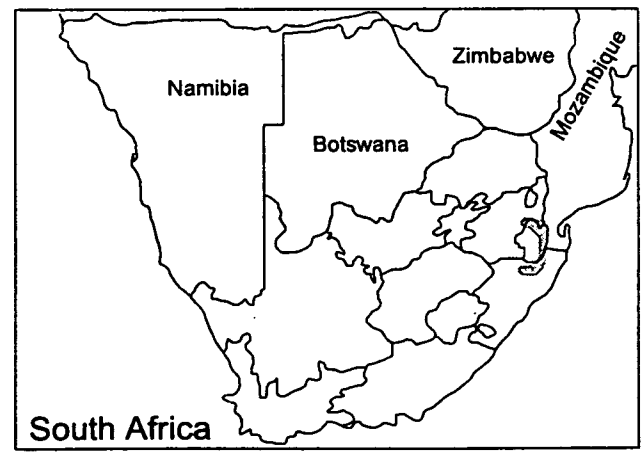
  Aloe series *Superpositae* (Reynolds, 1950).

- Samples analysed:

  The leaf exudate was investigated:

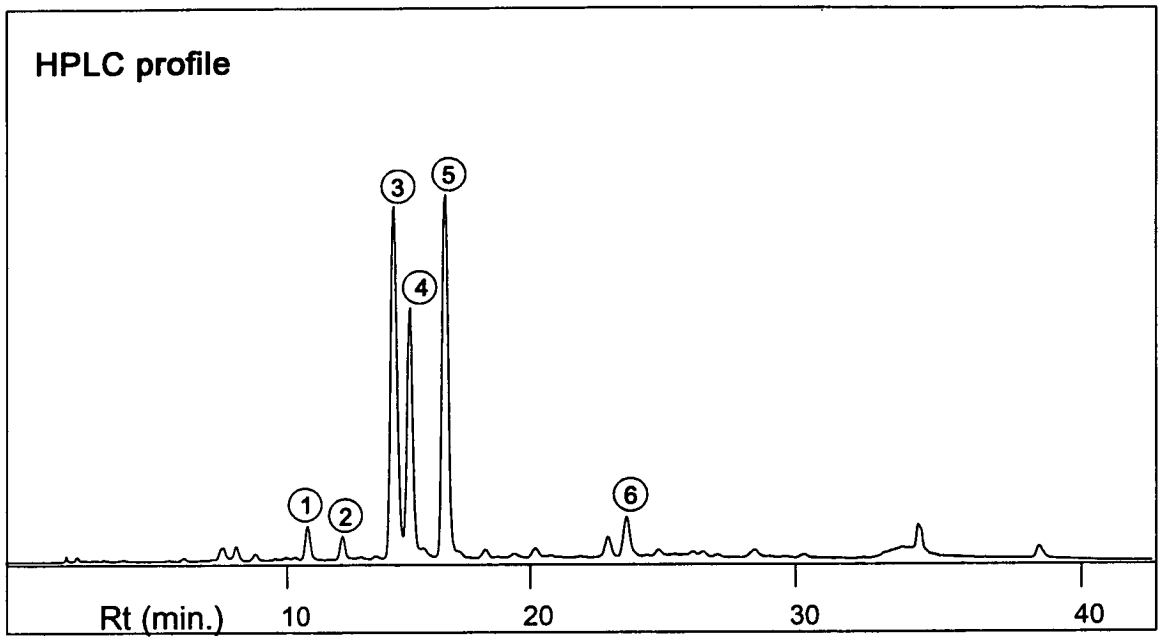
  - Louwsburg

Distribution



This species is found near Vryheid (KwaZulu-Natal) and along the Lobombo in Swaziland. It has also been recorded in Mpumalanga.

Aloe suzannae Decary



Peak number	Retention time	Compound	Percentage
1	11.42	unidentified flavonoid 1	2
2	12.75	unidentified flavonoid 2	2
3	14.70	unidentified flavonoid 3	29
4	15.33	unidentified flavonoid 4	20
5	16.66	unidentified flavonoid 5	30
6	23.40	unidentified flavonoid 6	3

A. suzannae is one of a few Malagasy species which contain flavonoids in the leaf exudate. *A. suzannae* is unique as it is the only species to contain both flavanones and flavones.

- Taxonomic position:

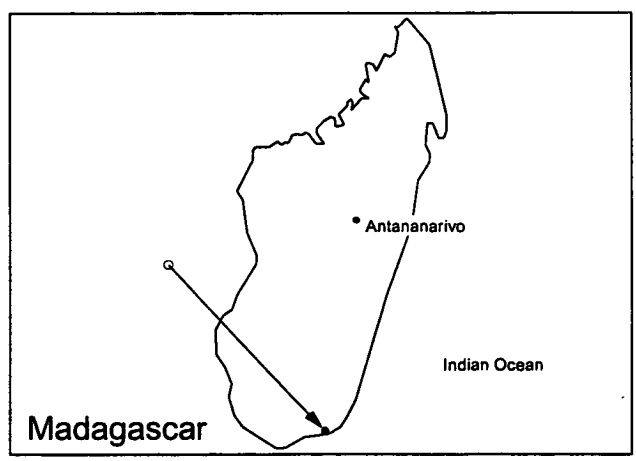
  Group 9 (Reynolds, 1966).

- Samples analysed:

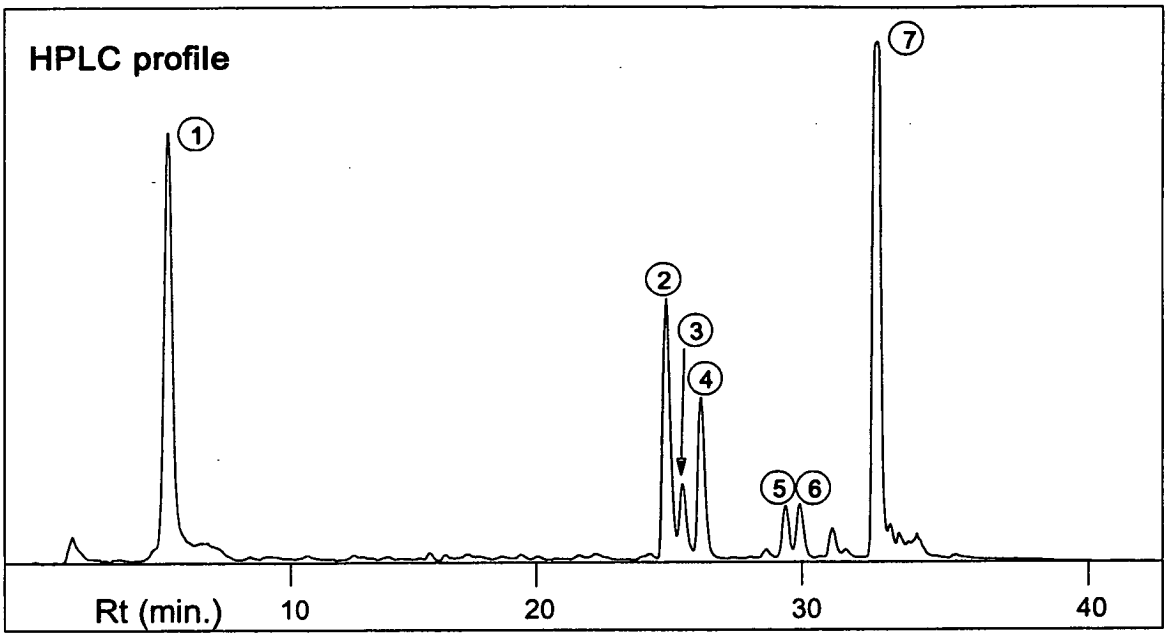
  The leaf exudate was investigated:

  - NBI 16988

Distribution



Aloe suzannae is restricted to the Ambovombe region in the southern part of Madagascar.



Peak number	Retention time	Compound	Percentage
1	5.82	aloesin	28
2	24.71	aloin B	14
3	25.33	unidentified chromone 1	4
4	26.03	aloin A	9
5	29.26	unidentified compound 1	3
6	29.81	unidentified compound 2	3
7	32.73	unidentified chromone 2	33

As suggested by the taxonomic affinity, the leaf exudate profile of this species is identical to the chemical pattern of species pertaining to *Aloe* sect. *Anguialoe*. The unidentified chromone (peak 3) probably relates to the coumaric acid containing chromones while the major compound (peak 7) has a UV spectrum identical to the cinnamoyl chromones.

- Taxonomic position:

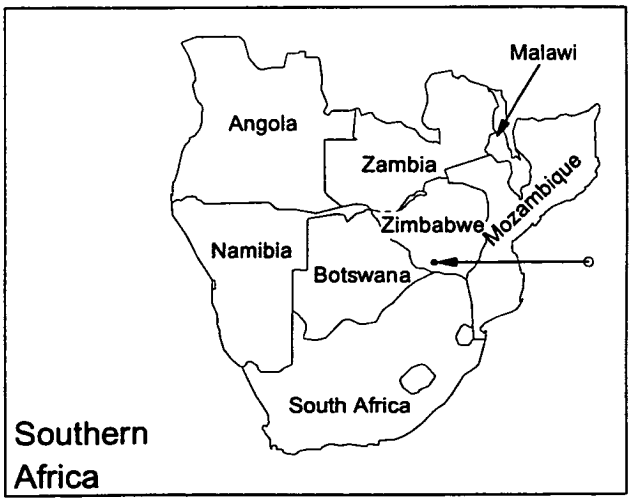
  Allied to *A. spicata* (Leach, 1968).

- Samples analysed:

  The leaf exudate was investigated:

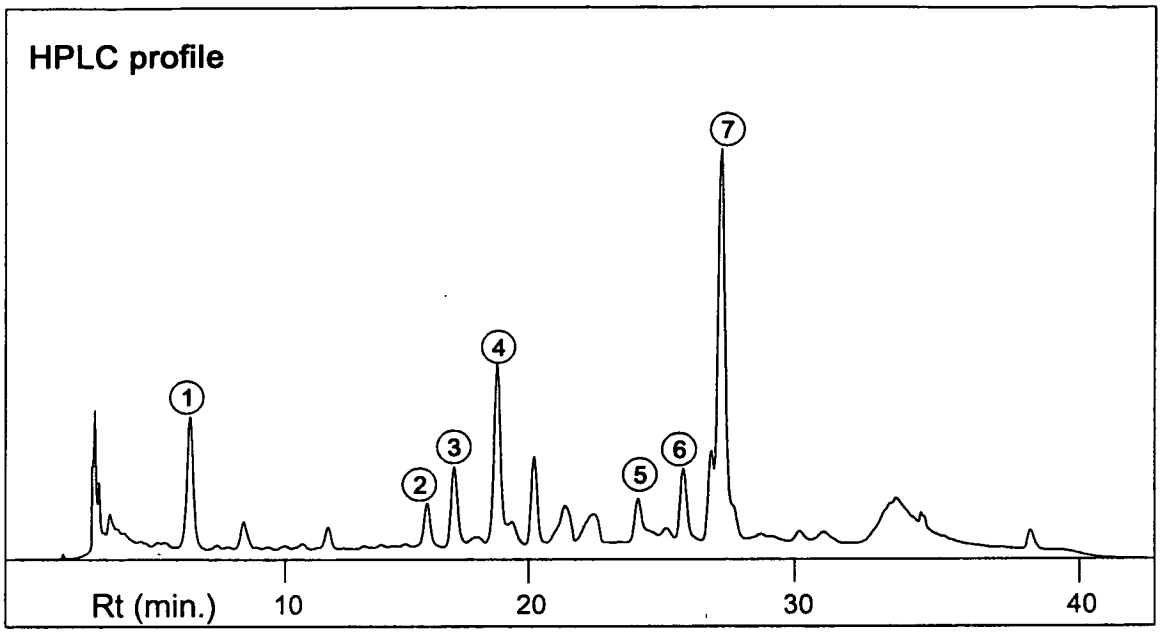
  - A. Ellert 547

Distribution



A. tauri grows near the Mnene Mission in the Belingwe District in southern Zimbabwe.

Aloe tenuior Haworth



Peak number	Retention time	Compound	Percentage
1	6.8	aloesin	8
2	15.9	unidentified flavone 1	3
3	16.9	unidentified flavone 2	5
4	18.6	isovitexin	11
5	24.0	aloin B	3
6	25.7	aloin A	4
7	27.1	unidentified chromone	29

An unknown chromone (aloeresin type compound) is the major phenolic in *A. tenuior*. The flavone, isovitexin occurs with two minor flavones (peak 2 & 3). All samples investigated displayed the general pattern depicted above.

- Taxonomic position:

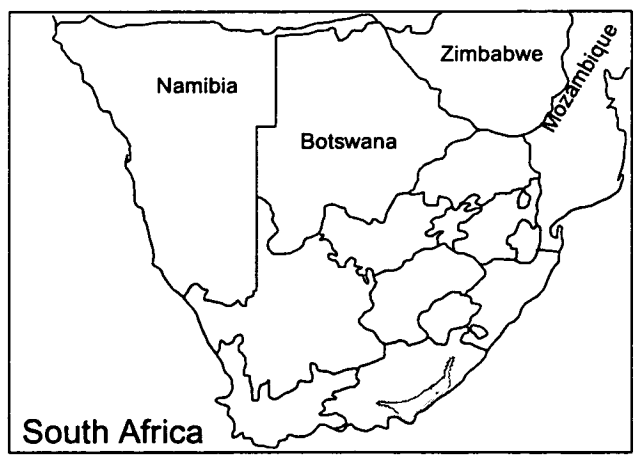
  Aloe series *Macrifoliae* (Reynolds, 1950).

- Samples analysed:

  The leaf extracts were investigated:

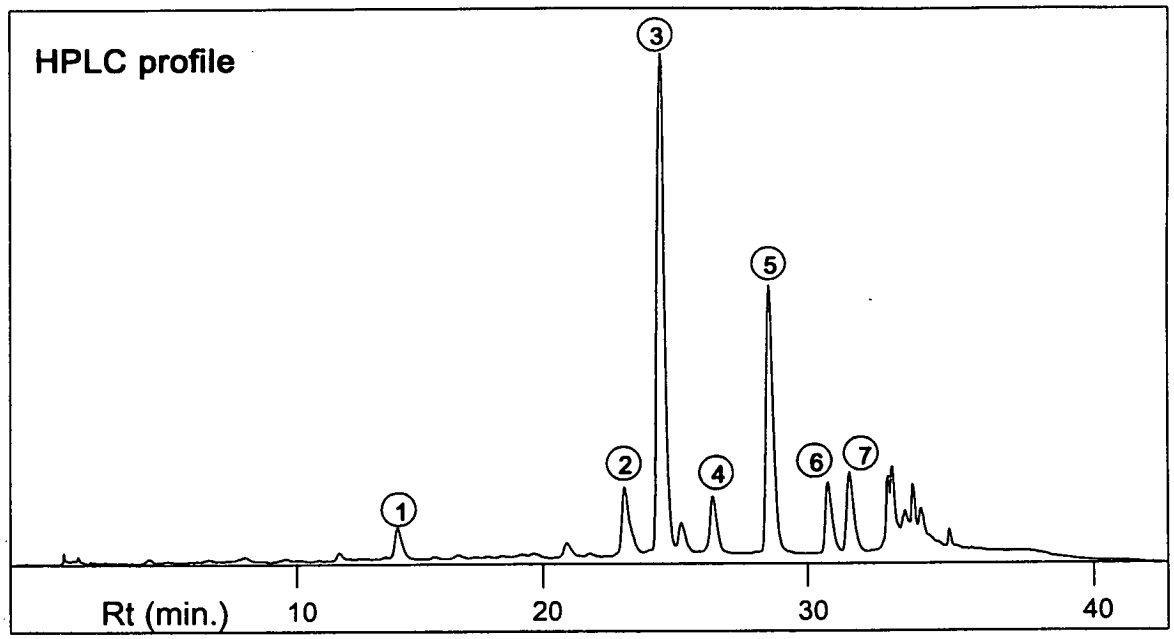
  - ex hort NBI (collected near Grahamstown)
  - ex hort NBI (collected near Transkei)
  - ex hort NBI (collected near Cape Town)

Distribution



Aloe tenuior has an extensive distribution from Cookhouse in the Eastern Cape Province to Tsolo just north of Umtata.

Aloe tewoldei M. G. Gilbert & Sebsebe



Peak number	Retention time	Compound	Percentage
1	14.32	dihydroisocoumaringlucoside	2
2	22.90	aloin B	5
3	24.23	aloin A	41
4	26.20	aloinoside B	4
5	28.35	aloinoside A	21
6	30.55	microdontin B	5
7	31.34	microdontin A	6

- Taxonomic position:

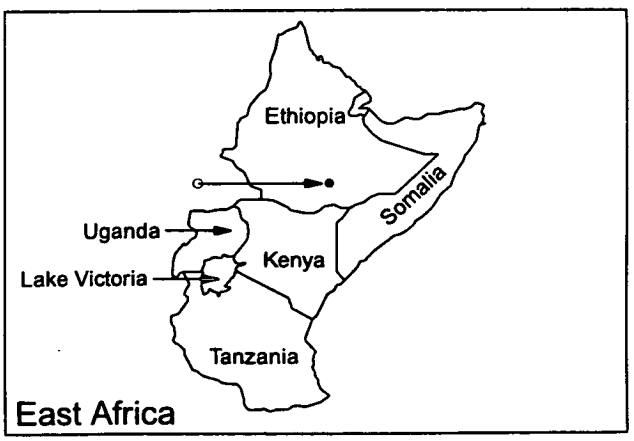
  Allied to *A. jacksonii* (Gilbert & Demissew, 1997).

- Samples analysed:

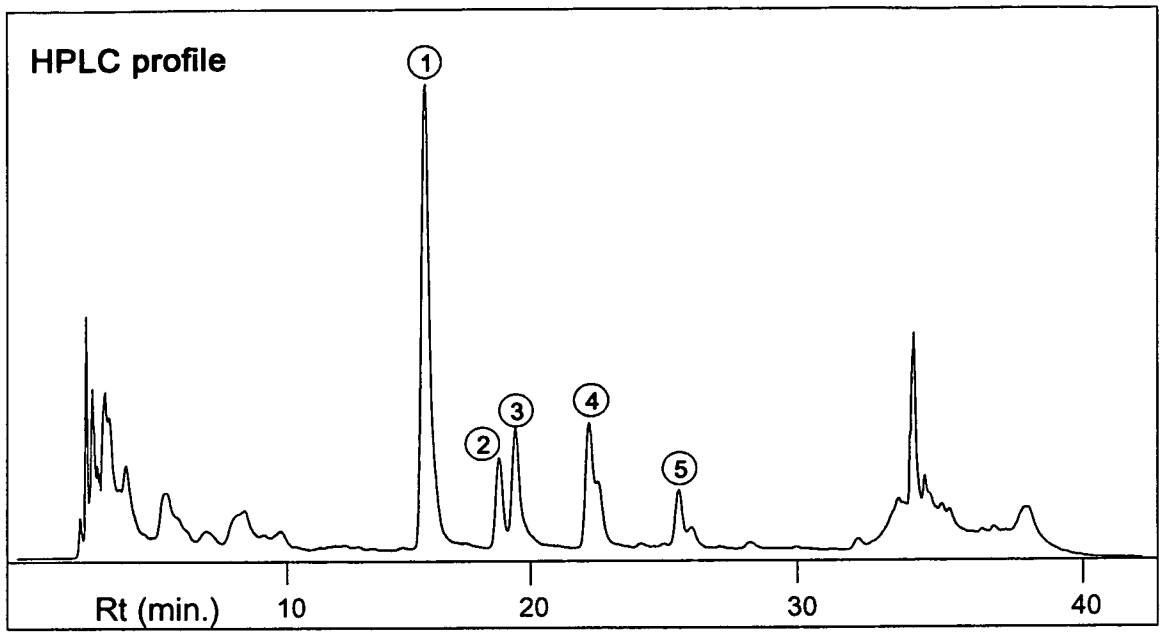
  The leaf exudate was investigated:

  - from type locality (ex Sebsebe)

Distribution



This species is only known to occur south of Asbe Teferri in the Harerge Province of Ethiopia.



Peak number	Retention time	Compound	Percentage
1	15.8	unidentified flavone 1	30
2	19.2	isovitexin	5
3	21.5	unidentified flavone 2	8
4	2222	unidentified compound 1	8
5	25.4	unidentified compound 2	3

The flavone, isovitexin co-occurs with the two unknown flavones. The unknown compounds (peak 4 and 5) reported in *A. saundersiae* is also present in *A. thompsoniae.*

- Taxonomic position:

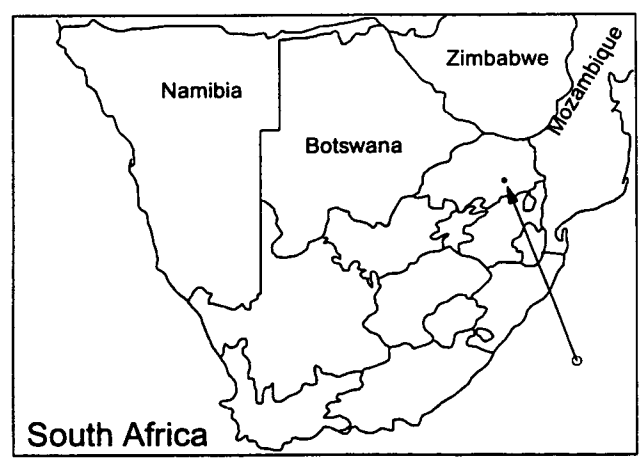
  Aloe section *Leptoaloe* (Reynolds, 1950).

- Samples analysed:

  The leaf extract was investigated:

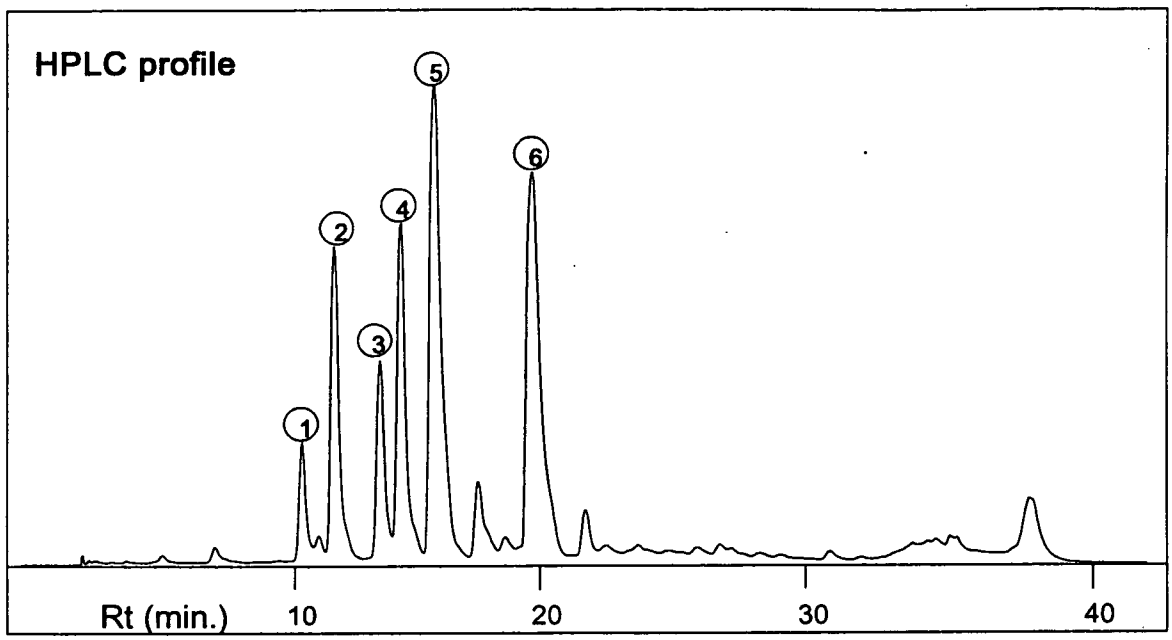
  - NBI 29456

Distribution



This species is only known from the Wolkberg in the Northern Province.

Aloe thorncroftii Pole-Evans



Peak number	Retention time	Compound	Percentage
1	10.66	unidentified flavonoid 1	4
2	11.89	unidentified flavonoid 2	12
3	13.73	unidentified flavonoid 3	7
4	14.50	unidentified flavonoid 4	13
5	15.78	unidentified flavonoid 5	25
6	19.53	unidentified flavonoid 6	23

Aloe thorncroftii represents one of the few examples of *Aloe* which contain flavonoids (flavanones / dihydroflavonols) in the leaf exudate as apposed to the frequently detected chromones and anthrones.

- Taxonomic position:

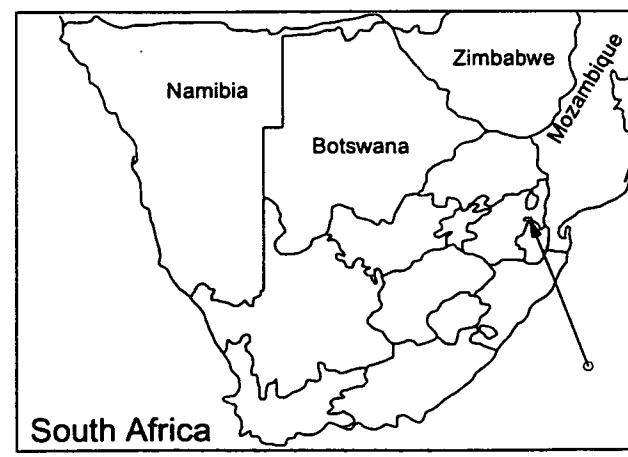
  Aloe series *Superpositae* (Reynolds, 1950).

- Samples analysed:

  The leaf exudate was investigated:

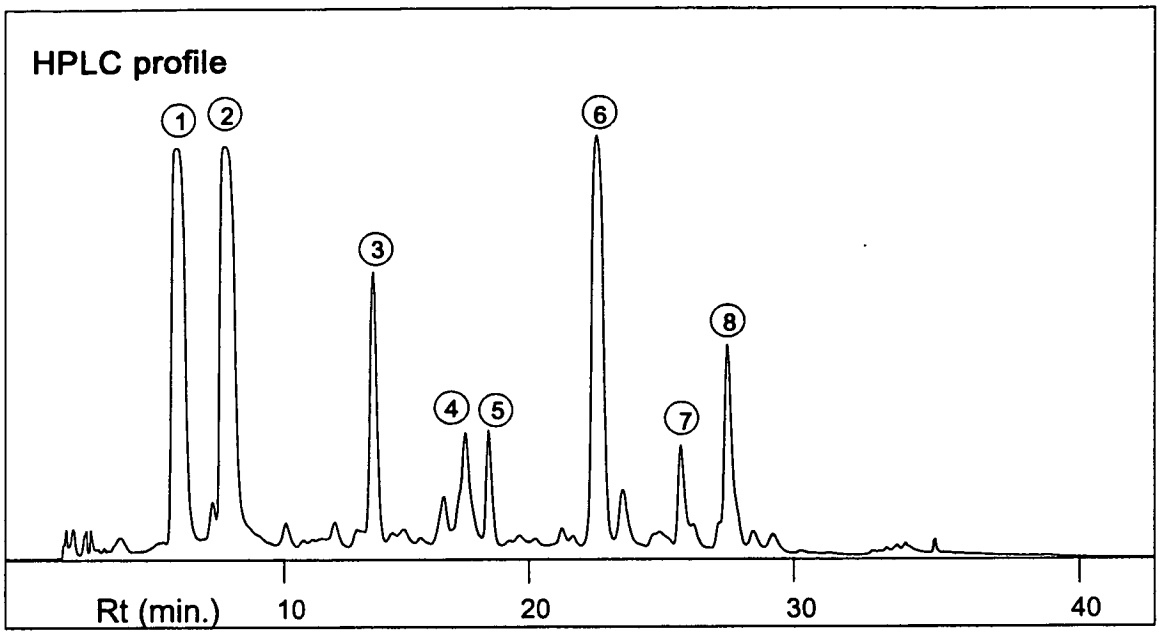
  - NBI 28436

Distribution



This high altitude species inhabits the mountains around Barberton in Mpumalanga.

Aloe thraskii Baker



Peak number	Retention time	Compound	Percentage
1	6.44	aloesin	20
2	8.26	7-*O*-methylaloesin	23
3	13.91	unidentified chromone 1	7
4	17.36	unidentified chromone 2	5
5	18.23	unidentified chromone 3	3
6	22.29	unidentified chromone 4	17
7	25.47	homonataloin A	3
8	27.23	homonataloin B	7

This species shows a high degree of correlation in terms of leaf exudate composition with *A. rupestris*. This species does however produce anthrones in addition to a series of unidentified chromones.

- Taxonomic position:

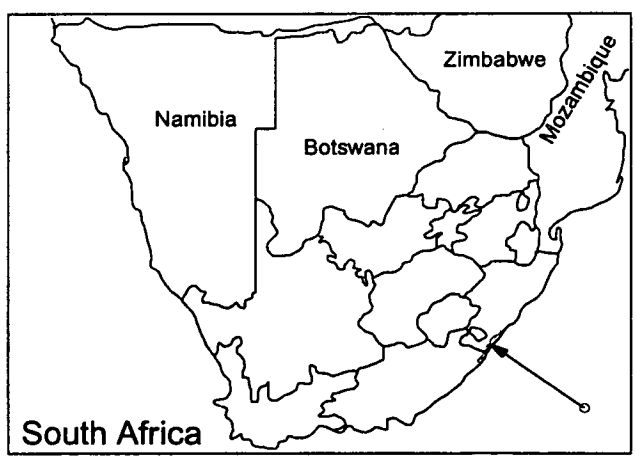
  Aloe section *Pachydendron* (Reynolds, 1950)

- Samples analysed:

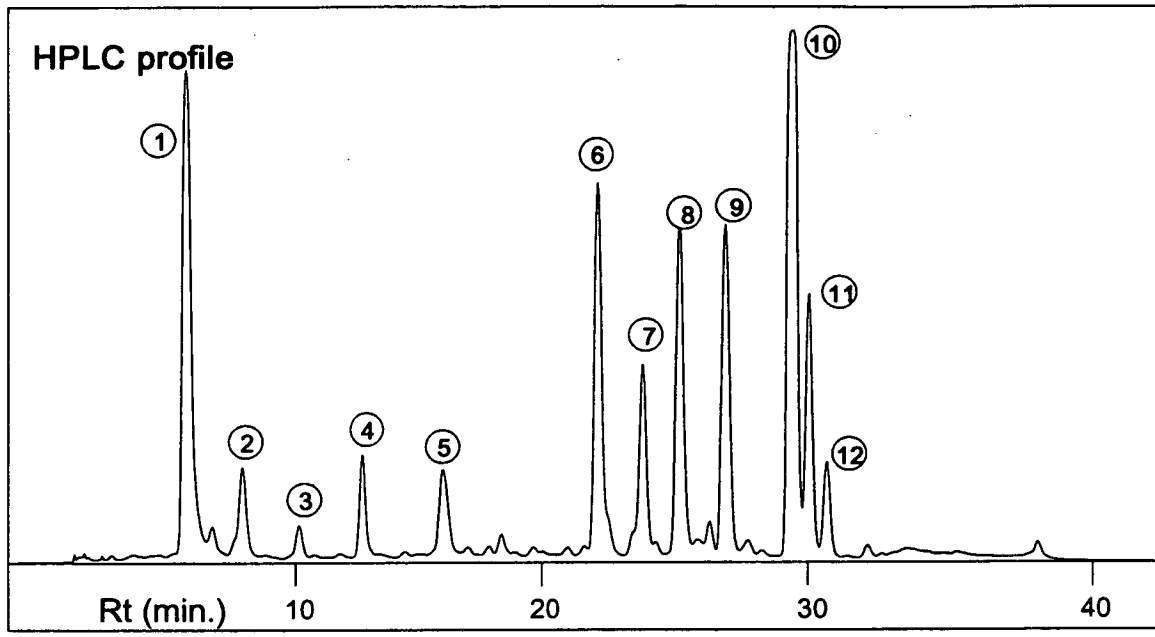
  The leaf exudate was investigated:

  - Illovo River
  - Zinkwasi
  - Umkomaas
  - Port Elizabeth

Distribution



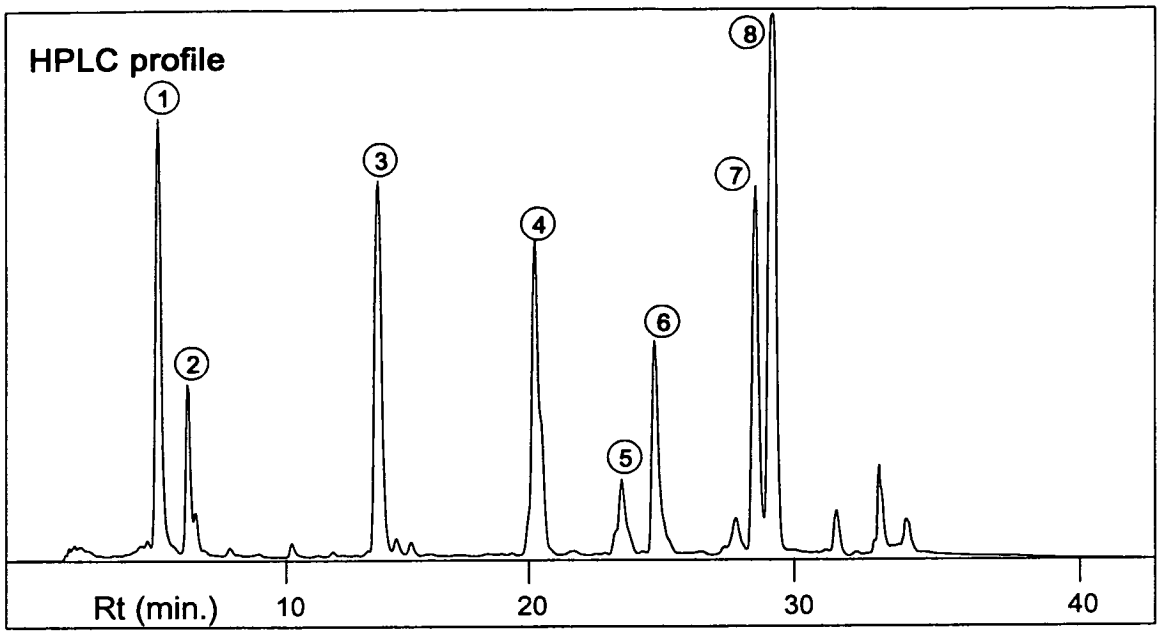
Aloe thraskii is found on the sand dunes of the east coast of South Africa.



Peak number	Retention time	Compound	Percentage
1	6.30	aloesin	17
2	8.43	7-*O*-methylaloesin	3
3	10.58	unidentified chromone 1	1
4	13.02	homonataloside B	3
5	16.08	dihydroisocoumaringlucoside	3
6	21.52	aloeresin D	11
7	23.69	unidentified compound 2	6
8	25.09	homonataloin B	10
9	26.24	homonataloin A	10
10	29.33	unidentified chromone 3	21
11	29.96	unidentified compound 4	7
12	30.62	unidentified chromone 5	3

Aloe tomentosa represents one of the most complex species in terms of leaf exudate composition. The unidentified chromones 1 and 3 are most probably cinnamoyl chromones while peak 12 could be a coumaroyl chromone. The UV spectra of the unidentified compounds 2 and 4 are identical and could not be ascribed to any known group of compounds.

cont/....



Peak number	Retention time	Compound	Percentage
1	5.51	aloesin	13
2	6.65	7-*O*-methylaloesin	4
3	14.00	8-*O*-methyl-7-hydroxyaloin	14
4	20.14	aloeresin D	10
5	23.35	aloin B	3
6	24.60	aloin A	8
7	28.42	unidentified chromone 1	12
8	29.07	unidentified chromone 2	23

This sample of *Aloe tomentosa* taken from the NBI (21758) correlates to the sample taken from the RBG (Kew) in that both contain aloeresin D and the unidentified cinnamoyl chromone.

- Taxonomic position:

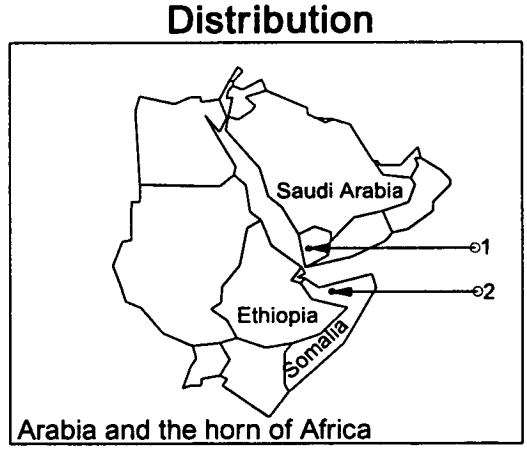
  Group 9 of the tropical aloes (Reynolds, 1966).

- Samples analysed:

  The leaf exudate was investigated:

  - RBG, Kew 305-70-02870
  - NBI 21758

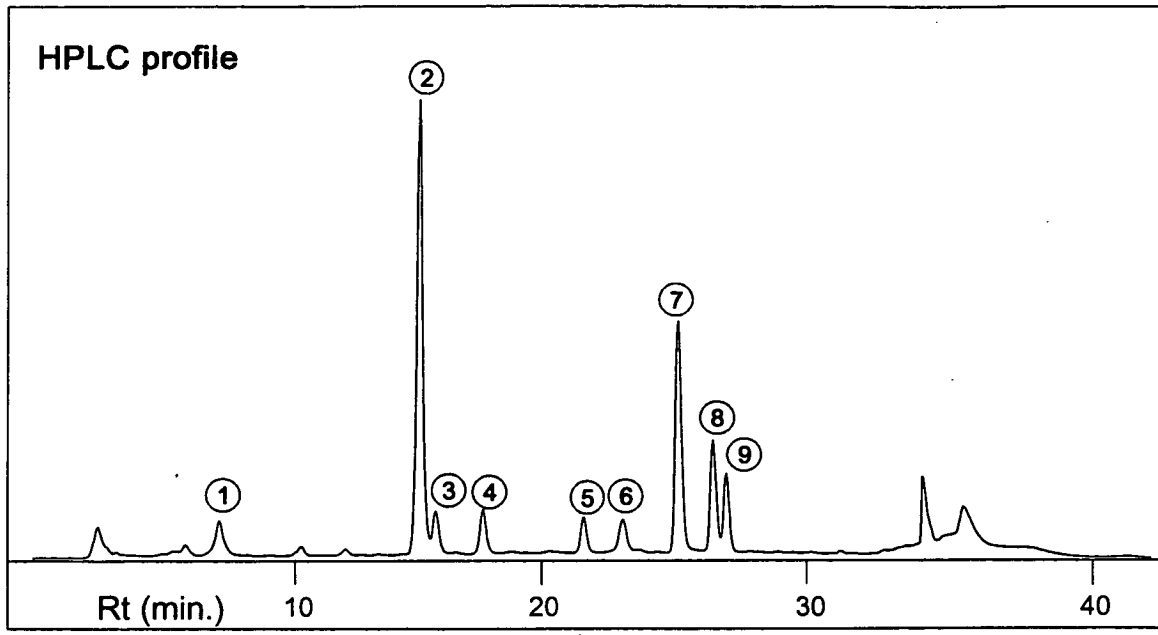
Distribution



Arabia and the horn of Africa

Aloe tomentosa is found near Bauan in the Yemen (1) and also in the vicinity of Erigavo (2) in northern Somalia

Aloe tororoana Reynolds



Peak number	Retention time	Compound	Percentage
1	7.12	7-*O*-methylaloesin	3
2	14.85	aloenin	38
3	15.48	unidentified anthrone 1	4
4	17.29	unidentified anthrone 2	4
5	21.19	unidentified compound 1	3
6	22.70	unidentified compound 2	3
7	24.84	aloin B and unidentified compound 3	20
8	26.17	aloin A	9
9	26.67	unidentified compound 4	6

The chemical pattern for *A. tororoana* seems to be similar to the *A. bussei* / *A. dorotheae* complex. The concentrations of the unidentified compounds were found to be too low to suggest a convincing match between this species and the others mentioned above.

- Taxonomic position:

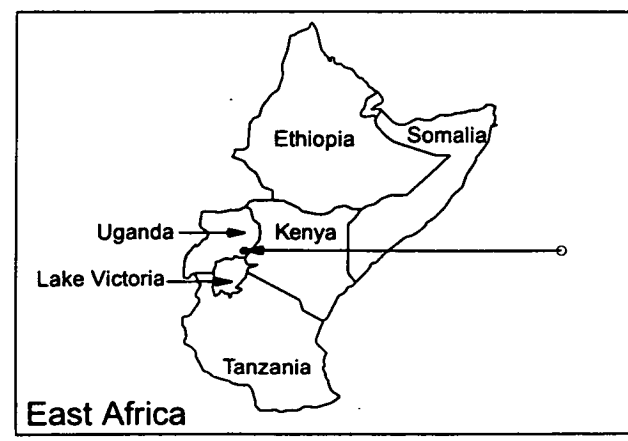
  Group 19 of the tropical aloes (Reynolds, 1966).

- Samples analysed:

  The leaf exudate was investigated:

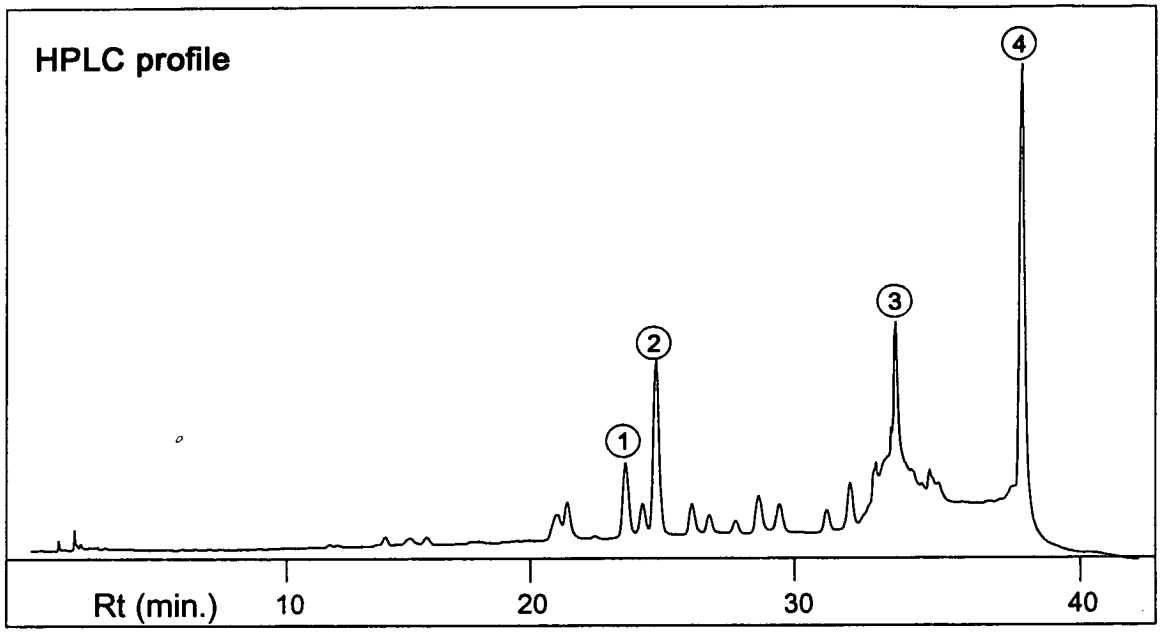
  - ex hort P. Favell

Distribution



This species is only known from the type locality which is near the summit of Tororo Rock in the south-eastern part of Uganda.

Aloe trichosantha A. Berger



Peak number	Retention time	Compound	Percentage
1	23.70	aloin B	tr
2	24.42	aloin A	25
3	33.71	unidentified compound 1	15
4	38.50	unidentified compound 2	60

The concentration of phenolic compounds are very low in this species. No class of compound could be ascribed to the two unidentified peaks.

- Taxonomic position:

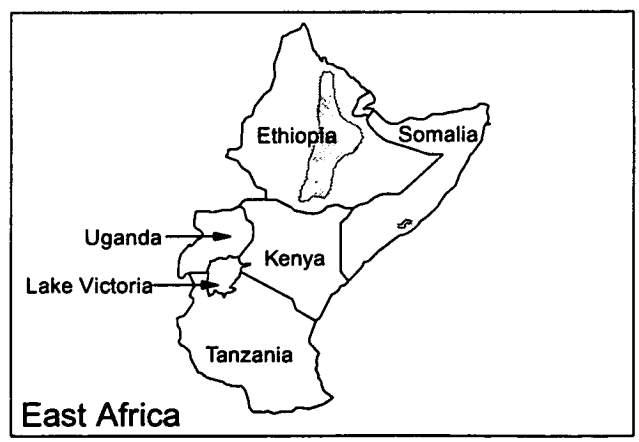
  Group 9 of the tropical aloes (Reynolds, 1966).

- Samples analysed:

  The leaf exudate was investigated:

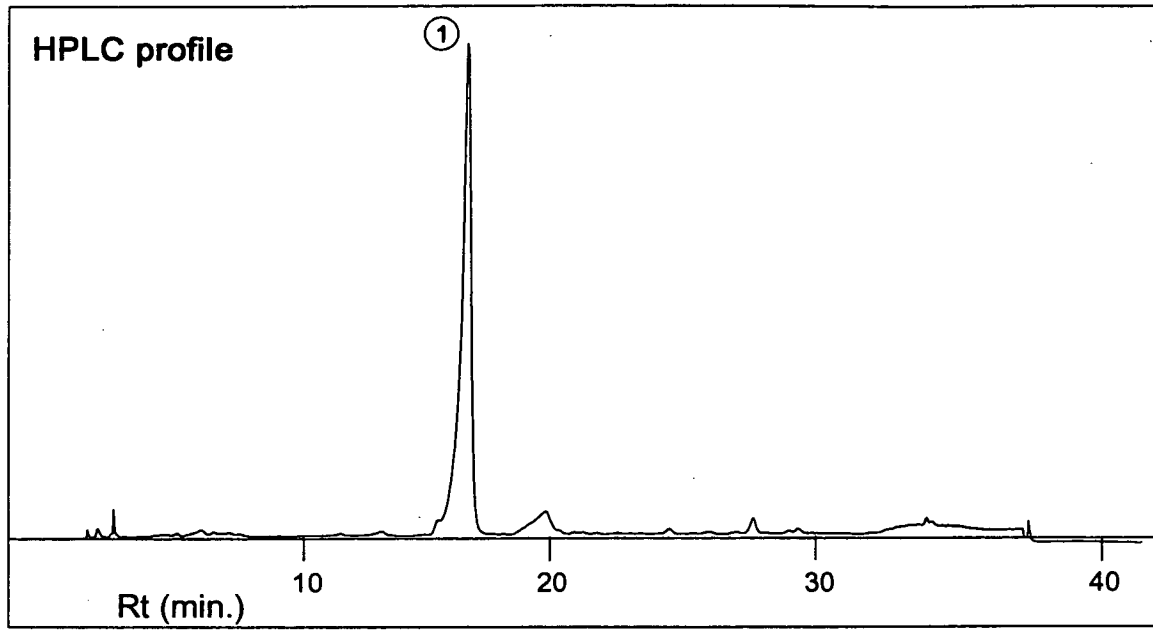
  - Sebsebe 4658
  - NBI 11217

Distribution



Aloe trichosantha is widely distributed in central Ethiopia. It extends from Nefasit in the north to Yavello in the south. Reynolds also reported plants north of Mogadishu in Somalia.

Aloe tugenensis L. E. Newton & Lavranos



Peak number	Retention time	Compound	Percentage
1	16.94	plicataloside	79

- Taxonomic position:

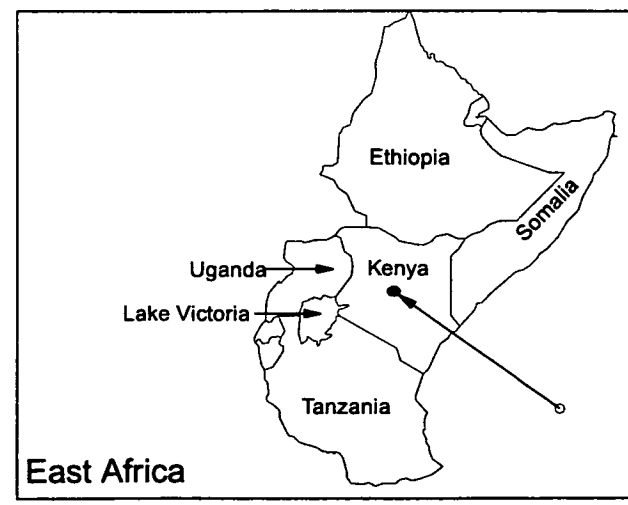
  Group 11 of the tropical aloes (Newton & Lavranos, 1990).

- Samples analysed:

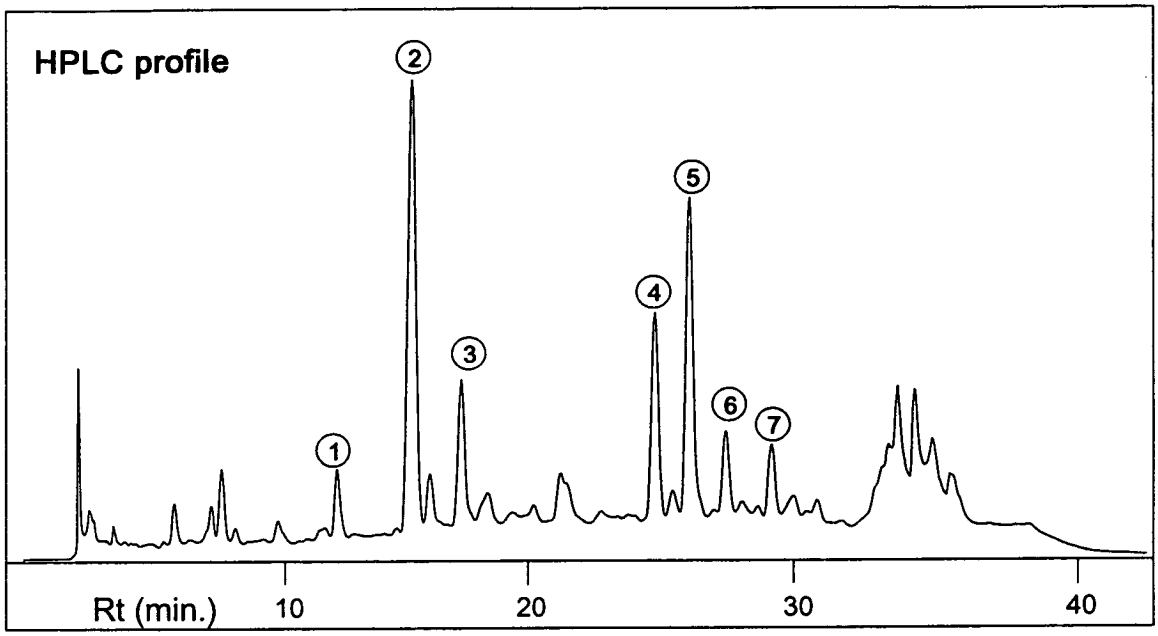
  The leaf exudate was investigated:

  - L. E. Newton 3514 (type plant)

Distribution



Aloe tugenensis is only known from the Baringo District in Kenya.



Peak number	Retention time	Compound	Percentage
1	12.11	unidentified compound 1	3
2	15.01	8-O-methyl-7-hydroxyaloin	34
3	16.93	unidentified compound 2	17
4	24.34	aloin B	14
5	25.63	aloin A	21
6	27.02	unidentified compound 3	5
7	28.50	unidentified compound 4	4

The compound denoted by peak 2 was isolated and identified from *A. schelpei* and its occurrence was confirmed in this species through co-injection on HPLC. No possible class of compound could be ascribed to any of the unidentified compounds.

- Taxonomic position:

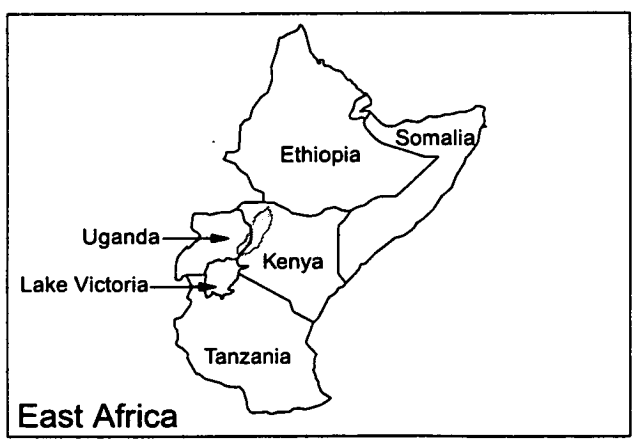
  Group 13 of the tropical aloes (Reynolds, 1966).

- Samples analysed:

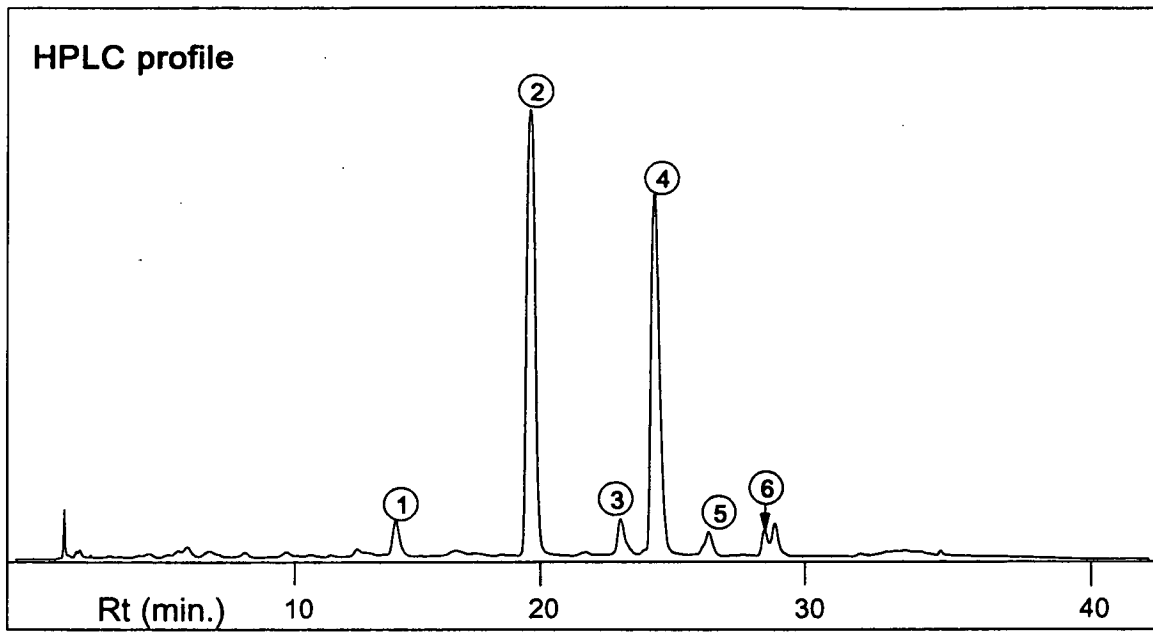
  The leaf exudate was investigated:

  - RBG, Kew 1977-3733

Distribution



Aloe turkanensis is found around Lake Turkana from where it extends south westerly to Amudat and the Toror Mountains in Uganda.



Peak number	Retention time	Compound	Percentage
1	14.38	dihydroisocoumaringlucoside	3
2	19.46	aloeresin D	46
3	22.92	aloin B	3
4	23.85	aloin A	38
5	26.09	aloinosides B	2
6	28.44	aloinosides A	2

- Taxonomic position:

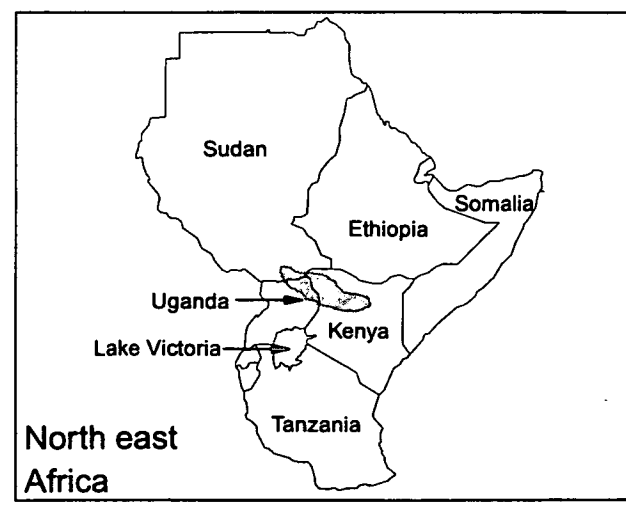
  Group 16 of the tropical aloes (Reynolds, 1966).

- Samples analysed:

  The leaf exudate was investigated:

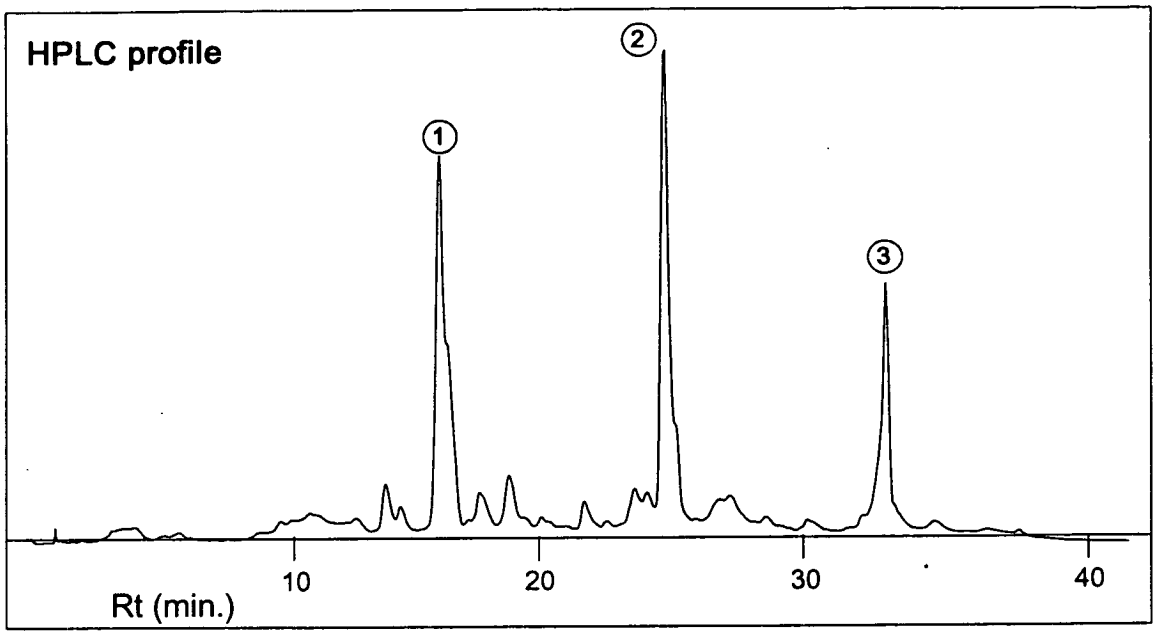
  - RBG, Kew 1970-1752

Distribution



This species has been recorded in the south-eastern parts of Sudan, NE Uganda and the northern parts of Kenya.

Aloe ukambensis Reynolds



Peak number	Retention time	Compound	Percentage
1	16.66	plicataloside	26
2	24.99	unidentified compound 1	32
3	33.64	unidentified compound 2	18

The naphthalene compound, plicataloside, co-occurs with two unidentified compounds unique to this species.

- Taxonomic position:

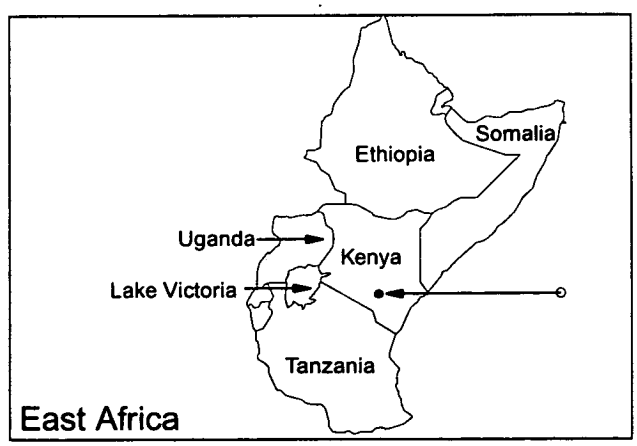
  Group 16 of the tropical aloes (Reynolds, 1966).

- Samples analysed:

  The leaf exudate was investigated:

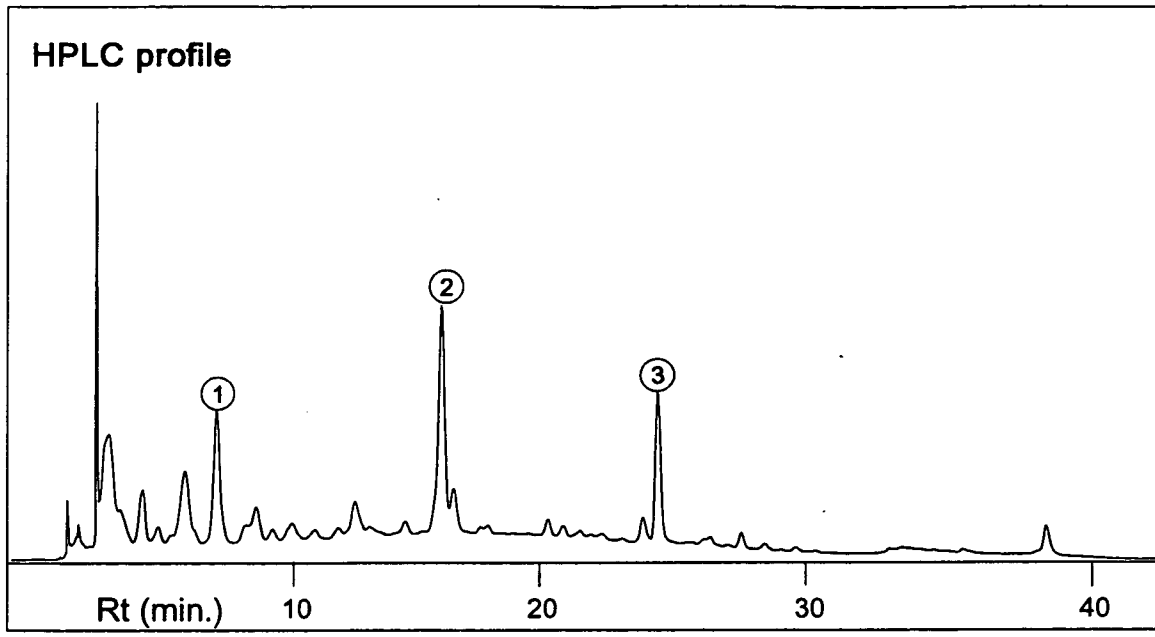
  - NBI 20505

Distribution



Aloe ukambensis is found on exposed rocky outcrops in the Fort Hall and Kitui Districts of Kenya

Aloe vacillans Forsskål



Peak number	Retention time	Compound	Percentage
1	7.65	unidentified compound 1	14
2	16.11	unidentified compound 2	23
3	23.66	unidentified compound 3	13

This species of aloe contains unique compounds in the leaf exudate. The UV spectra of all three the compounds are identical but do not match with any of the known classes of compounds screened for in this study. A second sample (also from Kew) was analysed and showed the same compounds to be present.

- Taxonomic position:

  Group 9 of the tropical aloes (Reynolds, 1966).

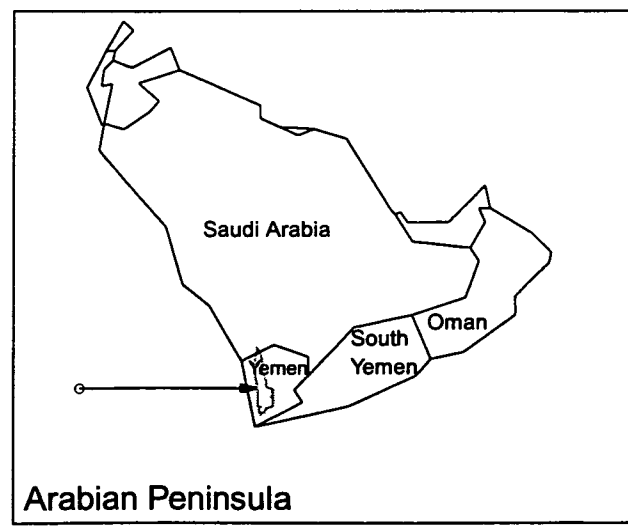
  Syn. *A. dhalensis* & *A. audhalica*.

- Samples analysed:

  The leaf exudate was investigated:

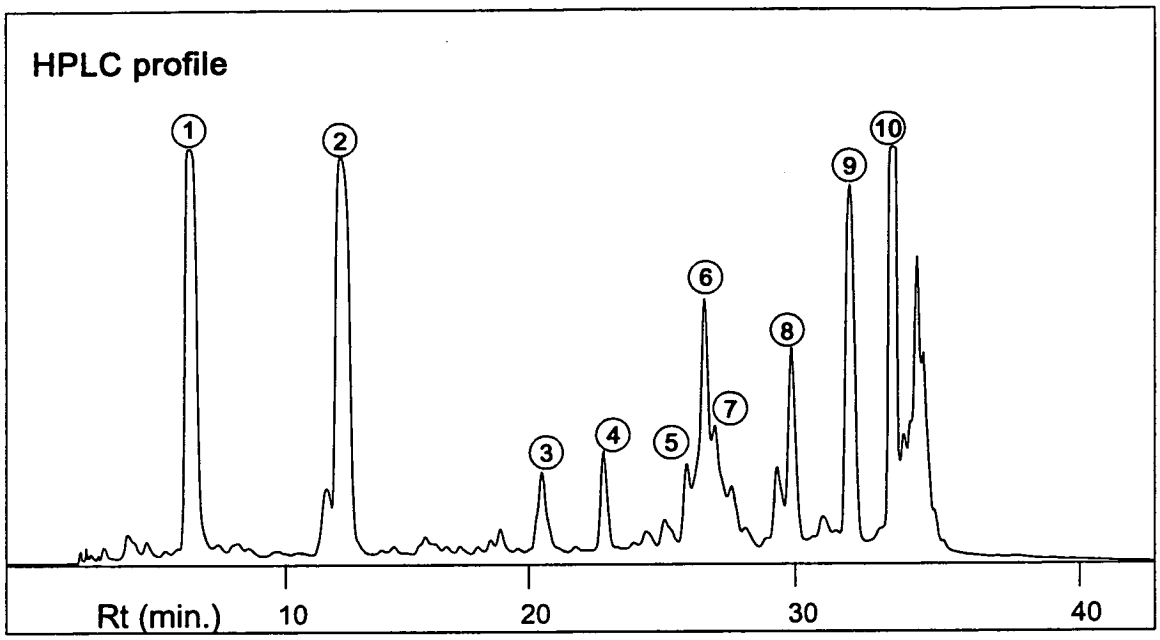
  - RBG, Kew 06077-00398
  - RBG, Kew 1977-3664

Distribution



Aloe vacillans is common on the western and southern escarpments of the Yemen from where it extends northwards into Saudi Arabia.

Aloe vanbalenii Pillans



Peak number	Retention time	Compound	Percentage
1	6.92	aloesin	14
2	12.65	unidentified compound 1	15
3	20.33	unidentified compound 2	2
4	22.54	unidentified compound 3	2
5	24.79	aloin B	1
6	25.61	unidentified compound 4	2
7	26.25	aloin B	7
8	29.49	unidentified chromone 1	5
9	31.67	unidentified chromone 2	10
10	33.27	unidentified chromone 3	11

The chemical profile of *A. vanbalenii* is dominated by a series of unidentified compounds and unknown chromones. The unidentified compounds (1 - 4) display UV absorbance spectra unique to this species while the two unidentified chromones are probably cinnamoyl chromones.

- Taxonomic position:

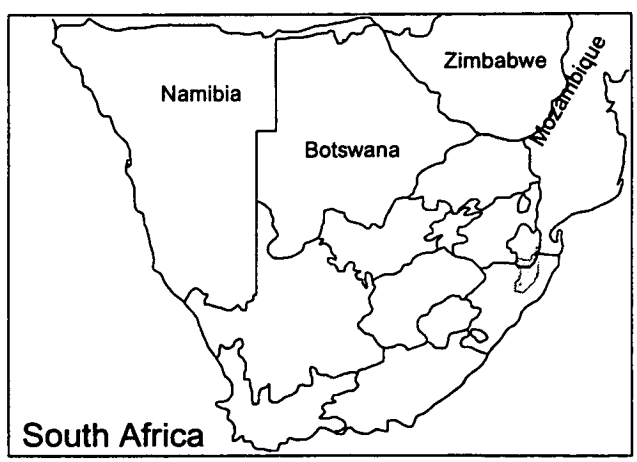
  Aloe series *Arborescentes* (Reynolds, 1950)

- Samples analysed:

  The leaf exudate was investigated:

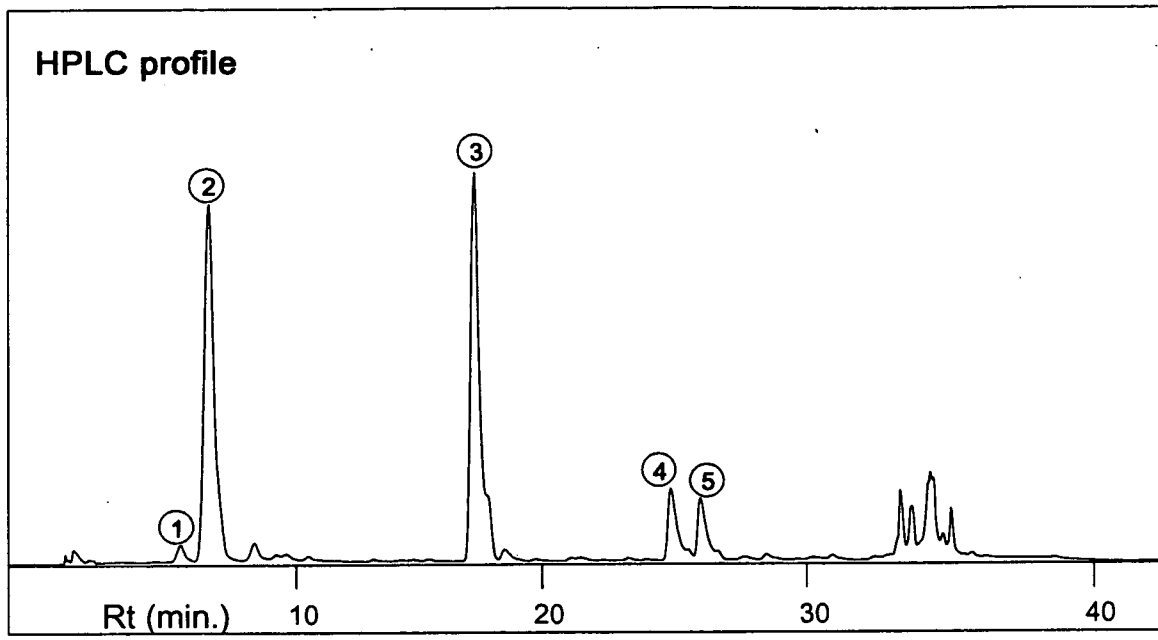
  - ex hort D. Hardy
  - ex hort The Wilds

Distribution



Aloe vanbalenii inhabits rocky outcrops in the Mpumalanga and KwaZulu-Natal Provinces of South Africa.

Aloe vaotsanda Decary



Peak number	Retention time	Compound	Percentage
1	6.37	aloesin	1
2	7.41	unidentified flavonoid 1	33
3	17.34	unidentified flavonoid 2	33
4	24.67	aloin B	7
5	25.78	aloin A	6

A. vaotsanda is another Malagasy endemic displaying a unique chromatographic profile as it contains two flavanones / dihydroflavonols as the main compounds together with the anthrone aloin.

- Taxonomic position:

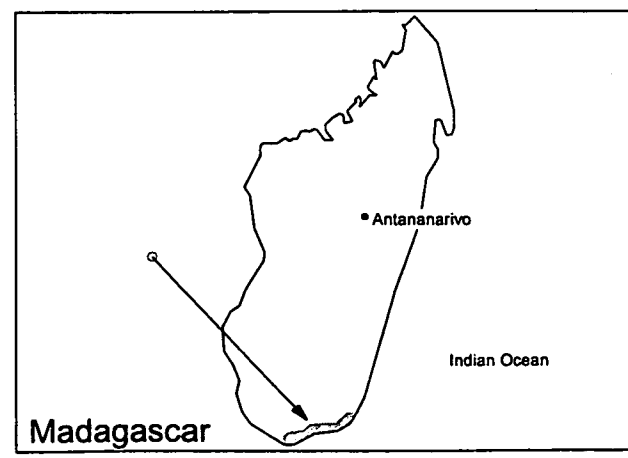
  Group 9 (Reynolds, 1966).

- Samples analysed:

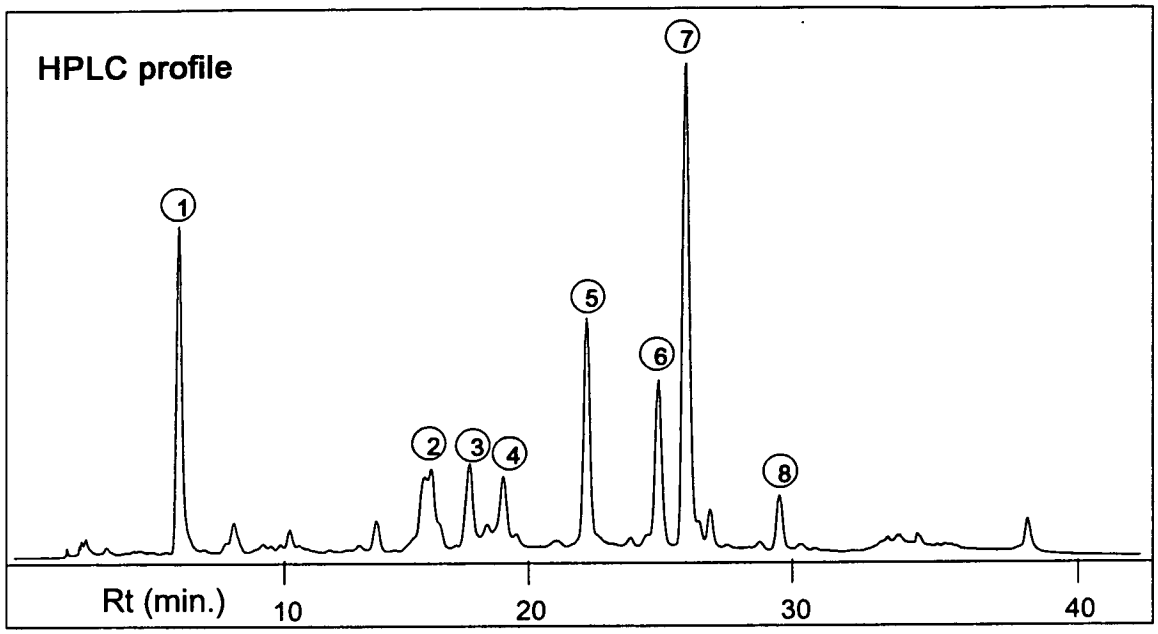
  The leaf exudate was investigated:

  - ex hort D. Hardy

Distribution



Aloe vaotsanda is found in the south-eastern parts of Madagascar. It is especially abundant near Tsihombe and Ambovombe.



Peak number	Retention time	Compound	Percentage
1	6.35	aloesin	14
2	16.07	unidentified compound	10
3	17.55	7-hydroxyaloin	5
4	18.83	unidentified chromone 1	5
5	22.02	aloeresin D	12
6	24.75	aloin B	10
7	25.78	aloin A	28
8	29.36	unidentified chromone 2	3

Aloe vera is characterised by the presence of the anthrones 7-hydroxyaloin and aloin A and B. The unidentified chromone 2 is probably related to the group of chromones containing a cinnamic acid ester.

- Taxonomic position:

  Group 9 of the tropical aloes (Reynolds, 1966).
  (syn. *A. barbadensis* Miller)

- Samples analysed:

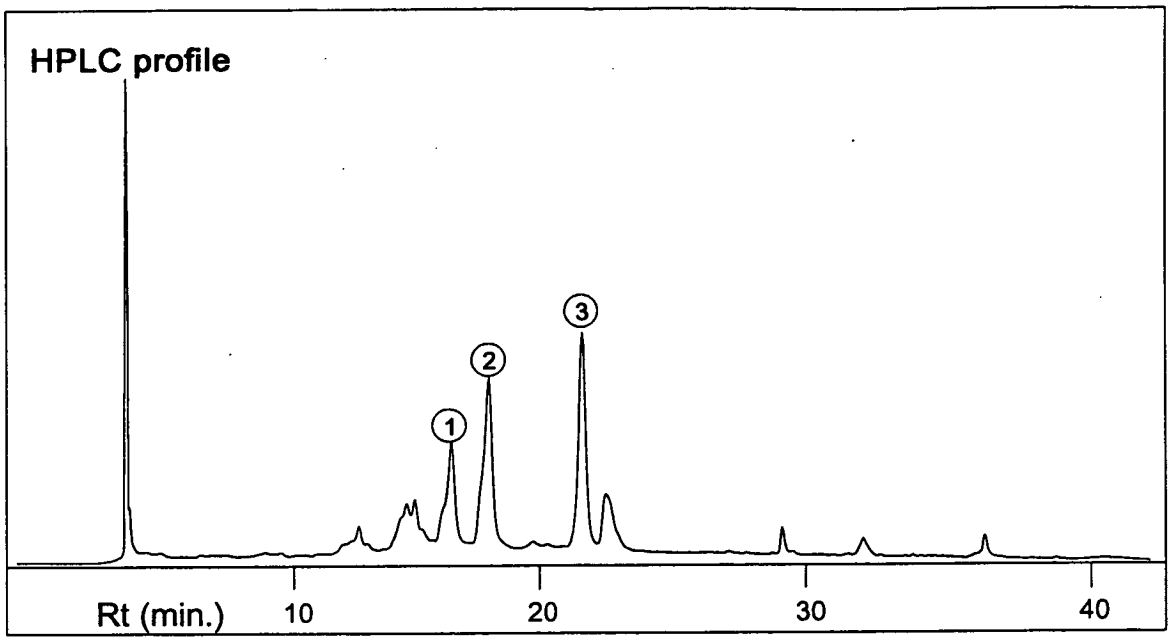
  The leaf exudate was investigated:

  - RBG, Kew 1969 12338
  - ex hort BSM

Distribution

The exact natural distribution of this species is unknown. It is believed that *A. vera* grew wild on the Canary Islands from where it was introduced to various areas of the world and has since become naturalised.

Aloe verecunda Pole-Evans



Peak number	Retention time	Compound	Percentage
1	15.1	unidentified flavone 1	9
2	16.4	isovitexin	23
3	20.94	unidentified flavone 2	25

Aloe verecunda collected at Melville Koppies in Johannesburg is the source from which isovitexin was isolated and identified in this study.

- Taxonomic position:

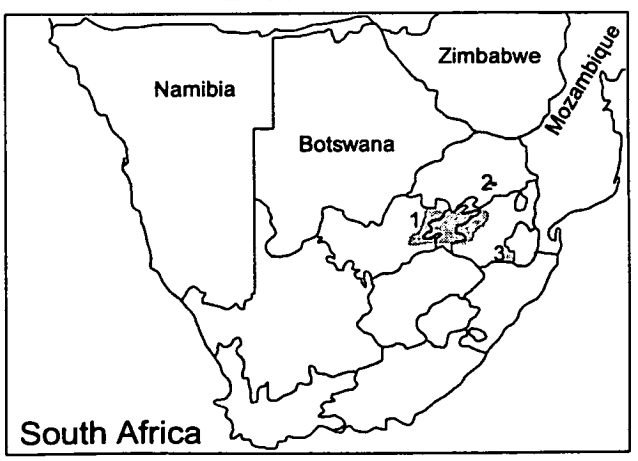
  Aloe section *Leptoaloe* (Reynolds, 1950).

- Samples analysed:

  The leaf extract was investigated:

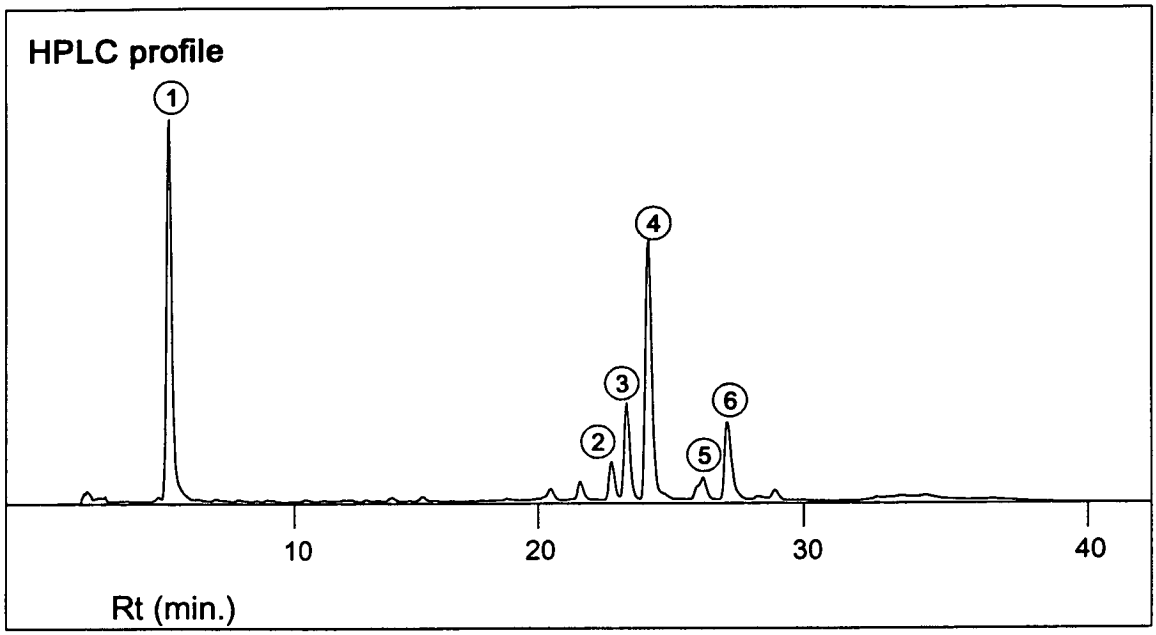
  - collected at Melville Koppies

Distribution



Anthropogenic factors could probably be responsible for the wide distribution of this species on the Witwatersrand (1). *A. verecunda* is also found in the Pietersburg area (2) and near Wakkerstroom (3).

Aloe veseyi Reynolds



Peak number	Retention time	Compound	Percentage
1	5.58	aloesin	38
2	22.99	unidentified chromone 1	4
3	23.59	unidentified chromone 2	11
4	24.41	unidentified chromone 3	29
5	26.53	nataloin B	3
6	27.48	nataloin A	10

An interesting leaf exudate composition as the series of unidentified chromones (probably of the coumaroyl type) have not been detected in another species. The anthrones nataloin A and B have a very restricted distribution in the genus *Aloe*.

- Taxonomic position:

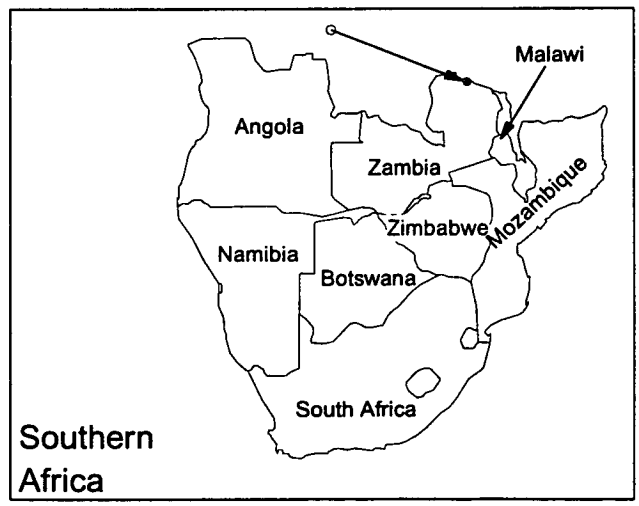
  Group 10 of the tropical aloes (Reynolds, 1966)

- Samples analysed:

  The leaf exudate was investigated:

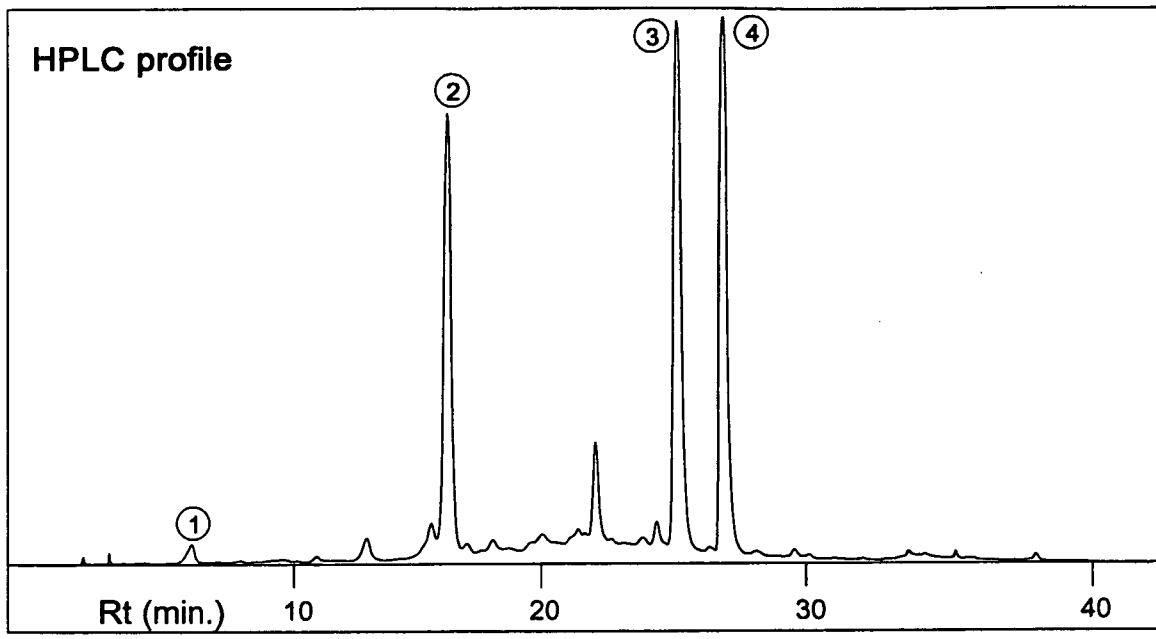
  - ex hort D. Hardy

Distribution



Aloe veseyi is only known from the type locality which is Kalambo Falls on the northern border of Zambia.

Aloe viridiflora Reynolds



Peak number	Retention time	Compound	Percentage
1	6.1	aloesin	1
2	15.74	aloeresin A	19
3	24.85	homonataloin B	25
4	26.61	homonataloin A	27

- Taxonomic position:

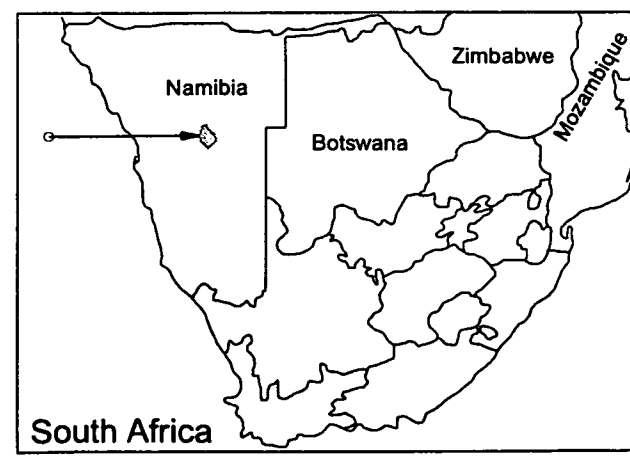
  Aloe series *Asperifoliae* (Reynolds, 1950).

- Samples analysed:

  The leaf exudate was investigated:

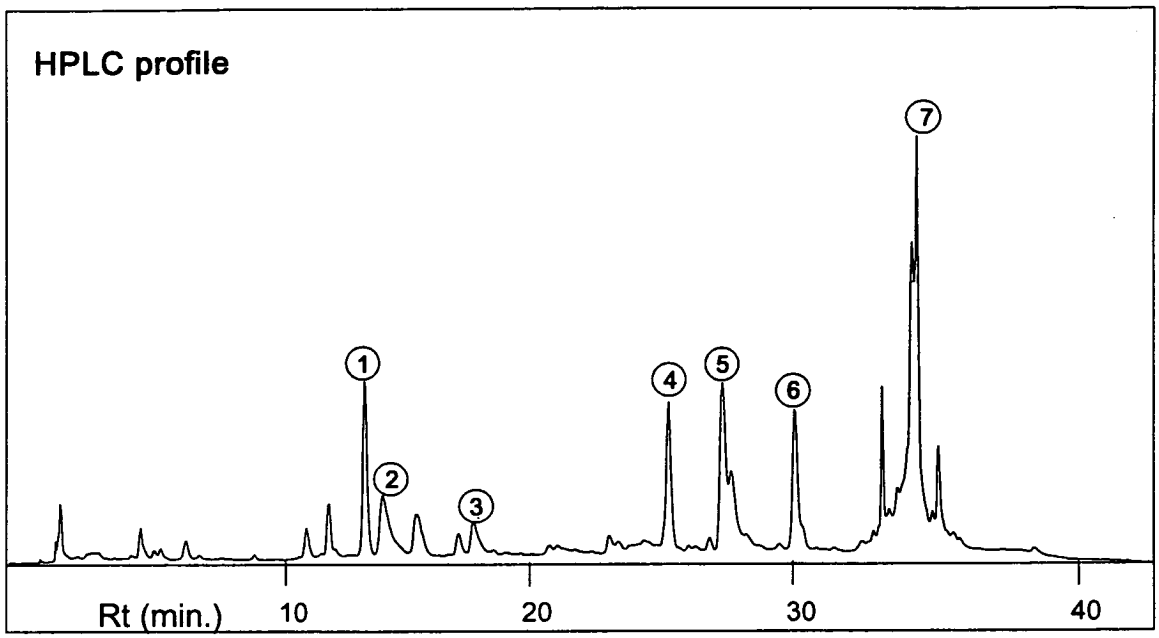
  - NBI 28700
  - ex hort JBG

Distribution



Aloe viridiflora has only been recorded east of Windhoek and north of Rehoboth in Namibia.

Aloe vaombe Decorse & Poisson var. *vaombe*



Peak number	Retention time	Compound	Percentage
1	13.61	8-*O*-methyl-7-hydroxyaloin	8
2	14.29	unidentified anthrone 1	4
3	17.70	unidentified anthrone 2	2
4	25.04	unidentified anthrone 3	8
5	27.09	unidentified anthrone 4	11
6	29.82	unidentified anthrone 5	8
7	34.29	unidentified compound	30

As is the case in most Malagasy species, *A. vaombe* produces a unique combination of anthrones. Peak 2, 3, 5 & 6 display UV spectra resembling the 7-hydroxyaloin and nataloin anthrones while peak 4 shows a homonataloin-like UV spectra.

- Taxonomic position:

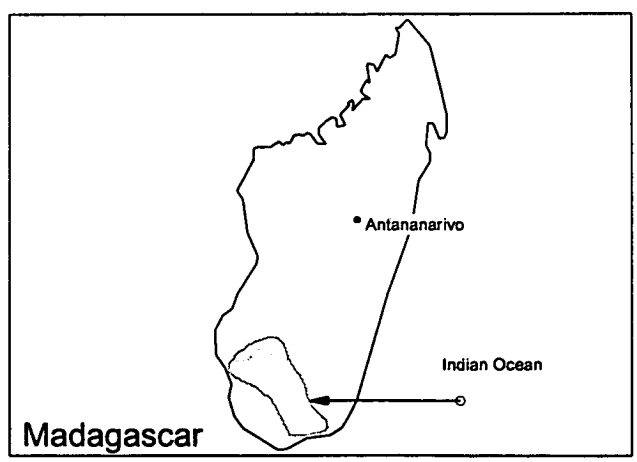
  Group 9 (Reynolds, 1966).

- Samples analysed:

  The leaf exudate was investigated:

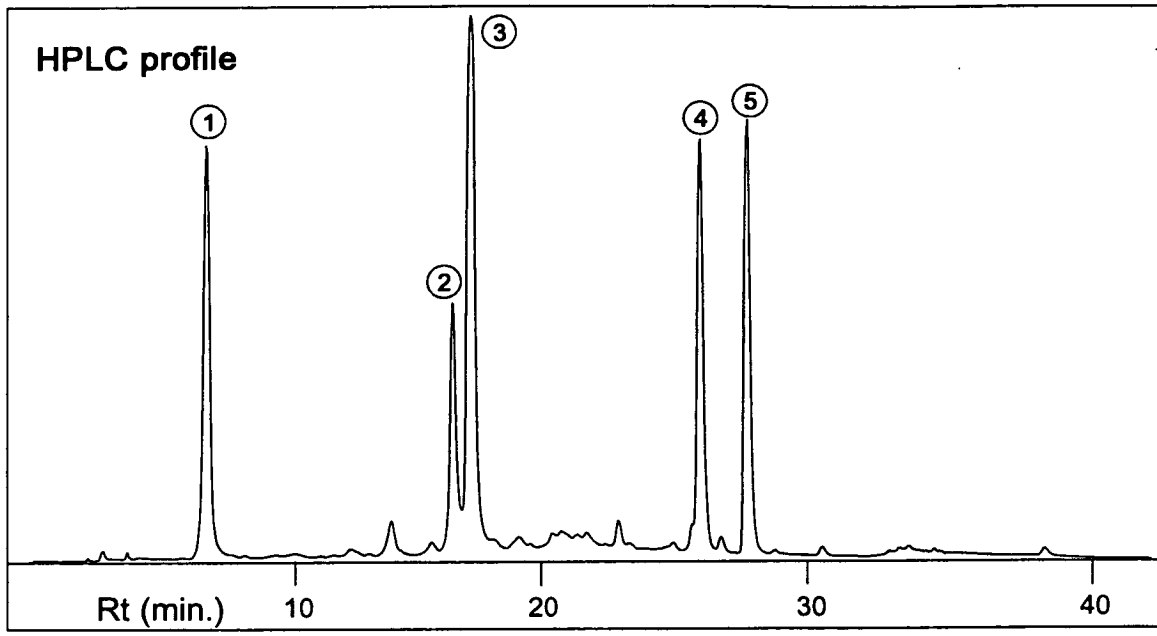
  - ex hort D. Hardy
  - ex hort NBI

Distribution



Aloe vaombe is widely distributed in the southern parts of Madagascar from Ambovombe to Tulear and Ranohira.

Aloe volkensii Engler ssp. *volkensii*



Peak number	Retention time	Compound	Percentage
1	6.65	aloesin	18
2	16.14	unidentified chromone	11
3	16.81	aloeresin A	29
4	25.66	homonataloin B	17
5	27.42	homonataloin A	17

The unidentified chromone displays the UV absorbance spectrum typical of the coumaroyl chromones (e.g. aloeresin A).

- Taxonomic position:

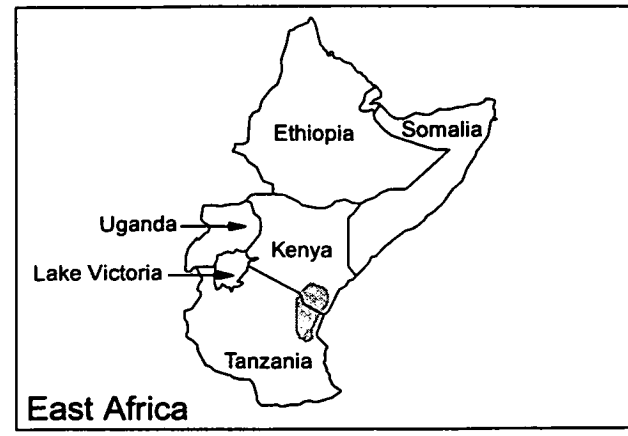
  Group 18 of the tropical aloes (Reynolds, 1966).

- Samples analysed:

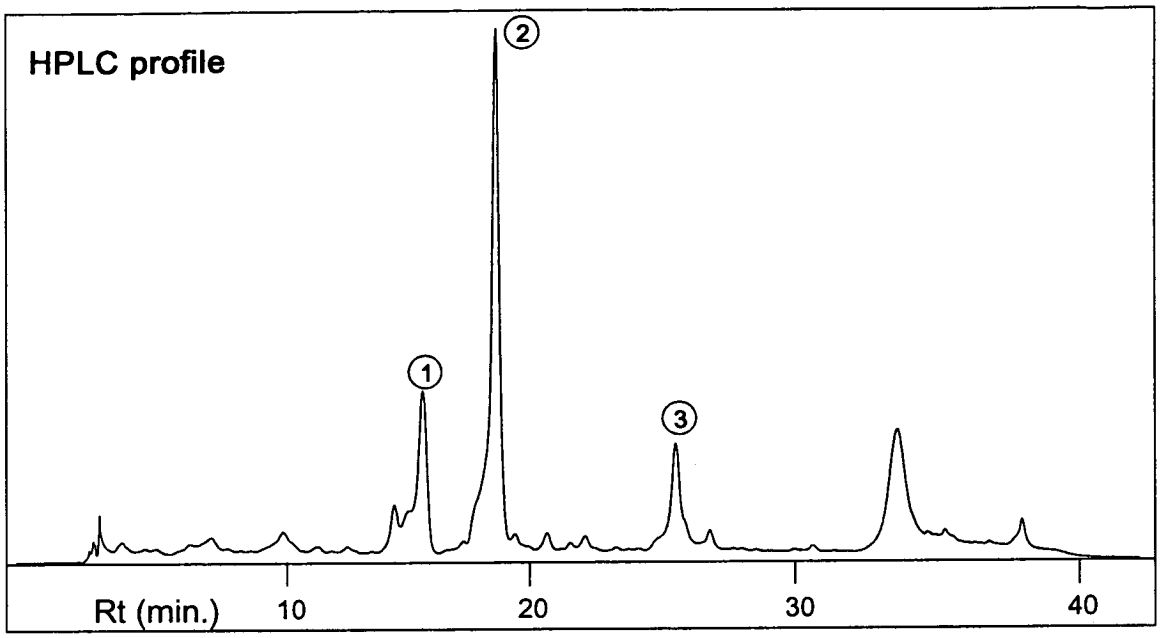
  The leaf exudate was investigated:

  - L. E. Newton 3770

Distribution



This species is often associated with riverine woodland in Kenya, Tanzania and unconfirmed reports in Zanzibar.



Peak number	Retention time	Compound	Percentage
1	15.7	unidentified flavone 1	7
2	18.5	isovitexin	43
3	25.4	unidentified flavone 2	10

Three flavones constitute the phenolic compounds in the leaf extract of *Aloe vossii*. Isovitexin is the major compound.

- Taxonomic position:

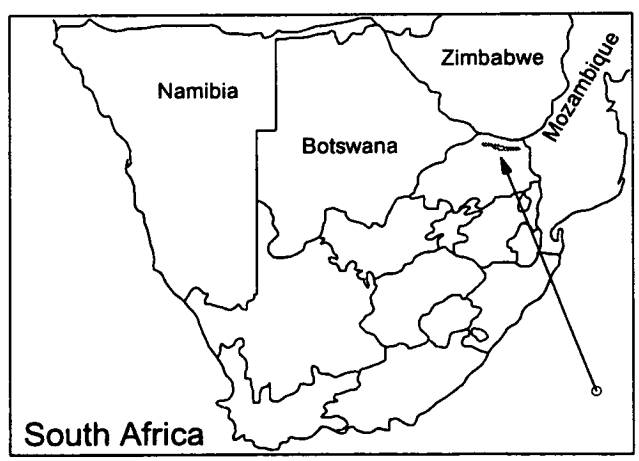
  Aloe section *Leptoaloe* (Reynolds, 1950).

- Samples analysed:

  The leaf extract was investigated:

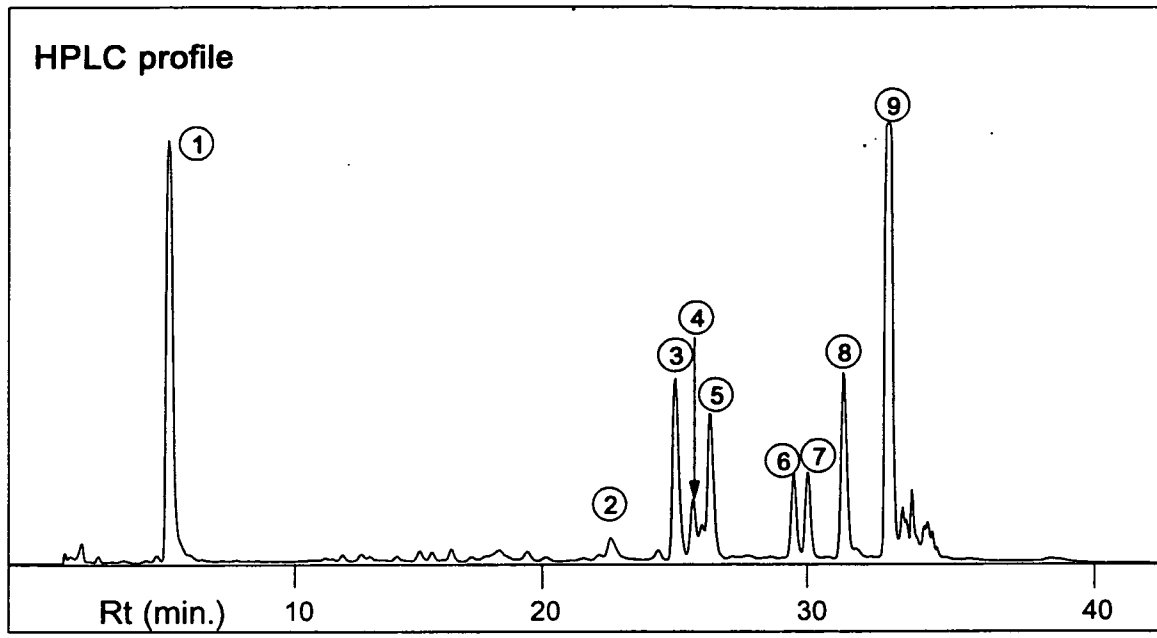
  - ex hort Craib (collected at Soutpansberg)
    Both the typical as well as the more robust form was analysed and found to be identical.

Distribution



This species is restricted to the Soutpansberg.

Aloe vryheidensis Groenewald



Peak number	Retention time	Compound	Percentage
1	5.84	aloesin	22
2	22.34	unidentified chromone 1	1
3	24.75	aloin B	8
4	25.39	6'-*O*-coumaroylaloesin	3
5	26.03	aloin A	7
6	29.16	unidentified chromone 2	4
7	29.69	unidentified chromone 3	4
8	31.02	unidentified chromone 4	9
9	32.67	unidentified chromone 5	28

With the exception of peaks 6 & 7 this HPLC profile is comparable to that recorded for *Aloe spicata*.

- Taxonomic position:

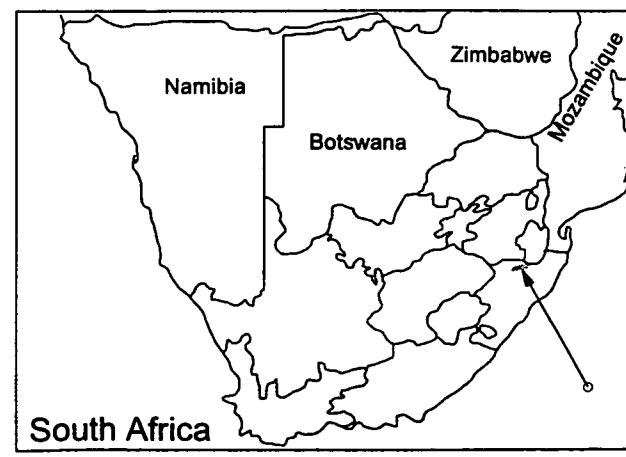
  Aloe section *Anguialoe* (Reynolds, 1950).

- Samples analysed:

  The leaf exudate was investigated:

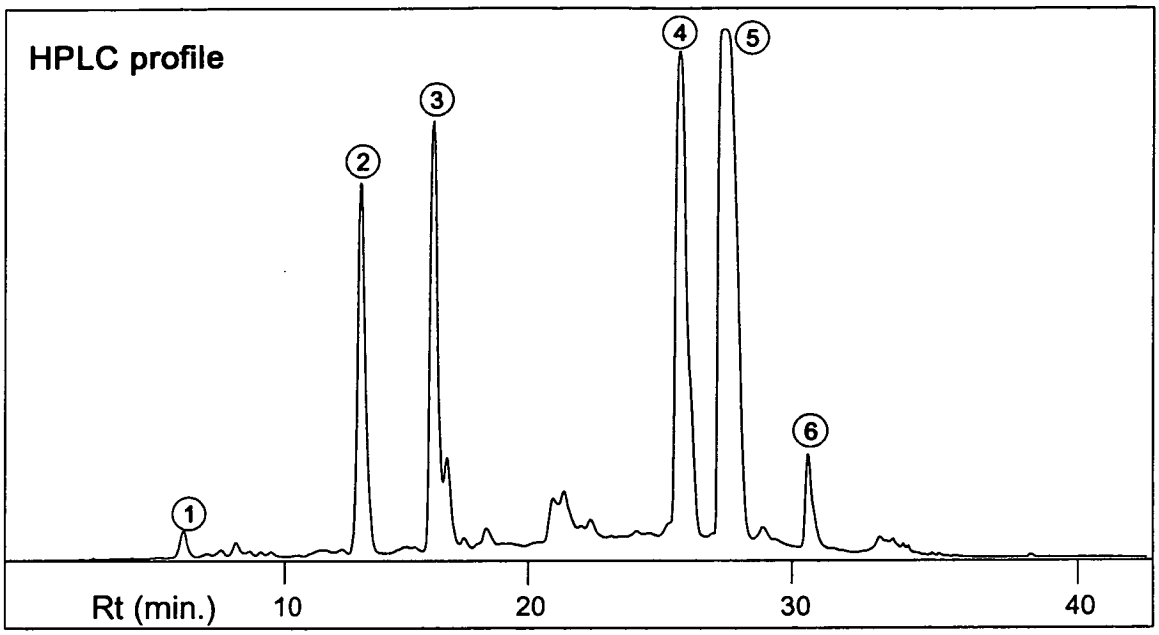
  - Vryheid/Louwsburg

Distribution



As suggested by the name, this species is found in the vicinity of Vryheid in northern KwaZulu-Natal.

Aloe wickensii Pole-Evans



Peak number	Retention time	Compound	Percentage
1	6.60	aloesin	1
2	13.45	homonataloside B	12
3	16.21	3'-*O*-coumaroylaloesin	14
4	25.50	homonataloin B	23
5	27.23	homonataloin A	37
6	30.36	3',6'-di-*O*-coumaroylaloesin	3

This combination of compounds is unique to species pertaining to *Aloe* series *Latebracteatae*. (see *A. cryptopoda* and *A. lutescens*).

- Taxonomic position:

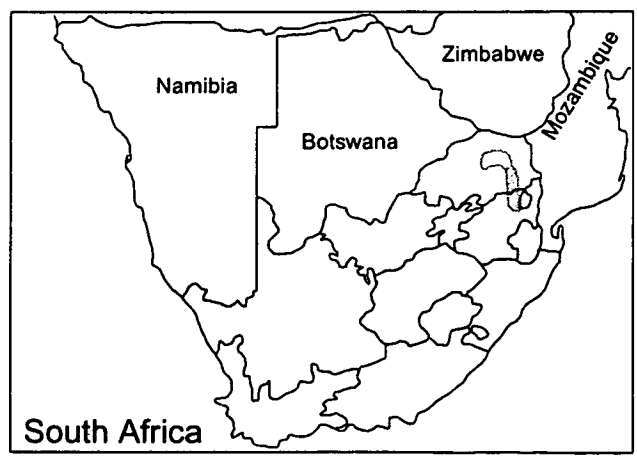
  Aloe series *Latebracteatae* (Reynolds, 1950).

- Samples analysed:

  The leaf exudate was investigated:

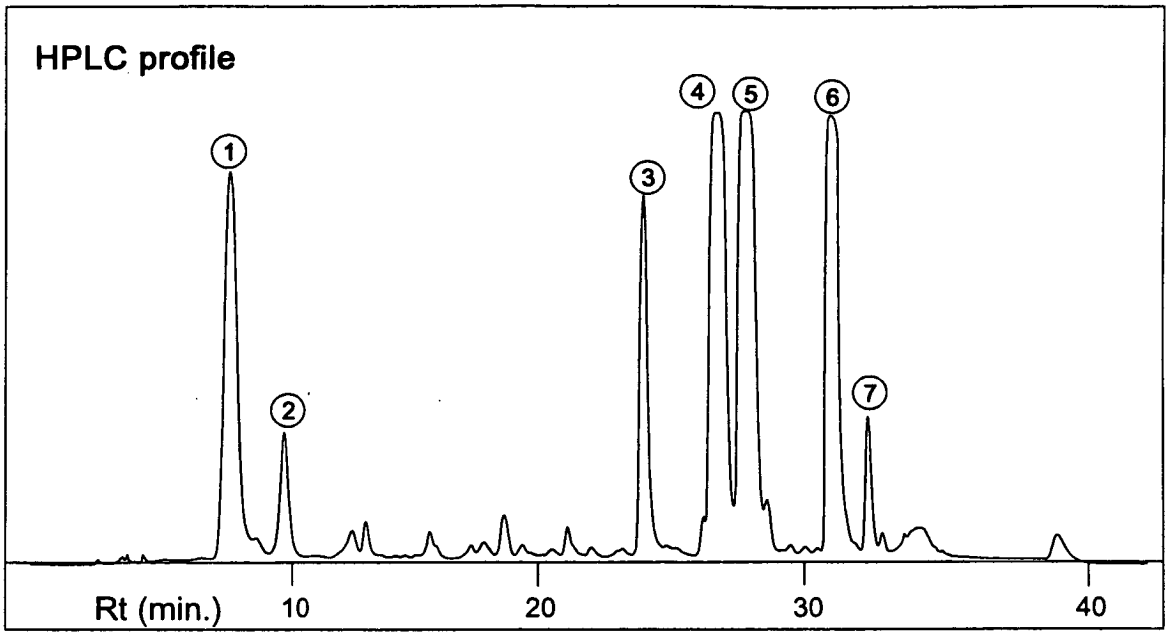
  - ex hort Nelspruit Botanical Garden
  - JBG 85-5-336

Distribution



Aloe wickensii is distributed in the Northern and Mpumalanga Provinces in South Africa.

Aloe wilsonii Reynolds



Peak number	Retention time	Compound	Percentage
1	6.63	aloesin	14
2	8.68	7-*O*-methylaloesin	3
3	22.63	aloeresin D	8
4	25.38	homonataloin B	21
5	26.49	homonataloin A	22
6	29.82	unidentified chromone	18
7	31.28	unidentified anthrone	3

The unidentified chromone displays the UV absorbance spectrum characteristic of the cinnamoyl chromones (e.g. aloeresin E and F). The UV absorbance of the unidentified anthrones correlates to that of aloin.

- Taxonomic position:

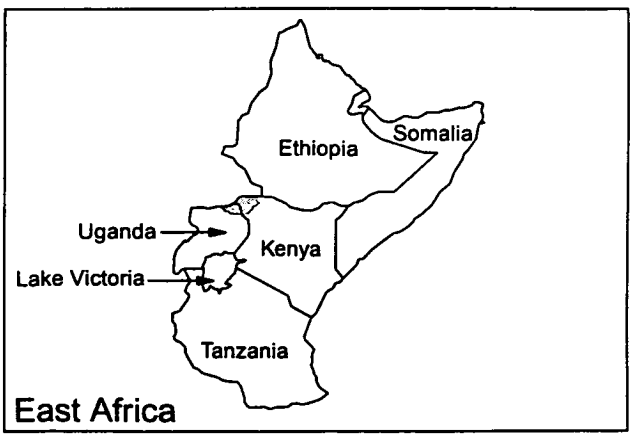
  Group 16 of the tropical aloes (Reynolds, 1966).

- Samples analysed:

  The leaf exudate was investigated:

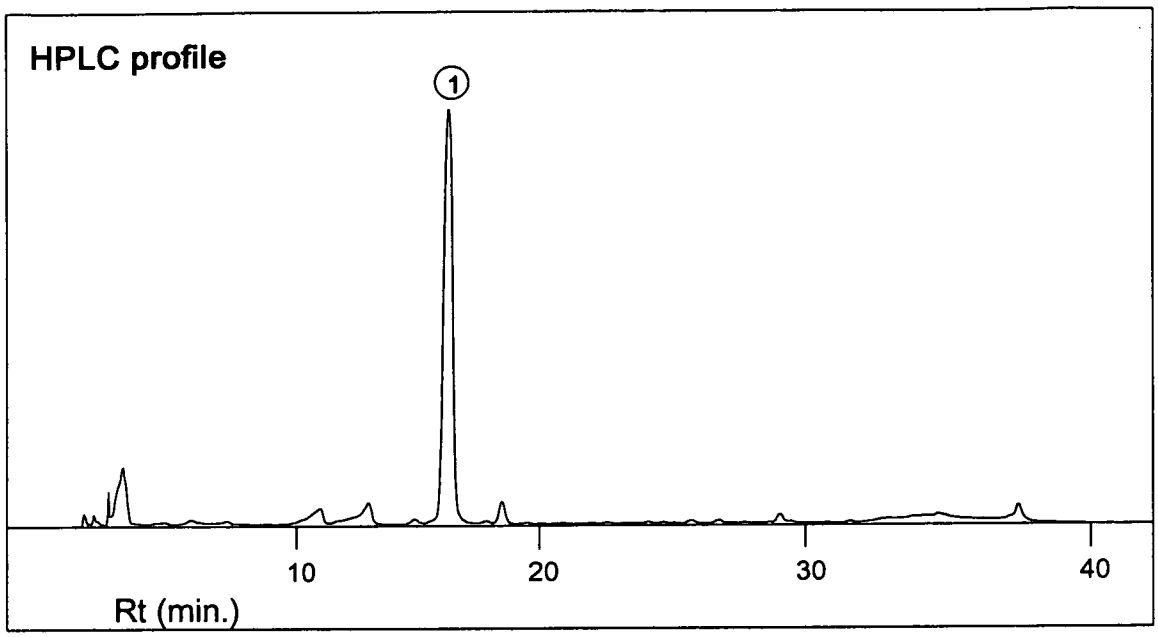
  - L. E. Newton 3509

Distribution



Aloe wilsonii is found in the Karamoja and Mbale Districts of Uganda and on the Sekerr Mts. in the West Suk District of Kenya.

Aloe wrefordii Reynolds



Peak number	Retention time	Compound	Percentage
1	17.02	plicataloside	78

- Taxonomic position:

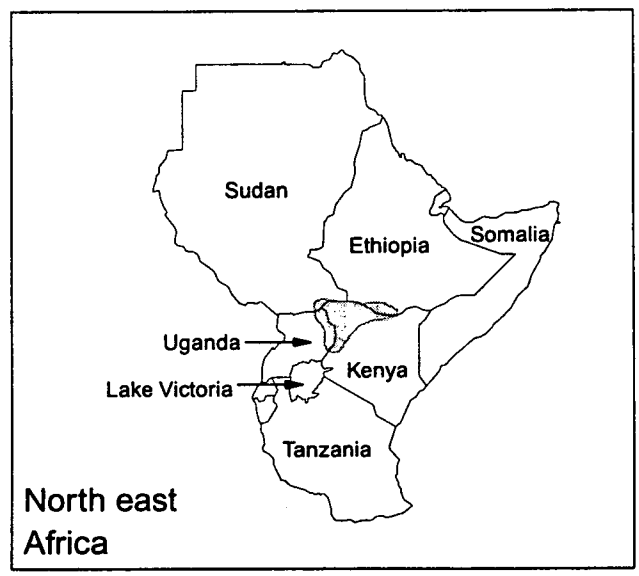
  Group 13 of the tropical aloes (Reynolds, 1966).

- Samples analysed:

  The leaf exudate was investigated:

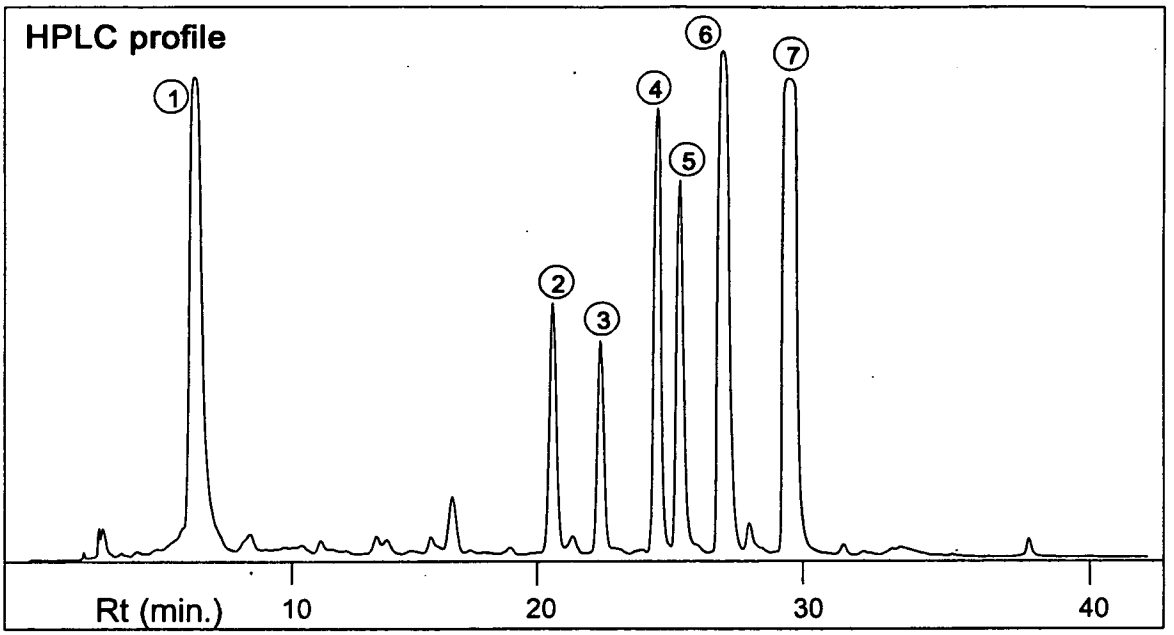
  - RBG, Kew 1977-4192

Distribution



This species is known from the Karamoja District in Uganda and the Turkana District in the north-east of Kenya. It has also been reportd from the south-eastern parts of Sudan and Ethiopia.

Aloe yavellana Reynolds



Peak number	Retention time	Compound	Percentage
1	6.26	aloesin	22
2	20.14	aloeresin E	6
3	21.98	unidentified chromone 1	5
4	24.18	aloeresin F	11
5	25.04	homonataloin B	9
6	26.64	homonataloin A	19
7	29.21	unidentified chromone 2	22

The HPLC profile of this species is similar to those of species pertaining to *Aloe* series *Mitriformes*. The unidentified chromone 1 displays the UV absorbance of the coumaric acid containing chromones, while peak 7 shows a spectrum identical to aloeresins E and F, the cinnamoyl chromones. Both samples analysed were identical.

- Taxonomic position:

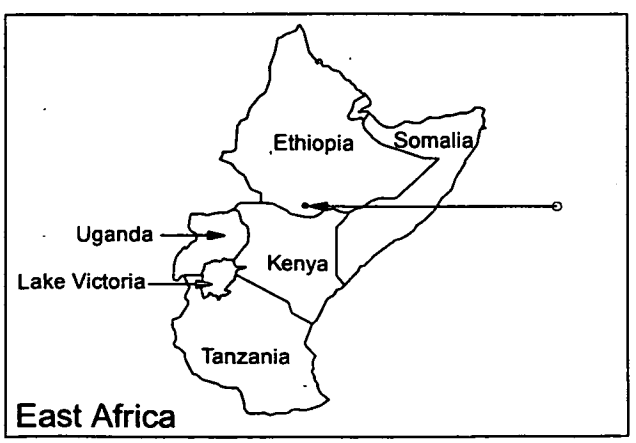
  Group 19 of the tropical aloes (Reynolds, 1966).

- Samples analysed:

  The leaf exudate was investigated:

  - ex hort L. E. Newton
  - ex hort RBG, Kew

Distribution



Aloe yavellana occurs near Yavello, south Ethiopia.