The Vigani Cabinet –
Analysis of historical resinous materials by gas chromatography - mass spectrometry and infrared spectroscopy

DISSERTATION

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Summary

Natural resins have been in use for a long time and for manifold purposes resulting in a long and complex terminological history. The investigation of this history has so far been based on the connection between nomenclature and chemical composition. Because resin chemistry and the botanical classification of source plants are connected as well, the investigation of natural resins can be enhanced by adding taxonomy as an additional dimension, providing a more complex and complete picture of resin chemistry and resin use.

The Vigani Cabinet, a collection of 300-year-old pharmaceutical and chemical materials owned by Queens' College, Cambridge (UK), allows doing just that. The materials are in a very good state of conservation, with their original labels still attached. The Cabinet was compiled by John Francis Vigani, who held the first Chair for Chemistry in Cambridge, at the beginning of the Enlightenment era, and is an important part of the developing and intensifying scientific research of that era. A wide range of historical literature provides information about contemporary terminology, botanical and geographical origin, manufacture, trade and properties of resinous materials from the 18th century. This contemporary context is a particular feature of the Cabinet, which allows adding a historical dimension to the correlations between terminology, chemical composition and taxonomy.

The dissertation thesis presented here provides an investigation of 17 botanical, 80 reference materials and samples from 24 natural resins from the Vigani Cabinet, studying these complex correlations and changes over time. The association of insights gained from the analysis of a broad spectrum of historical literature with comprehensive data profiles obtained from chemical analyses results in a new understanding of the link between historical and modern terminology and the chemotaxonomy of natural resins.

The analytical method employed in this study was gas chromatography-mass spectrometry (GC-MS) with and without methylation with trimethylsulfoniumhydroxide. This technique provided detailed molecular compositions of the studied materials. The work contributes systematic data for the differentiation of Pinaceae, Cupressaceae and *Pistacia* resins, improving their chemotaxonomical data profile. A wide range of reference samples from *Copaifera* provided an improved data profile for the differentiation of Copaiba sources by marker molecules. The mass spectra of phenylpropanoid methylesters found in commercial Balsam of Peru and Tolu (Myroxylon resins) are discussed. The analysis of legume copals from Fabaceae and Burseraceae resins revealed insights into the connection between terminology and chemical composition, which could be used to fill knowledge gaps regarding the wide range of similarly labelled materials from these groups. Finally, the identification of Baltic amber based on the analysis of its solvent-soluble fraction was investigated.

Materials from the Vigani Cabinet analysed in this work were labelled as "turpentines", "pix burgundica", "sandaracha", "copaiba", "balsamum peruvianum and tolutanum", "mastiche", "anime", "copal", "elemi", "tacamahaca" and "succinum". Historical nomenclature of natural resins has not always been unequivocally associated with a botanical origin. The availability of natural resins changed throughout the centuries. Lack of knowledge, in particular about resins from over-seas, or adulterations resulting from changing harvesting methods, led to changes in trade names or variations in the composition of products traded under the same name. Generic names were used for resins with similar properties but different botanical (and geographical) origin. The thesis shows that a chemotaxonomic reference system is suitable for the identification of unknown resinous materials, and a number of new insights into

the nomenclature of natural resins from the 17th and 18th century is obtained. The study of historical literature contributed in a significant way to the historico-cultural and archeometric research of the samples from the Vigani Cabinet and of natural resins in general and provided a basis for the interpretation of the chemical data from the Vigani samples. Table S.1 below summarises historical and modern names, botanical origin, chemotaxonomical markers and the scope of the investigation presented here.

The investigated "turpentines" (Cabinet number 1/8-1/11, 1/13) originated mainly from the family of Pinaceae. With reference to their historical reported botanical origin, the "Strasburg", "Venice" and "Chios turpentines" were adulterated, while a number of analyzed "turpentines" made from pine resin showed a strong connection to resin producing regions in South France reported in contemporary sources. The only exception from these findings was "Cyprus turpentine" (1/14), which turned out being a "Pistacia turpentine" from a *Pistacia* species, probably *Pistacia therebinthus* L. Another conifer resin was "Pix Burgundica" (A/24), which could be attributed to the resin of *Picea abies* Karst. in contrary to modern reference samples, which are obtained from pines. Main marker compounds for the Pinaceae resins were pimaric and sandaracopimaric acids and neutral labdane diterpenes. Based on the marker compounds hydroxy-sandaracopimaric, dehydroabietic acids and the phenols totarol and ferruginol, "sandaracha" (A/26) was obtained from the Sandarac cypress *Tetraclinis articulata* Mast., despite the tree was still unknown at the time of Vigani, which is why the material was named "juniper gum" in some of the sources. Several South American balsam resins called "Copaiba", "Balsamum Peruvianum or Tolutanum" (1/4, 1/31, 2/1, Z/17) could be characterized based on the results of the reference analysis, which shed some light on the confusing historical literature about these at the time of Vigani widely unknown South-American trees.

Another *Pistacia* resin was "mastiche" (A/11), which was obtained from *Pistacia lentiscus* L. A further group included the terminological connected materials labeled as "copal", "anime", "elemi" and "tacamahaca". "Anime" (A/5), a term which is if at all used today for American *Hymenaea* or *Protium* resins, could be attributed – by the presence of ent-labdane acids – to African Fabaceae resins as well as an unlabeled material from one of the lower drawers (La2/7). It could be shown that African legume copals were called "anime" at the time of Vigani. The term originally was used for antique African resins and was transferred by Portuguese traders to American materials. Other materials from this group (A/21, A/22, Z/1, A/24) belonged to the triterpene Burseraceae resins. The two "copal" and "elemi" resins originated from a *Protium* or *Canarium* species. The resins of both genera are composed so similar – markers are α- and β-amyrin, brein, maniladiol and tirucallane acids –, that a differentiation was not possible. Additionally, historical sources mention both "oriental" as well as "occidental" sorts of both "copal" and "elemi", which corresponds with the geographical distribution of *Canarium* and *Protium*. The today nearly unknown "tacamahaca" originated from a *Bursera* species, a genus connected to American "copals" today. Bursera resins can be distinguished from other American triterpene resins, for example from *Protium* species, by the presence of lupanes and the 3α-epimers of α- and β-amyrin.

The last group contained four samples labeled "succinum" (E/13-E/16). Their solvent soluble fraction contained the characteristic markers of Baltic amber. They were investigated additionally by FT-IR. A "black amber" variety, which appeared very similar to jet, showed the characteristic soluble fraction as well but lacked the Baltic shoulder in its FT-IR spectrum.

Modern name	Historical name	# Vigani	Botanical origins (historical)	Botanical origin (Vigani)	Marker compounds	Research focus
Strasburg turpentine	Therebinthia Argentoratensis	1/8	*Abies alba* Mill.	*Pinus* sp.	Pimaric and dihydroagathic acids	Adulteration, aging
Venice turpentine	Therebintina Veneta	1/10 1/11	*Larix decidua* L., *Abies alba* Mill., *Pinus* sp.	*Pinus* sp. Mixture of *Larix decidua* L. & *Abies alba* Mill	Pimaric and dihydroagathic acid Epimanoyloxide, *iso*-abienol, abienol, D8, D10 and L9, no pimaric acid	Nomenclature, adulteration, aging Ibid.
Common turpentine	Therebinthina vulgaris	1/9	*Pinus* sp., *Picea* sp., *Larix* sp.	*Pinus* sp.	Pimaric and dihydroagathic acids	Nomenclature, adulteration, aging
Pistacia turpentine	Chios Turpentine	1/13	*Pistacia terebinthus* L. *P. atlantica* Desf.,	*Pinus* sp.	Pimaric and dihydroagathic acids	Nomenclature, adulteration, aging
Pistacia turpentine	Cyprus Turpentine	1/14	*Pistacia terebinthus* L. *P. atlantica* Desf.	*Pistacia* sp.	Triterpenes (oleananes, tirucallanes, dammaranes)	Nomenclature, trade
Burgundy pitch	Pix Burgundica	A/23	*Picea abies* Karst., Pinus sp.	*Picea abies* Karst.	Pimaric and sandaracopimaric acids; cembrene, Δ13-*cis*-neoabienol, abienol, *cis*- and *trans*-abienol	Nomenclature, manufacture
Sandarac	Sandaracha	A/26	*Tetraclinis articulata* Mast.	*Tetraclinis articulata* Mast.	Oxygenated sandaracopimaric and dehydroabietic acids, phenols	Botanical origin, trade name
Copaiba balsam	Copaiba, Capivi	1/4	*Copaifera* sp.	*Copaifera* sp.	β-selinene, β-bisabolene, kauran-19-oic, polyalthic acids, eL17, cativic, ent-pinifolic acids	Botanical origin, diversity of *Copaifera* species used

Modern name	Historical name	# Vigani	Botanical origins (historical)	Botanical origin (Vigani)	Marker compounds	Research focus
Balsam of Peru	Balsamum Peruvianum	1/31, 2/1	*Myroxylon balsamum* Harms var. pereirae	*Myroxylon balsamum* Harms var. pereirae	Benzylbenzoate, -cinnamate, cinnamylbenzoate, -cinnamate, benzoic, cinnamic acids, trans-nerolidol	Botanical origin, different sorts used
Balsam of Tolu	Balsamum Tolutanum	Z/17	*Myroxylon balsamum* Harms var. balsamum	*Myroxylon balsamum* Harms var. pereirae	Benzylbenzoate, -cinnamate, cinnamylcinnamate, benzoic, cinnamic acids	Botanical origin, origin of adulteration
Mastic	Mastiche	A/11	*Pistacia lentiscus* L.	*Pistacia lentiscus* L.	Triterpenes (oleananes, tirucallanes, dammaranes)	Botanical origin, aging
Anime	Gum Anime	A/5	(West or East) African trees, *Hymenaea courbaril* L., Mexican *Bursera* or *Protium* sp.	*Daniellia* or *Guibourtia* sp. (Fabaceae)	18-hydroxy-, 18-methoxy-labda-8(20)-en-15-oic acids, hydroxy-labden-18-oic acid, 18-hydroxy-15-methoxy-labdane	Botanical origin, transfer of the term to American resins, confusion with copal
Copal	Gum copal	A/21	*Hymenaea* sp., *Rhus copallifera* L., *Protium* & *Bursera* sp.	*Protium* or *Canarium* sp.	α- and β-amyrin, brein, maniladiol, tirucallane acids	Botanical origin, transfer of the term to African & Asian resins, confusion with anime
Elemi	Gum elemi	A/24	*Canarium* sp., *Boswellia frereana* Birdw., *Dacryodes edulis* Lam., *Protium* sp., *Amyris elemifera* L.	*Protium* or (African) *Canarium* sp.	α- and β-amyrin, brein, maniladiol, tirucallane acids	Botanical origin, transfer of the term to American resins

Modern name	Historical name	# Vigani	Botanical origins (historical)	Botanical origin (Vigani)	Marker compounds	Research focus
Tacamahaca	Tacamahaca	A/22, Z/1	*Bursera* sp., *Calophyllum* sp., *Populus balsamifera* L.,	*Bursera* sp.	Epi-lupeol, 3α-epimers of α- and β-amyrin, T_{19}, T_{20}	Botanical origin
Amber	Succinum	E/13-E/16	-	-	Succinic acid, succinates, isopimaranes, abietanes, Baltic shoulder (FT-IR)	Identification of Baltic amber, Black amber

Tab. S.1 Summary of investigated materials, their contemporary nomenclature, botanical origin, identified marker compounds and research focus within the presented work

Zusammenfassung

Naturharze werden schon lange für sehr unterschiedliche Zwecke verwendet. Dies hat zu einer oft komplizierten Terminologie geführt, deren Untersuchung sich bisher auf den Zusammenhang zwischen dem Namen des Harzes und seiner chemischer Zusammensetzung stützte. Letztere ist aber auch mit der botanischer Herkunft und damit der Biochemie der Stammpflanze verknüpft, weshalb man chemotaxonomische Aspekte für die systematische Untersuchung von Naturharzen als zusätzliche Variablen nutzen kann. Dadurch erhält man, wie die gezeigt werden soll, ein vollständigeres und komplexeres Bild der Chemie und Nutzung von Naturharzen.

Die hier präsentierte Untersuchung beschäftigt sich mit dem Vigani-Kabinett, einer 300 Jahre alten pharmazeutischen Materialiensammlung, die sich im Queens‘ College, Cambridge (UK), befindet. Sie ist nach ihrem Erschaffer John Francis Vigani, dem ersten Inhaber des Lehrstuhls für Chemie in Cambridge, benannt und enthält eine Reihe sehr gut erhaltener und original beschrifteter zeitgenössischer Materialien. Durch die genaue Kenntnis der Entstehung dieses Kabinetts lässt es sich gut in den zeitgenössischen Kontext einordnen. Dieser ist charakterisiert durch die rasante Entwicklung von Wissenschaft und Technik während der Aufklärung. In der Literatur des ausgehenden 17. und des 18. Jahrhunderts finden sich zahlreiche Informationen zu Terminologie, botanischer und geographischer Herkunft, Verarbeitung, Handel und Eigenschaften von Naturharzen. Dadurch wird die historische Dimension des oben beschriebenen Zusammenhangs zwischen Terminologie, chemischer Zusammensetzung und Taxonomie erfahrbar.

In der Arbeit werden 17 botanische Proben, 80 moderne Referenzmaterialien und 24 Proben aus dem Vigani-Kabinett im Hinblick auf diese Zusammenhänge und Veränderungen untersucht. Durch die interdisziplinäre Untersuchung der chemischen Datenprofile und der historischen Quellen konnte so ein neues Verständnis des Zusammenhangs von historischer und moderner Terminologie und der Chemotaxonomie von Naturharzen gewonnen werden.

Die chemischen Analysen wurden mit gekoppelter Gaschromatografie-Massenspektrometrie mit und ohne Methylierung mit Trimethylsulfoniumhydroxid durchgeführt. Damit konnte die molekulare Zusammensetzung der Proben detailliert untersucht werden. Hinsichtlich der Analyse der botanische Proben und Referenzmaterialien konnten folgende Ergebnisse gewonnen werden. Die Unterscheidbarkeit von Harzen aus den Familien Pinaceae, Cupressaceae und dem Genus *Pistacia* wurde mithilfe von systematischen chemotaxonomischen Daten verbessert. Die Untersuchung einer Anzahl von kommerziell erhältlichen Copaibabalsamen ermöglichte die Unterscheidung der verschiedenen botanischen Quellen anhand von Markermolekülen. In der Gruppe der *Myroxylon*-Harze, wurden die Massenspektren von Methylestern in kommerziellen Peru- und Tolubalsamen untersucht. Leguminosen-Kopale aus der Familie Fabaceae und Burseraceae-Harze wurden im Hinblick auf die Verbindung zwischen Nomenklatur und chemischer Zusammensetzung untersucht, da sich hier verschiedene generische Namen wie Kopal, Anime und Elemi überschneiden. Dadurch konnten einige Lücken in dieser an kommerziell genutzten Harzen sehr reichen Gruppe gefüllt werden. Die Untersuchung und Identifizierung von baltischem Bernstein in dieser Arbeit basiert auf der Analyse seiner löslichen Fraktion, die einige charakteristische Verbindungen enthält.

Die untersuchten Proben aus dem Vigani-Kabinett waren sowohl englisch als auch Latein mit "turpentines", "pix burgundica", "sandaracha", "copaiba", "mastiche", "anime", "copal",

"elemi", "tacamahaca", "balsamum peruvianum and tolutanum" und "succinum" beschriftet. Zusammenfassend lässt sich sagen, dass die historische Nomenklatur von Naturharzen nicht immer eindeutig mit ihrem botanischen Ursprung verknüpft war. Zusätzlich veränderte sich die Erhältlichkeit der Harze im Laufe der Jahrhunderte. Durch fehlendes Wissen, insbesondere für Materialien und Pflanzen aus Übersee, oder Verfälschungen aufgrund von veränderten Fördermethoden veränderten sich die Handelsnamen dieser Materialien oder die Zusammensetzung von Materialien, die unter demselben Namen gehandelt wurden. Harze mit ähnlichen Eigenschaften aber unterschiedlichen botanischen (und geographischen) Ursprungs trugen generische Namen. Die Arbeit zeigt jedoch, dass ein chemotaxonomisches Bezugssystem die Identifizierung von unbekannten Harzen ermöglicht, und zeigt eine Reihe neuer Erkenntnisse über die Nomenklatur von Naturharzen des 17. und 18. Jahrhunderts. Die Untersuchung historischer Quellen trug dabei sehr zur Erhellung des historisch-kulturellen und archeometrischen Hintergrundes und zur Interpretation der chemischen Daten der Vigani-Proben bei. Die historischen und modernen Namen der Materialien, ihre botanischer Herkunft sowie chemotaxonomische Marker und Schwerpunkte der Untersuchung sind in obenstehender Tabelle S.1 zusammengefasst.

Die untersuchten "Terpentine" (Nummer im Kabinett 1/8-1/11, 1/13) konnten bis auf eine Ausnahme den Pinaceae-Harzen zugeordnet werden, wobei sowohl der "Straßburger", der "Venezianer" als auch der "Chiosterpentin" verfälscht waren. Einige "Terpentine" zeigten basierend auf ihrer Zusammensetzung und Informationen aus französischen Quellen des ausgehenden 17. Jahrhunderts eine starke Verbindung zu den harzreichen südfranzösischen Gegenden. Ein als "Zypernterpentin" (1/14) beschriftetes Material stammte von *Pistacia*, möglicherweise *Pistacia terebinthus* L. Diese Befunde spiegeln den Zustand des beginnenden 18. Jahrhunderts, wie er in den Quellen zu finden ist, wieder. Ein weiteres Koniferenharz war "Burgunder Pech" (A/24), welches im Gegensatz zu modernen Referenzen *Picea abies* Karst. zugeordnet werden konnte. Hauptmarker für die Pinaceaeharze waren Pimar- und Sandaracopimarsäure sowie neutrale Labdanditerpene. Basierend auf den Markerverbindungen Hydroxysandaracopimarsäure, Dehydroabietinsäure und den Phenolen Totarol und Ferruginol, stammt "Sandarak" (A/26) von der Sandarakzypresse *Tetraclinis articulata* Mast., obwohl der Baum zur Zeit von Vigani noch nicht entdeckt war und das Harz konsequenterweise in den Quellen gelegentlich "Wacholderharz" ("juniper gum") genannt wurde. Die Arbeit umfasst verschiedene südamerikanische Balsamharze (1/4, 1/31, 2/1, Z/17), die aufgrund der Marker aus den Referenzanalysen botanisch charakterisiert werden konnten, und damit etwas Licht in die teilweise verwirrende historische Literatur zu den südamerikanischen Stammpflanzen bringen konnte.

Unter den Triterpenharzen konnte "Mastix" (A/11) *Pistacia lentiscus* L. zugeordnet werden. Mehrere Materialien wurden aufgrund ihrer terminologischen Verbindung in einer Gruppe zusammengefasst, dazu gehörten u.a. als "Kopal", "Anime", "Elemi" und "Takamahaka" bezeichnete Harze. "Anime" (A/5), ein Begriff der heute wenn überhaupt für amerikanische Hymenaea-oder Protiumharze verwendet wird, wurde aufgrund der Anwesenheit von ent-Labdansäuren den Fabaceaeharzen zugeordnet, ebenso wie ein unbeschriftetes Material aus einer der unteren Schubladen (La2/7). Bei diesen heute als Leguminosenkopale bezeichneten Harzen zeigte sich somit ein Namenstransfer vom antiken "Anime" für afrikanische Harze zu modernen amerikanischen Materialien, die aufgrund der portugiesischen Handelsrouten zustande kam. Die anderen Materialien dieser Gruppe (A/21, A/22, Z/1, A/24) gehörten den Burseraceaeharzen an. "Elemi" und "Kopal" aus dem Kabinett stammten von *Protium* oder *Canarium* Spezies*.* Die Harze dieser beiden Genera sind sehr ähnlich zusammengesetzt –

Marker sind α- and β-Amyrin, Brein, Maniladiol und Tirucallansäuren –, sodass eine Unterscheidung nicht möglich war. Zusätzlich bleibt die geographische Herkunft unklar, da in historischen Quellen sowohl "orientalische" als auch "okzidentalische" Sorten erwähnt werden, was der geographischen Verbreitung von *Canarium* und *Protium* entspricht. Das heute fast unbekannte "Takamahaka" stammte von einer amerikanischen *Bursera* Spezies, ein Genus, der vor allem mit amerikanischen Kopalen in Zusammenhang gebracht wird. Harze dieses Genus können von anderen amerikanischen Triterpenharzen, zum Beispiel von *Protium*, unterschieden werden, da sie Lupane und die 3α-Epimere von α- and β-Amyrin enthalten.

Als letzte Gruppe wurden schließlich vier Proben untersucht, die mit "succinum" bezeichnet waren (E/13-E/16). Alle zeigten die für baltischen Bernstein typischen Marker in der löslichen Fraktion und konnten bis auf E/16 auch mittels FT-IR identifiziert werden. "Schwarzer Bernstein" (E/16), dessen Äußeres sehr stark an Gagat erinnerte, zeigte zwar die charakteristische Zusammensetzung der löslichen Fraktion aber ein für baltischen Bernstein untypisches Infrarotspektrum.

CONTENTS

Abbreviations

The standard author abbreviations of modern botanical names with an official status are not listed here, but only the one from historical botanical names. Sometimes, the abbreviations referred to the name of the author and sometimes to a specific publication.

The labels of the chemical compounds are explained in chapter 3.1.4.

Historical terms are written in quotations marks such as "copal" to indicate that they were taken from historical sources and do not necessary have the same meaning as the eponymous modern terms. In contrary, scientific terms without quotations marks are modern terms. Botanical names are written in italics with the author standard abbreviation in normal letters. Historical botanical names (in quotation marks) are written in the same way, although there was no standard author citation at Vigani’s time.

Used literature is cited in parenthesis with the name of the author(s), the year and in the case of books the page. In case the full name of a published work is mentioned within the text, it is written in italics such as *Medulla Chymiae* to distinguish it from historical terms. Single quotes are used to refer to (sub)titles of single chapters within this work. Text citations are included in the text except for long passages, which are written in smaller font size and indented.

AFAD	Academy of Fine Arts Dresden
Birdw.	Birdwood, George Christopher Molesworth (1832-1917)
Breyn.	Breyne, Jakob (1637-1697)
$C_{\#}$	Carbon number length, other letters with subscript numbers are explained in chapter 3.1.4
C-#	Carbon number referring to position within a chemical structure
C.B.(P.)	Caspar Bauhin (1560-1624) (*Pinax theatri botanici*, first edition published 1623 in Basel)
Clusius/Clusii	de l’Écluse, Charles, also Carolus Clusius (1526-1609)
CPP	Copalyldiphosphate
d.	abbreviation for old english monetary unit penny, derived from denarius
Desf.	Desfontaines, René (1750-1833)
DHA	Dehydroabietic acid
(di)ME	(di)methylester
DMAPP	Dimethylallylpyrophosphate
Dod./ Dodon.	Dodoens, Rembert (1516/17-1585), a Flemish physician and botanist
EIC	Extracted ion chromatogram
f.	Filius
f	Following (page)

FPP	Farnesylpyrophosphate
Gaertn.	Gaertner, Joseph (1732-1791)
Ger.	Gerard, John (1545-1611/12), an English botanist
GGPP	Geranylgeranylpyrophosphate
HD	Hexadecane
Hern./Hernd.	Hernandez de Toledo, Francisco (1514 –1587)
Ibid.	Ibidem
IPP	Isopentenyldiphosphate
J.B.	Bauhin, Johann (1541–1613)
KCount	Kilocount
L.f.	Linné the Younger, Carl von (1741-1783)
L. /Linn.	Linné, Carl von (1707-1778)
m/z	Mass-to-charge ratio
Marcgr(ave) / Marg./ Margg.	Marcgrave, Georg (1610-1644)
Mast.	Masters, Maxwell Tylden (1833 – 1907)
MCount	Megacount
min	minute
MMA	Museum of Modern Arts New York
MW	Molecular weight [Da]
Offic./Officinarum	from Latin officina, a shop where goods are manufactured, refers the a drug available under the name
Park./Par.	Parkinson, John (1567-1650)
P.B.P.	Hermann, Paul (1646-1695): *Paradisus Batavus*, first edition published 1698 in Leiden
Pluk.	Plukenet, Leonard (1641–1706)
P.P.	Plukenet, Leonard: *Phytographia,* four volumes, first edition published 1691 to 1692 in London
Plumier	Plumier, Charles (1646-1704)
P.T.	Tournefort, Joseph de Pitton (see Tournef.) (1656-1708)
Pis(o)	Piso, Willem (1611-1678)
R.H./ Raii Hist./Ray	Ray, John (1627-1705): *Historia plantarum*, three volumes, first edition published 1686, 188 and 1704
SA	Succinic acid
Tab.	table
TDA	Tridecanoic acid, tridecanoate (in methylated extracts)

Terent.	Johannes Schreck, latinized Joannes Terrentius, who contributed to the compilation of Monardes works by Nardo Antonio Recchi 1648 and 1651 *Rerum Medicarum Novae Hispaniae Thesaurus*
TIC	Total ion current
TMSH	Trimethylsulfoniumhydroxide
Tournef. / Tourn.	Tournefort, Joseph Pitton de (see P.T.)
t_R	Retention time

List of sources

FIGURE 2.5 The two subfamilies of Cupressaceae

Farjon A. (2005) A monograph of Cupressaceae and Sciadopitys, Royal Botanic Gardens, Kew, p. 643

FIGURE 2.14 Partial chromatograms of Burseraceae resins

a, c - Stacey, R.J., Cartweight, C. and McEwan, C. (2006) Chemical characterisation of ancient Mesoamerican 'Copal' resins: Preliminary results. Archaeometry, 48(2), 323–340

b - de la Cruz-Cañizares, Juana, Doménech-Carbó, María-Teresa, Gimeno-Adelantado, José-Vicente, Mateo-Castro, Rufino and Bosch-Reig, Francisco (2005) Study of Burseraceae resins used in binding media and varnishes from artworks by gas chromatography - mass spectrometry and pyrolysis-gas chromatography–mass spectrometry. Journal of Chromatography A, 1093, 177–194.

FIGURE 5.28 Historical trees connected with "sandaracha"

a, b, c - Lemery, Nicolas, Schneider, Ulrich Johannes (2007) Vollständiges Materialien-Lexicon, Directmedia Publishing GmbH, Berlin, p. 1833, 3541, 859;

d, e - Image courtesy Missouri Botanical Garden, www.botanicus.org,

FIGURE 5.33 Historical plants mentioned in connection with "capivi"

a, b, c - Marcgrave, Georg (1648) Historiae rerum naturalium Brasiliae (eds Margrave, Georg and Piso, Willem), Francisus Hackius, Leiden, apud Lud. Elzevirium, Amsterdam, pp. 1 – 293, Image courtesy Missouri Botanical Garden, www.botanicus.org

d - Piso, Willem (1658) De Indiae utriusque. Re naturali et Medica, Ludovico and Daniel Elzevirios, Amsterdam., Image courtesy Missouri Botanical Garden, www.botanicus.org

FIGURE 5.34 Historical plants mentioned in connection with "capivi" 2:

a - Jacquin, Nikolaus Joseph (1763) Selectarum stirpium Americanarum Historia, Vol. 2, Ex officina Krausiana, Vienna, Image courtesy Missouri Botanical Garden, www.botanicus.org

b - Lemery, Nicolas, Schneider, Ulrich Johannes (2007) Vollständiges Materialien-Lexicon, Directmedia Publishing GmbH, Berlin, p. 499

FIGURE *5*.39 Historical plants mentioned in connection with "occidental anime"

a - Bauhin, Johann and Cherler, Heinrich (1650) *Historia plantarum universalis nova et absolutissima cum consensu et dissensu circa eas*, Vol. 1, Dominik Chabree & Franz Ludwig von Graffenried, Yverdon-les-Bains, books.google.de

b - Piso, Willem (1658) *De Indiae utriusque. Re naturali et Medica*, Ludovico and Daniel Elzevirios, Amsterdam., Image courtesy Missouri Botanical Garden, www.botanicus.org

FIGURE *5*.47 Historical plants mentioned in connection with "Balsam of Peru"

a - Hernández, Francisco (1651) *Nova plantarum, animalium et mineralium mexicanorum historia*, Sumptibus Blasij Deuersini, Zanobij Masotti Bibliopolarum, Typis Vitalis Mascardi, Rome, http://openlibrary.org b - Piso, Willem (1658) *De Indiae utriusque. Re naturali et Medica*, Ludovico and Daniel Elzevirios, Amsterdam., Image courtesy Missouri Botanical Garden, www.botanicus.org

c - Lemery, Nicolas, Schneider, Ulrich Johannes (2007) Vollständiges Materialien-Lexicon, Directmedia Publishing GmbH, Berlin, p. 503

FIGURE *5.*63 The "copal-bearing trees" ("copalliferae arbores") of Hernandez

Hernández, Francisco (1651) *Nova plantarum, animalium et mineralium mexicanorum historia*, Sumptibus Blasij Deuersini, Zanobij Masotti Bibliopolarum, Typis Vitalis Mascardi, Rome, http://openlibrary.org

FIGURE *5.*64 Other botanical sources of "copal"

a – Plukenet, Leonard (2010) Phytographia, Gale Ecco Print Editions, Farmington Hills

b - Hernández, Francisco (1651) *Nova plantarum, animalium et mineralium mexicanorum historia*, Sumptibus Blasij Deuersini, Zanobij Masotti Bibliopolarum, Typis Vitalis Mascardi, Rome, http://openlibrary.org

c - Piso, Willem (1658) *De Indiae utriusque. Re naturali et Medica*, Ludovico and Daniel Elzevirios, Amsterdam., Image courtesy Missouri Botanical Garden, www.botanicus.org

d - Lemery, Nicolas, Schneider, Ulrich Johannes (2007) Vollständiges Materialien-Lexicon, Directmedia Publishing GmbH, Berlin, p. 1072

FIGURE *5.*69 Historical botanical sources of "elemi"

a - Lemery, Nicolas, Schneider, Ulrich Johannes (2007) Vollständiges Materialien-Lexicon, Directmedia Publishing GmbH, Berlin, p. 1331

b - Piso, Willem (1648) De Medicina Brasiliensi libri quatuor, in *Historia naturalis Brasiliae,* (eds Margrave, Georg and Piso, Willem), apud Francisum Hackium, Leiden, apud Lud. Elzevirium, Amsterdam, pp. 1 – 122, Image courtesy Missouri Botanical Garden, www.botanicus.org

c - Plukenet, Leonard (2010) Phytographia, Gale Ecco Print Editions, Farmington Hills

d - Aublet, Fusée (1775) Histoire des plantes de la Guiane Francoise, Vol. 3, P. F. Didot , London, Paris, Image courtesy Missouri Botanical Garden, www.botanicus.org

FIGURE *5.*73 Historical botanical sources of "tacamahaca"

a - Hernández, Francisco (1651) *Nova plantarum, animalium et mineralium mexicanorum historia*, Sumptibus Blasij Deuersini, Zanobij Masotti Bibliopolarum, Typis Vitalis Mascardi, Rome, http://openlibrary.org

b - Plukenet, Leonard (2010) Phytographia, Gale Ecco Print Editions, Farmington Hills

c - Lemery, Nicolas, Schneider, Ulrich Johannes (2007) Vollständiges Materialien-Lexicon, Directmedia Publishing GmbH, Berlin, p. 3327

d - Jacquin, Nikolaus Joseph (1763) *Selectarum stirpium Americanarum Historia,* Vol. 2, Ex officina Krausiana, Vienna, Image courtesy Missouri Botanical Garden, www.botanicus.org

PICTURES TAKEN BY DR. BIAN CALLINGHAM, QUEENS‘ COLLEGE, CAMBRIDGE

Figure 1.1 (left), 5.1. 5.4, 5.8, 5.12, 5.16, 5.19, 5.26, 5.30, 5.36, 5.37, 5.42, 5.45, 5.49, 5.55, 5.58, 5.61, 5.67, 5.71, 5.78, 5.81, 5.87, 5.91, 5.96

PICTURES TAKEN BY PROF. DR. CHRISTOPH HERM

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PICTURES TAKEN BY LISA STERTZ

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All other pictures are taken by the author.

1. INTRODUCTION

Natural resins are widely used by humans as raw materials for lacquers, drugs, adhesives and for spiritual purposes. Because of their common use in particular in former times, they can be found in nearly every area of life. Their exact ecological function is still not totally clarified such is their complex chemical composition. A literature review reveals that resin chemistry has to be investigated more detailed (see chapter 2). The need for reference materials close to original materials used and the presence of the Vigani Cabinet provide a starting point for the investigation of natural resins from the 18th century. In order to understand works of fine art, craftsmanship, chemistry and pharmacy and also religious practices it is necessary to investigate the botanical origin, terminology and chemical composition of natural resins more closely. This work provides an important contribution to this endeavour by studying materials obtained from a historical collection. This "materia medica" collection was compiled by John Francis Vigani at the beginning 18th century, and is now in the possession of the Queens' College, Cambridge. Studying these historical sources is helpful as it allows to draw a more detailed and more-dimensional picture of historical and contemporary use of natural resins. In this work, the question is raised whether an investigation of the connection between taxonomy and chemistry may lead to a new understanding of historical and modern terminology. For that purpose, various resinous materials from the Vigani Cabinet will be analysed and information from contemporary scientific literature is used to compile a picture as complete as possible of the 300-year-old materials.

1.1 Natural resins in a historical and modern context

In the 17th and 18th century, the terms "resin" and "gum" were used differently from today. In particular, several resins were called "gums". The different exudates from plants were arranged under "resins", "gum resins" and "gums". In the 17th century, the main difference between "gum resins" and "gums" was the solubility in water:

> "Resina, ρατινα, lacryma seu liquor est pinguis ac oleaginosus tum sponte ex arboribus profluens, tum interdum accedente vulneratione. Estque duplicis consistentiae, liquidiuscula aut duriuscula. [..] Gummi resinas voco concretas arborum lacrymas in oleo quidem promptiùs, attamen & in aqua, licèt difficulter, solubiles. [..] Gummi stirpibus ferulaceis seu gummata sunt concreti liquores, aqueis faciles solutu, profusi tum è stirpibus ferulaceis, tum ex fructicibus, tum ex arboribus excelsis". (Manget 1687: 64)[1].

Towards the end of the 17th century three groups existed: water (wine, vinegar, herb juice) soluble, oil soluble and irregular materials, which are difficult to dissolve in both oil and water (Manget 1687: 64; Harris 1704: Resin; Pomet 1717: 353; Lemery 1721: 949f).

This changed at the beginning of the 18th century. A third solvent, "spirit of wine", "spirituous solvent" or "rectified spirit", was introduced to distinguish "gums" and "resins" (Chambers 1728a: 191; Chambers 1728b: 998). The differentiation was originally made earlier. Chambers mentions that Tournefort defined "gum-resins" as soluble partly in "spirit of wine" and partly in water (ibid.).

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[1] "Resin, is a thick and oily tear or liquid, which flows spontaneously out of trees, sometimes caused by wounding. It is of twofold consistence, somewhat liquid or somewhat solid [..] Gum resins I call the concrete tears of trees, which are soluble in oil quite promptly, nevertheless, and in water more difficult [..] Gums or gummata are the concrete liquids, which are readily soluble in water, of ferulaceous plants, fruits and elevated trees" (own translation).

> "Resin, Resina, a fat, viscid, sulphurous Juice, oozing either spontaneously, or by Incisions, from several kinds of Trees, particularly the Pine, Fir, &c. [(Mastic, Camphor, best class is turpentine, the coarsest Rosin)] Resin is properly a Juice of the Bark only. [..] Resins will incorporate with Oil, or rectified Spirits, but not with an aqueous Menstruum. The Difference between Resins and Gums, consists in this, that Resins are more sulphurous, and Gums more aqueous; so that the first dissolve in Spirit of Wine, and the last in Water." (Chambers 1728b: 998).

> "Gum, Gummi, a vegetable Juice exuding thro' the Pores of certain Plants, and there hardening into a tenacious transparent Mass. Gum is properly one of the Juices of the Bark: It is drawn thence by the Sun's Warmth, in Form of a glutinous Humour; and by the same Cause is afterwards inspissated, concocted, and render`d tenacious. [..]The Character of Gums, whereby they are distinguished from Resins and other vegetable Juices, is, that they are dissoluble in Water, and at the same Time inflammable by Fire. / In general they are more viscid, and less friable, and generally dissoluble in any aqueous Menstruum; whereas Resins are more sulphurous, and require a spirituous Dissolvent." (Chambers 1728a: 191).

Thus, the plant exudates were no longer distinguished by their solubility in oil but by their solubility in water and in alcohol. The old classification still existed alongside the new one (Chambers 1728a: 119): "Aqueous and resinous gums" were distinguished instead of "gums" and "resins". This is the reason why some materials are called "gum" even though they are listed under "resins". The term "resin" was used by some chemists in a more comprehensive way, such as in the lecture notes of John Vigani: "Resin/rosin in reality is nothing else but solid oil of vegetables, as oil is really nothing but liquid resin rarefied by distillation" (Lecture notes undated: 4f; Lecture notes 1707: 104; Harris 174: rosin). The resinous parts of a plant are extracted by heating with "spiritus vini" until the "menstruum be thoroughly impregnated with the Resinous parts" (Lecture notes undated: 4f; Lecture notes 1707: 104). The "spiritus vini" is the distillate of wine, ethanol, and "menstruum" is another word for solvent (Wagner 2007: Vol. 4, glossary). Afterwards the solution is distilled. The part remaining in the retort is put into cold water, which urges the resinous part to precipitate: "This is the method [to draw the resin] from all parts of the vegetable Kingdome" (Lecture notes undated: 4f; Lecture notes 1707: 104). Thus, the term "resin" described a material dissoluble in alcohol.

"Resins" consisted of different relative amounts of "salt", "spirit" and "oil". These "principles", together with "earth" and "phlegm", were thought to be "Sorts of Bodies, which may by Fire be drawn from many Mix'd Natural Bodies" (Harris 1704: Principles). They were, however, "not truly and properly the Elements of Constituent Principles of Natural Bodies, nor indeed do we known any such" (ibid.). The "constitutive principles" of matter are described by Vigani as "atoms of various figures, with innate qualities of motion, figure, magnitude and place", which form the "elements" (cited after and translated by Guerrini 1994). Those "atoms", however, were not detectable through chemical experiments (Guerrini 1994), and therefore chemical analysis remained sense-perceptive. Even though some analyses, which were carried out to understand the plant constitution rather than identify individual compounds (Geoffroy, Thicknesse 1749; Campell 1978), the majority of such analysis reports were made for comparing different materials and manufacturing operations.

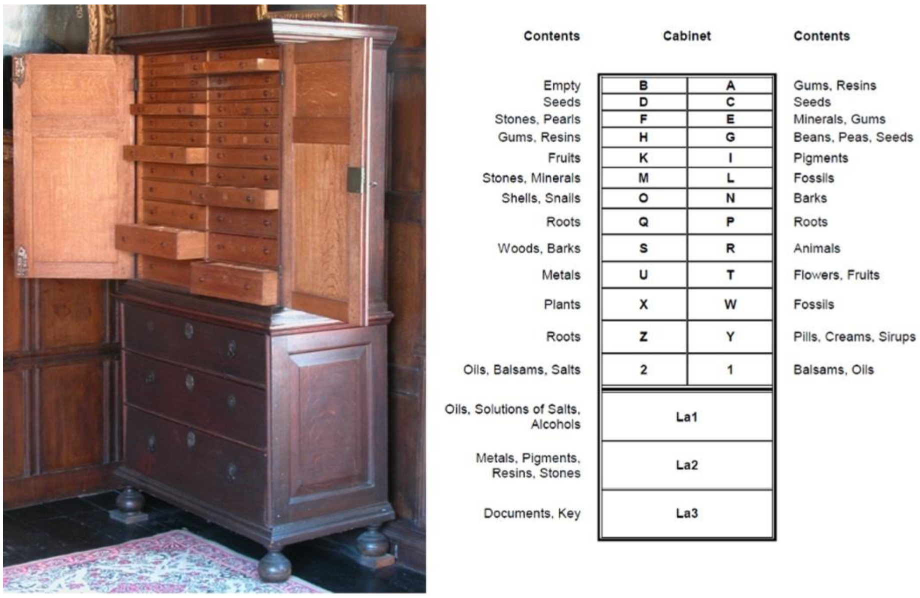
Today, natural resins are defined as plant exudates, particularly from trees, which share common (chemical and physical) properties such as solubility, state of matter and application characteristics (Howes 1950; Kühn 2001: 360; Langenheim 2003: 23). They consist of hydrocarbon secondary metabolites, mainly terpenoids and terpenes, the latter a group of compounds which are reducible to isoprene, a C-5 hydrocarbon (Breitmaier 2005: 1-3). Apart from a more elaborate idea of the constituting "principles", these definitions do not differ very much from the historical ones. They are made under the assumption of similar or equal properties or composition. This tends to be exclusive, because there are resins containing polysaccharides and other non-terpenoid constituents, exuding at different places of the plant, produced by insects or with changing solubility, state of matter and chemical properties.

Chemotaxanomical investigations have led to a more detailed picture of resin chemistry, and the availability of phytochemical data greatly improved the identification of unknown resinous materials. Chemotaxonomy is based on the assumption of a connection between botanical taxonomy and chemical composition. Basically, the separation of the biosynthesis of resins into different pathways leads to separated occurrences of the main chemical groups found in resins: mono- and triterpenes, sesqui- and diterpenes and phenylpropanoid compounds (Lynen 1964; Abe et al. 1993; Rohmer 1999; Lichtenthaler 1998; Bohlmann et al. 1998; Eisenreich et al. 1998; MacMillian, Beale 1999; Haralampidis et al. 2002; Breitmaier 2005: 3-9; Vogt 2010). There are exclusions, and compounds from different pathways have been found in the same resin (Langenheim 2003: 373), but the (predominant) occurrence of a certain group or the common occurrence of a specific group of compounds can be used for taxonomical assignment, although, due to phytochemical diversity, resin chemistry is extremely variable (Otto, Wilde 2001; Lardos et al. 2011).

A definition based on the ecological role of resins is relatively new, because the reason why plants produce resins is still under discussion. The ecological role of resins is strongly connected to their biosynthesis, which in turn influences chemical composition. Catabolism, storage and exudation mechanism are also important parameters. For example, whether a species or genus tends towards induced or constitutive resin production is indicated by the enzymatic system for the biosynthesis and the storage structure (Langenheim 2003: 32, 122ff; Sturm 1982). Complex resin secretory and storage structure mainly in the secondary xylem is related to high quantities of constitutive resin, while secretory structures in the cortex are mainly related to induced resin (Langenheim 2003: 31). Terpene synthase enzymes are able to synthesize multiple terpenes, which is thought to be the reason for the fixed ratios of specific compounds in constitutive resins. In contrast to this, resin compounds induced by injury are produced by single-product synthases, which is why the composition of constitutive and induced resins may differ (Langenheim 2003: 31-32; Sturm 1982). On the other hand, high resin production – for example in the Pinaceae – is associated with few quantitative changes between constitutive and induced resin, because the enzymatic activity through injury is greater for trees with low resin production and less complicated secretory structures (Langenheim 2003: 120).

1.2 The Vigani Cabinet and its historical background

The Vigani Cabinet is a collection of various medical, pharmaceutical and chemical materials compiled by the Italian chemist and pharmacist Giovanni Francisco (anglicised John Francis) Vigani. He was born in Italy, in or near Verona, around 1650. Little is known about his education, but he seems to have travelled through Europe for some time to further his education. His only published work, the *Medulla Chymiae* (Marrow of Chemistry), was first printed in Gdańsk in 1682 (Vigani 1682). Several further editions and reprints of this work were published in London and Leiden (Haley 2002: 3; Wagner 2007: Vol. 1, 13) and it was reviewed in Rotterdam, Leipzig and Paris (Schaffer, Stewart 2005). In 1682, he settled in Newark-on-Trent in the north of Cambridge, England. Shortly thereafter, he began to lecture in pharmacy and chemistry as a private tutor or college lecturer mainly in Queens' and St Catherine's College



Contents	Cabinet		Contents
Empty	B	A	Gums, Resins
Seeds	D	C	Seeds
Stones, Pearls	F	E	Minerals, Gums
Gums, Resins	H	G	Beans, Peas, Seeds
Fruits	K	I	Pigments
Stones, Minerals	M	L	Fossils
Shells, Snails	O	N	Barks
Roots	Q	P	Roots
Woods, Barks	S	R	Animals
Metals	U	T	Flowers, Fruits
Plants	X	W	Fossils
Roots	Z	Y	Pills, Creams, Sirups
Oils, Balsams, Salts	2	1	Balsams, Oils
Oils, Solutions of Salts, Alcohols	La1		
Metals, Pigments, Resins, Stones	La2		
Documents, Key	La3		

Left – present location at the President's Loge of Queens' College, Cambridge, right - layout of the Vigani Cabinet with content of several drawers (right) (Wagner 2007. Vol. 2)

Fig. 1.1 The Vigani Cabinet

in Cambridge (Haley 2002: 3). In 1703, he was appointed as the first "Professor of chemistry" at the University in Cambridge, probably because of his good reputation as a lecturer of chemistry (Guerrini 1994; Haley 2002: 5). He continued to lecture and to carry on an apothecary service until he died in Newark in 1712 (Wagner 2007: Vol. 1, 8-12).

Vigani compiled the Cabinet named after him in 1703/1704, while he was lecturer for "materia medica" at Queens' College in Cambridge (Wagner 2007: Vol. 1, 1). It contains more than 570 raw materials from plants and animals, inorganic materials such as pigments, stones and metals, and 50 manufactured drugs, as well as oils and several unidentified fluids in glass bottles, nearly 700 materials in all. Most of the Cabinet survived until today in an almost untouched condition. A compilation of the materials inside the Cabinet, with a focus on fine art materials, was made by Lisa Wagner. She additionally provided a transcription of several manuscripts found inside the Cabinet and in the library of Queens' College (Wagner 2007: Vol. 4). Those manuscripts include a number of invoices and lecture manuscripts associated with Vigani and the Cabinet (MS Quns Vig. 2-11; Lecture notes undated, Lecture notes 1707). The invoices cover almost 450 (almost two thirds) of the conserved materials in the Cabinet. The majority of the materials inside the Cabinet is labelled, which makes it possible to reconstruct names, prices and acquisition dates for most of these materials.

All materials were purchased from druggists in London and paid for by the College. The Cabinet is made of oak and cost 10 pounds (Wagner 2007: Vol. 1, 71-76). According to the preserved invoices, "materia medica" cost 35 pounds, 6 shillings and 1 ½ pence, glass bottles, papers and transportation 5 pounds and 15 shillings (Wagner 2007: Vol. 1, 76). A calculation made by Vigani and the College purser reveals a deficit of 6 s and 3 pence, which probably covers part of the materials not mentioned in the preserved invoices. Another 22 pounds and 3 shillings not listed in the invoices are mentioned by the purser (Wagner 2007: Vol.1, 77). The associated materials may never have been delivered, or may have been lost or stored elsewhere.

Vigani left Queens' College soon after the completion of the Cabinet. As the Cabinet was owned by the college, it remained there. Around 1730, it was under the supervision of the

College's Master (Bradley 1730). Later, it disappeared from sight. In 1922, it was rediscovered underneath the staircase in the old library of Queens' College. In 1933, some of the materials were removed for analysis (Evers 1933), and the Cabinet was used for lectures. A typed inventory of the materials (the old inventory) found in the Cabinet also dates from that time. Some time before 1970, the Cabinet was removed to its current location in the President's Loge (Wagner 2007: Vol.1, 64-65; Fig. 1.1).

The Cabinet is arranged in 29 drawers (Fig. 1.1). The bottom drawer La3 is nowadays used as a repository for the documents related to the Cabinet, while the one above La2 is a storage drawer for stock and spare materials (Wagner 2007: Vol. 1, 63). The other drawers are arranged in a systematic manner, which partly reflects the contemporary classification of "materia medica" found in corresponding publications (Dale 1693; Pomet 1694; Lemery 1698; Bradley 1730; Hill 1751). Obviously, Vigani aimed to compile a systematic collection of "materia medica" (Wagner 2007: Vol.1, 64). This is in contradiction to his written work, which focusses on experimenting, observing and deducing rather than systematic theoretical considerations (Guerrini 1994; Wagner 2007: Vol.1, 17-22). The circumstances of the Cabinet's compilation – the high quality of the materials, the short acquisition time of one year and the high costs paid by the College – suggest that he intended to compile a collection for display and not for use. Nevertheless, Haley mentions its use for pharmaceutical preparations (Haley 2002: 6).

The Vigani Cabinet was compiled at the beginning of the Enlightenment era, a time when scientific research began to focus on experimental work (Boyle 2000). It was accompanied by intensified publication and the beginning compilation of knowledge (Harris 1704; Chambers 1728). Particularly in England, the Royal Society started to collect observations from learned witnesses of integrity. A determining element of the time was the contrast between the more theoretical natural philosophy and the practical experimental work. The *Medulla Chymiae* itself was, for example, intended as a practical textbook for Vigani's courses and not as a compilation of chemical knowledge (Vigani 1682). A more theoretical approach with a similar experimental section was pursued by the French chemist Nicolas Lemery (Lemery 1675). In general, chemistry was a subject of experimenting and performing operations and not of theoretical considerations (Guerrini 1994). It was taught mainly in connection with pharmacology and medicine (Gascoigne 1989: 62f.; Schaffer and Stewart 2005). Other related field were pharmacognosy – or the art of the "material medica" – and botany (Guerrini 1994). A broad variety of pharmacological and medical treatises from this time provides useful information on the properties, geographical and botanical origins, collection methods, storage and trading details of the materials (Manget 1687; Blanckaert 1690; Dale 1693; Woodward 1695; Tournefort 1717; Zwinger 1724; Bradley 1730; Geoffroy 1743; James 1747; Linné 1749; Hill 1751). Not all of these compilations were made out of theoretical interests but also for practical purposes such as the identification of adulterations. Due to the importance of taste, smell, and appearance for such analyses, books about commodity sciences (in German "Warenkunde") were widely distributed (Pomet 1694; Lemery 1698; Lemery 1721; Lemery 1737; Geoffroy 1743; Geoffroy, Thicknesse 1749). Based on theoretical considerations about the nature of "elements" by Boyle and the mechanical concept of matter and motion of Newton, chemistry slowly began to search for the principle indestructible part of matter (Guerrini 1994; Boyle 2000; Schaffer and Stewart 2005). Another important process was the development of botanical taxonomy. Based on early works by Caspar and Johann Bauhin, John Ray and Joseph Pitton de Tournefort, Carl von Linné established modern taxonomy with the S*ystema naturae* and *Species plantarum* (Bauhin, Cherler 1650-1651; Bauhin 1623; Ray 1690; Ray 1693; Tournefort 1694; Linné 1735; Linné 1753).

1.3 Aim of the thesis - outline

The Cabinet contains 43 natural resins or gum-resins, resinous balsams and products thereof in different drawers. That includes several European resins such as sandarac, Venice turpentine or amber, but also exotic materials such as anime, copal, elemi, tacamahaca, Balsam of Peru and Tolu and Copaiba balsam. The analytical investigation of natural resins made important progress in the last years (for example Pastorova 1997; Koller et al. 1997a; Mills, White 1999; van der Werf et al. 2000; van den Berg et al. 2000; van den Berg et al. 2002; Langenheim 2003; Scalarone et al. 2003; de la Cruz-Caňizares et al. 2005; Stacey et al. 2006; Chiavari at al. 2008; Doménech-Carbó et al. 2009; Colombini, Modugno 2009; Pitthard et al. 2011). Due to the high number of constituents to be analysed and significant changes after exudation, it remains a complex process, however. Additionally, natural resins show a complex and sometimes confusing terminology, which tends to change over time (Tschirch 1935: 265-6; Boisson 1988; Mills, White 1999: 98, 102-3; Stross 1997; Koller et al. 1997b; Langenheim 2003: 357-359; de la Cruz-Caňizares et al. 2005; Rüdiger et al. 2007; Regert et al. 2008; Doménech-Carbó et al. 2009). Apart from the good conservation state of the materials from the Vigani Cabinet, the chance to set the materials into their historical context is a particular feature of the Cabinet. It allows the use of contemporary scientific literature in addition to the manuscripts from the Cabinet, which in turn facilitates the investigation of the interrelation between the chemical composition, botanical origin and terminology of natural resins.

The complex chemotaxonomical and phytochemical data about resin chemistry are connected with the available terminology to a three-dimensional picture. The presence of several 300-year-old natural resins conserved in the Vigani Cabinet adds an historical dimension to these connections. With contemporary information from written sources about their origin, trade and manufacture, a chemical analysis of the resinous materials from the Vigani Cabinet would lead to a detailed picture of resinous materials in history and present, their terminology and botanical origin.

Chapter 2 provides a review of (phyto)chemical literature and from archaeometry about the chemical composition of certain resins. The data are presented based on the taxonomy of their botanical sources. The current state of knowledge is evaluated and at the end research deficits are discussed. This serves to provide a basis for the investigation of reference materials and a discussion about possible biomarker compounds for the different resins.

Chapter 3 contains the experimental section. The main analysis method of this work is coupled gas chromatography and mass spectrometry. The samples are dissolved and methylated with trimethylsulfoniumsulfate. For amber samples from the Cabinet additional solvents and infrared spectrometry is used. The chapter presents these methods and gives a short introduction to the compounds investigated and some methodological problems that arose during the work.

Chapter 4 presents, based on the consideration made at the end of chapter 2, the results of the analyses of a wide range of reference materials. They originate from several endemic plants (botanical samples) and from references collections. The analytical method is coupled gas chromatography and mass spectrometry. The results are presented based on the taxonomy developed in chapter 2. Because the connection of nomenclature and chemical composition is sometimes the object of investigation, the names of the materials may also be chosen as subtitles. The chapter provides data profiles of the investigated resins as completely as possible. The following discussions focus on chemotaxonomical interrelations and open questions, which arose from the literature review.

Due to the high number of chemically different materials, a short discussion of the results is provided for every single order. The chapter concludes with a discussion of research deficits similar to that of the literature review, and a summary of the improvements made, as a basis for the investigation of the materials from the Vigani Cabinet.

The chapter 5 presents data profiles of the materials from the Vigani Cabinet together with a data collection of their contemporary context. The results are presented in data sheets, one for each analysed material. These sheets include a description of the material, and references in historical sources, together with information about terminology, botanical and geographical origin, manufacture, trade and properties taken from the historical sources. One or more possible chemical compositions based on the historical information and the modern chemical data are discussed. This is followed by the results from the chemical analysis and a discussion. The individual items of the data sheets are explained in detail at the beginning of chapter 5.

The results from the materials from the Vigani Cabinet are discussed and interpreted based on the information from the historical sources and the chemical data from the literature and reference analyses made in this work. The main connection between historical and modern data is the botanical and geographical origin of the materials, which additionally may points to changes in their terminology.

Chapter 6 summarizes the main results of the investigation of reference materials and the individual materials from the Vigani Cabinet obtained in this thesis, answering the following questions:

1. Do chemotaxonomical and phytochemical data provide a reasonable reference system for identifying unknown materials? Which open questions could be answered and which could not?

2. In which way was the historical information about the materials found in the Cabinet helpful for filling knowledge gaps about natural resins from the 18th century?

3. What new insights could be gained regarding the individual materials from the Cabinet?

In doing that, the chapter provides an outline of the core contributions of this dissertation thesis.

2. LITERATURE REVIEW

Resin producing plants can be principally divided in Gymnosperms and Angiosperms. All gymnosperm species producing resins belong to one order, the Pinales, commonly called conifers. This is not the case with angiosperm plants, here the resin production is widely spread and various orders include important resin producing species. The botanical classification is shown in Fig. 2.1. It should be noted that there are a number of additional resin producing families, which are not discussed in this work.

Resins from gymnosperms are mainly used on the northern hemisphere, commonly referred to as conifer resins, but also southern hemisphere conifers produce resins. They are discussed in chapter 2.1. The volatile fraction of conifer resins consists mainly of monoterpenes and is generally very large (20 – 50 %). The non-volatile fraction is characterised by diterpenes.

Angiosperm resins are produced by plants distributed over the whole world. They are of varying chemistry compared to conifer resins, because they originate from a much larger and diverse group of plants. In Leguminosae (Fabaceae) resins sesquiterpenes dominate and non-volatile fraction is composed of diterpenes. Another family from that order (*Myroxylon*) produces phenolic resins (chapter 2.2). Finally, in the order Sapindales families produce resins composed of mono-, sesqui- and triterpenes (chapter 2.3). The last chapter is about fossil resins, which are – although mainly exuded by extinct plant species – classified by their chemical composition relating to distinct plant species. They are discussed in one chapter, because this work focuses on Baltic amber (chapter 2.4). The chapter concludes with a discussion of the presented data and their completeness relating to the present work (‘research deficits’).

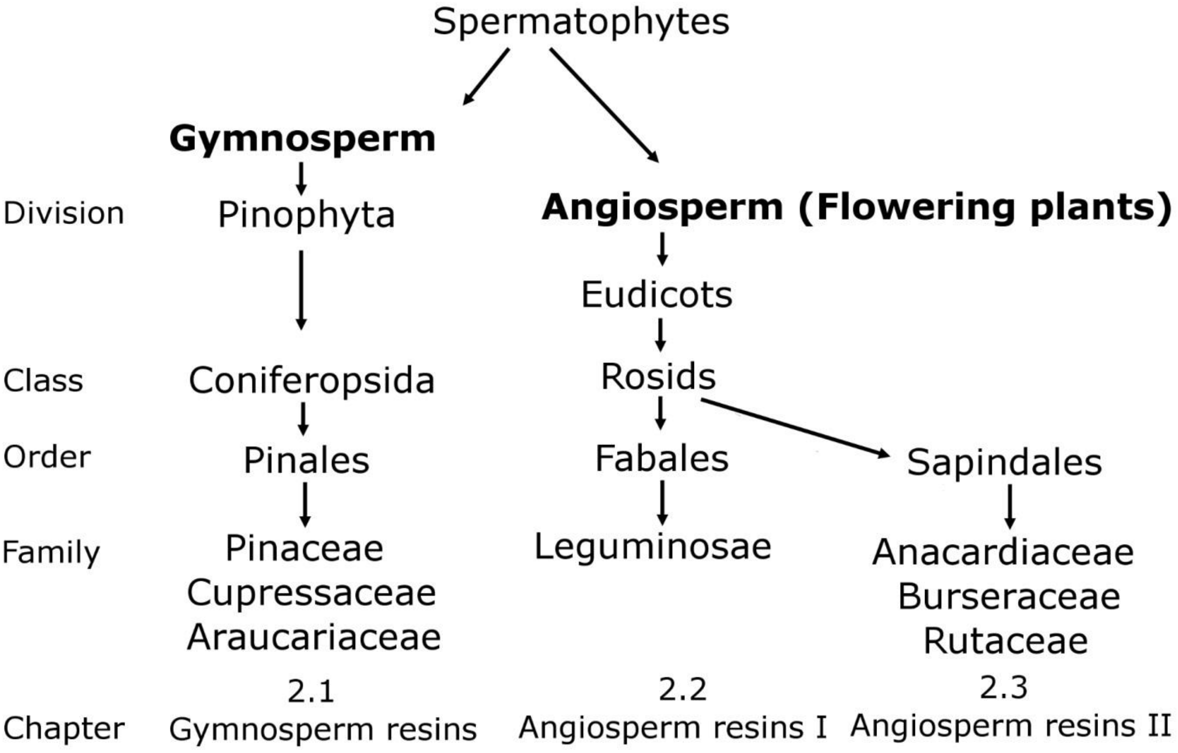


Fig. 2.1 Botanical classification of resin producing families

2.1 Gymnosperm resins – conifer resins and products

Coniferous resins originate from the families Pinaceae (northern hemisphere conifers), Cupressaceae and Araucariaceae (southern hemisphere conifers) (Fig. 2.1). Main compounds in these families are di- and tricyclic diterpene abietanes, (iso)pimaranes and labdanes (Fig. 2.2, 2.6), which are synthesised from CPP and syn-CPP (see appendix).

2.1.1 Pinaceae

Pinaceae resins exude as more or less viscous solids, which hardens thereafter or by human treatment. The most common turpentines, resins and products of this family are listed with their modern name in table 2.1.

Pinaceae resins consist mainly of diterpene acids of the (iso)pimarane and abietane type (Mills, White 1999: 100-2; Scalarone et al. 2002). The most abundant diterpenes are (iso)pimaric, sandaracopimaric, palustric, abietic, neoabietic and dehydroabietic acids (Fig. 2.2), whereas dehydroabietic acid is thought to be an aging product and not an original constituent (Pastorova et al. 1997; Chiavari et al. 2008).

Non polymerizing labdane alcohols and also acids are found occasionally in *Pinus* and *Picea* species (Hegnauer 1962: 377-8, 383-5; Mills, White 1977; Sturm 1982: 24, 25). In *Pinus* species small amounts of C-8 oxygenated labdanes are found (Arrabal et al. 2002; Papajannopoulos et al. 2001). Resins of *Pinus* species from the section Cembrae contain high amounts of copaiferic and lambertianic acid, both biosynthesised from CPP (Lisina et al. 1972; Raldugin et al. 1976; Raldugin et al. 1978). Also communol, communic and merkusic acids are found in *Pinus* resins (Joye, Lawrence 1963; Coppen et al. 1993; Mills, White 1999: 100; Bambang et al. 2006).

In *Larix* species non-polymerizable labdane alcohols and their derivatives are familiar. The high amounts of epimanool, larixol and larixylacetate are used as biomarkers for larch resins (Mills 1973; Koller et al. 1997a; van den Berg et al. 2000; Osete-Cortina et al. 2004). The resin from the European larch is found to differ also by high amounts of isopimaranes and lower amounts of abietanes from other Pinaceae resins (van den Berg et al. 2000). Labdanes with conjugated double bonds in the side chain are found in *Abies* (Norin 1972; Mills, White 1977; Shmidt et al. 1982; Serpico, White 1998) and *Picea* species (Shmidt, Pentegova 1977; Smidt et al. 1982; Raldugin et al. 1991; Breitmaier 2005: 53; Martin et al. 2002). For *Abies* resin the polymerisation of phellandrene and *cis*-abienol is reported (White, Kirby 2001). A compilation of the literature data is given in table 2.2.

Processing

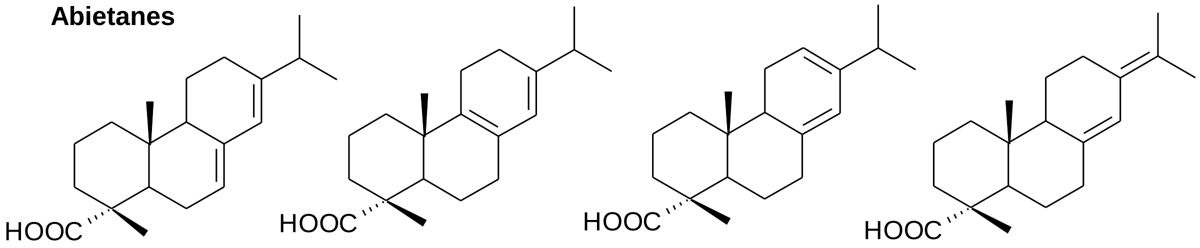
Pinaceae resins are heated to obtain oil of turpentine and colophony as well as pitch and tar. Modern terminology distinguishes two processing types, distillation and pyrolysis, which do not fully correspond with historical terms.

Distillation is mainly used for the separation of the volatile and non-volatile fraction of pine resins. It takes place in a batch or continuous still at temperature range 150-180°C. The mono- and sesquiterpene fraction is removed. It is called oil of turpentine or (gum) turpentine, the latter to distinguish it from wood or sulphate turpentine (Falbe, Regnitz 1995). This turpentine differs from the "turpentine" used in historical sources or nonangloamerican publications, and refers only to the volatile fraction separated by a distillation process. The remaining fluid mass in the batch contains mainly diterpenes, which

Genus	Species	Derived resinous material
Larch (Larix)	European Larch (L. decidua Mill.)	Venetian turpentine
Fir (Abies)	Silver Fir (A. Alba Mill.)	Strasbourg turpentine
Pine (Pinus)	European Black Pine (P. nigra J F. Arnold)	Colophony
	Swiss Pine (P. cembra L.)	Carpathian turpentine, Colophony
	Maritime Pine (P. pinaster Aiton)	Bordeaux turpentine, Colophony
Spruce (Picea)	Norway Spruce (P. Abies (L.) H. Karst.)	Colophony, Burgundy Pitch

Tab. 2.1 Tree species and their resins from the family of Pinaceae (Mills, White 1999: 98; Koller et al. 1997a)

Abietanes



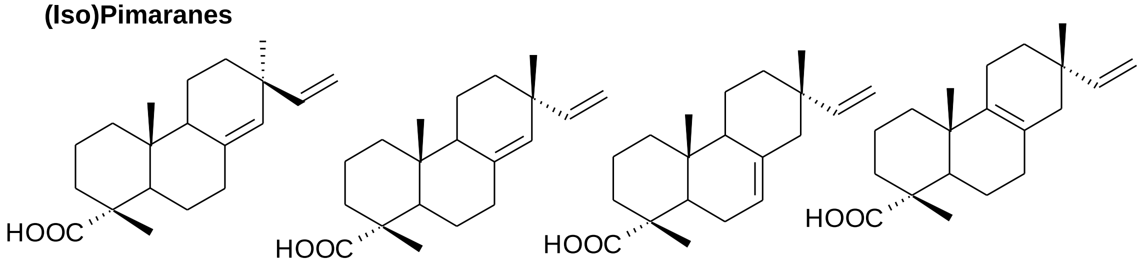
abietic acid
or abieta-7,13-dien-18-oic acid

palustric acid

levopimaric acid

neoabietic acid

(Iso)Pimaranes



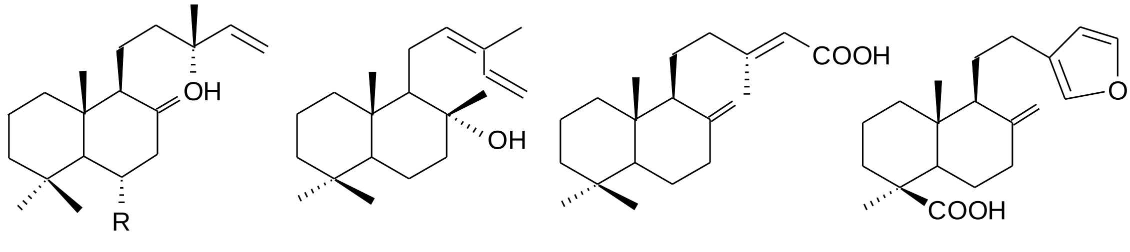
pimaric acid or
pimara-8(14),15-diene-18-oic acid

sandaracopimaric acid

isopimaric acid

Δ8-isopimaric acid

Labdanes



R= H **Epimanool**
or labda-8(29)-14-diene-13-ol
R=OH **Larixol**
R=OAc **Larixy acetate**

***cis*-abienol**

copaiferic acid
labda-8(20),13-diene-15-oic acid

lambertianic acid

Fig. 2.2 Structures of compounds found in Pinaceae resins

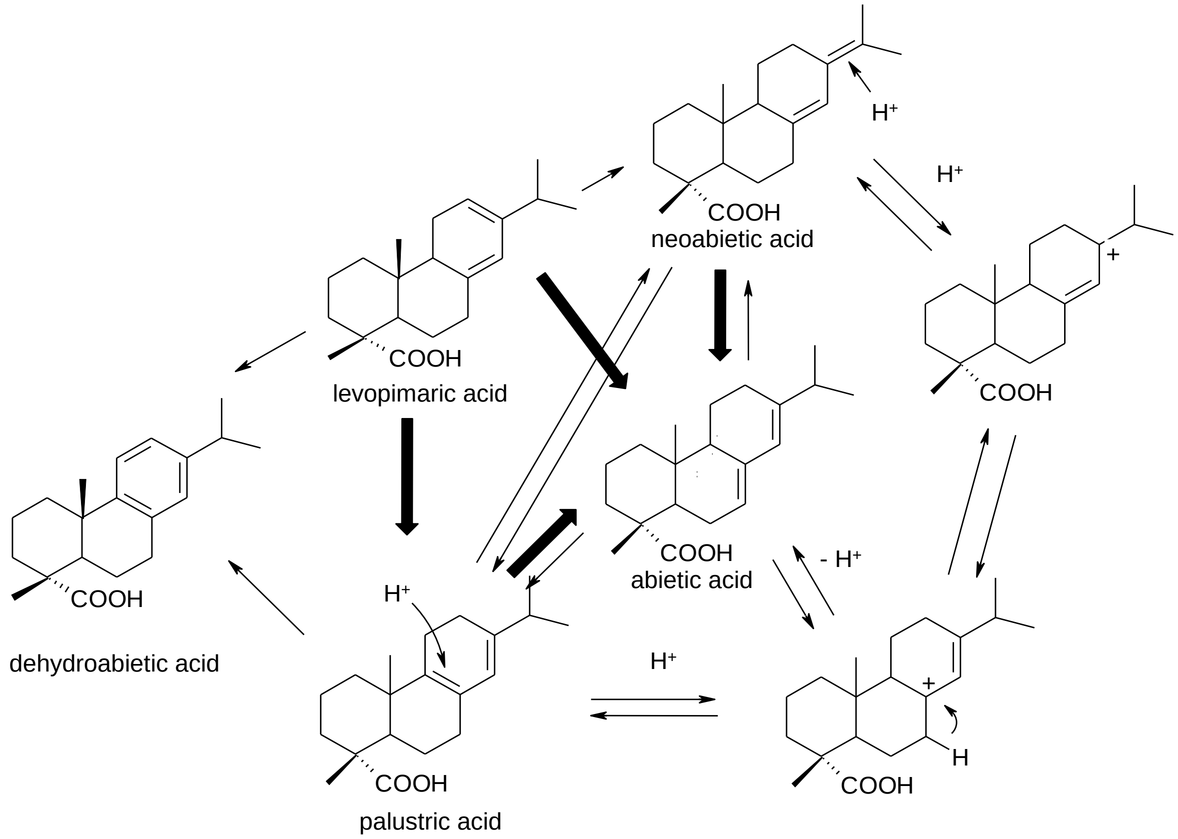


Fig. 2.3 Isomerisation pathways of abietanes (Loeblich et al. 1955; Baldwin et al. 1956; Ritchie, McBurney 1950; Loeblich Lawrence 1957; Joye, Lawrence 1961; Takeda et al. 1968; Enoki 1976; Portugal et al. 1996; Pastorova et al. 1997; Morales et al. 1992)

are isomerised and to a minor content oxidised and fragmented (Loeblich, Lawrence 1958; van den Berg et al. 1996: 933; van den Berg et al. 2000; Chiavari et al. 2002; Osete-Cortina, Doménech-Carbó, 2005; Chiavari et al. 2008). Abietane acids readily isomerize under heat conditions (Mills, White 1977; Portugal et al. 1996; Pastorova et al. 1997). The reaction is catalysed by protons primarily from the intermolecular carboxyl group but also from acidic environments (see below) (Loeblich, Lawrence 1958). This leads to a significant decrease of isomerisation when the carboxyl group is methylated (Loeblich, Lawrence 1958). From a molecular point of view levopimaric acid is the most unstable abietane acid due to its lower substituted and exocyclic double bond. Therefore it is transformed the fasted and found only in very fresh resins (Proefke, Rinehart 1992; van den Berg et al. 2000; Mills, White 1999: 100). With increasing stability neoabietic, palustric and abietic acid are formed, but also back and forth reactions occur (Fig. 2.3). Oxidation also occur, mainly dehydroabietic acid is formed (van den Berg et al. 1996: 933; van den Berg et al. 2000; Chiavari et al. 2002; Osete-Cortina, Doménech-Carbó, 2005; Chiavari et al. 2008).

Burgundy pitch or Burgundy resin is melted in hot water and purified by straining through cloth. It is sometimes called spruce resin. Its botanical origin is *Picea abies* Karst. (Pitthard et al. 2011; Kremer 2011; Scents of the Earth 2012). Today it is produced all over the world and not only in Burgundy, from where it is thought to be originally supported (Pitthard et al. 2011). Therefore, other species are possible for its production. Pitthard et al. found methyl-6,7-dehydroabietate, which is probably 7-methoxy-Δ6(7)-dehydro-dehydroabietate (Pastorova et al. 1997; van den Berg et al. 2000), 15-hydroxy-dehydroabietate and methyl-6,7,15-dimethoxy-dehydroabietate as marker compounds in a modern burgundy pitch (Pitthard et al. 2011).

Historically, similar products were produced by melting or cooking pine resin in water or as the remaining of the distillation process for the production of oil of turpentine. These materials are called colophony, Greek pitch or rosin (Manget 1687: 64; Lemery 1721: 330; Hill 1751: 708f). In modern literature different methods are described: melting and heating of raw resins in earth pits as well as in retorts and boiling the resin in water (Koller et al. 1997a; Petit-Dominguez, Martinez-Maganto 2000; Koller et al. 2003). Koller et al. cooked the resinous balsam of larch in water according to recipes from the early 18th century. They found decreasing amounts of larixol and larixylacetate but increasing amounts of detectable resin acids in the methanol extract. This indicates mainly isomerisation reactions of the abietane compounds (Koller et al. 1997c).

The second processing type is called pyrolysis, dry or destructive distillation. The main differences are the combined use of resin and resinous wood, the higher operation temperature and the absence or controlled presence of oxygen. Materials produced with that methods are called tar or pitch. Distillation carried out in a retort may be accompanied by pyrolysis processes, and historically the terms resin and pitch are overlapping.

Typical chemical processes are aromatisation, defunctionalisation, decarboxylation and skeletisation. High amounts of dehydroabietic and didehydroabietic acid are formed (Weser et al. 1998; Colombini et al. 2003; Pérez-Arantegui et al. 2009), together with diterpene hydrocarbons such as retene, tetrahydroretene, abietatriene and norabietatriene (Beck et al. 2002, 181). The degree of decarboxylation, defunctionalisation and loss of angular methyl groups in general is related to the operating temperature (Beck et al. 1998; Beck et al. 2002; 182). Above 300°C decarboxylation of the resin acids takes place, between 300 and 350°C oxidised acids are formed (mainly 7-oxo-dehydroabietic acid), which are decomposed above 450°C (Beck et al. 1998). Formation of norabietatrienes and retene is increased at temperature above 350°C with different rates (Beck et al. 1998). At temperatures above 400°C an isomerisation rate of 0.5 – 2 % was observed (Beck et al. 2002: 182). Ring cleavage products are considered typically for those materials, they are thought to be formed from levopimaric acid (Takeda et al. 1969; Beck et al. 2002: 182). Additionally, low amounts of pimaric and isopimaric were found in pitch related materials (Pérez-Arantegui et al. 2009). Natural methylesters mainly of dehydroabietic acid found in those materials are considered as biomarkers for the use of wood (Weser et al. 1998; Beck et al., 1998; Colombini et al. 2003).

Aging

After harvesting with and without further treatment or application the resins undergo different aging processes. Main reactions are isomerisation and oxidation. They are strongly influenced by environmental conditions such as light, temperature and presence or absence of oxygen. In general, pimaranes are relatively stable against oxidising environments due to their lack of conjugated double bonds, while abietanes are decomposed to a much greater content. Aged Pinaceae resins can consist nearly entirely of aging compounds. This distinguishes them from other resins, which are due to another chemical composition not that prone to isomerisation and oxidation processes.

Isomerisation is the main process in the dark, especially when a polar solvent is involved. Both thermal (see above) and acidic isomerisation are similar reactions (Loeblich, Lawrence1958). However, thermal isomerisation is less effective than isomerisation in an acidic environment (Baldwin et al. 1956).

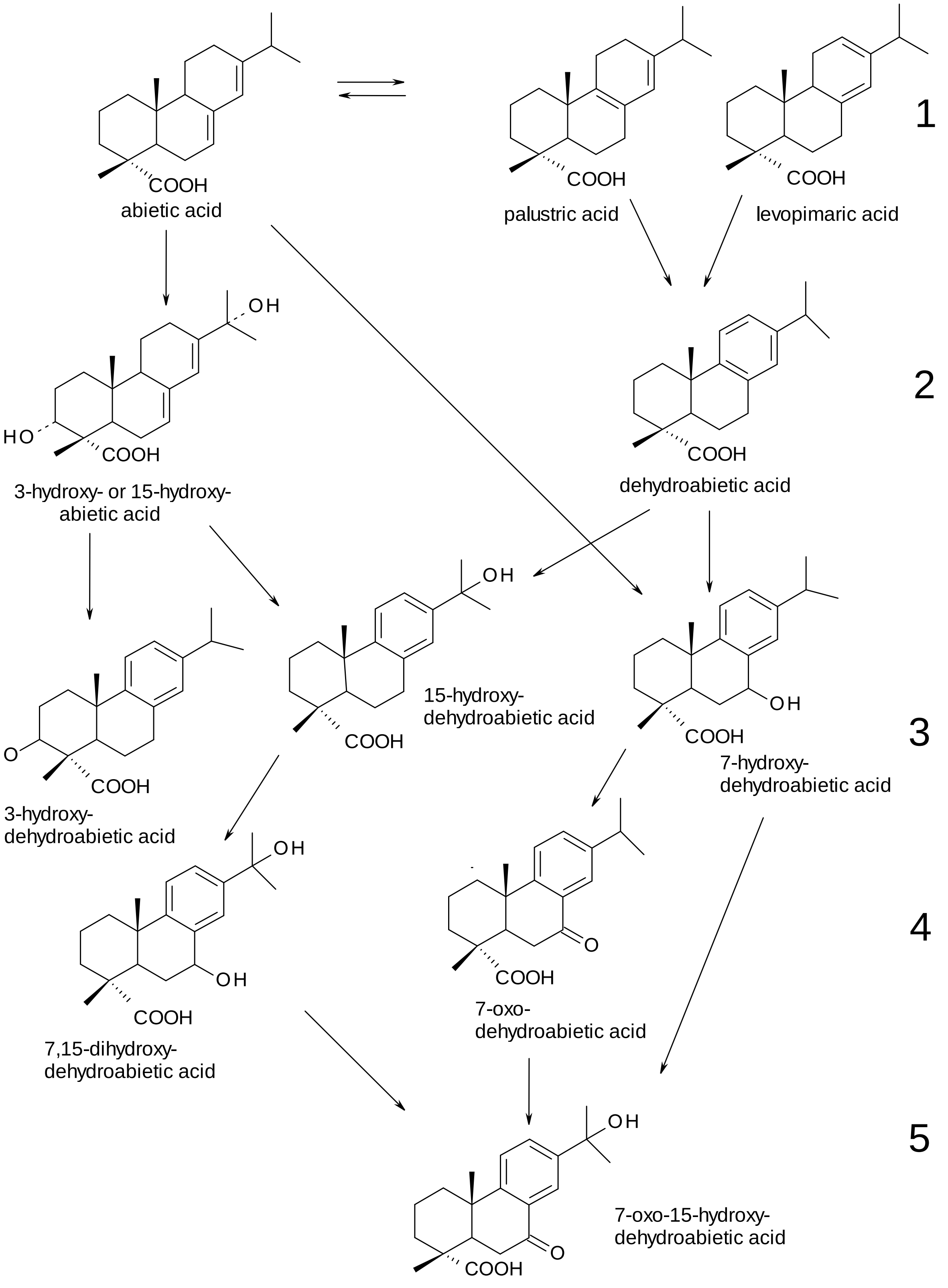


Fig. 2.4 Main aging products with proposed oxidation pathways, numbers describe the increasing oxidation state (Pastorova et al. 1997; van den Berg et al. 2000; Enoki, Kitao 1974; Enoki, Kitao 1975; Osete-Cortina, Doménech-Carbó 2005)

<u>Dehydrogenation</u> is observed mainly through the production of dehydroabietic acid, which is particularly in decomposed samples considered as a marker of Pinaceae resins. Investigations have shown that mainly homoannular dienoic acids as palustric and levopimaric acid

yield dehydroabietic acid (Enoki 1976) (Fig. 2.3). Other compounds reported are the dehydrogenation products di- and tetradehydroabietic acid (Andreotti et al. 2006; Weser et al. 1998; Koller et al. 1998; Scalarone et al. 2002; Colombini et al. 2005).

Abietanes yield dehydroabietic acid and higher oxidised derivatives of it by further incorporation of oxygen (Pastorova et al. 1997; Scalarone et. al. 2003). Artificial aging experiments showed that under exposure to light and oxygen oxidation is the predominately process (van den Berg at al. 2000; Scalarone et al. 2002; Scalarone et. al 2003). There is a wide range of reported findings of highly oxidised dehydroabietic acids in literature, 7-hydroxy-, 7-oxo- and 7-oxo-15-hydroxy-dehydroabietic acid are the most common (e.g. Anderson, Winans 1991; Krohn et al. 1992; Pastorova et al. 1997; van den Berg et al. 2000; Colombini et al. 2003; Andreotti et al. 2006; Fig. 2.4).

Literature mentions different proposed mechanism for the oxidation of abietane acids (Moore, Lawrence 1958; Schuller et al, 1960; Schuller, Lawrence, 1961; Das et al. 1994: 75; van den Berg et al. 1996; Egenberg, Glastrup 1999; van den Berg et al. 2000; Osete-Cortina, Doménech-Carbó 2005). Oxidation at C-7 and C-15 is preferred to C-3, because positions next to double bonds are of allylic nature. The C-15 position is steric favoured (Das et al. 1994: 75). Oxidation mainly starts with dehydroabietic acid but also the oxidation of abietic acid to 7- or 15-hydroxyabietic acid was proposed (Kutney et al. 1982; van den Berg et al. 1998; Osete-Cortina, Doménech-Carbó 2005). All pathways are shown in Fig. 2.4.

Under indoor conditions mainly isomerisation and oxidation were observed. Exposure to light led to a small degree of polymerisation in Pinaceae resins, which normally do not tend to polymerisation due to their endocyclic double bonds. If labdane compounds are present, the process was accelerated (Scalarone et al. 2002; van den Berg et al. 2002).

Artificial outdoor conditions – lower temperature, higher light intensity and a greater wavelength range – led to stronger degradation reactions of the original constituents and their oxidation products. Abietane compounds are degraded to a higher content than under indoor conditions. Additionally photo-induced cleavage reactions were observed, which led to an increasing amount of diterpene fragments (Scalarone et al. 2002). Levopimaric acid was proposed to be the precursor of these cleavage products (Takeda et al. 1969; Portugal et al. 1996). Also pimaranes are decomposed to a higher content. It is not known which products are formed. Apart from seco-pimaranes oxygen containing derivatives of dehydroabietic acid are proposed (Kutney et al. 1981; Portugal et al. 1996).

Next page: Tab. 2.2 Composition of Pinaceae resins, amounts [%] of diterpene acids and labdanes compounds in resinous balsams from Pinaceae species or products derived from them; x – present without quantification; tr – treasures; (1) Mills, White 1999: 101; (2) Arrabal et al. 2002 (different samples, amounts are averaged); (3) Lange, Weißmann 1991; (4) Rezzi et al. 2005; (5) Raldugin et al. 1976; (6) Raldugin et al. 1976b; (7) Lange et al. 1994; (8) Hafizoğlu, Reunanen 1994 (bark and cone resin); (9) Raldugin et al. 1991 (also native methylesters of all resins acids except SPS); (10) Ostete-Cortina, Doménech-Carbó 2005 (Venice Turpentine from Talens; Strasburg Turpentine from Kremer) (11) van den Berg et al. 2000 (Venice Turpentine from Schmincke); (12) Scalarone et al. 2002; (13) Mills, White 1977 (Abies alba resin collected in the Pyrenees); (14) Mills 1973.

	Pimaric	Sandaracopimaric	Isopimaric	Levopimaric and/or Palustric		Dehydroabietic	Abietic	Neoabietic	Other compounds
Pinus pinaster (1)	8	2	12	39		4	14	18	
P. pinaster (2)	7	1.6	8	42		3	13	17	iso-abienol, abienol, labda-11,13-dien-8-ol
P. sylvestris (1)	19	3	1,5	34		4	28	10	
P. sylvestris (3)	7.9	1.5	1.8	55.9		6.8	10.3	12.6	
P. nigra spp. (4)	2.1 - 5-7	0.6 – 1.6	1.8 – 7-6	2.7 – 26.0	6.8 – 15.0	2.3 – 17.8	4.2 – 13.5	2.8 – 11.8	
P. halepensis (1)	1.2	10	39	37		-	10	1,5	
P. ponderosa (1)	7.5	3	15	40		8	11	11	
P. palustris (1)	5.5	1	10	52		8	9	13	
P. pumila (5)		1	16	3		1.2	9	3.5	49,3% copaiferic, cis-abienol, iso-cembrol
P. cembra (6)	1.9	0.5	21.4	3.5		4.6	30.3	2.2	35,6% lambertianic
P. lambertiana (1)	Δ8 0.5	3	22	4		8	4	2	56 % lambertianic acid
P. peuce (7)	~3	1.6	33	9.9		5.8	34.3	6.7	abienol, (iso)cembrene
P. merkusii (1)		10	15	38		8	16	3	10 % merkusic acid
P. elliottii (1)	4.5	1.5	21	38		4	9	3	4 % communic acid
P. resinosa (3)	6.2	1.4	1.4	58.7		5.4	8.2	12.4	
P. pinea (3)	5.5	1.5	13.7	26.8		3.9	32.1	13.5	
Picea shrenkiana (9)	2.3	4.9	29	16.1	16.1	13.8	10.7	7.1	labda-8(17),13-dien-15-ol, iso-cembrol, cis-abienol, (epi)manoyloxide

	Pimaric	Sandaracopimaric	Isopimaric	Levopimaric and/or Palustric	Dehydroabietic	Abietic	Neoabietic	Other compounds
Picea orientalis (8) (bark resin)	-	0.8	4.9	5.0	2.7	8.1	7.6	trans-abienol
P. orientalis (8) (cone resin)	-	1.0	-	6.5	2.1	21.4	9.0	
Strasburg Turp. (10)		x	x	x	x	x	x	
Abies alba (13)		1	1.5	12	0.6	20	17	
A. nordmanniana (8) (bark resin)	-	0.5	0.5	8.9	0.6	11.4	5.5	trans-abienol
A. nordmanniana (8) (cone resin)	-	0.7	1.2	2.7	1.1	19.8	10.7	

	Pimaric	Sandaracopimaric	Isopimaric	Levopimaric and/or Palustric	Dehydroabietic	Abietic	Neoabietic	Epimanool	Larixol	Larixylacetate
Venice Turp (10)	x	x	x		x	x	x			x
Venice Turp. (11)		x	x		x	x	x	x	x	x
Larix decidua (1)	0.5	1	18.5	12.5	1.8	7.6	5.6	7.5	3.1	33
L. gmelinii (12)	-	1.9	16.4	6	5.1	5.6	2.2	13	23.7	16.6
L. russica (12)	tr	1.5	7.5	2	0.5	2.7	tr	12.8	-	-
L. occidentalis (14)	1.55	1.35	22.8	11.95	7.65	12.7	5.1	4.4	-	-
L. pendula (12)	0.4	1.6	18.6	7.3	8.6	5.3	1.6	10.7	3.5	12.2
L. kaempferii (14)	1.7	0.85	21.0	6.7	5.9	8.25	3.55		-	-

Tab. 2.2 Composition of Pinaceae resins, details see page 14

2.1.2 Cupressaceae

The family of Cupressaceae is mostly known for one important resin, called sandarac. It can originate from different genera within the family (Fig. 2.5). True sandarac originates from the Sandarac Cypress *Tetraclinis articulata* (Vahl) Mast., a monotypic tree from the genus *Tetraclinis*. But also resins from other genera were called sandarac in the past, namely junipers (*Juniperus*) and cypress (*Cupressus*) (Mills, White 1999: 102-3; Arends 2005: 307). The botanical separation of the genus *Juniperus* and the sandarac tree was established at the end of the 18th century, the tree was called *Thuia articulata* Vahl. then (Desfontaines 1799: 353). Until the end of the 19th century it bared several names for example *Callitris quadrivalis* Vent. (Tschirch 1935: 558). Then it was described as the monotypic tree (Masters 1893). The so called Australian Sandarac is gained from several Australian cypress trees from the genus *Callitris* (Hegnauer 1962: 352; Mills, White 1999: 103), which belongs to another subfamily than the other three genera (Fig 2.5).

Chemical investigation of this botanical group is not that advanced like it is for Pinaceae resins. Many investigations are limited to volatile constituents of the essential oils obtained from different sources such as wood, leaf and berries. Investigations of the different genera based on diterpenoid compounds are rather rare. The different genera are discussed below in detail. In general abietane type compounds are widely absent though dehydroabietic acid was found occasionally (Mills, White 1977; van den Berg et al. 2002). The most abundant constituents seem to be pimaranes, especially sandaracopimaric acid, and labdanes synthesised from CPP such as communic acid (Mills, White 1977) (Fig. 2.6). The last-mentioned tends to polymerisation due to its exocyclic double bonds and the resulting polycommunic acid is the reason for the greater hardness and brittleness of these resins compared to the softer Pinaceae resinous balsams (van den Berg et al. 2002). Because pimaranes do not tend to degradation and the labdane communic acid mainly polymerises sandarac does not show typical aging markers like Pinaceae resins.

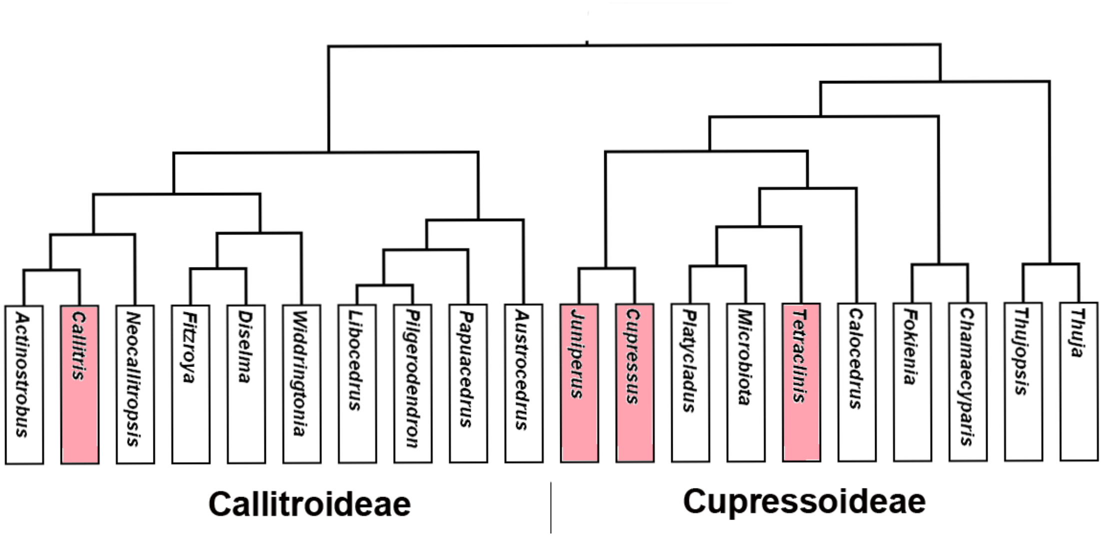


Fig. 2.5 The two subfamilies of Cupressaceae, possible genera for resins called sandarac are marked in pink (Farjon 2005: 643)

Juniper

Junipers do not produce very much pure resin but resin rich leaves, berries and wood which is used today almost exclusive for the production of essential oils and other products for medical and cosmetic industry (Langenheim 2003: 329f; Hegnauer 1962: 368-71). The use of the resin is reported in different modern sources (Fox, Heron 1995; Mills, White 1999: 103; Arends 2005: 307); investigations about the chemical composition of the non-volatile fraction, however, are limited to solvent extracts of leaves and berries. In berries sandaracopimaric and pimaric acid as well as different derivatives of isocommunic acid were found. Extracts of leaves show different amounts of the isomers of communic acid dependent on the belonging to different subsections of the genus (de Pascual et al. 1983; elSawi, Motawe 2008).

The only work found about juniper resin and its diterpene constituents deals with juniper tar. It is mainly produced from stems and branches of junipers as the residue during the production of cade oil. It can therefore be regarded as a form of colophony made from the resin rich wood and other parts of junipers. Its diterpene constituents were found to be pimaric (3.8 %), sandaracopimaric (1.4 %) and isopimaric acid (5.2 %), palustric (5.1 %), abietic (15.0 %) and neoabietic acid (3.1 %) and high amounts of dehydroabietic acid (32.2 %) (Hafizoğlu 1994).

Cypress

In contrast *Cupressus* species produce a sandarac-like resin, which contains *cis*- and *trans*-communic acid and sandaracopimaric acid (Gough, Mills 1970; Mills, White 1999: 103; Hegnauer 2001: 493) as well as ferruginol and totarol (Mangoni, Belardini 1967; Hegnauer 2001: 493; Cox et al. 2007) which would makes them very similar to sandarac. Cox et al. do not find communic acid in cypress resins (Cox et al. 2007).

Different C-19 and C-15 oxygenated labdane for example agathic acid (Fig. 2.6) are reported to be part of resins from *Cupressus* species (Cox et al. 2007). In chemotaxonomic studies the structural isomer of agatholic acid isocupressic acid, the C-13 oxygenated labdanes cupressic acid and torulosol are found in in *Cupressus* resins (Hegnauer 2001: 493). The dihydro-derivative of isocupressic acid (imbricataloic acid) is found in some Asian and American *Cupressus* species (Gough, Mills 1970; Cox et al. 2007: 348).

Sandarac Cypress

So called true sandarac is obtained from the sandarac cypress *Tetraclinis articulata* (Vahl) Mast. The bark of the living tree contains schizolysigenous cavities, which are full of resin (Howes 1950). The resin is collected from natural exuded drops direct from the bark or by ripping the tree and collecting the emerging resin (Krünitz 1824: 74; Koller et al. 1997b: 383).

Investigations of sandarac called resins are more widespread but mostly do not provide clear evidence on the botanical origin. The investigated resins mainly consist of *cis*- and *trans*-communic acids; the polymeric fraction of the resin is composed of these two isomers and communol (van den Berg et al. 1999; van den Berg et al. 2002; Scalarone et al. 2003b). The other main constituent is sandaracopimaric acid, furthermore the 12-acetoxy- and a hydroxy-derivative of sandaracopimaric acid and other pimaranes as isopimaric and pimaric acid were found (Colombini et al. 2000a; van den Berg at al. 2002; Chiavari at al. 2008; van Keulen 2009). Often the presence of sandaracopimaric acid is taken as a marker for the use of sandarac in the analysis of complex samples (Dunkerton et al. 1990; Chiavari et al. 2002; Marinach et al. 2004). White and Kirby mention more correctly that the presence of sandaracopimaric acid in aged or complex samples indicate the use of a “Cupressaceae resin from the genera *Tetraclinis*, *Juniperus* or possible *Cupressus*” (White and Kirby 2001).

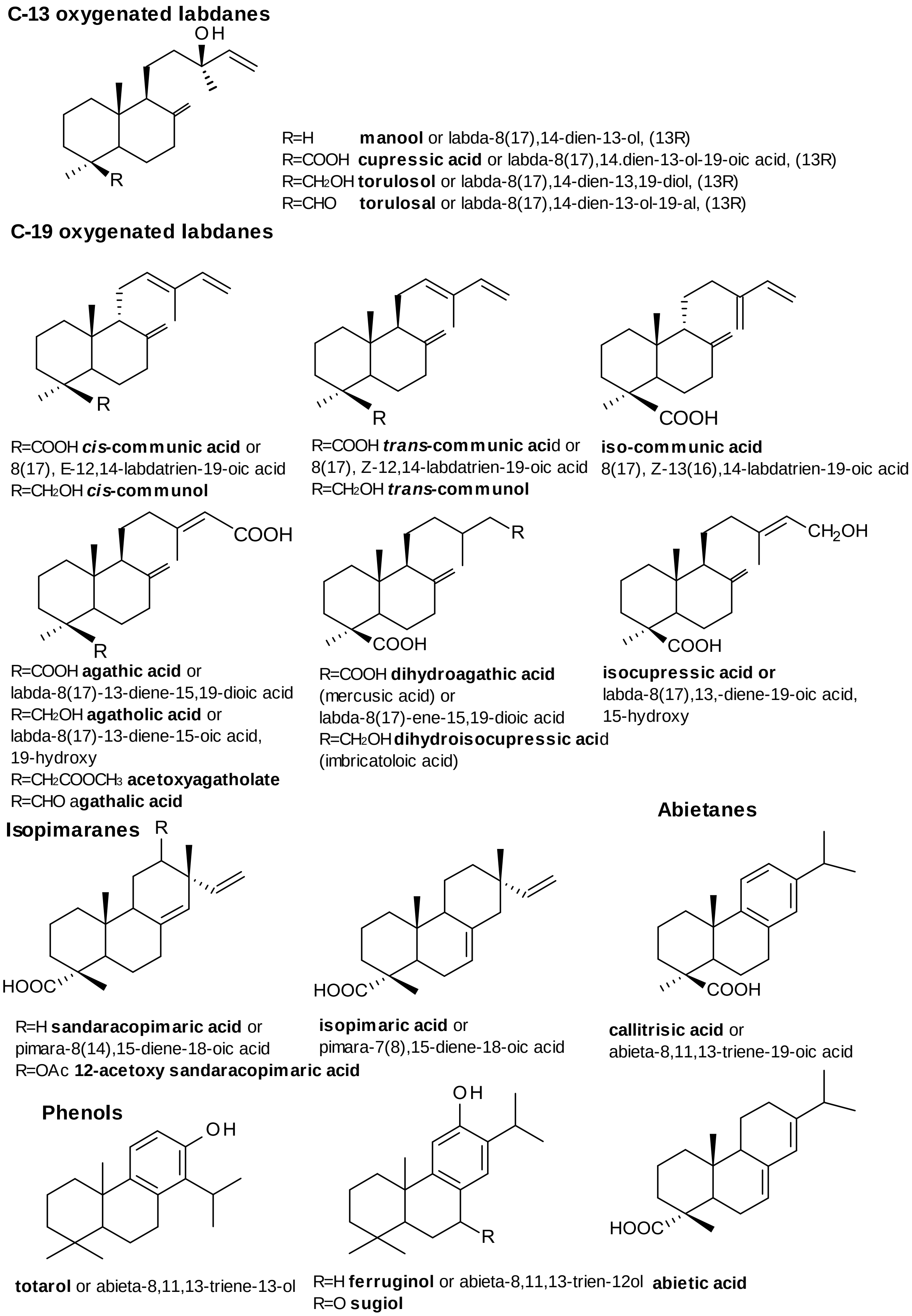


Fig. 2.6 Structures of compounds found in Cupressaceae and Araucariaceae resins

Additionally labdanes as agathic, agathalic and agatholic acid together with acetoxyagatholic acid are reported as constituents of sandarac (Scalarone et al. 2003; Scalarone et al. 2003b). Phenolic compounds such as totarol and ferruginol are reported to be characteristic for sandarac (Chiavari et al. 1995; Chiavari et al. 2002), but they are difficult to detect if a metylation agent is used (Koller et al. 1997b). Small amounts of abietane type compounds were found in samples of sandarac in both the soluble and the polymerized fraction as well (Mills, White 1977; van den Berg et al. 2002). Abietic acid seems to polymerize due to its double bonds and dehydroabietic acid was found in the soluble fraction (ibid.).

2.1.3 Araucariaceae

Southern hemisphere conifers include the genera *Araucaria* and *Agathis*, the last one yielding the common Manila and Kauri copal. Manila copal is obtained from *A. dammara* (Lamb.) Rich., Kauri copal from *A. australis* (D. Don) Steud. The copal resin is obtained by tapping living trees or by digging it from the ground in former existing forest.

Araucariaceae resins consist of a mixture of all known structure types (Fig. 2.2, 2.6): pimaranes (only sandaracopimaric acid), labdanes (agathic acid and derivatives) and abietanes (abietic and oxygenated derivatives). In *Agathis* resins high amounts of sandaracopimaric, communic, agathic, acetoxy-agathic as well as cupressic acid are found (van den Berg et al. 2002; Scalarone et al. 2003; Cox et al. 2007; Chiavari et al. 2008). In Manila copal also the aging product agatholic acid is present (Scalarone et al. 2003). Kauri copal contains sandaracopimarol (van den Berg et al. 2002) and small amounts of abietic, neoabietic and 7-hydroxy-dehydroabietic acid (van den Berg et al. 2002; Cox et al. 2007). The polymeric fraction is composed of communic and in the case of Kauri copal of equal amounts of communic acid and communol (van den Berg et al. 2002; Scalarone et al. 2003; Chiavari et al. 2008).

Araucaria species are native to Australia and neighbouring regions and tropical South America. *Araucaria* resins are composed very variable. Australian *Araucaria* resins contain communic, sandaracopimaric and abietic as well as hydroxy-abietanes (Caputo et al. 1974; Cox et al. 2007). But also cupressic, isocupressic and a Δ12-double bond isomer of agathic acid were found (Caputo et al. 1974; Cox et al. 2007). In contrary the resin of *A. bidwilli* contains no communic and only small amounts of sandaracopimaric acid, but high amounts of agathic, Δ12-agathic, agatholic, agathalic and acetoxy-agathic acid (Caputo, Mangoni 1974; Cox et al. 2007). In the resin of *A. imbricata* also the dihydro-derivative of isocupressic acid, imbricatoloic acid, is present (Weismann et al. 1965).

Additionally in *Araucaria bidwilli* copalic acid and two clerodanes – kovalenic and Δ4(17)-kovalenic acid – are found (Caputo, Mangoni 1974; Cox et al. 2007) (Fig. 2.8). This species seems to be a rare example in the order Pinales for the co-occurrence of compounds derived from CPP (labdanes) and ent-CPP (ent-labdanes), which normally does not occur together (Mills, White 1977).

2.2 Angiosperm resins I – Fabales

In the class Rosids, order Fabales mainly the family of Fabaceae – formerly called Leguminosae or trivial legumes – produces reliable quantities of resins. They are characterized by polymerising diterpenes mainly of the ent-labdane type synthesised from ent-CPP dissolved in sesquiterpenes. Diterpenes originating from CPP are present only exceptionally in contrary to the labdane containing conifers where it is the other way round (chapter 2.1.3). Other possible diterpene constituents are clerodanes or kauranes. Diterpene compounds are shown in Fig. 2.8, sesquiterpene in Fig. 2.7.

Additionally, the genus *Myroxylon* is part of the family of Fabaceae. It contains only two species in South America, which produces a resinous balsam. It is composed totally different to the other genera of this family, namely of phenylpropanoids and triterpenes. Triterpenes occur in different series derived from the protosteryl and the dammarenyl cation (see appendix), but they are separated not as strict as diterpenes.

Copaifera

Trees from the genus *Copaifera* produce viscous resins in their trunks, stems and leaves (van der Werf et al. 2000; Plowden 2003). There are about thirty species in South America and four in Africa producing reliable quantities of resin. African *Copaifera* species produce harder resins with high amounts of polymerizing diterpenes, which lead to the formation of hard copals (Plowden 2003). Mentioned species are *C. mildbradeii* Harms, *C. baumiana* Harms, *C. religiosa* J. Léonard, *C. letestui* (Pellegr.) Pellegr. and *C. salikounda* Heckel (Salgues 1957; Langenheim 2003: 394). They are composed very similar to South American *Copaifera*.

The resins of South American species contain higher amounts of sesquiterpenes and are therefore more viscous and liquid (Plowden 2003). The most common product is called Copaiba balm, in some areas also Copaiba oil, Para balm (Pará in Brazil), Maracaibo balm (Venezuela), Pau-D'oleo (Brazil) and Canime (Colombia) (Tschirch 1936: 1359f, 1366f; van der Werf et al. 2000; Cascon, Gilbert 2000; Gérard et al. 2009). *Copaifera* trees were found to possess a canal secretory system similar to *Pinus* species. In the cambium axial canals are arranged in circles, which are sometimes interconnected (Langenheim 2003: 122; Plowden 2003). On the other hand, in Amazonian species only low resin quantities were found in bark and sapwood, but high quantities of constitutive resin in the heartwood of middle aged trees (Plowden 2003). Copaiba balm is traded from different parts of South America, from Northeastern Brazil, Venezuela, Colombia, Guyana, French Guyana and Suriname (Tschirch 1936: 1359f, 1366f; Pinto et al. 2000; Cascon, Gilbert 2000; van der Werf et al. 2000). Species are listed in table 2.3 together with their chemical composition. The resin of *Danillia oliveri* (Rolfe) Hutch. & Dalziel is also called Africa copaiba or Illurin balsam (Ammon, Hunnius 2004: 191) (for chemical composition see *Daniellia* section below).

The colour, viscosity and chemical composition vary very much between the different materials. Main compounds from *Copaifera* resins from South America are copalic acid, caryophyllene and bergamotene (Fig. 2.7, Fig. 2.8). It is very difficult to assign botanical species to names or harvesting regions, particularly because of taxonomical uncertainties and lacking knowledge of traditional names and harvesting practises (Plowden 2003). A specific material is not necessarily obtained from only one species and also within a given species chemical differences can be very broad. In a sample from *C. duckei* from Pará, Brazil, kauranes were found, which was not the case with *C. duckei* from the more northern territory Amapá. Instead eperuic and crolechinic acid were found in the samples from Amapá (Cascon, Gilbert

2000). Additionally, a commercial available material could have been blended from different resinous balsams to obtain the wished viscosity (Tschirch 1936: 1359f, 1366f).

In a broad analysis of commercially available samples of Copaiba balm and samples from European collections two different types of samples were distinguished by their chemical composition. First sample type is characterized by high amounts of copalic acid and hardwickiic acid, as well as the minor constituents eperuic, cativic and ent-pinifolic acid and was assigned to *C. multijuga* or *C. cearensis* (type A in table 2.3). Second sample type is characterized by high amounts of the ent-kauranes kaur-16-en-19-oic and kauran-19-oic acid, polyalthic, hardwickiic and ent-pinifolic acid and was assigned to *C. duckei*, *C. guianensis* or *C. langsdorfii* (type B in table 2.3) (van der Werf et al. 2000 and literature in table 2.3). *C. officinalis*, the former synonym of the Copaiba balsam producing trees, is not investigated in the scientific literature. An analysis of the terpenoid constituents of stem wood suggest an attribution to type A, because main constituents of volatile compounds are β-caryophyllene (53.3, 13.2), α-humulene (6.64, 1.45), germacrene D (256.18, 50.83), β-selinene (3.34, 0.54), α-auurolene (6.12, 0.64), γ-cadinene (4.17, 0.80) and δ-cadinene (3.17, 0.53) (Chen et al. 2009).

In analysis from literature high amounts of sesquiterpenes correspond with low amounts of diterpenoid acids, associated with seasonal changes or maybe aging (Cascon, Gilbert 2000; Maistro et al. 2005). In aging experiments mainly the clerodanes such as hardwickiic acid but also polyalthic acid were found to be unstable, whereas labdane constituents eperuic, copalic, agathic and ent-pinifolic acid as well as kauranes were found to be relatively stable against aging through light and oxygen (van der Werf et al. 2000). Caryophyllene oxide is thought to be a genuine compound of the secondary metabolism and not an aging product (Cascon, Gilbert 2000). Copaiba balsam is mentioned as highly adulterated mainly in the 19th and beginning 20th century (Tschirch 1936: 1359f; van der Werf et al. 2000). It was mixed with pine resin or made of a mixture of distilled copaiba oil and colophony (van der Werf et al. 2000; Langenheim 2003: 395). Gurjun balsam, Segura or Hardwickia balsam were used an alternative or adulteration (van der Werf et al. 2000). Gurjun balsam is obtained from *Dipterocarpus* species in Southeast Asia and India and consists of 60 – 80 % essential oil, composed mainly

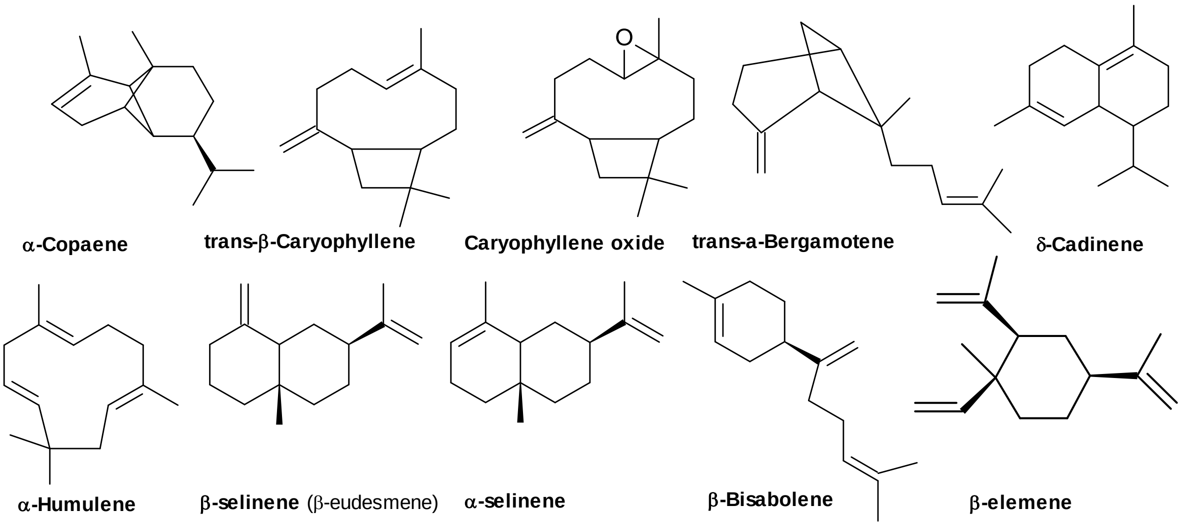
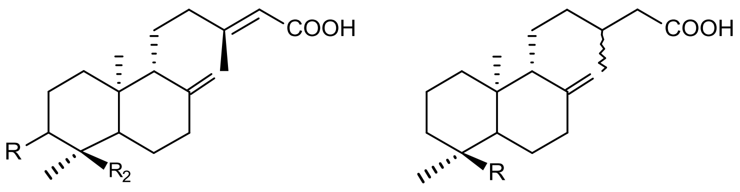


Fig. 2.7 Sesquiterpene compounds found in resins of *Copaifera* species

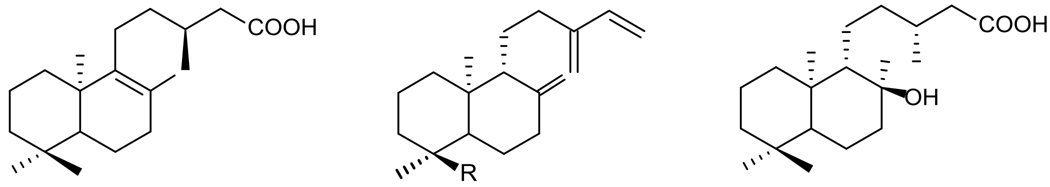
of α-gurjunene (Bombarda et al. 1997). Hardwickia balsam is obtained from the Indian species *Hardwickia pinnata* Roxb., now *Kingiodendron pinnata* (Roxb. ex DC.) Harms (Schaer 1916; Ammon, Hunnius 2004: 191). Main constituents are α-caryophyllene, kovalenic and hardwickiic acid (*Hymenaea, Guibourtia, Tessmania, Daniellia*; Misra et al. 1979).

ent-Labdanes



13α
R=H **Eperuic acid**
(labda-8(20)-en-15-oic acid)
R=COOH **enantio-Pinifolic acid**
(labda-8(20)-en-15,18-dioic acid)
R=CH_3OH **Labda-8(20)-en-18-ol-15-oic acid**
13β
R=COOH **Oliveric acid**
(13β-labda-8(20)-en-15,18-dioic acid)

R/R_2=H **Copalic acid**
labda-8(20),13-dien-15-oic acid
R=AcO, R_2=H **3-Acetoxy-copalic acid**
R=H, R_2=COOH **Guamáic acid**
(labda-8(20),13-diene-15,18-dioic acid)

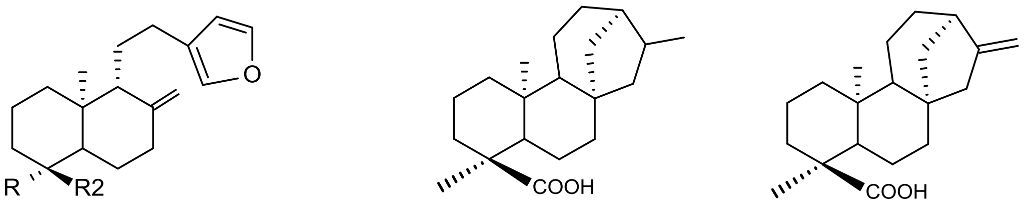


13(14)en **Labda-8-en-15-oic acid**
13(14)diene **Δ8-Copalic acid**

R=H **enantio-Biformene**
R=COOH **iso-Ozic acid**
labda-8(2),13(16),14-triene-18-oic acid
R=CH_3OH **Ozol**

enantio-Labdanolic acid
labdan-8β-ol-15-oic acid

ent-Kauranes

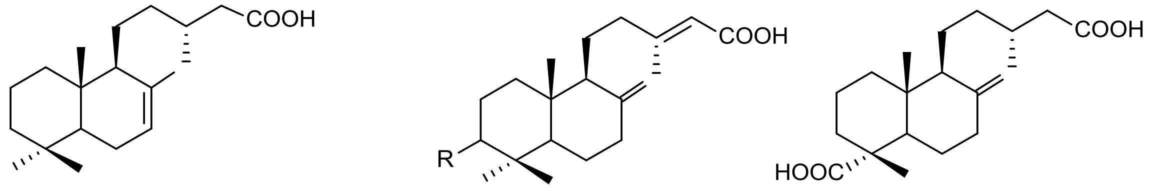


R=COOH, R2=H **Daniellic acid** (illurinic acid)
R=H, R2=COOH **Polyalthic acid**

kaur-16-en-19-oic acid

kauran-19-oic acid

Labdanes

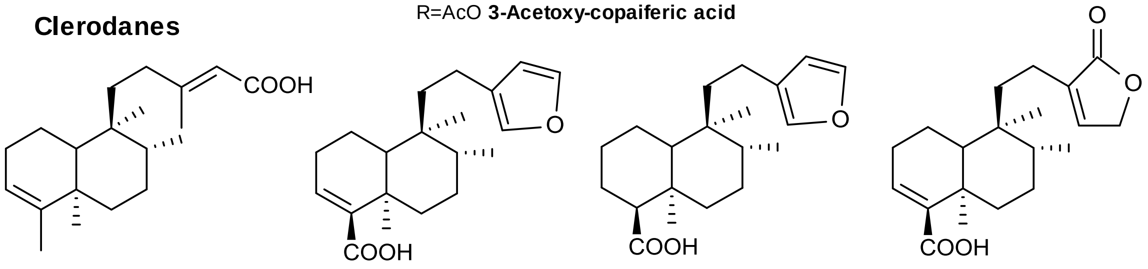


Cativic acid
labda-7-en-15-oic acid

R=H **Copaiferic acid** (anticopalic acid)
labda-8(20),13-diene-15-oic acid
R=AcO **3-Acetoxy-copaiferic acid**

Pinifolic acid

Clerodanes



kovalenic acid
cleroda-3,13-diene-15-oic acid

hardwickiic acid

crolechinic acid

patogonic acid

Fig. 2.8 Compounds found in resins of *Copaifera*, *Hymenaea*, *Guibourtia*, *Tessmania* and *Daniellia* species

	C. duckei Dwyer[1,2]	*C. multijuga* Hayne[2,6]	*C. guianensis* Desf[2]	*C. langsdorffii* Desf.(5, 11)	*C. cearensis Ducke (3,4,9)*	*C. reticulata* Ducke (7,10)
Region[1]	Eastern Amazon, Bolivia	Western and middle Amazon (Bahia, Mato Grosso, Pará)	Northern Amazon (Amazonas, Pará), Guyana, Suriname	Southern Amazon (Mato Grosso, Bahia, Ceará), Bolivia, Argentina, Paraguay	Eastern Brazil (Bahia, Ceará)	Western Amazon (Amapá, Rondonia), Suriname, Bolivia
Sesquiterpenes						
α-Copaene	--	2.1-5.2; 1.4	0.6	yes (main)	8.2	--, 0.2-0.6
β-Elemene						--, 0.5-13.4
trans-β-Caryophyllene	4.5; 0.3-17.7	42.9-60.3; 60.2	4.7	yes (main); 53.3	19.7	0.7-62.6
trans-α-Bergamotene	1.0; 0.4-19.7	2.0-7.0; 6.4	7.2		2.1	11.2-36.9
α-Humulene	0.7; --	yes; 8.6	yes	yes	3.7	--, 1.1-9.2
γ-Muurolene		--; 2.7				--, 0.3-1.6
β-Selinene	--; 0.5-14.8	--	1.5			--, 0.1-35.7
α-Selinene	--; 0.2-8.2	--				--, 0.2-23.2
β-Bisabolene	1.0; 1.0-12.1	--	2.1	yes (main)	2.8	12.7-50.3
δ-Cadinene	--	1.6-2.9; 1.9	--		7.2	--, 1.1-3.5
β-Caryophyllene oxide	--	8.8; 0.2	19.1		1.5	0.1-15.2
Diterpenes						
Eperuic acid					yes	
Cativic acid[2]					yes	
Kaur-16-en-19-oic acid	--; 19.8-24.5 (not in all samples)	--	17.5	yes	--	

	C. duckei (1,2)	*C. multijuga* (2,6,8)	*C. guianensis* (2)	*C. langsdorffii* Desf.(5, 11)	*C. cearensis Ducke (3,4,9)*	*C. reticulata* Ducke (7,10)
Kauran-19-oic acid	--	--	0.9	yes		
Copalic acid	3.7; 0.6-4.8 (not in all samples)	1.9-11.0; 9.5	1.4		yes (main)	
Kovalenic acid		--; yes			yes	
Polyalthic acid	27.1; 9.9-27.7	--	10.6	yes (main)	--	
Crolechinic acid					yes (main)	
Hardwickiic acid	59.3; 8.0-24.3	--	11.0		yes (main)	
3-Hydroxy-copalic acid[3]		; 0.8				
3-Acetoxy-copalic acid[3]	--	0.8-6.2; 1.0	--		--	
7-Acetoxy-hardwickiic acid (8)		yes				
Patagonic acid					yes	

Tab. 2.3 Amounts [%] of sesquiterpenes, labdanes, kauranes and clerodanes in resinous balsam from different *Copaifera* species, amounts higher than 50% for some sesquiterpenes refer only to the volatile fraction, see referenced literature; x – present without quantification; -- – not present; main – main constituent; empty – not specified; literature (1) Maistro et al. 2005; (2) Cascon, Gilbert 2000; (3) Braga et al. 1998; (4) Pinto et al. 2000; (5) Ferrari et al. 1971; (6) Sant'Anna et al. 2007; (7) Herrero-Jáuregui et al. 2011, (8) van der Werf et al. 2000 (only acetoxy-hardwickiic acid), (9) Veiga Junior et al. 2007, (10) Zoghbi, Andrade 2009, (11) Gramosa, Silveira 2005; typical constituents of the two samples types identified by van der Werf et al. are marked in orange (type A) and blue (type B) (van der Werf et al. 2000). Only the main constituents are given in each case, respectively.

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[1] Used literature for habitats: Tschirch 1936: 1359-1360; GRIN 2012a; others species mentioned as sources for Copaiba balm are: *C. officinalis* (formerly *C. jacquinii* Desf.) (Venezuela, Guyana, Colombia) and *C. martii* Hayne (Brazil). *C. reticulata* is mentioned as the main source for modern Copaiba balm (Tschirch 1936: 1359f; Ammon, Hunnius 2004: 191; Gérard et al. 2009) but also *C. multijuga* (Sant'Anna et al. 2007).

[2] Van der Werf et al. found labdanic acid in samples of type B, equating between eperuic and cativic acid (van der Werf et al. 2000). That compound is not mentioned in the publications used for this table (Ferrari et al. 1971; Braga et al. 1998; Cascon, Gilbert 2000; Pinto et al. 2000; Maistro et al. 2005).

[3] Cascon & Gilbert report 3-acetoxycopalic acid in Copaiba balm from *C. multijuga*, while van der Werf et al. list 3-acetoxy-copaiferic acid as typical constituent of Copaiba balm type A (Cascon, Gilbert 2000; van der Werf et al. 2000). Both refer to Braun & Breitenbach and Zinkel & Magee, who described the enantiomer 3-acetoxy-copaiferic (or anticopalic) acid (3-acetoxylabda-8(20),13-dien-15-oic) (Braun & Breitenbach 1977; Zinkel & Magee 1987). Sant'Anna et al. also identified hydroxy- and acetoxy-copalic acid by standard comparison, but the origin of the standard compound is not given (Sant'Anna et al. 2007).

Legume copals - *Hymenaea*, *Guibourtia*, *Tessmania*, *Daniellia*

These families are regarded as the source of so called diterpene (leguminous) copals, originating mainly from Africa (*Hymenaea*, *Guibourtia*, *Daniellia*, *Tessmania*) and tropical America (*Hymeneae*). There are also African copals obtained from *Copaifera* species (Plowden 2003). The widely used Manila and Kauri copals, which are of diterpene composition, too, originate from Gymnosperm conifers growing in the southern hemisphere (Araucariaceae) (chapter 2.1.3). Leguminous copals differ from these materials mainly through the presence of high amount of ent-labdanes, which were found only exceptionally in Araucariaceae species. Additionally labdanes synthesised from CPP are nearly absent, only cativic acid was reported for some *Hymeneae* resins (Fig. 2.8).

All but one *Hymenaea* species are native to the neotropis, which produce a soft resin called copal or anime (Langenheim 2003: 398; Case et al. 2003). *Hymenaea* species accumulate a resin in lysigenously formed cavities in the trunk, which is collected together with older resin digged from river bed and shores (Cunningham et al. 1973; Langenheim 2003: 394f.). This pocket secretory structures distinguishes leguminous copal producers from *Copaifera* species, which yield a more fluid resinous balsams from an interconnected canal system (Langenheim 2003: 122). Main species mentioned in literature are *H. courbaril* L., *H. oblongifolia* Huber, *H. intermedia* Ducke, *H. parvifolia* Huber. The resin of *H. courbaril* is described as pale yellow to reddish and called 'goma anime de México' (Case et al. 2003). Some resins are called Jatobá (or Jutaicica, Jutahyica, Yatoba) and related to *H. courbaril* L., too, or to *H. stigonocarpa* Mart. (Nakano, Djerassi 1961; Langenheim 2003: 398; Doménech-Carbó et al. 2009).

Some American *Hymenaea* resins possess a significant polymeric fraction and are traded as hard copals or amber-like materials (Anderson et al. 1992; Anderson, Botto 1993; Anderson 1994), other are softer without a significant polymeric fraction (Doménech-Carbó et al. 2009). They consist of high amounts of labdane diterpenes synthesised from ent-CPP with an enantiomer configuration at positions C-10 and C-9 including eperuic, labda-8-en-15-oic and copalic acid as main compounds together with ent-labdanolic acid, its Δ13-dehydroderivative (ent-labda-13(14)-en-8β-ol-15-oic acid) and guamáic acid. Iso-ozic and ent-pinifolic acid were found in lower amounts, small amounts of clerodanes such as kovalenic acid were found, too. From the CPP-series only cativic acid is present in such resins (Cunningham et al. 1973; Cunningham et al. 1974; Doménech-Carbó et al. 2009). It was shown that there are as significant differences between species as between other leguminous genera (Cunningham et al. 1973).

Hymenaea verrucosa Gaertn. grows on the east coast of Africa (Mozambique copal) and neighbouring islands (Madagascar, Zanzibar copal). The resin is digged at the east coast and has a characteristic goose-skin-like surface (Langenheim 2003: 396). Earlier investigations showed high amounts of copalic, the 13-epimer of ent-eperuic, ent-pinifolic, ent-labdanolic, Δ13-dehydro-labdanolic, enantio-labda-8(20)-en-18-ol-15-oic and 18-acetoxy- enantio-labda-8(20)-en-15-oic acids (Hugel et al. 1966). In the neutral fraction caryophyllene oxide, 13-epimanool, 18-hydroxy-epimanool and enantio-labda-8(20)-en-15,18-diol were found (ibid.) The fresh resin contains up to 95% of iso-ozic acid, which polymerises and yield a copal of very high hardness (Langenheim 2003: 396; Regert et al. 2008).

Other African genera related to copal resins are *Guibourtia*, *Daniellia* and *Tessmania*, mainly for the West African regions (Salgues 1957; Meyer et al. 1991; Langenheim 2003: 393-399; Regert et al. 2008; Doménech-Carbó et al. 2009). Materials are named after the region they

Name	Species
Congo copal	*Guibourtia demeusei* (Harms) Léonard, *Tessmania africana* Harms, *T. anomala* Harms, *T. yangambiensis* J. Leonard, *Daniellia alsteeniana* Duvign., *D. klainei* Pierre ex De Wild, *D. mortehani* De Wild, *D. oliveri* Hutch. & Dalziel, *D. pynaerti* De Wild, *Copaifera baumiana* Hars., *C. mildbradeii* Harms, *Cynometra sessiflora* Harms
Angola copal	*Guibourtia carrissoana* (Exell) Léonard
Akra or Accra copal	*Daniellia similis* Craib ex Holland
Sierra-Leone copal	*Guibourtia copallifera* Benn., *Daniellia thurifera* Benn.
Benin copal	*Daniellia caudata* Craib.
Kamerun copal	*Daniellia thurifera* Benn., *Guibourtia demeusei* (Harms) Léonard
West African copal	*Guibourtia ehie* (Chev.) Léonard, several *Daniellia* sp. such as *D. alsteeniana* Duvign., *D. ogea* (Harms) Rolfe ex Holland, *D. thurifera* Benn., *D. klainei* Pierre ex De Wild

Tab. 2.4 African leguminous copals and their botanical origin (Leonard 1950; Salgues 1957; Langenheim 2003: 393-399, de la Estrella et al. 2010)

were collected. These trading names not necessarily refer to only one species (table 2.4). Congo copaliers exude the resin after traumatic damage in high amounts, which covers whole plant parts and fall down on earth. The resin is collected from superficial formations in the marshy forests or during the flood at several rivers and seas in the Congolese basin. The most important copaliers are *Guibourtia demeusei* Leonard, *Cynometra sessiloflora* Harms, *Daniellia pynaerti* De Wild and *Copaifera mildbraedii* Harms (Leonard 1950).

Chemical analysis of a Congo copal revealed a significant polymeric fraction consisting of polyozic acid, ozol and enantio-biformene. Free acids were eperuic, labda-8-en-15-oic, cativic, copalic and kovalenic acids as well as several unidentified methylated labdane acids with molecular weights of 336, 320 and 368 (van den Berg et al. 1999; van den Berg et al. 2002). Another African copal analysed in that study was composed similar in the lower eluting region but different in the higher eluting region. It contained high amounts of two unidentified methylated labdane acids with MW of 350 and ent-pinifolic acid (van den Berg et al. 2002). Sierra Leone copal is reported to be deficient in copalic acid and its oxygenated products (White, Kirby 2001). It is found to be easy distinguishable from other African copals, which is not the case with materials labelled Congo copal (Mills, White 1999: 104).

There is some confusion about the resin of *Daniellia oliveri* (Rolfe) Hutch. & Dalziel, which is sometimes called African copaiba (Mills 1973; Langenheim 2003: 395; Ammon, Hunnius 2004: 191), sometimes African copal (Leonard 1950; Salgues 1957; Bevan et al. 1968; Haeuser et al. 1970). It contains labdane alcohols, aldehydes and labdane acids including contain daniellic and oliveric acid (enantio-13β-labda-8(17)-en-15,18-dioic acid) (Haeuser et al. 1961; Haeuser et al. 1970). Other *Daniellia* species seem to contain only traces of these acids (Mills 1973).

Myroxylon

Two varieties of *Myroxylon balsamum* (L.) Harms, *M. balsamum* var. *balsamum* and *M. balsamum* var. *pereirae (Royle) Baill.*, yield Tolu and Peru balsam.

Peru balsam is obtained from *M. balsamum* var. *pereirae*. The tree grows in Central America, mainly at the balsam coast in San Salvador and Guatemala, and in Ecuador ((Harms 1908; Mammerler 2007: 6). Its name is derived from the original trading route from Central America over Peru to Spain (Harms 1908; Mammerler 2007: 5, 6). Balsam of Peru is obtained by fumigation of the trunks of the trees after the removal of the bark (Ammon, Hunnius 2004: 191). Rags are wrapped around the tree and afterwards boiled in water. The balsam sinks to the ground and is collected (Mammerler 2007: 6). It is not a constitutive but an induced resin (Ammon, Hunnius 2004: 191). Another described method is the scorching and beating of the bark, whereby the balsam is extracted by boiling (Mammerler 2007: 6). Today it is produced mainly in El Salvador (Hausen et al. 1995). It is described as dark brown and transparent oily liquid with an aromatic smell of cinnamon (fresh) and vanilla (aged), not sticky and with a bitter taste (Ammon, Hunnius 2004: 191; Mammerler 2007: 5f)

It consists of small amounts of free benzoic acid and cinnamic acids as well as their methylesters together with 45 – 70 % benzyl benzoate and benzyl cinnamate (cinnamein). Additionally vanillin, α- and β-nerolidol (3-5 %) and farnesol were found (Hausen et al. 1995; Mills, White 1999: 109; Mammerler 2007: 6). Other reported compounds are cinnamic alcohol, cinnamyl cinnamate, eugenol, coniferyl benzoate, hydroconiferyl benzoate, coniferyl cinnamate, hydroconiferyl cinnamate, benzyl alcohol, ferulic acid and benzyl ferulate (Hausen et al. 1995; Mills, White 1999: 109; Hausen 2001). An unknown compound with the total formula $C_{26}H_{26}O_6$ was found, too (Hausen et al. 1995). Structures can be found in Fig. 2.9. Coniferyl benzoate decomposes very quickly. After ten years of storage it can hardly be identified anymore (Hausen et al. 1995).

Tolu balsam is obtained from *M. balsamum* var. *balsamum*. The classification of the two varieties originates from Harms, who named the source of Balsam of Tolu *M. balsamum* var. *genuinum* Baill. (Harms 1908). It could not be find out by whom it was reclassified. The tree grows in Panama and in South America (Venezuela, Colombia, Ecuador, Peru).

Tolu balsam contains a mixture of aromatic and terpene compounds, namely benzoic and cinnamic acids, the corresponding alcohols, aldehydes and several ethyl, benzyl and cinnamyl esters of benzoic and cinnamic acid. Additionally, methyl cinnamate, styrene, eugenol, vanillin, benzyl ferulate or isoferulate and ferulic acid were found. Additionally reliable quantities of triterpenes were found (Wahlberg et al. 1971; Wahlberg, Enzell 1971; Wright, Wheals 1987) (Fig. 2.9). Triterpenes present were dammaradienone, 20R-hydroxydammarenone, 20S-dammarenediol, hydroxyhopane, oleanolic acid, sumaresinolic acid, 3-oxo-6β-hydroxyolean-12-en-28-oic acid, urs-12-en-3-on-28-al, 22-hydroxyhopanone and 20R,24ξ_2-ocotillone (Wahlberg et al. 1971; Wahlberg, Enzell 1971). The last one is called also 20,24-epoxy-25-hydroxy-dammaren-3-one and was found to be an aging compound of dammaranes in mastic resins (van der Doelen et al. 1998) (see chapter 2.3.1). Wahlberg et al. mention the presence of α- and β-amyrin related compounds, which they could not identify due to low amounts (Wahlberg et al. 1971). Friedel and Matusch identified guaiadienes in Tolu balsam (Friedel, Matusch 1987).

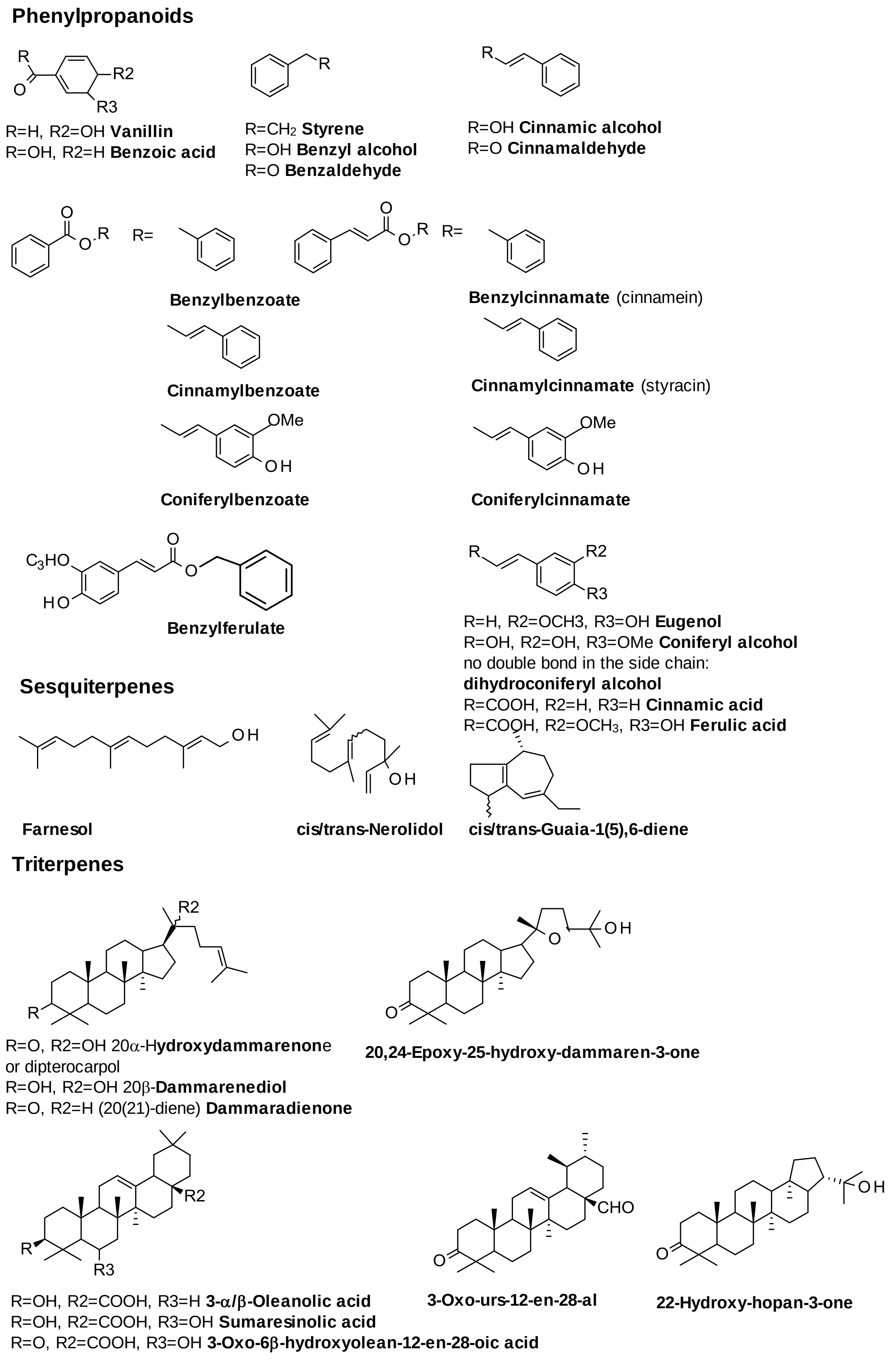


Fig. 2.9 Phenylpropanoids and triterpenes in resins of *Myroxylon* species

2.3 Angiosperm resins II – Sapindales

Resins from the Sapindales (order Rosids) originate from three families, the Anacardiaceae, Burseraceae and Rutaceae (Fig. 2.1). Main compounds in these families are tetra- and pentacyclic triterpenes of the ursane, oleanane, lupane and dammarane skeleton. Additionally tirucallanes were found to be part of resins from this group, in the Burseraceae also lanostanes and hopanes (Mills, White 1977; de la Cruz-Caňizares et al. 2005; Colombini, Modugno 2009: 13). They are non-polymerizing but easy oxidising (Mills, White 1999: 105). The botanical origin, particularly on the level of genera, does not allow clear forecasts of the chemistry of a particular resin as it is possible for conifer resins (Mills, White 1999: 105). But, within limits, it is possible to distinguish families and in same case genera by their chemistry.

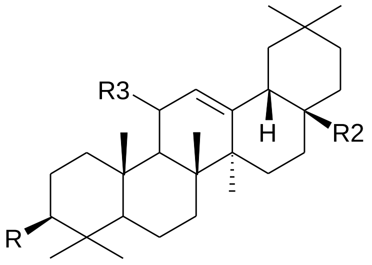
2.3.1 Anacardiaceae

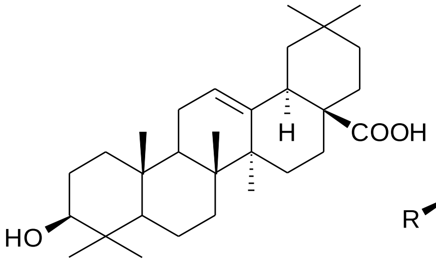
***Pistacia lentiscus* L.**

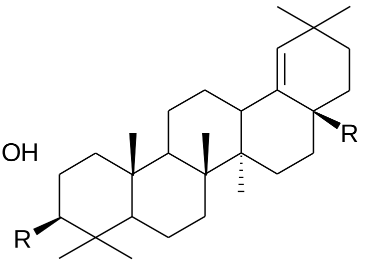
This family includes the genus *Pistacia* which is the source of mastic. It is obtained from several varieties of the Mastic tree *Pistacia lentiscus* L. It grows in coastal Mediterranean areas. Typically, resin canals of *Pistacia lentiscus* are found restricted to the vascular rays in the xylem, which indicates that the resin is produced traumatically (Koller et. al. 1997c; Langenheim 2003: 386). It is produced and stored in secretory tissue of the bark. After vertical incisions are made into the bark the resinous balsam exudes and coagulates for some weeks to solid tears, which drop down or are stripped off (Koller et al. 1997c; Langenheim 2003: 386f; Ierapetritis 2010). The collection is limited to a period in summer and autumn, because the resin collected in winter is of minor quality (Koller et al. 1997c; Langenheim 2003: 385). In contrast, during the Genoese reign on Chios the resin obtained from an additional harvest in February and March was regarded to be of the highest quality (Freedman 2011). A regular trade of the resin is known mainly from the island Chios but also Cyprus and Sicily are mentioned occasionally (Koller et al. 1997c; Langenheim 2003: 385; Ierapetritis 2010). On Chios the male trees of *P. lentiscus* var. chia are cultivated for the production of mastic, mainly in the South-eastern part of the island (Koller et al. 1997c; Langenheim 2003: 386; Ierapetritis 2010). The mastic trade in the the 17th and 18th century is summarised by Ierapetritis (Ierapetritis 2010).

In mastic resin triterpene compounds with a bi-, tri-, tetra- and pentacyclic skeleton were found (Boar et al. 1984; Marner et al. 1991; Langenheim 2003: 387; Colombini, Modugno 2009: 16f.). Main components of the mastic resin are pentacyclic triterpenes with an oleanane skeleton. High amounts of oleanonic and moronic acid, β-amyrin and β-amyrone as well as oleanonic aldehyde were found (Mills, White 1977; van der Doelen et al. 1998; Colombini et al. 2000b; Langenheim 2003: 387; Dietemann 2003: 44). Another group of pentacyclic triterpenes, lupanes, are reported occasionally for mastic (Dietemann 2003: 44; Langenheim 2003: 387). The second important group includes tetracyclic triterpenes with the tirucallane or dammarane skeleton. Main tirucallane compounds found in mastic are tirucallol, tirucallone and the acids (iso)masticadienonic and (iso)masticadienolic acid (Marinach et al 2004; Mills, White 1977; van der Doelen et al. 1998; Colombini et al. 2000b; Langenheim 2003: 387; Dietemann 2003: 44). Also lanostanes such as lanosterone and lanosterol with a second double bond at position C-7 or C-8 are mentioned for mastic (Dietemann 2003: 44; Colombini, Modugno 2009). Dammaranes were also found (Colombini et al. 2000b; Dietemann 2003: 44).

Oleananes





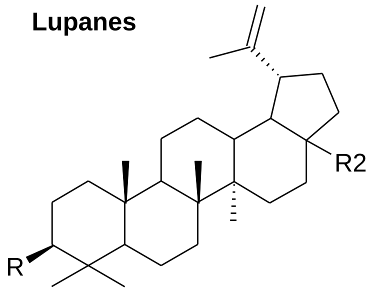


R=OH, R2=CH3, R3=H **β-Amyrin** (olean-12-3β-ol)
R=O, R2=CH3, R3=H **β-Amyrone**
R=OH, R2=COOH **Oleanolic acid**
(3β-hydroxy-olean-12-en-28-oic acid)
R=O, R2=COOH **Oleanonic acid**
(3-oxo-olean-12-en-28-oic acid)
R=O, R2=CHO **Oleanonic aldehyde**
R=OH, R2=CHO **Oleanolic aldehyde**
R=O, R2=COOH, R3=O **11-Oxo-oleanonic acid**

18α-Oleanolic acid

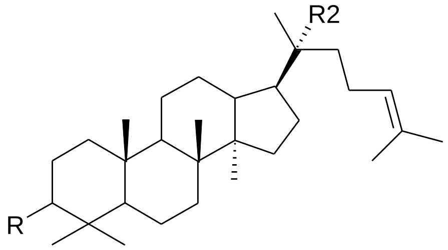
R=O, R2=COOH Moronic acid
(3-oxo-olean-18-en-28-oic acid)
R=OH, R2=CH3 **Germanicol**
(olean-18-en-3-ol)

Lupanes



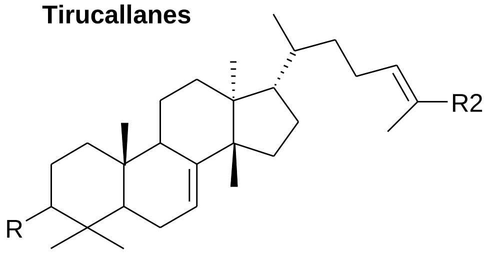
R=OH, R2=CH3 **Lupeol** (lup-20(29)-en-3β-ol)
R=O, R2=CH3 **Lupenone**
R=O, R2=COOH **3-Oxo-lup-20(29)-en-28-oic acid**

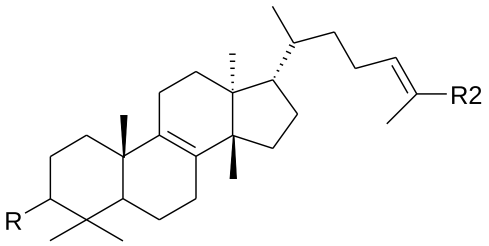
Dammaranes



R=O, R2=OH **Hydroxydammarenon**e or dipterocarpol
R=AoC, R2=OH **3-O-acetyl-hydroxydammaranone**
R=O, R2=H (20(21)diene) **Dammaradienone**

Tirucallanes

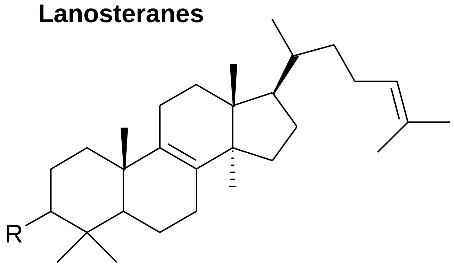




R=O, R2=COOH **Masticadienonic aci**d
R=OH, R2=COOH **Masticadienolic acid**
R=AcO, R2=COOH **3α-O-acetyl-masticadienolic acid**

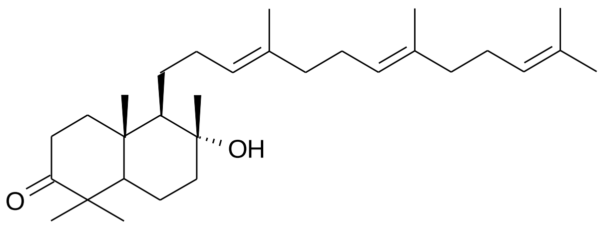
R=OH, R2=CH3 **Tirucallol**
R=O, R2=CH3 **Tirucallone**
R=O, R2=COOH **Isomasticadienonic acid**
R=OH, R2=COOH **Isomasticadienolic acid**
R=AcO, R2=COOH **3α-O-acetyl-isomasticadienolic acid**

Lanosteranes



R=OH **Lanosterol**
R=O **Lanoster-3-one**

Miscellanous



3-Oxo-8-hydroxy-polypoda-13E,17E,21-triene

Fig. 2.10 Compounds found in *Pistacia* resins

MW	Original constituents	Aging constituents
358		Hexakisnor-dammaran-3,20-dione
410		28nor-ß-amyrone, 28norlup-20(29)-en-3-one, 28norolean-17(18)-3-one,
412		28nor-ß-amyrin
414		3-oxo-trisnor-dammarano-20,24-lactone
424	dammaradienone, ß-amyrone, olean-18-en-2-one, lanoster-3-one, lupenone, tirucallone, 3-oxo-malabarica-14(26),17E,21-triene	
426	tirucallol, ß-amyrin, lanosterol, germanicol, lupeol, 3-hydroxy-malabarica-14(26),17E,21-triene	17β-hydroxy-28-norolean-12-en-3-one
438	oleanonic aldehyde	
440	oleanolic aldehyde	28-hydroxy-ß-amyrone
442	hydroxydammarenone, (8R)-3-oxo-8-hydroxypolypoda-13E,17E,21-triene	
444	(3L,8R)-3,8-dihydroxypolypoda-13E,17E,21-triene	
454	oleanonic acid, moronic acid, masticiadienonic acid, isomasticadienonic acid	3-oxo-lup-20(29)-en-28-oic acid
456	oleanolic acid, 18α-oleanolic acid , 3-epi-masticadienolic acid, 3-epi-isomasticadienolic acid	
458		20,24-epoxy-25-hydroxy-dammaren-3-one
460		20,24-epoxy-25-hydroxy-dammaren-3-ol
482		11-oxo-oleanonic acid
486	3-acetoxy-hydroxydammarenone	
498	3-O-acetyl-3-epi-masticadienolic acid, 3-O-acetyl-3-epi-isomasticadienolic acid	

Tab. 2.5 List of compounds found in mastic resin from literature (Dietemann 2003: 77, 110; Assimopoulou, Papageorgiou 2005a; White, Kirby 2001; Marner et al. 1991; Langenheim 2003: 387; van der Doelen 1999). Additionally various hydroxy-, methoxy and acecoty-derivatives of 28-nor-olean-17-ene, 28-norolean-12-ene, moronic acid and a dihydro derivative of 3**β**-acetoxy-6**β**-isomasticadienolic acid were found (Assimopoulou, Papageorgiou 2005a)

In mastic samples a low molecular polymer was found. It consists of monoterpenoid units of *cis*- and *trans*-β-myrcene. Measurements showed that oxidative crosslinking is a minor process during the formation of this polymer, which is therefore formed mainly by the polymerisation of the conjugated double bonds (van den Berg et al. 1998). The essential oil fraction of mastic consists of α-pinene, β-myrcene and small amounts of limonene, β-pinene and camphene (Koller et al. 1997c; Langenheim 2003: 387).

Other Pistacia species

The only other important product from that genus is Pistacia turpentine, also called Chios, Cyprus or Venice turpentine. There is a particular inconsistency in literature about the botanical source of Pistacia turpentine, both *P. terebinthus* L.. and *P. atlantica* Desf. are mentioned (Koller et al. 1997c; Mills, White 1999: 108; Langenheim 2003: 389; Lardos et al. 2011). Koller et al. mentioned *P. atlantica* in connection with a minor sort of mastic, while Mills and White wrote it to be the true botanical source of Pistacia turpentine (Koller et al. 1997c; Mills, White 1999: 108). Tschirch mentioned *P. terebinthus* (Tschirch 1935b: 383). According to Mills and White that confusion was caused by past nomenclature considering *P. atlantica* as a variety of *P. terebinthus* (Tschirch 1935b: 383; Mills, White 1999: 108). There are indications in literature that Cyprus turpentine is obtained from a different species or variety than Chios turpentine, the former possibly from *P. atlantica* (Hairfield, Hairfield 1990; Lardos et al. 2011). The mentioned tree grows in the whole Mediterranean region in coastal areas, some species also in the Nearer East and Asia (Koller et al. 1997c; Mills, White 1999: 108).

This resinous balsam is composed very similar to mastic. The monoterpene fraction however is a 10 times higher than that of the mastic resin and consists of α-pinene, β-phellandrene and smaller amounts of limonene, caranol, campholenaldehyde, thymol, bornylacetate and camphene (Koller et al. 1997c). It contains no or only small amounts of β-myrcene and other polymerisable components in the essential oil fraction. This is the reason of the much more fluid consistence compared to mastic (van den Berg et al. 1998).

There are many mentions of this resinous balsam particularly in connection with findings of archaeological resinous materials (Mills, White 1989; Hairfield, Hairfield 1990; Serpico, White 2000; Stern et al. 2008). It proved to be very difficult to distinguish different *Pistacia* resins by GC/MS. Chudolij et al. presented a differentiation based on low molecular constituents such as tricyclene, β-myrcene, α-methyl-anisole, linalool and others (Chudolij et al. 2005; Chudolij et al. 2007). But their results were never published in detail. Hairfield and Hairfield found differences between mastic resin and Chios- and Cyprus turpentine by thin layer chromatography, which could not be clarified until now by other analytical methods. The turpentines showed to contain several compounds in the ether extract of lower polarity and in the ethanol extract of higher polarity, which were not found in mastic (Hairfield, Hairfield 1990).he resin of *P. terebinthus* var. *Chia* contains seco-28-norolean-12-en-3oic acid, 18α-oleanonic acid, morolic aldehyde and dammaradienol, which are not present in the resin of *P. lentiscus* var. *Chia* (Assimopoulou, Papageorgiou 2005a; Assimopoulou, Papageorgiou 2005b). Stern et al. finally stated that it is impossible to distinguish different species with actual analytical methods (Stern et al. 2008).

Aging

In general aged *Pistacia* resins tend to yield poorly resolved chromatograms with a high background of degradation products (Edwards et al. 2007). Only the aging of dammaranes results in a few predominant epoxy-compounds. From the lateral chain of the dammarane skeleton a tetrahydrofuranic ring is formed via cyclisation and further degraded. It was found that light is necessary for this aging process (Colombini et al. 2000b; van der Doelen et al. 1998; van der Doelen, Boon 2000). In aged samples therefore 20,24-epoxy-25-hydroxy-dammaren-3-one and 3-oxo-25,26,27-trinordammarano-20,24-lactone have been found (Assimopoulou, Papageorgiou 2005a; Colombini, Modugno 2009: 16). Consequently, hydroxydammarenone, which is present in high amounts in fresh samples, vanishes with aging (Fig. 2.11).

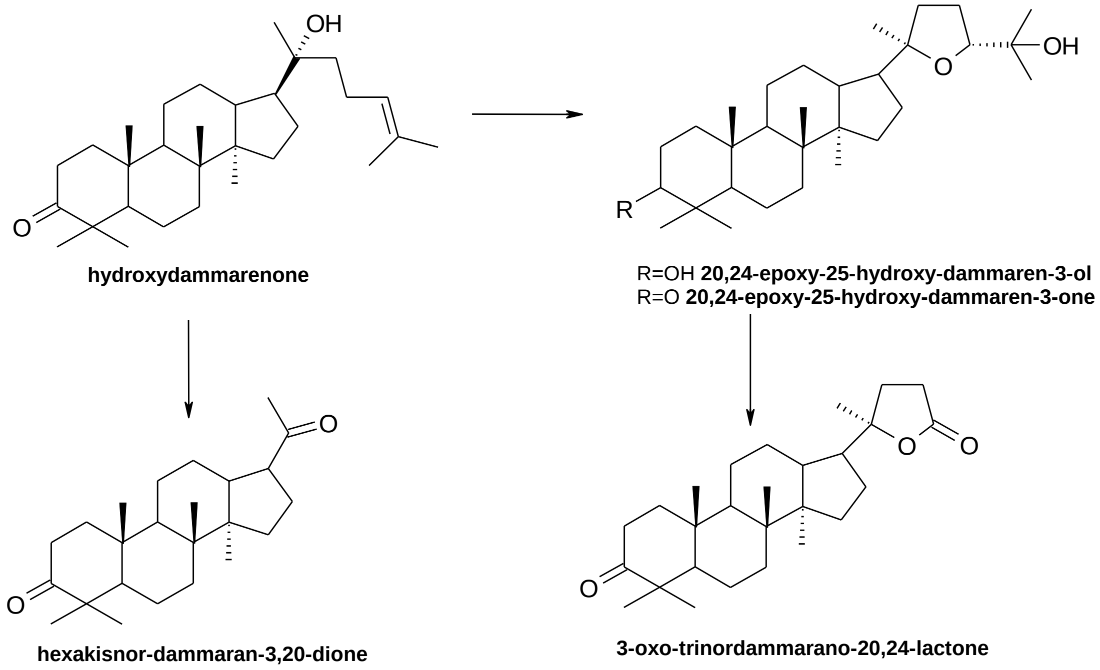


Fig. 2.11 Aging reaction of dammarane compounds: cyclisation of the dammarane side chain leads to an epoxy-compound, which is further oxidised to a lactone, hexakisnor-dammaran-3,20-dione was proposed to be directly formed from hydroxydammarenone (van der Doelen, Boon 20000)

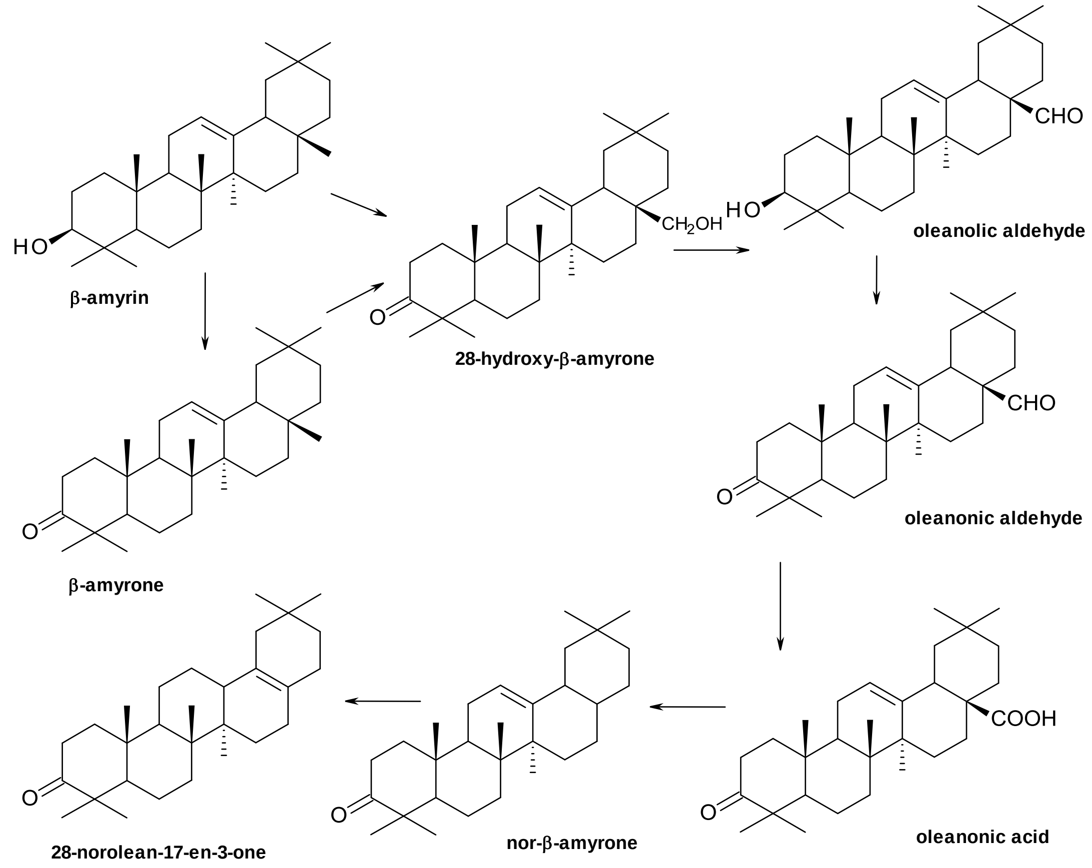


Fig. 2.12 Aging reaction of oleanane compounds: β-amyrin or β-amyrone are oxidised stepwise to oleanonic acid, which is decarboxylated. A hydrogen shift leads to a 28-noroleanen-3-one (Marner et al. 1991; Pastorova 1997: 104)

However, tirucallanes and oleananes seem to yield a greater amount of low concentrated aging products, which are difficult to detect with GC-MS (Dietemann 2003: 143; Edwards et al. 2007). Moronic and oleanonic acid are fairly visible in aged samples, even though moronic acids seems to be more stable (Mills, White 1997: 107; Colombini, Modugno 2009: 16). Oleanonic aldehyde decomposes very quickly, particularly in heated samples. It is thought to oxidise to the corresponding acid (White, Kirby 2001). Tirucallanes as (iso)masticadienonic acids are good markers for aged samples (Colombini et al. 2000b), while tirucallol seems to oxidise to tirucallone (White, Kirby 2001).

Another typical aging product is 28-nor-olean-17(18)-en-3-one, which can be found together with moronic acid and 20,24-epoxy-25-hydroxy-dammaren-3-one also in very degraded samples (Edwards et al. 2007). In laboratory heating *Pistacia* resins up to 400°C yielded an increasing amount of nor-oleananes but in archaeological samples no relation between heated materials (for incense purposes) and the amount of noroleanone could be found (Stern et al. 2003). The artificial aging experiment was carried out under the absence of oxygen, therefore particularly the presence of 28-nor-olean-17(18)-en-3-one is correlated to smouldering processes rather than incense practices (Colombini, Modugno 2009: 17).

Other nor-derivatives such as nor-β-amyrone and nor-β-amyrin are reported also for fresh or commercially available mastic (Marner et al. 1991; Colombini et al. 2000b), which is the consequence of the exposure of the resin to light and air after exudation before harvesting. As a possible formation pathway a stepwise oxidation at the C-28 position starting from β-amyrone or β-amyrin to a carboxylic acid and subsequent decarboxylation is proposed by Marner et al. (Marner et al. 1991). Thus β-amyrin or β-amyrone oxidises to oleanonic or oleanolic aldehyde and further to oleanonic acid, which is then decarboxylated. The decarboxylation followed by a hydrogen shift is described by Pastorova (Pastorova 1997: 104) (Fig. 2.12). A possible intermediate of this process 28-hydroxy-β-amyrone is found (Marner et al. 1991). It is proposed that findings of 3-oxo-norlup-20(29)-en-28-oic acid are based on the same reaction (Marner et al. 1991).

2.3.2 Burseraceae

The family of Burseraceae is the source of over 600 resin producing genera (de la Cruz-Caňizares et al. 2005). Resins from Anacardiacae and Burseraceae are chemically related (Langenheim 2003, 88), but data from literature are far more rarely than for *Pistacia* resins. Additionally, the names of the different resins – elemi, copal, anime or tacamahaca – often represent generic terms. This makes it difficult to correlate resin names and genera or species unequivocally. The different names and resin producing trees are summarised in table 2.6.

Nomenclature

Elemi today refers to the resin from *Canarium luzonicum* (Blume) A. Gray native to the Philippines, which is the main source for the so called Manila elemi, a soft, malleable and whitish resin with a strong pleasant citrus odour (Mills, White 1999: 105, 108). It is of greenish, yellow colour and becomes yellow and white with aging. Its whitish opaque appearance is caused by crystallized resin acids, additionally it contains a high amount of sesquiterpenes. It was imported to Europe not later than in the early 17th century, although references from the 15th century are found, too (Tschirch 1935: 265-6; de la Cruz-Caňizares et al. 2005).

From antique times to middle ages the term seems to be applied to resins from Africa and the Orient, particularly Arabia. That resin was possible obtained from *Boswellia frereana*

Birdw. (Hugh 1910b: 259; Mathe et al. 2009), it occurs in tears or stalactite pieces with a transparent dark yellow interior (de la Cruz-Caňizares et al. 2005). A modern African elemi is derived from *Canarium schweinfurthii* Engl., Other African species mentioned are *Dacryodes edulis* Lam.(= *Canarium edule*) and *C. zeylanicum* (Retz) Blume (Gurib-Fakim, Brendler 2004: 158; University of Melbourne 2006; Regert et al. 2008). African elemi is colourless when fresh and becomes yellow with time (Langenheim 2003: 357).

Finally, different resin from tropical America of the genus *Protium* are called (Brazilian) elemi as well. *Protium* is sometimes called *Icica*, but both genera are also mentioned to be discrete (de la Cruz-Caňizares et al. 2005; GRIN 2012b). Indigenous names of *Protium* trees from different geographical regions were partly transferred to the resin. Additionally, identification of *Protium* species is difficult and they are confounded with other species of the Burseraceae family (Rüdiger et al. 2007). Brazilian elemi is therefore known under many different names such as anime, caraño or caraná balsam, animecillo, copal, copalillo, almécega, almíscar, galbano, breu, breu branco, breu vermelho, jauaricica and goma-limão (Hugh 1910a: 54; Langenheim 2003: 357-359; Rüdiger et al. 2007). They are used as frankincense, varnish ingredient and plasticiser (Martínez 1997: 102; Siani et al. 2004; de la Cruz-Caňizares et al. 2005). *Protium* resin is obtained by collecting natural exuded lumps and by making incisions in the bark to accelerate the resin flow (Langenheim 2003: 358f, 360). The resin of *Protium copal* is collected by making incision in the bark, mainly in the wet season. The resin is collected one week later (Langenheim 2003: 360).

The term copal appeared first in Europe in the second half of the 16th century for a resin from New Spain. It was originally used as incense (Case et al. 2003). The Nahuatl term was adopted by the Maya, but also the original Maya word "pom" or combination of both can be found still today (Watson 1938; Langenheim 2003: 359f; Stacey et al. 2006). The main source of incense in Vera Cruz, Oaxaca, Yucatán and Guatemala *Protium copal* Engl. grows on the Yucatán Peninsula in Central America (Case et al. 2003). It is also the main source for pom (ibid.).

Copal and pom called resins from Mexico can be obtained also from *Bursera* species (Stross 1997; Case et al. 2003; Langenheim 2003: 359; Stacey et al. 2006). *Bursera* is the New World relative to *Commiphora* and *Boswellia* resins (Olibanum and myrrh), all three families belonging to the subfamily Bursereae (Langenheim 2003: 87, 362, 373). The resins of Mesoamerican *Bursera* resins are opaque, sometimes translucent fragments or cylindrical pieces of pale-yellow or white colour and with a fragrant smell. Common trading names are “Copal blanco”, “Copal oro” and “Copal negro”, which refers to the method of collection and not the botanical origin (Case et al. 2003). *Bursera* resins contain mono-, sesqui and triterpenes as well as sometimes diterpenes from canals in the bark (Langenheim 2003: 88).

Boswellia is the source of frankincense or olibanum. The main species are listed in table 2.6. *Commiphora* resins are usually known as the source of myrrh (*C. myrrha* (Nees) Engl.), but the genus comprises several species producing trees, for example an oleoresin called Balm of Gilead or the Mecca myrrh (*C. gileadensis* (L.) C. Chr., formerly *C. opobalsamum* (L.) Engl.). Langenheim mentions African species of that genus as possible sources of triterpene copal resins, because *Commiphora* is chemically related to *Bursera*, the source of American triterpene copal resins (Langenheim 2003: 88). Frankincense from *Boswellia* is harvested by pastoral families in the dry season by wounding the tree third times, and only the resin exuded the third time is regarded as of best quality (Langenheim 2003: 366). Some resins

Species	Family	Burseraceae				
	(Sub)Tribe	Canariaeae	Protiae	Bursereae		
Name	Genus	*Canarium*	*Protium*	*Bursera*	*Boswellia*	*Commiphora*
Elemi		*C. luzonicum* (manila elemi) *C. schweinfurthii* (African elemi) *C. saphu* (African elemi)	*P. icicariba* (Brazilian elemi) *P. heptaphyllum* (elemi from Colombia & Venezuela also called tacamahaca) *P. guianense* (elemi from Guyana)		*B. frereana* (African elemi)	
Copal		*Canarium* sp. (African copal) *Canarium bengalense* Roxb. (East Indian copal)	*P. copal* (copal, pom, Guatemala, Yucatán)	*B. cuneata*, *B. excelsa*, *B. bipinnata*, *B. copallifera* (Mexican copal) *B. jorullensis, B. microphylla, B. simaruba*		*Commiphora* sp. (African copal) Probably *C. boranensi*, *C. corrugate*
Anime			*Protium* sp.			
Tacamahaca			*P. heptaphyllum* (also called elemi from Colombia & Venezuela)			
Miscellaneous		*C. strictum* (black dammar)	*P. carana* (Caraná balsam)			*C. gileadensis* or C. opobalsamum (Balm of Gilead)

Tab. 2.6 Burseraceae resin producing species with associated names of the resins (Meyer et al. 1991; Martínez 1997: 102; Stross 1997; Langenheim 2003: 88, 358, 374; Mathe et al. 2004; de la Cruz-Caňizares et al. 2005; Stacey et al. 2006; Rüdiger et al. 2007; Regert et al. 2008; Mathe et al. 2009; GRIN 2012b; Basar 2005: 36)

have a white cloudy appearance, which is caused by polysaccharides, incorporated from the walls of the epithelials cells of the secretory structures into the resin during exudation. *Commiphora* trees have a great number of secretory canals in the bark possibly forming interconnected cavities. From these cavities the resin flows without wounding (Langenheim 2003: 369). From the schizogenously cell walls of the canals polysaccharides are incorporated into the resin (Langenheim 2003: 125, 369).

Chemistry

Elemi

Elemi resins consist mainly of the pentacyclic alcohols α- and β-amyrin, their keto derivatives (Mills, White 1999: 108; Chiavari et al. 2008; Regert et al. 2008) and acids of the tirucallane series (Mills, White 1999: 108; Langenheim 2003: 256; Fig. 2.13)

Manila elemi (*Canarium luzonicum*) additionally contained maniladiol, brein and epi-Ψ-taraxastandiol (Morice, Simpson 1941; Morice, Simpson 1942; Khalid 1983). Main tirucallanes are 3α-hyroxy-tirucall-7,24-dien-21-oic and 3α-hydroxy-tirucall-8,24-dien-21-oic acid (α- and β-elemolic acid), together with minor amounts of 3β-hydroxy-tirucall-8,24-dien-21-oic, 3-oxo-tirucalla-7,24-dien-21-oic (elemonic) and 3α-acetoxytirucall-8,24-dien-21-oic (3α-acetoxy-β-elemolic) acids (Cotterrell et al. 1970; Argay et al. 1997; Mathe et al. 2009). Finally, *Canarium* species are good sesquiterpene accumulators, Manila elemi contained limonene, the phenylpropanoid (iso)elemicin, elemol, β-eudesmol and α-phellandrene (Khalid 1983; Marinach et al. 2004; Chiavari et al. 2008; Fig. 2.13).

A sample of modern Manila elemi analysed by de la Cruz-Cañizares et al. contained elemol, β- and γ-eudesmol and elemicin in the sesquiterpene and α-amyrin and β-amyrin in the triterpene region (de la Cruz-Cañizares et al. 2005). No brein, maniladiol and tirucallane related compounds were found in that investigation, but several minor peaks in the corresponding region of chromatogram were not labelled. Aging compounds were ursa-9(11),12-diene-3-one, olean-9(11),12-dien-3-ol, ursa-9(11),12-dien-3-ol, α-amyrone and β-amyrone formed through artificially light aging (de la Cruz-Cañizares et al. 2005). Elemicin was decomposed through light aging (de la Cruz-Cañizares et al. 2005). Additionally, neoolean-3(5),12-diene was found in an 12-year-old sample of Manila elemi. It was suggested to be an (thermal) alteration product – defunctionalisation and rearrangement of the A-ring – of β-amyrin. It was found in a 6 year old samples of Mexican copal, too (ibid.).

The resin of *C. schweinfurthii* ('African elemi') contained α-, β-elemolic and elemonic acids and their 3β-epimers and isomasticadienonic acids (Khalid 1983), the resin of *C. strictum* ('black dammar') α-amyrin, β-amyrin, β-amyrin acetate, Ψ-taraxasterol, epi-Ψ-taraxastandiol, 11-β-hydroxy- and 11-keto-α-amyrin (Hinge et al. 1965). Other African *Canarium* species contain amyrins and manelemic acid, the latter probably an old term for elemolic or elemonic acids (*C. madagascariensis* Engl.) (Gurib-Fakim, Brendler 2004: 158). In *C. zeylanicum* (Retz) Blume canaric acid, a 3,4-seco-lupen-3-oic acid, is found as well as in *Dacroydes edulis* Lam. (Baas 1985). Those seco-compounds are seldom found and reported for several Burseraceae genera (see above).

Main compounds of *Protium* resins are α-amyrin and β-amyrin in a 2:1 ratio and α- and β-amyrone accompanied by minor amounts of maniladiol, brein and friedelan-3-one (Stacey et al. 2006; Rüdiger et al. 2007; Marques et al. 2010). In the resin of *P. heptaphyllum* additionally lupenone was found as well as the 9(11)-diene of α- and ß-amyrin and amyrones, respectively. Taraxastan-3-one-20-ol, taraxastan-3β-20-diol, their Δ20(21)-Ψ-epimers, maniladiol and brein were found, too (Susunaga et al. 2001; Rüdiger et al. 2007; Fig. 2.13). The resins of *P. heptaphyllum*, *P. crenatum* Sandwith and *P. hebebatum* Daly contained α- and β-elemolic acids, the latter also elemonic acid (Rüdiger et al. 2007; Mora et al. 2001; Marques et al. 2010). No such compounds were found in the resin of *P. kleinii* Cuatrec. (Brazil), but the 11- and 16-hydroxy derivatives of α- and β-amyrone (Rüdiger et al. 2007).

Stacey et al. investigated different *Protium* resins, all related to elemi called materials (*P. heptaphylla*[2] labelled as "British Guiana Elemi", *P. heptaphyllum*, *P. icicariba*). Main compounds were α-amyrin and β-amyrin in a ratio of 2 to 1 accompanied by minor amounts of α-amyrone, maniladiol and brein (Stacey et al. 2006).

The volatile fraction of the resins from *South American Protium* species (*P. heptaphyllum, P. icicariba, P. bahianum, P. strumosum, P. spruceanum*) main compounds are α-pinene, sabinene, α-phellandrene, p-cymene, limonene, α-terpinolene and high amounts of p-cym-8-ol. Some species (*P. nitidifolium, P. paniculatum, P. hebetatum, P. altisonii*) do not contain α-terpinolene and p-cymen-8-ol (Siani et al. 1999; Ramos et al. 2000; Machado et al. 2003; Siani et al. 2004; Pontes et al. 2007). In *P. heptaphyllum* a more prominent sesquiterpene fraction with α-copaene, β-elemene, methyleugenol, β-selinene, myristicin, elemicin and high amounts of dillapiole is found (Siani et al. 1999; Rüdiger et al. 2007).

In summary, the non-volatile fraction of *Canarium* and *Protium* resins is composed very similar with a high variability within the genus. All contain α-amyrin and β-amyrin as well as α-amyrone, maniladiol and brein. Tirucallanes such as α- and β-elemolic acids as well as taraxastanes such as taraxastandiol, taraxastonol and structural related compounds are reported occasionally for single species in both genera. Some *Protium* resins are reported to contain small amounts of friedelan-3-one, *P. heptaphyllum* lupenone, which are both not mentioned for *Canarium* resins. From the published data it stays unclear whether this is of chemotaxonomic significance. For Manila elemi from *Canarium luzonicum* a characteristic sesquiterpene composition with high amounts of elemicin, elemol and eudesmol is reported. For the volatile fraction of resins from other *Canarium* species no data are found. Therefore only Manila elemi is distinguishable by its sesquiterpene fraction clearly from *Protium* resins, which show a higher monoterpene fraction with high amounts of p-cymene, terpinolene and p-cymen-8-ol together with phenylpropanoids in *P. heptaphyllum*.

Copal

An investigation about the triterpenes constituents of *Protium copal* Engl. could not be found. Langenheim mentions a highly variable chemistry for *Bursera* resins including mono-, sesqui-, di- and triterpenes and even phenylpropanoid compounds (Langenheim 2003: 373). No investigation about diterpenes and phenylpropanoids in *Bursera* resins is found and Langenheim gives only references for other plant parts. Main compounds are ursanes, oleananes and lupanes, which are present either predominantly as alcohols and ketones or as acids.

In the resin of *Bursera excelsa* high amounts of α-amyrin and lupeol, lower of isomers of α-amyrin and β-amyrin (probably the 3-epimers) and lupenone are present (Stacey et al. 2006). The lupeol identified by them is probably 3-epi-lupeol (Itoh et al. 1982; Mathe et al. 2004; see also Fig. 2.14c).

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[2] Another botanical classification was used in that paper, so that it is not clear which name that species bears in the APG classification, but Guyana elemi today is related to *Protium guianense* (see table 2.6).

The resin of *B. simaruba* (L.) Sarg. contains epi- and lupeol, epiglutinol, α-amyrin, β-amyrin and lup-20(29)-en-3β,23-diol (Peraza-Sánchez et al. 1995). A different composition is found for the resin of *B. penicillata* (DC.) Engl. – formerly *B. delpechiana* Poiss. ex Engl. It contains α-amyrin and ursanes such as ursonic acid, ursolic acid, 11-oxo-ursolic acid, 11-oxo-acetoxy-ursolic acid, acetoxy-ursolic acid and 3β-acetoxy-ursa-11(12)-en-28-oic-13,(28)-lactone. No lupeol and β-amyrin are found in this investigation (Syamasundar et al. 1991). Similar results are reported for the resin of *B. fagaroides* (Kunth) Engl. var. *fagaroides*, which consists of oleanonic and ursonic acids and aldehydes (Stacey et al. 2006; Fig. 2.13).

Case proposed a connection of different Mexican resin names and species based on literature data, colour, consistence and amount of essential oil of the samples and chemical investigation by infrared spectroscopy (Case et al. 2003). The investigated samples were purchased in the USA:

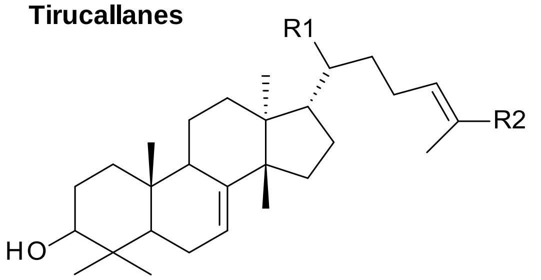
- Copal oro from *Hymeneae courbaril* (see chapter 2.2): high amounts of α-pinene and limonene accompanied by lower amounts of β-pinene, p-cymene, α-copaene and α-terpinyl acetate.
- Copal negro from *Protium copal*: high amounts of α-pinene, sabinene and δ-3-carene accompanied by lower amounts of 1,8-cineole, γ-terpinene, p-cymene, terpinen-4-ol, β-caryophyllene and α-terpineol.
- Copal blanco from *Bursera bipinnata: high amounts* of α-copaene, and germacrene D accompanied by lower amounts of β-bourbonene, β-ylangene, β-elemene, β-caryophyllene, α-humulene and bicyclogermacrene, no α-pinene.

De la Cruz-Caňizares investigated a Mexican copal attributed to *Bursera cuneata*. Its monoterpene fraction was composed very similar to the "Copal negro"-type of Case et al. with high amounts of o-cymene, α-pinene, limonene, γ-terpinene and 4-terpineol together with lower amounts of β-pinene, α-terpinene, α-terpinolene, sabinol, verbenone and carvacrol. No reliable quantities of sesquiterpenes were present. Its triterpene fraction contains α-, β-amyrin and hop-22(29)-en-3β-ol, the latter a constitutional isomer(C-18, C-21) of lupeol (de la Cruz-Caňizares et al. 2005; Fig. 2.14).

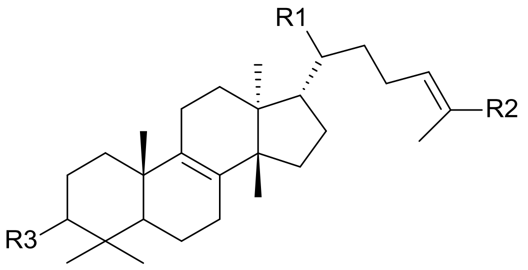
Stacey et al. analysed three samples of "Copal blanco", "Copal negro" and a "Copal de piedre" from a Mexican market place and found two amyrin-isomers (probably 3-epimers), epi-lupeol, β-amyrin, lupenone, α-amyrin, 3β-hydroxy-olean- and –urs-12-en-11-one (Stacey et al. 2006). Because this is different from the composition of (elemi related) *Protium* resins but similar to *Bursera excelsa* they present in the same paper (Fig. 2.14a, c), they conclude that the commercial samples were obtained from *Bursera* or *Amyris* species than rather than *Protium* (ibid.). This is consistent with mentions in literature that *Bursera* resins are the main source for copal resins in Mexico (Stross 1997; Langenheim 2003: 359).

A "Copal lágrima" investigated by Stacey et al. is found to consist of boswellic acids (Stacey et al. 2006). Boswellic acids are typical for *Boswellia* resins (frankincense) (Pardhy, Bhattacharyya 1978b; Hairfield et al. 1989; Mathe et al. 2004; Mathe et al. 2009), a genus not native to Mesoamerica. Thus, the material was either adulterated or until now a not investigated *Bursera* species contains oleanane and ursane acids with the carboxyl group at the C-24 position. This would be reasonable because *Bursera* and *Boswellia* are closely related (Langenheim 2003: 362, 373).

Tirucallanes

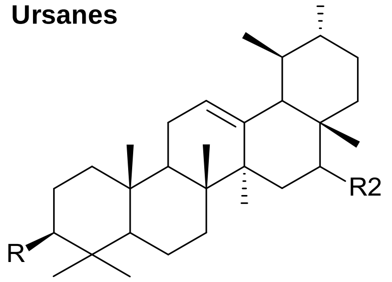


R1=H, R2=COOH **Masticadienonic acid**
R1=COOH, R2=H **β-Elemolic acid**
(3α-hydroxy-tirucall-7,24-dien-21-oic acid)



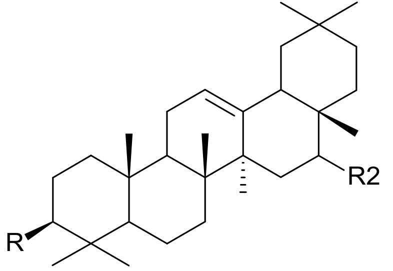
R1=H, R2=COOH, R3=O **Isomasticadienonic acid**
R1=COOH, R2=H, R3=OH **α-Elemolic acid**
(3α-hydroxy-tirucall-8,24-dien-21-oic acid)
R1=COOH, R2=H, R3=O **Elemonic acid**
(3-oxo-tirucall-8,24-dien-21-oic acid)

Ursanes

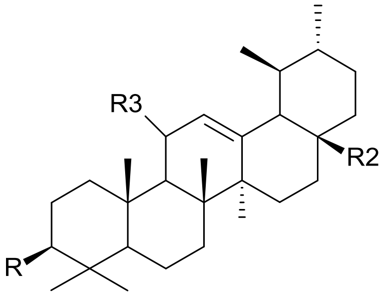


R=OH, R2=H **α-Amyrine** (urs-12-en-3β-ol)
R=O, R2=H **α-Amyrone**
R=OH, R2=OH **Brein** (urs-12-en-3b,16β-diol)

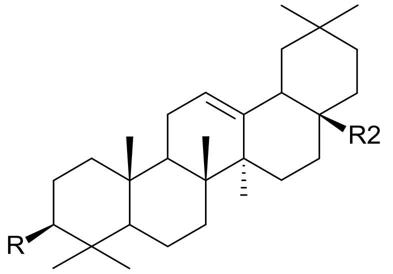
Oleananes



R=OH, R2=H **β-Amyrin** (olean-12-en-3β-ol)
R=O, R2=H **β-Amyrone**
R=OH, R2=OH **Maniladiol** (olean-12-en-3β,16β-diol)

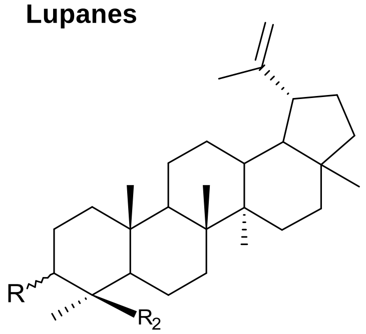


R=OH, R2=COOH **Ursolic acid** (3β-hydroxy-urs-12-en-28-oic acid)
R=O, R2=COOH **Ursonic acid** (3-oxo-urs-12-en-28-oic acid)
R=OH, R2=COOH, R3=O **11-Oxo-ursolic acid**
R=AoC, R2=COOH, R3=O **11-Oxo-3-acetoxy-ursolic acid**
R=AoC, R2=COOH, R3=H **3-Acetoxy-ursolic acid**



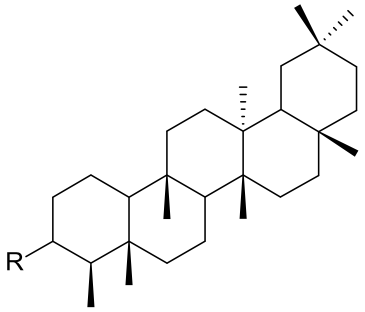
R=OH, R2=COOH **Oleanolic acid**
(3β-hydroxy-olean-12-en-28-oic acid)
R=O, R2=COOH **Oleanonic acid**
(3-oxo-olean-12-en-28-oic acid)
R=O, R2=CHO **Oleanonic aldehyde**

Lupanes



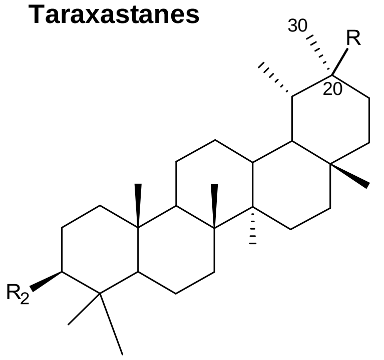
R=OH **Lupeol** (lup-20(29)-en-3β-ol)
R=OH **Epi-lupeol** (lup-20(29)-en-3α-ol)
R=O **Lupenone**
R=AoC **Lupenyl acetate**
R=OH, R2=COOH **Lupeolic acid**

Friedelanes



R=O **Friedelan-3-one** (friedelin)
R=OH 5(6) en **Epiglutinol**
(friedolean-5-en-3α-ol)

Taraxastanes

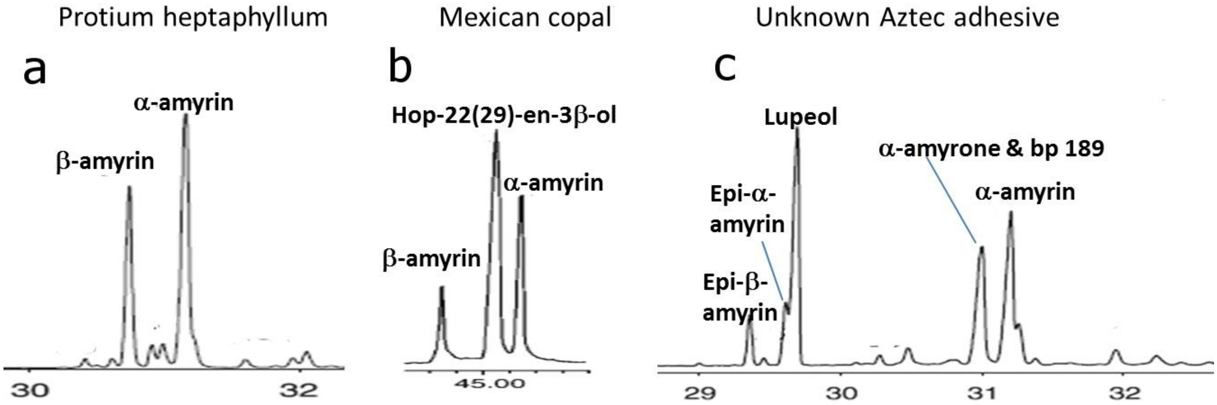


R=H, R2=OH 20(30)ene **Taraxasterol**
R/R2=OH **Taraxastan-3β,20-diol**
R=OH, R2=O **Taraxastan-3-one-20-ol**

Fig. 2.13 Triterpenes compounds in Burseraceae resins

De la Cruz-Caňizares et al. investigated artificial light aging for a Mexican copal attributed to *Bursera cuneata* as they did with Manila elemi (see above). They report ursa-9(11),12-diene-3-one, olean-9(11),12-diene-3-ol, ursa-9(11),12-dien-3-ol and β-amyrone (de la Cruz-Caňizares et al. 2005). These compounds are also found in aged Manila elemi and in the resin of *Protium heptaphyllum* (Susunaga et al. 2001; Rüdiger et al. 2007). In general, de la Cruz-Caňizares et al. find dehydration and oxidation of the present C-3 hydroxyl group rather than further oxidation at other positions such as C-11, C-16 or C-28.

In summary, *Bursera* resins contain high amounts of (epi)-lupeol and lupenone together with amyrin-epimers, which distinguish them from other South American *Protium* copals and from elemis. They also have a smaller volatile fraction. Two Mexican *Bursera* species, which are not commonly mentioned in connection with Mesoamerican copal resins consist of oleanane and ursane acids.



a - resin of Protium heptaphyllum (Stacey et al. 2006), b – Mexican copal (de la Cruz-Caňizares et al. 2005) and c – unknown adhesive at an Aztec artefact, bp – base peak, the lupeol labelled peak is very likely epi-lupeol due to the elution order given by Itoh et al. (Itoh et al. 1982; Stacey et al. 2006)

Fig. 2.14 Partial chromatograms of Burseraceae resins, triterpene region (TIC)

<u>Other Burseraceae resins</u>

Boswellia resins have a characteristic composition of oleananes and ursane acids particularly with the carboxyl group at C-24 and higher amounts of 3α- then 3β-substituted compounds (Pardhy, Bhattacharyya 1978b; Hairfield et al. 1989; Mathe et al. 2004; Mathe et al. 2009). α- and β-boswellic acids together with their 3α-acetoxy-derivatives and oxygenated derivatives at position C-11 (Fattorusso et al. 1983; Culioli et al. 2003; Büchele et al. 2003; Mathe et al. 2004; Basar 2005: 37-38). In the neutral part 3epi-α-amyrin, 3epi-β-amyrin, their acetates, α- and β-amyrone are present (Basar 2005: 38). In Indian frankincense (*B. serrata*) additionally α- and β-elemolic acids, elemonic acid, 3α-acetoxy-β-elemolic acid and an epoxy-tirucallane were identified (Pardhy, Bhattacharyya 1978a; Singh, Bhakuni 2006; partly shown in Fig. 2.13).

In the volatile fraction of frankincense verticilla-4(20),7,11,triene and an isomeric dimer of α-phellandrene were found as biological markers (Mertens et al. 2009). α-phellandrene dimerises under exposure to sunlight (Basar 2005: 84-90). Other compounds present in relative high amounts in different *Boswellia* resins were cembrene A, cembrene C, incensole, (iso)incensol oxide and incensole acetate (Mertens et al. 2009), all synthesised from GGPP (Khalid 1983; Basar 2005: 42-59; Melese 2007: 8).

In *Boswellia carteri* Birdw. α- and β-boswellic acid, their 3-acetoxy-derivatives, 11-hydroxy- and 11-hydroxy-3-acetoxy-β-boswellic acid and 3,4-secours-12-en-3-oic acid (dihydroroburic acid) are present (Fattorusso et al. 1983; Basar 2005: 142). Additionally, small amounts of β-elemolic, elemonic acids and several dehydration products of the boswellic acids are present (Basar 2005: 142). Dihydroroburic acid is also reported for the resin of *B. carteri* (Baas 1985). In Eritrean olibanum α- and β-boswellic acids, 3α-hydroxy-lup-20(29)-en-24-oic acid (lupeolic acid) are present (Culioli et al. 2003). Lupeolic acid and its acetoxy-derivative are found in other (African) frankincense resins as well, an in form of 11α-hydroxy-β-boswellic and acetyl-11-oxo-β-boswellic acids (Büchele et al. 2003; Basar 2005: 37-38; Fig. 2.13). In the resin of *B. rivae* α-, β-boswellic, 11-hydroxy-β-boswellic and 3-acetoxy-β-boswellic acids are present (Basar 2005: 150; Fig. 2.13)

Some African *Boswellia* species are composed different. In the resin of *B. neglecta* α-amyrin, α-amyrone, epi-α-amyrin, small amounts of α- and β-boswellic and canaric acids are found (Basar 2005: 149; Melese 2007: 8). The major constituent of African elemi (*B. frereana*) is (3-epi-)lupeol together with smaller amounts of lupenone, α-, β-boswellic and elemonic acids (Mathe et al. 2004; Mathe et al. 2004b; Fattorusso et al. 1985; Basar 2005: 148; Mathe et al. 2009). In the resin of *B. frereana* several dammaranes such as 3β,20-dihydroxydammar-24-ene, 3β,12,20-trihydroxydammar-24-ene, 3β-acetoxy-20-hydroxydammar-24-ene and 3β-acetoxy-16,20-dihydroxydammar-24-ene are identified (Fattorusso et al. 1985). Oxygenated dammaranes are reported occasionally for resins from *Boswellia* and *Commiphora* (see below) species. Chemotaxonomically, the presence of dammaranes is used to distinguish them from New World Burseraceae, which were not found to contain dammaranes in any part of the plant so far (da Paz Lima et al. 2004).

Commiphora resins consist of 30 – 60 % gum and 25 – 50 resin and show an even more varying chemical composition. The resin fraction contains high amounts of sesquiterpenes, furanosesquiterpenes and triterpenes. Main compounds of the resin of *C. myrrha* (Nees) Engl. are germacrene B, furanodiene, lindestrene, furanoeudesma-1,3-diene and β-elemene, (sesquiterpene fraction). Main compounds of the triterpene fraction are 3-epi-lupenyl acetate, lupenone, 3-epi-α-amyrin and α-amyrone (triterpene fraction) (Langenheim 2003: 371; Hanuš et al. 2005). For the resin of *C. confusa* Vollesen 3α,20-dihydroxydammar-24-ene, 3α-acetoxy-20-hydroxydammar-24-ene, cabralediol 3-acetate and α-amyrin are reported (Dekebo et al. 2002). In the resin of *C. incisa* Choiv. mansumbianes are found. These C_{22} compounds derive via the loss of the side chain from dammaranes. Main compounds are mansumbione, mansumbinol and 3,4-mansumbinoic acid together with 16,20β-dihydroxydammar-24-en-3-one (Provan, Waterman 1986). The resin from *C. pyracanthoides* Engl. from Southern Africa is rich in the C-24-oic comic acids A, B, C, D and E, whereby comic acid B is β-boswellic acid (Hanuš et al. 2005; partly shown in Fig. 2.13).

2.3.3 Rutaceae

Trees of the genus of *Amyris* yield elemi resins, for example *A. elemifera* L., the so called Yukatán- or Mexican Elemi (Mills, White 1999: 108). Additionally *Amyris plumieri* Engl./DC. is mentioned, which is possible another name for the same species (Pernet 1972; Stacey et al. 2006). The trunks of *Amyris* species exude the resin, which is hard, yellow, translucent and aromatic (Pernet 1972; White, Kirby 2001; Langenheim 2003: 361). The resin *of A. elemifera* L. was investigated by Stacey et al. and found to contain high amounts of lupeol and α-amyrin together with smaller amounts of lupenone and unidentified isomers of α- and β-amyrin (Stacey et al. 2006). Compounds are shown in Fig. 2.13. This resembles very much the composition of Mesoamerican *Bursera* resin, further investigations of *Amyris* could not be found. Langenheim mentions flavonoids especially flavones and flavonols to be part of resins from tropical members of Rutaceae but without detailed information (Langenheim 2003: 91).

2.4 Fossil resins

Fossil resins can be found all over the world, the terms fossil resin, amber and resinite are used interchangeable (Langenheim 2003: 143, 147f). Fossil resins are divided into subgroups according to the nature of their polymerizable monomers, from which the macromolecular structure is derived (Anderson et al. 1992; Anderson, Botto 1993; Anderson 1994; Langenheim 2003: 154f):

- Class I: labdanoid diterpenes (labdatriene carboxylic acid, alcohols, hydrocarbons); This class is subdivided into class Ia: labdanoid diterpenes with regular configuration (communic acid, communol, succinic acid); Ib: communic acid, communol, biformene and no succinic acid present; Ic: labdanoid diterpenes with an enantiomer configuration (ozic acid, ozol, enantio-biformene, zanzibaric acid)
- Class II: bicyclic sesquiterpenoid hydrocarbons (cadinene and related isomers)
- Class III: polystyrene (phenolic compounds as cinnamic acid and esters thereof)
- Class IV: non polymeric sesquiterpenes based on cedrane skeleton preserved in small amounts
- Class V: non-polymeric diterpenoid carboxylic acid (abietane, pimarane, isopimarane) preserved in small amounts

Fossilization starts with polymerisation of these monomers followed further chemical changes in the resin including cross-linking, isomerisation and cyclization. This process is called maturation and its duration is a matter of discussion (Langenheim 2003: 144-146). Langenheim takes the limit of carbon-14-dating (40–60000 years), which is dependent on the detection limit, as the minimum age for a fossilized resin (Langenheim 2003: 146). On the other hand, the term fossil in biology mainly refers to specimen died out before the Holozän (10.000 to 12.000 years before). Therefore, fossil resins can be considered as more than 10.000 to 60.000 years old. Oldest known dated samples are 310 million years old (Langenheim 2003: 147). Reported plant sources – recent or extinct – for fossil resins date from cretaceous over tertiary to Pleistocene (Langenheim 2003: 171).

Fossil resins are deposited in sediments formed in bays or river deltas of continental coastal zones. The resin is dug in the soil around the tree from which it exuded, washed out into nearby streams and carried downriver. It is buried in anaerobic sediments (Langenheim 2003: 147-9). This description resembles modern and also historic descriptions of copal deposits and digging sites (Pomet 1717: 403-4; Lemery 1721: 336-7; Tschirch 1936: 1016-21; Cunningham et al. 1973; Langenheim 2003: 394f).

Baltic amber

Baltic amber or succinite refers to the great group of north and eastern European fossil resins. They originate from early Tertiary (Oligocene). Other deposits are in East and Southeast Europe (Black Sea, Carpathians) as well as Great Britain and Denmark (Vavra 2009). Their plant source is a matter of discussion, particularly because of conflicts between the paleobotanical and chemistry data (Langenheim 2003: 164). While plant material survived together with the resin indicates an extinct conifer, several chemotaxonomic considerations point to an extinct *Pseudolarix*-like (succinic acid) or *Agathis* (high amounts of polymerisable labdanes but no succinic acid) genus as well as an extinct representative of Koyamaki pine (*Sciadopitys verticillata* Luerss.) (Langenheim 2003: 164-169; Wolfe 2009). Differences in the results of physical and chemical investigations on succinite repeatedly lead to the conclusion that more than one species was involved in the formation of the resin (Kohlmann-Adamska 2001).

The constituents of succinite are divided into the soluble and insoluble (polymerised) part of the resin (Fig. 2.16). The soluble part (extracted with different solvents such as cold ether, methanol, chloroform and diethyl ether) contains in the monoterpene fraction typically high amounts of succinic acid as well as camphene, o-, p-, m-cymenes, fenchone, fenchyl alcohol, camphor, (iso)borneol, bornyl formate and bornyl acetate (Mills et al. 1984/85; Stout et al. 2000; van Keulen 2009; Ribechini et al. 2009; Yamamoto et al. 2006). Koller et al. found free succinic acid only in the opaque aged crusts of former clear samples of Baltic amber (Koller et al. 1997d). There are indications in literature that succinic acid is no original constituent of the amber forming resin but a product of early anoxic diagenesis of the entombed resin (Czechowski et al. 1996; Wolfe et al. 2009) or the result of a microbiological process (Vavra 2009). It would be of no chemotaxonomic significance then.

Monoterpanyl esters of succinic acid – fenchyl, (iso)bornyl, fenchyl bornyl, difenchyl and di(is)bornyl esters – are reported by several authors together with dimonoterpanyl succinates as characteristic compounds, the latter not known from extant conifers (Mills et al. 1984/85; Czechowski et al. 1996; Koller et al. 1997d; Yamamoto et al. 2006; Vavra 2009; Wolfe et al. 2009). Additionally, monoterpanyl diterpenoates such as fenchyl- and (iso)bornyl-Δ8-isopimarate, -(dehydro-)Δ8-pimarate, dehydroabietate and abietate have been observed together with esters of pimarane and abietane alcohols with succinic acid (dehydroabietyl succinate) (Mills et al. 1984/85; Czechowski et al. 1996; Yamamoto et al. 2006; Fig. 2.15).

Koller et al. mention high amounts of monoterpenes and lower amounts of sesquiterpenes as characteristic for Baltic amber (Koller et al. 1997d). In the sesquiterpene fraction α-ionene, isomeric derivatives of (dihydro)cadinene, bergamotene, ledol, dihydro-ar-curcumene, calamenene, calamine and palustrol are found (Mills et al. 1984/85; Czechowski et al. 1996; Yamamoto et al. 2006; Stout et al. 2000). Ionene, methylionene and hydroxymethylionene are formed from labdane structures by degradation (Yamamoto et al. 2006)

The other main part of the soluble part is composed of diterpene acids with an abietane or pimarane skeleton (Mills et al. 1984/85; Koller et al. 1997d; van Keulen 2009; Ribechini et al. 2009). Abietic, levopimaric and dehydroabietic acid were found together with changing amounts of pimaranes such as (Δ8-)isopimaric, pimaric and sandaracopimaric acids together with the corresponding dihydro compounds dihydrosandaracopimaric, dihydroisopimaric and dihydroabietic acid (Mills et al. 1984/85; Koller et al. 1997d; van Keulen 2009; Ribechini et al. 2009). Additionally agathic acid, dihydroagathic acid (merkusic acid) and its Δ8-isomer were found together with several unidentified compounds possessing a molecular ion at m/z 262. Mills et al. speculate them to be products of the cyclisation of agathic acid (Mills et al. 1984/85).

Several authors reported minor peaks for degradation products of abietanes and pimaranes: 1,2,3,4-tetrahydronaphthalenes, dihydroabietatriene, abietatriene, dehydroabietatriene, retene, 18- and 19-norabietatrienes, 13-methylpodocarpatriene, 18- and 19-nor-13-methylpodocarpatrienes and podocarpatriene-18-oate (Botta et al. 1982; Mills et al. 1984/85; Koller et al. 1997d; Czechowksi et al. 1996; Stout et al. 2000). These compounds are formed during maturation by acid-catalysed isomerisation, aromatisation, defunctionalisation, decarboxylation and other skeletal modification reactions (Botta et al. 1982). Finally, homologous alkane series have been reported for some succinate samples (C_{20} – C_{28}, C_{22} - C_{33}) (Czechowksi et al. 1996; Islas et al. 2001). n-Alkanes are interpreted by Czechowski et al. as biodegraded lipid detritus, but not from plant wax as found in brown coal. Yamamoto et al. found alkanoates (C_{21} - C_{32}) and alkanodioates (C_{12} – C_{27}) in black amber (stantienite), which assumingly derive from higher plant lipids and biopolymers or from suberins, respectively, deposited with and incorporated into the resinous material (Yamamoto et al. 2006).

The insoluble polymerised part of the resin is composed of labdatriene diterpenoid carboxylic acids such as communic acid, copolymerised with communol, and esterified with succinic acid (cross-linking) (Czechowski et al. 1996; Vavra 2009). It is therefore a class 1a resinite (see above). The maturation process can be summarised in three steps: 1. Degradation of exomethylene functionalities, 2. rearrangement of double bonds to Δ8-position and 3. defunctionalisation of ring systems (Vavra 2009). It was mainly investigated with infrared spectroscopy and pyrolysis-GC-MS. Typical pyrolysis products of succinite are bicyclic degradation products: tri-, tetra- and pentamethylocta- and decahydronaphthalenes. Furthermore several monoterpenes, sesqui- and diterpenes (dehydroabietic, abietic) and succinic acid are found in the pyrolysis fraction (Stout et al. 2000; Ribechini et al 2009).

The infrared spectrum of succinite is very close to that of the polymer fraction of modern *Agathis australis* resins (Kauri copal). It is an esterified polymer of communic acid, communol and succinic acid. Firstly, communic acid and communol polymerise via an radical 1,2 addition across the terminal double bond. The free hydroxyl groups of this polymer are then esterified with succinic acid (succinylation) or free carboxyl groups of abietanes (Mills et al. 1984/85; Stout et al. 2000). Also isomerisation of the exocyclic double bond into the ring (Δ8 position) was observed (ibid.). An acid-catalysed polymerisation was proposed (Botta et al. 1982).

A typical feature of the infrared spectrum of most European ambers is the Baltic shoulder, a flat region between 1,175 – 1,250 cm^{-1} flanked by a peak at 1,164 cm^{-1} (Wolfe et al. 2009). It is not found in non-Baltic fossil resins including those containing succinic acid (Beck 1986). Other typical bands are given by Golubev and Martirosyan (Golube, Martirosyan 2012). Stout et al. took fourier transformed infrared (FTIR) spectra of several succinites, gedanites and gedano-succintes before and after solvent extraction of the samples. They summarize that the spectra of the solvent extracted samples are "in all major respects" identical with those of the whole resin. This would make the infrared spectra of the whole resin representative of the insoluble, polymeric part of the resin (Stout et al. 1995).

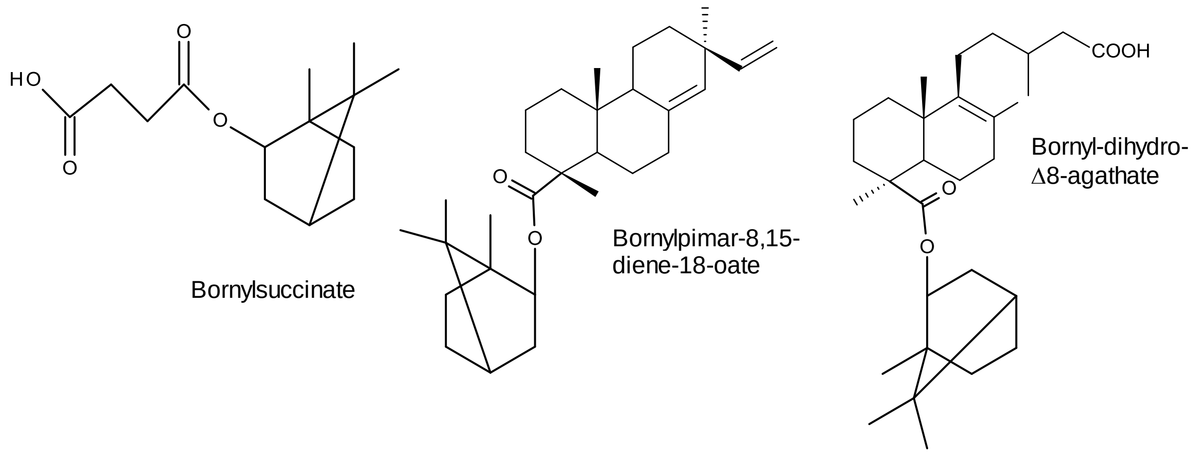


Fig. 2.15 Monoterpanyl ester in succinite, exemplary shown for borneol

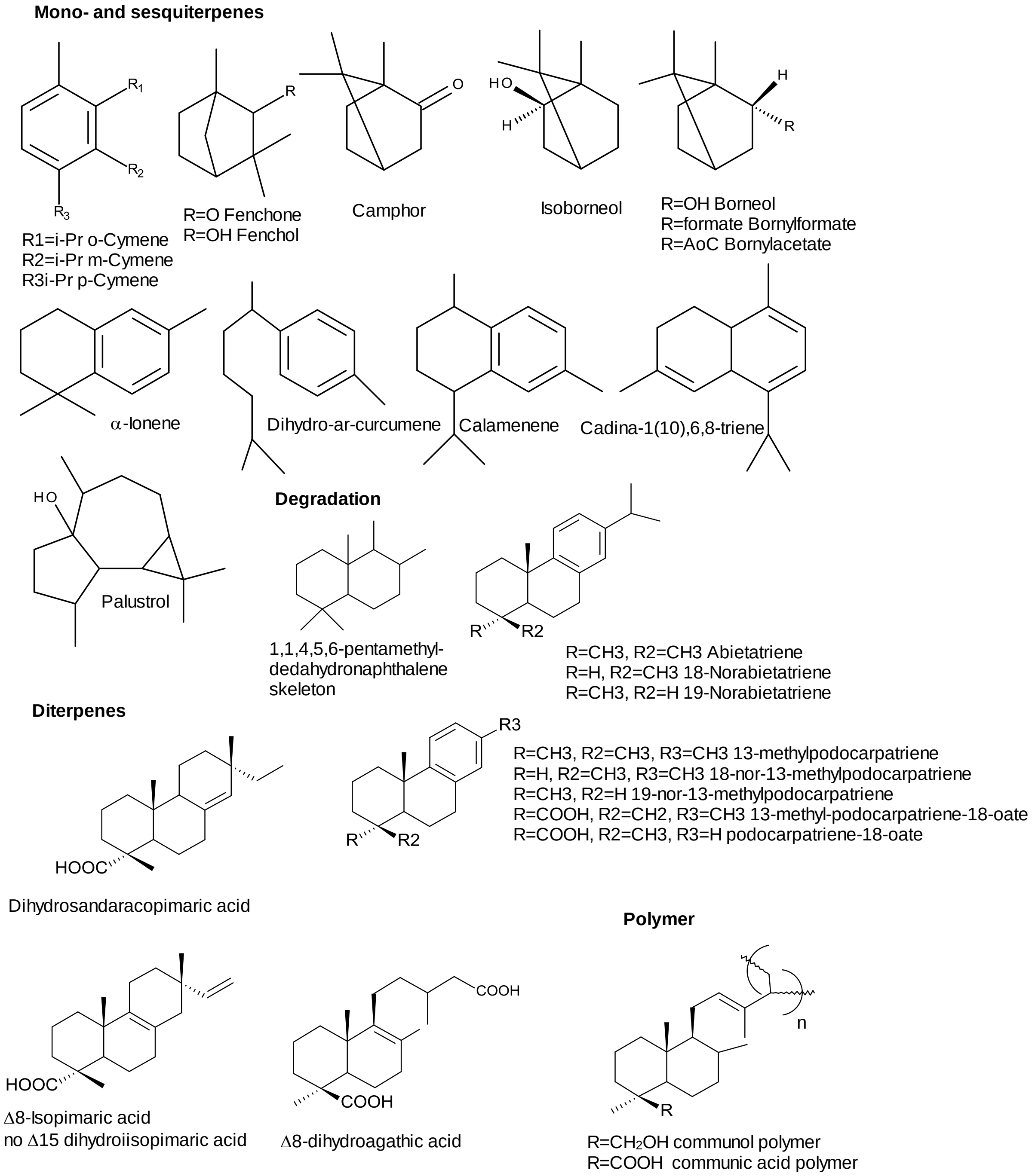


Fig. 2.16 Compounds of the soluble fraction of Baltic amber, other diterpenes see Fig. 2.2 and 2.6

2.5 Summary and research deficits

The chapter provides an overview about the state of knowledge for the different composed resins investigated in this work. It shows to which extent the knowledge can differ. In general, the five groups - pimarane, abietane and labdane compounds (conifers), ent-labdanes (Fabaceae), phenylpropanoids (Fabaceae), triterpenes (Sapindales) and abietanes and succinic acid and their derivatives (soluble fraction of amber) – are well distinguishable, but within the groups there is still need for further research. The following discussion summarizes these gaps and partly provides a basis for the investigation of the reference materials.

Conifer resins

What is known? In which way does this knowledge serve the investigation of botanical and other reference materials?

- Conifer resins consist of diterpenes synthesised from CPP and syn-CPP – abietanes, pimaranes and (syn-)labdanes. The single compound classes appear separated from each other in the different families with only few exceptions. Conifer resins are distinguishable very well by high amounts of specific compounds: Pinaceae – abietane and pimarane acids, Cupressaceae – sandaracopimaric and C-19 oxygenated labdane acids and Araucariaceae – C-19 oxygenated labdane, pimarane and abietane acids.
- Aging reactions of Pinaceae resins are investigated in detail mainly for the aging at light and air. Aging reactions caused by thermal treatments seems to be mainly isomerisation of the abietane acids.
- Cupressaceae resins consist of high amounts sandaracopimaric and communic acids, apart from that, literature data suggest a similar composition for resins from different genera (*Juniperus, Cupressus, Tetraclinis*), even though data are not very detailed.
- Araucariaceae resins are connected to the large group of copal called resins. Conifer copals are well distinguishable also among from other resins called copal and from each other.

What has yet to be investigated?

- The different genera of Pinaceae resins are probably distinguishable by minor amounts of labdane alcohols and acids, but no comprehensive investigation or review is found. Typical compounds are abienols (*Abies, Picea*), labdane acids (*Pinus*, section Cembrae) and labdane alcohols (*Larix*). In particular, *cis*-abienol is found in several species together with changing amounts of other abienols, but data are incoherent. Another differentiation criterion may be the relative amounts of pimaric and sandaracopimaric acids, which is mentioned in literature but never been published in detail. Particularly, the genera *Pinus*, *Picea* and *Larix* probably contain differing contents of these acids.
- Aging reactions of Pinaceae resins caused by thermal treatments are investigated for modern colophony, but no detailed report for Burgundy pitch is found. For the latter not even details of the production process are known.
- The composition of *Juniperus* resins is unknown. By comparison, the composition of *Cupressus* resins is probably distinguishable from that of Sandarac cypress by C-15 and C-19 oxygenated labdane acids. But it cannot be said from the present data

whether these compounds occur in the whole genus or only in single species. The resin of the Sandarac cypress *Tetraclinis articulata* Mast. is not investigated and the detailed analyses of a variety of commercial sandarac samples do not have a botanical background.

- Because Araucariaceae copals consist of a mixture of all compound types found in conifers (pimaranes, abietanes, labdanes) it may be difficult to identify them in mixtures. The presence of agathic acids and its oxidised derivatives is reported also for some Cupressaceae resins. Because in this work only pure materials are investigated with known terminology this is of low significance. However, a chemical and probably chemotaxonomic connection between Cupressaceae and Araucariaceae resins earns more detailed investigation.

Fabaceae resins

What is known? In which way does this knowledge serve the investigation of botanical and other reference materials?

- The family of Fabaceae yields a wide range of resins with a varying chemistry, mainly originating from tropical or arid regions in Africa and America. The chemistry is dominated by ent-labdane and in the case of the bark resin of *Myroxylon* of phenylpropanoids. A clear correlation between terminology and botanical origin as it is common for conifer resins, it not found in this family. Apart from lacking chemical data, limited availability of the materials in Europe and unknown harvesting and trading details, literature data allow the conclusion that the wide range of resin producing species even within one genus and the related materials are not correlated in an unambigious way.
- Copaiba balsam from *Copaifera* is of varying composition due to the use of different species for its production. A typification reported in literature was made mainly of samples from European collections, but botanical analyses indicate a similar distribution.
- Legume copals originate from a wide range of different African Fabaceae species (*Hymenaea, Guibourtia, Tessmania, Daniellia*), which are mentioned in literature. Particularly, *Hymenaea* resins, which also include soft South American resins and not only hard copals, are investigated comparatively well, but a high variability within the genus is also mentioned.
- *Myroxylon* resins are well distinguishable due to high amounts of phenylpropanoid compounds. Main compounds are benzyl, cinnamyl and coniferyl alcohol and benzoic, cinnamic and ferulic acids. p-Coumaryl alcohol and p-coumaric acid are not found. Other compounds are present only in small quantities. The different varieties of *M. balsamum* show a significant different composition.

What has yet to be investigated?

- The data profile of Copaiba balsams and the related botanical sources partly contradicts or is incomplete. Additionally, nearly nothing is known about production methods and used species in detail. Analysis should focus whether there is a connection of the imprecise and unknown production methods and the variable chemical composition.

- The data basis for the legume copals is fragmentary. African copals are investigated only sporadically and South American *Hymenaea* resins for single species. Data are not sufficient to distinguish between different legume copals, additionally a various constituents are mentioned but not identified.
- Literature about *Myroxylon* resins lacks mass spectrometric data of the several esterified phenylpropanoids, particularly when no silylation is used.

Sapindales

What is known? In which way does this knowledge serve the investigation of botanical and other reference materials?

- *Pistacia* resins, particularly mastic, are investigated in detail. Because the resin starts to change directly after exudation even fresh materials may show a highly complex composition. A few major compounds are found in all materials, but the composition of minor compounds tends to be very variable.
- A wide range of Burseraceae resins are connected with materials used by humans, such as copal, elemi, anime, tacamahaca and others (see table 2.6). The family shows a tendency to produce a wide range of slightly different resins known under the same generic names. Often one species is the main source of a particular resin, but several other species of the genus produce smaller quantities of a similar resin, which is traded sometimes under the same sometimes under a different name. The reverse, a particular material originates from different genera, which are of quite different composition, is found, too. It will be difficult to assign a material of a certain name – whether common or rarely used – to a specific botanical (and geographical) origin, when the chemical composition of the species in question is unknown or can be estimated only by chemotaxonomical considerations.
- Within the Burseraceae, elemi resins originate from several species from three different genera (*Canarium, Protium, Boswellia*), from which only the resin of *Boswellia frereana* is clearly distinguishable from the others. *Canarium* and *Protium* contain α- and β-amyrins, maniladiol, brein and tirucallane acids, but other compounds (taraxastanes, lupenone, friedelane), which may serve as biomarkers for single species or genera, seem to occur only occasionally. Copal resins may originate from *Canarium, Protium, Bursera* and *Commiphora*, for which only American *Bursera* copals are investigated. They are distinguishable by the presence of lupanes and the absence of maniladiol, breine and tirucallane acids. There are several *Bursera* resins, which consist of oleanane and ursane acids, but these species are not mentioned in connection with copal resins.
- There is a difference in the reported aging reactions for pentacyclic triterpenes. Both are based on (β-)amyrin. For *Pistacia* resins a stepwise oxidation at C-28 followed by decarboxylation is reported, the last compound being 28-norolean-17-en-3-one. For *Canarium* and *Bursera* resins mainly Δ9(11)-dehydrogenation and oxidation at the present C-3 functional groups is reported, some phytochemical data includes compounds with additional hydroxyl or carbonyl groups at C-11 and C-16, in lupanes also at C-23. It cannot be said why the different resins show such different aging reactions.

What has yet to be investigated?

- The underlying processes of the aging characteristic of *Pistacia* resins have been investigated to some extent, but far from being fully understood.
- *Pistacia* species are undistinguishable by GC-MS and the identification of Pistacia turpentine is mainly achieved by non-chemical considerations. It is not yet clarified whether *P. atlantica* or *P. terebinthus* are the source of Pistacia turpentine. Botanical analyses of these resins with GC-MS are not found.
- Investigation of Burseraceae resins suffers from taxonomical problems and lacking systematic knowledge due to the large number of materials used.
- Data profiles of the genera from Burseraceae are incomplete. While *Canarium* and *Protium* resins are investigated comparatively well, the data about resins from *Bursera*, *Commiphora* and *Boswellia* are fragmentary, for the latter two also focusses on the widely used gum resins frankincense and myrrh but not related copal or elemi resins. The chemistry of *Canarium* and *Protium* copals is unknown and can only be deduced from that of the softer elemis from the same genera.
- Because most investigations of Burseraceae resins reported here are phytochemical reports without a (detailed) GC-MS section, detailed mass spectra, elution order and relative amounts are sometimes open.
- The family of Rutaceae is discussed mainly for completeness, because only one investigation about a copal producing Mesoamerican *Amyris* species is found. The composition is very similar to *Bursera* resins. To which extent *Amyris* species exude commercial used copal resins or whether they can be distinguished from Burseraceae resins stays uncertain.

Fossil resins – amber

What is known? In which way does this knowledge serve the investigation of botanical and other reference materials?

- The composition of the soluble part of Baltic amber is well known and described. It is characteristic for the resin.
- Literature mentions a black amber, labelled stantienite, which is composed mainly of homologues series of alkanes and alkanodioic acids and triterpenes.

What has yet to be investigated?

- The applicability of the sample preparation for the historical samples has to be investigated.

3. EXPERIMENTAL

3.1 Coupled gas chromatography and mass spectrometry

3.1.1 Materials

Chemicals

Used chemical were: methanol HiPerSolv, HPLC-gradient (VWR, #20864.320), isooctane for HPLC (AppliChem, #A1627), oxalic acid anhydrous (Fluka, #75688-250G), trimethyl-sulfoniumhydroxide(TMSH)-solution (Fluka, # 92732-10X1ML), chloroform for HPLC (VWR, #83626.320) and dichloromethane LiChrosolv (VWR, #23373.320). Internal standards were tridecanoic acid (TDA; Fluka, #91988) and hexadecane (HD; Fluka, #52210).

Reference materials

The main part of the investigated reference samples originate from the reference collection of binding media at the Academy of Fine Arts in Dresden (AFAD), Hochschule für Bildende Künste, Güntzstrasse 34, 01307 Dresden, Germany. Other reference samples were obtained from the Laboratory of the Bavarian State Authority for the Conservation of Monuments, Saxon State Authority for the Conservation of Monuments, Prof. Dipl. Rest. Ulrich Schießl, Prof. Dr. Christoph Herm and Nanke Schellmann. Several materials were purchased from Kremer, Kremer Pigmente GmbH & Co. KG, Hauptstraße 41-47, 88317 Aichstetten, Germany and Eggebrecht, Gerhard Eggebrecht, Doppelreihe 1a, 25361 Süderau, Germany.

Botanical reference samples originate from the Sylvan Botanical Garden (Forstbotanischer Garten), Department of Forest Sciences at the Technical University of Dresden in Tharandt, the Botanical Garden at the Technical University of Dresden, the Botanical Garden Berlin-Dahlem at the Free University of Berlin, the Botanical Garden of the University of Potsdam and the Botanical Garden of the Pillnitz Castle.

Reference materials were sampled mainly in the Laboratory for Archaeometry of the Academy of Fine Arts in Dresden. Botanical samples were sampled both from the staff of the botanical gardens (Sylvan Botanical Garden Tharandt, Botanical Garden Berlin-Dahlem) and personally (Botanical Garden Dresden, Botanical Garden Pillnitz).

All reference samples are described in detail in chapter 4 in the form of tables within the chapters they are analysed. For every material the label, when known the year it arrived in the reference collection, the date of sampling, a picture and a detailed description is given.

Samples from the Vigani Cabinet

Samples from the Vigani Cabinet were sampled personally in April 2007 and March 2009 in the Queens' College, Cambridge, at the University of Cambridge. The first time only materials stored in the drawers and in already opened bottles or bottles with loose caps were sampled. The second time the restorer Lisa Stertz opened still closed bottles for further sampling. The sample of "Gum Anime" (A/5) was sampled by Dr. Brian Callingham in March 2011. They were stored in glass vials in the dark until analysis. Detailed descriptions of the materials and the sampling are given in chapter 5 together with their analysis.

3.1.2 Sample preparation

The sample preparation was adapted from literature (Koller, Baumer 2000) and presented in detail at the GCMS Workshop at the MASC Group Meeting in Philadelphia PA, USA, in september 2007 by Ursula Baumer (Baumer et al. 2009). Based on the extraction scheme, solvents are isooctane, methanol and a mixture of methanol and chloroform (3:7). Isooctane is used mainly for waxes, but also extracts neutral constituents of resins. Methanol is recommended for the dissolution of many resins, the methanol-chloroform mixture, however, only for shellack, bitumen and the soluble part of amber. In literature further solvents are given for the extraction of the soluble part of amber resins, mainly methanol and dichloromethane (Koller et al. 1997a; Czechowski et al. 1996; Baumer et al. 2007). The solubility in methanol is improved by heating at 40°C (Koller et al. 1997a).

The derivatisation agent is trimethylsulfoniumhydroxide (TMSH) (Yamauchi et al. 1979; Koller, Baumer 1997; Breidenich 2000; Baumer et al. 2007), which is available as a 0.25 molar methanol solution. It was added directly to the solvent extract (supernatant). The mixture was slightly shaken and injected. TMSH is suitable for carboxyl groups and aromatic hydroxyl groups (Yamauchi et al. 1979). An investigation on drying oils recommended a stoichiometric ratio of 2:1 for TMSH and fatty acids and about half an hour of reaction time (Dron et al. 2004). Heating the derivatized solvent extract for 10 minutes at 100°C increases the conversion rate (Yamauchi et al. 1979; Baumer et al. 2009).

The methanol extract is treated with oxalic acid in order to separate unmethylated resins acids. Oxalic acid causes a temporarily polarisation of the column and is useful in particular for the separation of resins with high amount of acids, which are not specific enough for identification (Koller et al. 1997b; Baumer et al. 2009). The acidified methanol extract has to be measured within 4 hours after preparation (Koller et al. 1997b).

This method was selected from a wide range of sample preparation methods presented in literature because a great variety in the chemical composition, solubility and derivatisation reactivity could be anticipated for the materials to be investigated. Additionally, the sample preparation was comparatively simple and sufficient for the pure samples from the Vigani Cabinet and a complex pre-treatment as it is common for mixed samples was not necessary.

All samples apart from amber were measured as their solvent extracts, solvents were isooctane and methanol. A sample (1 – 10 mg) was dissolved in 200 μl to 2 ml solvent in order to achieve a concentration of 5 mg/ml. The mixture was shaken and homogenized. The sample was centrifuged and the supernatant was removed. 200 – 300 μl of the solvent extract were mixed with 27 μl hexadecane and injected. Then 100 μl of this solution were transferred to an autosampler vial and 5 μl tridecanoic acid and 33 μl TMSH solution were added, slightly shaken and after half an hour injected. The remaining solvent extract was acidified with 10 to 20 mg oxalic acid (only for the methanol extract) and injected. The residue was evaporated to dryness under a gentle stream of nitrogen and dissolved in the following solvent and treated in the same way (Fig. 3.1 left).

In the case, the concentration was too high, 200 to 300 μl of the remaining original solvent extract were transferred and diluted with 1 to 1.5 ml solvent in order to achieve a concentration of 1 mg/ml. 160 μl hexadecane were added and the sample was injected. Then 100 μl of this solution were transferred to an autosampler vial and 5 μl tridecanoic acid and 7 μl TMSH solution were added and after half an hour injected. The remaining solvent extract was acidified with 110 to 170 mg oxalic acid (only for the methanol extract) and injected.

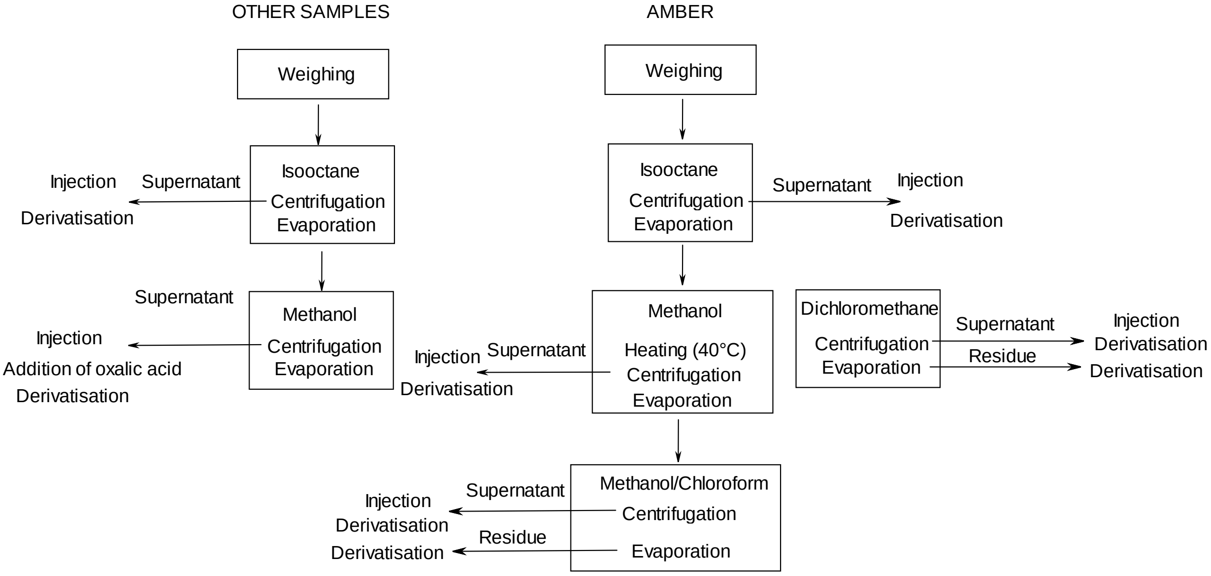


Fig. 3.1 Solvent extraction scheme

1 to 10 mg coarsely powdered amber samples were dissolved in isooctane. For the isooctane and methanol extracts the used quantities and concentrations were the same as for the other samples, except for the dilution, which was not necessary. They were centrifuged and the supernatant was removed. One part was injected and another was methylated with trimethylsulfoniumhydroxide (TMSH) at room temperature for half an hour. The residue was evaporated to dryness under a gentle stream of nitrogen and dissolved in methanol. The methanol extracts were heated at 40°C for 30 minutes and for 24 hours and proceeded as described for isooctane. The dried residue was dissolved in the methanol-chloroform mixture. After centrifugation, the supernatant was evaporated to dryness before 100 to 200 µl of the TMSH-solution, 10 µl hexadecane and 10 µl tridecanoic acid were added. This concentration step was included to improve the intensities. In the amber samples from the Cabinet (E/13 – E/16, chapter 5.4.1 – 5.4.4) the methanol-chloroform extract was heated after the TMSH-solution was added for 10 minutes at 100°C and injected. A second sample (1 - 10 mg) was dissolved in 200 µl to 2 ml dichloromethane, centrifuged and the supernatant removed. It was evaporated to dryness before 100 to 200 µl of the TMSH-solution, 10 µl of hexadecane and 10 µl tridecanoic acid were added.

The analyses done in this work showed that TMSH methylates only carboxyl groups under the described conditions. In some cases, mostly when the original compound was present in high amounts, also hydroxyl groups were methylated to a minor extent. This is also reported in literature (Yamauchi et al. 1979; Brondz 2002). Consequently, both compounds, the hydroxy-terpenoate and the methoxy-terpenoate, were present in the methylated extract. The reason is very likely that the reaction was carried out at room temperature, which prevented a complete conversion of hydroxyl groups. According to the literature, TMSH yield good results for aromatic hydroxyl groups and poor for others, but the experiments were carried out at reaction temperatures up to 100°C (Yamauchi et al. 1979). For this work a lower reaction temperature was chosen – except for some amber samples -, because of the sensitivity of the resin's constituents.

Whether a methylester or methoxyether is naturally or originates from the derivatisation, was visible from the chromatograms by comparison of the unmethylated and methylated extracts. When the unmethylated extracts are not shown, the presence of related compounds was examined during identification of the constituents of the methylated extract.

Natural methylester were generally seldom, and in case of their presence, this is discussed in the text.

With oxalic acid typical compounds present only in small amounts become visible. On the other hand oxalic acid increases the isomerisation process of resin acids in the solution, while the isomerisation rate can be very different. Pimarane acids are relatively stable, whereby abietanes acids are isomerised within minutes. The addition of oxalic acid increases the methylation of resin acids through the solvent, which can be observed always to a minor content. These methylesters proved to be relatively unstable compared to that formed with TMSH (own results).

Due to the differing solubility of the analysed samples, different solvents, methylation and the addition of oxalic acid were of varying significance. The state of investigation is also varying for the chemical and botanical different groups. Therefore, single chapters do not present the same selection of chromatograms. In the case, the methylated and unmethylated extracts are presented together, the methylated resin is treated as its methylester (for example abietate instead of abietic acid). Whether the methylesters are naturally or artificial can be seen from the text, the chromatograms and the compound tables.

3.1.3 Instrumentation

Analyses were carried out on a Varian GC-MS 4000 (ion trap) with split injection and an injection temperature of 250°C. A VF-5ht column (30 m x 0.25 mm ID x 0.1 μm df) was used (column A). Temperatures were: transfer line 280°C, source temperature 180°C. MS was carried out with extern electron ionisation (70eV), scan range from 50-500 and 50-600 m/z depending on the chemical class of the compounds and tuning with PFTBA. Helium was used as a carrier gas. Varian MS Workstation 6.6 was used for GC/MS control.

For the measurements carried out in June and July 2011 a Restek Rxi-5Sil MS column (30 m x 0.25 mm ID x 0.25 μm df) was used (column B). Due to the higher film thickness the retention times increased. Additionally, it was no high temperature column (maximum operating temperature 350 °C). The temperature program for triterpenes was modified accordingly. Although those experiments generated different retention times no change regarding the elution order was observed.

The oven program was dependent on the used solvent and the chemical class of the investigated compounds. All temperature programs used for the presented measurements are given in table 3.1. For diterpene materials mainly the program ‘Diterpenes’ was used, only Copaiba balsam (Diterpene 2) and the dichloromethane extracts of amber (Diterpene 3) were measured with a different temperature program. Copaiba balsam possesses a complex sesquiterpene fraction, whereas ‘Diterpene 2’ was modified for this region. Dichloromethane has a lower boiling point than methanol. For triterpene three different temperature programs were used. The aim was to optimize the elution with a simultaneous short acquisition time due to the high quantity of analysed materials. The composition within triterpene resins is highly variable and some materials consist of only few compounds present in high amounts, while others show a complex mixture of many different compounds. Therefore, different gradients within the triterpene region were tested. The temperature program ‘Triterpene 1’ was finally selected. Because several of the samples analysed with differing temperature programs (Triterpene 2, Triterpene 3), retention times may differ. The used temperature program is given for each compound table.

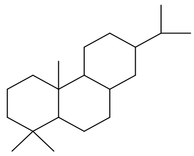
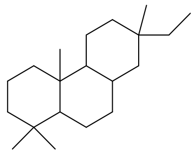
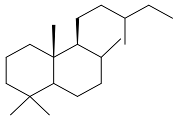
Name	Solvent	Temperature program, retention times of the terpene fractions	Reference materials	Vigani samples
Diterpenes 1	Isooctane, methanol, methanol-chloroform	**55°C (2min), 14°C/min to 200°C, 8°C/min to 320°C (2 min)** Monoterpene fraction t_R 0 – 8 minutes Sesquiterpene fraction t_R 6 – 12 minutes Diterpene section t_R 12 – 22 minutes */14 – 24 minutes*	Pinus cembra, P. pinaster, Picea abies, P. omorica, Larix decidua, L. gmelinii, L. kaempferii, Abies alba DD, 5.3.3, 5.3.4, VTII, 5.7.1, STI, 4.17.1, 4.1.2, 4.17.1, 4.1.1, 4.1.2, 4.1.7, BP1, BP3, VT5, 4.1.2aged, *4.7.1*, 4.7.6, *JC*, TADD, TABD, BLaD11, BLaD8, AABD, 4.3.6a, 4.3.6b, 4.15.1, 4.15.2	1/4, 1/8, 1/9, 1/10, 1/11, 1/13, 2/2, 2/3, *A/5*, A/23, A/26 E/13, E/14, E/15, E/16
Diterpenes 2	Methanol	**55°C (2min), 5°C/min to 200°C, 8°C/min to 320°C (2 min)** Sesquiterpene fraction t_R 13 – 28 minutes/*17 – 31 minutes* Diterpene section t_R 28 – 40 minutes/*31 – 42 minutes*	BLaD5, *5.1.3, 5.1.6*	
Diterpenes 3	Dichloromethane	**30°C (2 min), 14°C/min to 200°C, 8°C/min to 320°C (2 min)** Monoterpene fraction t_R 0 – 10 minutes Sesquiterpene fraction t_R 8 – 14 minutes Diterpene section t_R 14 – 24 minutes	4.3.6a, 4.3.6b	E/14, E/15
Triterpenes 1	Methanol	**55°C (2min), 8°C/min to 270°C, 2°C/min to 310, 8°C/min to 360°C (2 min)/ *350°C (no isotherm)*** Sesquiterpene fraction t_R 9 – 20 minutes/14 – 22 minutes Triterpene fraction t_R 27 – 52 minutes/29 – 54 minutes	PTDD, 4.4.21, 4.4.22, E1, 5.4.3, *4.15.1*, *4.15.2*, 5.6.1, 5.6.2/*5.6.2*, 5.2.2/*5.2.2*	1/14, A/11, 1/16, 2/4, A/24
Triterpenes 2	Methanol	**55°C (2min), 8°C/min to 290°C, 2°C/min to 360°C (2 min)** Triterpene fraction t_R 27 – 52 minutes	4.5.3, 4.5.4, 4.5.7, MaSI, MaSII	
Triterpenes 3	Methanol	**55°C (2min), 8°C/min to 360°C (2 min)** Triterpene fraction t_R 27 – 37 minutes	4.4.13, AS07	A/22, Z/1, A/21
Phenylpropanoids 1	Methanol	**55°C (2min), 8°C/min to 230°C, 4°C/min to 360°C (2 min)** Sesquiterpene fraction t_R 9 – 20 minutes		2/1
Phenylpropanoids 2	Methanol	**55°C (2min), 4°C/min to 270°C, 8°C/min to 360°C (2 min)** Sesquiterpene fraction t_R 16 – 37 minutes		1/31, Z/17

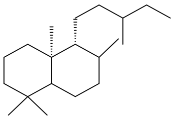
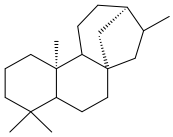
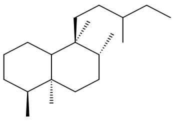
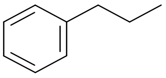
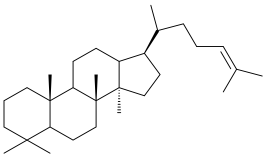
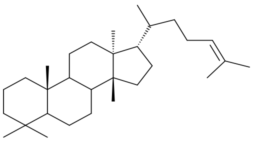
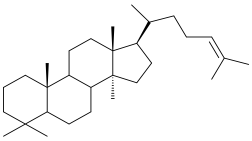
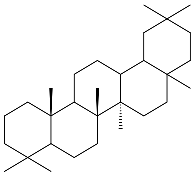
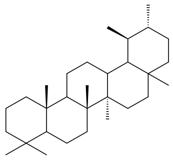
Tab. 3.1 Temperature programs used for the analyses presented in chapter 4 and 5, labels printed in italic were measured with a RESTEK column (column B), other with a Varian column (column A) (details see above)

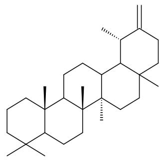
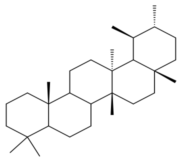
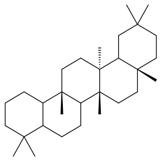
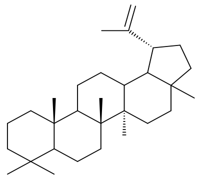
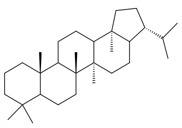
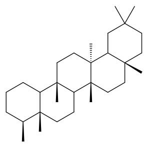
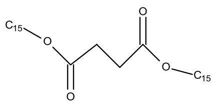
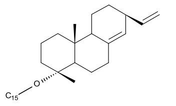
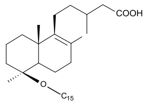
The phenylpropanoid materials from *Myroxylon* species analysed with 'Triterpenes 1' proved to generate poorly chromatograms because of the high amounts of some single compounds. Therefore, for the Vigani samples different temperature programs were tested in order to improve the results (Phenylpropanoids 1 and 2). The experiments did not yield satisfying chromatograms.

3.1.4 Data-Evaluation

The data achieved from the GC-MS instrument were surveyed with MS Workstation 6.6 on the GC-MS control station. AMDIS was used for further chromatographic and mass spectroscopic evaluation. A self-developed database composed of mass spectra from the measurement of reference samples was then used for the evaluation of the samples from the Vigani Cabinet. Identification of mass spectra was obtained by comparing them with data from different sources. The main source was the database of the National Institute of Standards and Technology (NIST). Additionally, a collection of mass spectra kindly provided by Dr. Patrick Dietemann was used (Dietemann 2007) and a variety of published mass spectra from literature. The source for its identification is given for each compound in the compound tables shown in the appendix. In some case the retention time and elution order were used for the identification, then t_R is given. This is mainly the case for not methylated resin acids, of which no mass spectral data are available, but which have highly characteristic mass spectra.

Group	Base structure	Chapter, notes	Figures	Label
Monoterpenes	C_{10}	2.3.2, 2.4, 4.3	2.16	M
Sesquiterpene	C_{15}	Mono- and bicyclic compounds, 2.2, 2.4, 4.2.1, 4.2.3, 4.3.1	2.7, 2.16	S
Diterpenoids	C_{20}	Diterpenes with an unknown structure or compounds derived from diterpenes (f.i. by degradation); structures with no own category	2.16	D
Abietane		2.1, 2.4, 4.1, 5.1	2.2, 2.6	A
Pimarane		2.1, 2.4, 4.1, 5.1	2.2, 2.6, 2.16	P
Labdane		2.1, 4.1, 4.2, 5.1, 4.4, 5.4	2.2, 2.6, 2.8, 2.16	L

Group	Base structure	Chapter, notes	Figures	Label
ent-Labdane		2.2, 4.2, 5.2	2.8	eL
Kaurane		2.2, 4.2.1, 5.2.1	2.8	K
Clerodane		2.2, 4.2.1, 4.2.2, 5.2	2.8	C
Phenylpropanoid		Natural metabolites derived from cinnamic acid; see also biosynthesis in the appendix; 2.2, 5.2.4-5.2.6	2.9	PP
Triterpenes	C_{30}	Unknown structure; structures with no own category		T
Dammaranes		Includes (via loss of the side chain) C_{22}-derivatives of dammaranes called mansumbuiones; 2.2, 2.3, 4.3, 5.3	2.9, 2.10, 2.16	Da
Tirucallanes		2.3, 4.3, 5.3	2.10, 2.13	Ti
Lanosterane		2.3, 4.3.1, 5.3.1, 5.3.2	2.10	La
Oleananes		2.2, 2.3, 4.2.3, 4.3, 5.3	2.9, 2.10, 2.13	Ol
Ursanes		2.2, 2.3, 4.3, 5.3	2.9, 2.13	Ur

Group	Base structure	Chapter, notes	Figures	Label
Taraxastane		2.3, 4.3.2, 5.3.3-5.3.6	2.13	Ta
Baueranes		4.3.2, 5.3		Ba
Glutinanes		4.3.2, 5.3		Gl
Lupanes		2.2, 2.3, 4.3, 5.3	2.10, 2.13	Lu
Hopanes		2.2, 4.2.3	2.9	Ho
Friedelanes		5.3	2.13	Fr
(Di)monoterpanyl succinates		2.4, 4.4, 5.4	2.15	(d)MS
Monoterpanyl diterpenoates		2.4, 4.4, 5.4	2.15	MD
Monoterpanyl labdanoates		2.4, 4.4, 5.4	2.15	ML

Tab. 3.2 Principal structures and labels of identified compounds

All compounds are listed in tables in the corresponding chapter with their label, retention time and characteristic mass fragments. The base peak is given in bold, the molecular ion underlined. They were labelled according to the chemical class they belong to with a letter and then numbered consecutively according to their retention time. Base structures of compounds found in this work are given in table 3.2 above. In case the compound could not be identified it was labelled with ‘U’ for unknown. All compounds mentioned in the text and tables are listed arranged by their base structures in the appendix, where a literature reference is given, which was used for their identification. The elution order proved to be most important for an unambiguous identification as well, which is also referenced in the appendix. In some case the base structure was deducible from the mass spectrum, even though no identification could be achieved.

3.2 Fourier transformation infrared spectroscopy

3.2.1 Sample preparation

The samples from the Vigani cabinet were mechanically prepared on a diamond anvil cell (High Pressure Diamond Optics).

3.2.2 Instrumentation

Analyses were carried out on a Fourier transformation infrared microscope from Bruker Hyperion 2000/Tensor 27 in transmission mode with a 4 cm^{-1} resolution, sample 32 scans.

3.2.3 Data evaluation

The data achieved from the Fourier transformation infrared microscope were surveyed with OPUS. Peaks were identified by automatic peak identification with OPUS between 4000 and 580 cm^{-1}.

4. RESULTS – REFERENCE MATERIALS

The compilation of literature data on resin chemistry presented in chapter 2 provides a basis for further investigations. Chapter 2.5 outlines research deficits with regard to the materials from the Vigani Cabinet, which need analyses. In order to gain data profiles for the different resin groups and to answer some of the questions raised in chapter 2.5, reference materials were selected for chemical analysis. The presentation of this chapter is arranged corresponding to the presentation of chapter 2.

References of Gymnosperm resins (chapter 2.1) are presented in chapter 4.1. Literature provides abundant and detailed data for this group, the investigation therefore focuses on a chemotaxonomic differentiation of the different genera. For this purpose, a wide range of botanical samples are analysed in addition to samples taken from reference collections.

References of Angiosperms resins from Fabaceae (chapter 2.2) are presented in chapter 4.2. For some genera, in particular *Copaifera* resins, plenty of data has been presented in the literature. Other genera have not been examined in such a detail. For these other genera, the chapter focuses on the identification of compounds found in references by their mass spectra. Because no reliable botanical samples were available, only samples taken from reference collections are analysed.

References of Angiosperm resins from Sapindales (chapter 2.3) are in the focus of chapter 4.3. *Pistacia* resins have been broadly examined, systematic data for the large number of resins from the Burseraceae, however, are rare. Due to the lack of reliable botanical samples, the chapter focuses on the connection between nomenclature and chemical composition.

Baltic amber (chapter 2.4) is presented in chapter 4.4, with a main focus on sample preparation and solubility.

Each chapter concludes with a summary of the presented data. In chapter 4.5 the results are discussed with regard to research deficits given in chapter 2.5 and the analysis of the materials from the Vigani Cabinet.

4.1 Gymnosperm resins – conifer resins and products

In this chapter, references of coniferous resins from the families Pinaceae (4.1.1), Cupressaceae (4.1.3) and Araucariaceae (4.1.3) are investigated. Literature data (chapter 2.1) suggest a very consistent chemical composition within a genus but differences between the families. Therefore an analysis of a variety of reference materials is carried out in order to gain a data profile on the chemical composition of resins from this order. The aim of the investigation is to achieve a more detailed picture of the connection between botanical origin and chemical composition on the one hand and nomenclature on the other.

4.1.1 Pinaceae – Coniferous turpentines

Several reliable botanical samples from the main genera of Pinaceae (table 4.1) are analysed in order to identify phytochemical markers. In the following, various commercially available materials are investigated (table 4.6) to acquire a more detailed picture regarding the connection between modern terminology and phytochemical marker compounds (chapter 4.1.1.1). Modern materials are labelled as turpentines (German Terpentin), which refers to the semi-liquid resin and not the distilled oil. The origin of the term is discussed in chapter 5.1.1, ‘terminology’. The botanical origin of such materials is shown in table 2.1.

For the investigation of Burgundy pitch, the aging characteristic of Pinaceae resins, either caused by light aging or by heating, are examined as well (chapter 4.1.1.2).

4.1.1.1 Phytochemical markers – detection of adulterations

Botanical samples

For the investigation four samples of *Pinus*, three of *Picea*, three of *Larix* species and two of *Abies alba* Mill. are analysed. All botanical samples are described in table 4.1. Results are summarised in table 4.2.

In Fig. 4.1, the chromatograms of the (methylated) methanol extracts of the resins from two *Pinus* and one *Picea* species are shown as examples for these analyses. All three contain high relative amounts of pimaranes and abietanes such as pimaric, sandaracopimaric, isopimaric, palustric, abietic and neoabietic acid and their methylester, respectively. *Picea* species contain more sandaracopimarate than pimarate, and *Pinus* species contain more pimarate than sandaracopimarate (Fig. 4.1a, b). The resins of *Picea abies* and *P. pungens* contain cembrene, iso-cembrol, Δ13-trans-, *cis*- and *trans*-abienols (Fig. 4.1e), that of *P. omorica* epimanool, *iso*-abienol, abienol, high amounts of *cis*-abienol and lower of *trans*-abienol (not shown). Such compounds were found in none of the analysed *Pinus* species. The only exception from these findings is the resin of *Pinus cembra*, which contains no pimaric and high amounts of the labdane lambertianate and relatively high amounts of isopimarate (Fig. 4.1c). It also contains cembrene, iso-cembrol (Fig. 4.1f). Palustrate is not present. Both, the relatively higher amounts of isopimaranes and the presence of high amounts of labdane acids relates to literature data for pine species from the subsection Strobus (see table 2.2).

The abietane acids and their methylester, respectively, show a distribution depending on the aging state of the resins. The two *Picea* resins, which were still sticky when sampled (*Picea abies, Picea pungens*, see table 4.1), contain decreasing relative amounts with increasing retention time: high amounts of palustrate, intermediate of dehydroabietate and lower of abietate and neoabietate (Fig. 4.1b). In contrary, dried up samples (all *Pinus* species, *Picea omorica*, see table 4.1), contain high relative amounts of dehydroabietate flanked by intermediate amounts of palustrate, abietate and small amounts of neoabietate (Fig. 4.1a). That bell-curved shape visible in the analysis is typical for an advanced isomerisation process of the abietane acids (see Fig. 2.3).

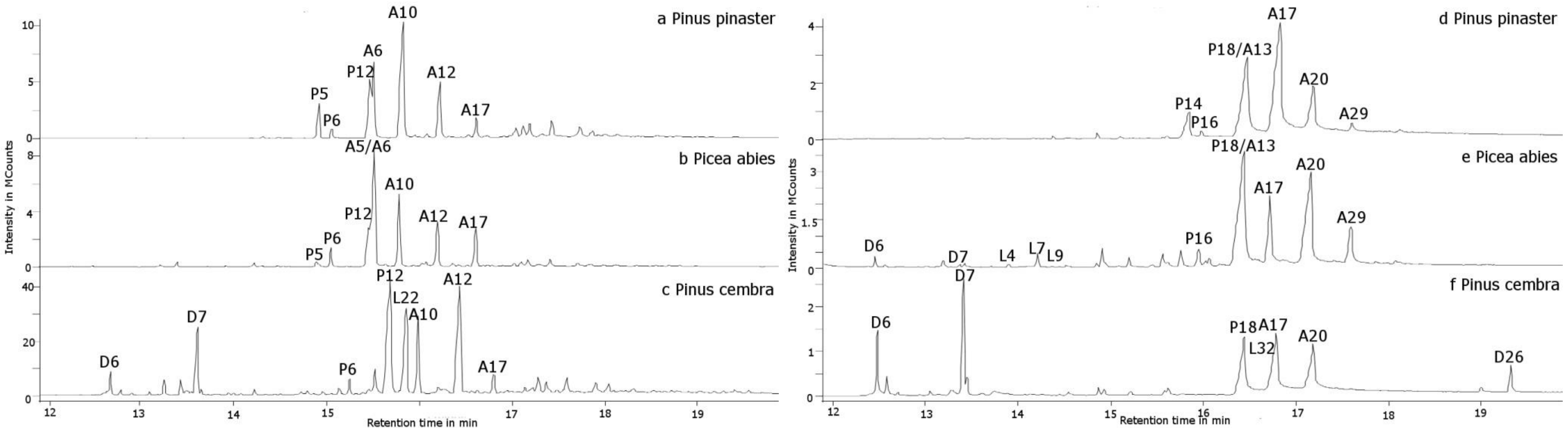
In Fig. 4.2, the chromatograms of the (methylated) methanol extracts of the resins from three *Larix* species are shown. All of them contain mainly sandaracopimaric, isopimaric, dehydroabietic and abietic acids and their methylester, respectively. The resin of *Larix decidua* contains in addition palustrate and neoabietate, that of *L. gmelinii* neoabietate acids (Fig. 4.2a). No pimarate is found in the samples.

All *Larix* resins contain high amounts of epimanool, larixol and larixylacetate. In the resin of *Larix decidua* larixol and larixylacetate are the main constituents (Fig. 4.2d). The resin of *L. gmelinii* contains significant amounts of larixol and lower amounts of larixylacetate, the resin of *L. kaempferi* small amounts of both compounds (Fig. 4.2d-f). Both, however, contain high relative amounts of epimanool, similar to the resin of *L. decidua*. In addition, the resins of *L. kaempferi* contains small amounts of cembrene (Fig. 4.2e, f).

The resin of *L. decidua* shows an abietane acid distribution similar to that of less aged *Picea* resins, however dehydroabietate is present in lower amounts compared to the other abietanes in *L. decidua*. Similar results are obtained for the resin of *L. gmelinii*, which is in a more advanced aging state. Finally, the resin of *L. kaempferii* contains high amounts of dehydroabietate but also of isopimarate.

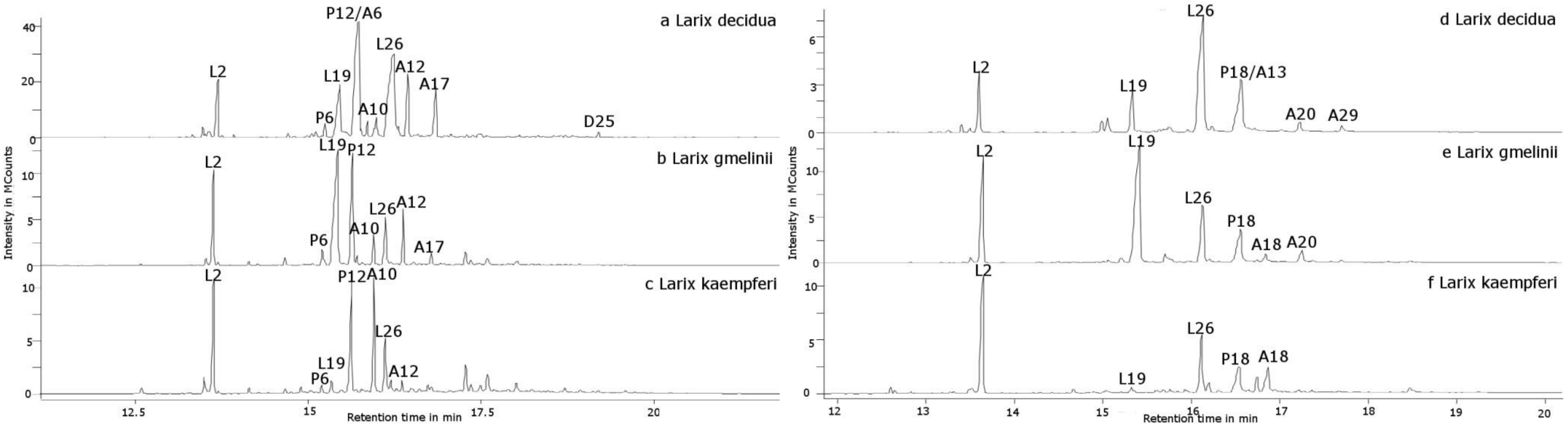
Label	Description	Picture	Sampling: date; description
Pinus nigra	*Pinus nigra* J. F. Arnold Botanical Garden Tharandt		05.04.2008; almost globular pieces, dark yellow, dark red to brown, weathered surface, inside dark red and opaque; weak smell of pine
Pinus sylvestris	*Pinus sylvestris* L. Botanical Garden Tharandt		05.04.2008; small pieces with a green, white and mossy surface, somewhat moldy; colour from dark red (inside) to brown (surface); opaque with a few small yellow spots; faint spicy resinous smell
Pinus cembra	*Pinus cembra* L. Botanical Garden Tharandt		05.04.2008; black brown, sticky mass with a few very viscous pieces and small yellow spots; smell of pine with a faint medical scent
Pinus pinaster	*Pinus pinaster* Aiton Botanical Garden Tharandt		05.04.2008; small yellow pieces, transparent; faint smell of pine
Picea abies	*Picea abies* (L.) H. Karst. Botanical Garden Tharandt		05.04.2008; sticky mass with single very viscous pieces; yellow, orange and brown colour; smell of pine
Picea omorica	*Picea omorica* (Pančić) Purk. Botanical Garden Tharandt		05.04.2008; dirty yellow and sticky pieces; faint smell of pine
Picea pungens	*Picea pungens* Engelm. Botanical Garden Tharandt		05.04.2008; yellow, red and black crumbly mass, somewhat sticky, smell of pine
Larix decidua	*Larix decidua* Mill., Sylvan Botanical Garden Tharandt		05.04.2008; dirty white to yellow, cloudy, very viscous liquid with dirt and pieces of the bark; another sample contains dried up more solid orange to red pieces; sample was sent in a plastic bag, which was leak
Larix gmelinii	Larix gmelinii var. japonica (Larix gmelinii (Rupr.) Rupr. var. japonica (Maxim. ex Regel) Pilg.), Botanical Garden Pillnitz		March 2009; a piece of the bark covered with resin exuded after pruning; surface dark green and mossy, some yellowish, glossy and sticky drops from inside are sampled, resinous medical smell
Larix kaempferi	*Larix kaempferi* (Lamb.) Carr., Botanical Garden Pillnitz		March 2009; a piece of the bark covered with resin exuded after pruning; surface dark green and mossy with yellowish and glossy drops inside, which are viscous but more solid than that of Larix gmelinii
Abies alba DD	*Abies alba* Mill., Botanical Garden Dresden		17.02 2009: small drop of resin from the bark of a detached tree, pale yellow colour and opaque
Abies alba PD	*Abies alba* Mill., Botanical Garden PD		12.03.2009; small white to yellowish and dark drops taken directly from the bark, opaque

Tab. 4.1 Description of botanical reference samples analysed in chapter 4.1.1.



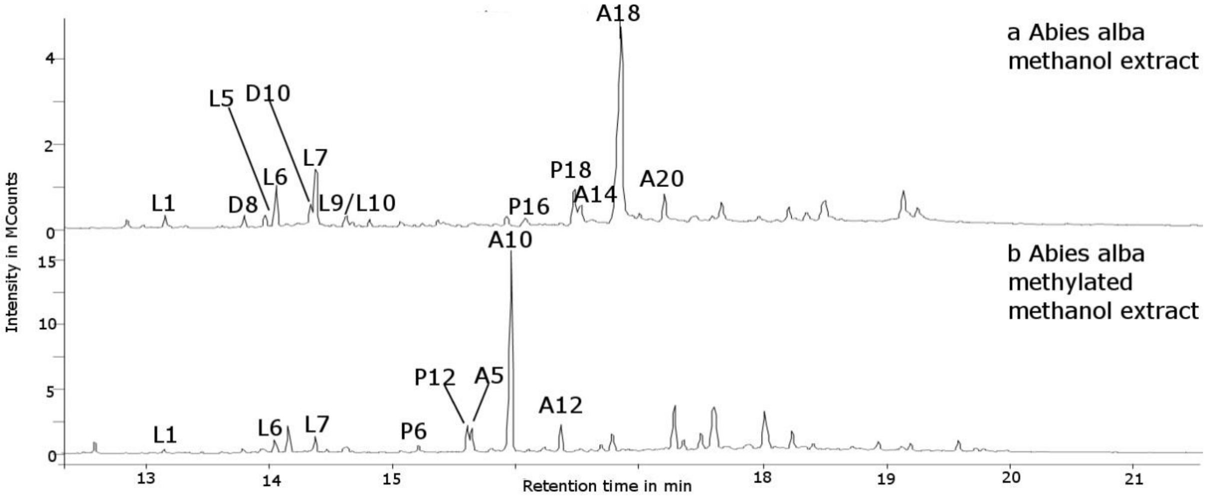
Left – methylated methanol extracts, right – methanol extracts, a, d - Pinus pinaster, b, e - Picea abies and c, f - Pinus cembra (labels, see table 4.3)

Fig. 4.1 Gas chromatograms of resins from different genera of Pinaceae, diterpene section (TIC)



Left – methylated methanol extracts, right – methanol extracts, a, d - *Larix decidua* , b, e - *Larix gmelinii* and c, f - *Larix kaempferi (labels, see table 4.3)*

Fig. 4.2 Gas chromatograms of resins from different species of Larix, diterpene section (TIC)



Top (a) - *methanol extract and bottom (b) - methylated methanol extract (labels, see table 4.3)*

Fig. 4.3 Gas chromatograms of the resin from Abies alba DD, diterpene section (TIC)

Fig. 4.3 shows the chromatograms of the (methylated) methanol extracts of the resin from *Abies alba* DD. The sample contains epimanoyloxide, compound D8, *iso*-abienol, abienol, compound D10, high amounts of *cis*-abienol, lower amounts of compound L10 and *trans*-abienol (Fig. 4.3a). It contains mainly sandaracopimaric, isopimaric, dehydroabietic, abietic and neoabietic acids and their methylester, respectively. The main compound is dehydroabietate (Fig. 4.3b). No pimarate and palustrate are present. Instead of palustrate, the sample contains the compound A5. Its mass spectrum resembles that of levopimarate. The same compound is found in the sticky resins from *Pinus cembra*, *Picea abies* and *Picea pungens*, but not in the dried up resins from *Picea omorica*, the remaining *Pinus* and none of the *Larix* resins. In methanol extracts the corresponding acid is present as well (A14). Levopimaric acid is known to be usually present only in fresh resins (van den Berg et al. 2000). In literature, the isomerization of abietanes to abietic acid was found to be reversible (Takeda et al. 1968). Additionally, dehydroabietic acid is reported to be produced by air oxidation not from abietic

	Pinus	Picea	Larix	Abies alba
				
Pimaranes	More pimaric than sandaracopimaric acid	More sandaracopimaric than pimaric acid	No pimaric acid	No pimaric acid
Others	*P. cembra*: high amounts of isopimaric acid		High amounts of isopimaric acid	
Marker	*P. cembra*: cembrene, cembrol, lambertianic acid	*P. abies, P. pungens*: cembrene, cembrol, Δ13-*cis*-neoabienol, *cis*-/*trans*-abienol *P. omorica*: epimanool, (*iso*-) abienols, *cis/trans*-abienols	Epimanool, larixol, larixylacetate	Epimanoyloxide, D8, D10, (*iso*-)abienols, *cis*-/trans-abienols, L10

Tab. 4.2 Characteristic compounds of botanical reference samples analysed in chapter 4.1.1.1

acid but from levopimaric and palustric acids (Enoki 1976). Because compound A5 and A14 are present only in slightly aged samples, levopimaric acid is probably an intermediate product of the isomerization process. It seems that, after the almost complete isomerization to abietic acid, small amounts of levopimaric acid are regenerated and can be further oxygenated to dehydroabietic acid. The other sample of *Abies alba* Mill. (Abies alba PD) is composed similiar.

Label	t_R	Name	Main mass fragments
D6	12.48	Cembrene	79, **93**, 105, 119, 145, 229, 257, 272
L1	13.16	Epimanoyloxide	81, 177, 191, **257**, 275, (290)
D7	13.41	*iso*-Cembrol	81, **93**, 107, 121, 147, 189, 229, 257, 272, 290
L2	13.49	Epimanool	**81**, 95, 137, 257, 272, (290)
D8	13.69	Unidentified	**67**, 81, 95, 109, 123, 135, 191, 207, 235
L4	13.89	∆13-*cis*-neoabienol	81, 95, 107, 121, **177**, 191, 290
L5	14.05	iso-Abienol	81, 95, 109, **191,** 217, 235, 255, 272, 290
L6	14.05	Abienol	81, 95, 109, **191,** 217, 235, 255, 272, 290
D10	14.34	Unidentified	81, 95, **109**, 121, 161, 217, 235, 245, 260, 278
L7	14.37	*cis*-Abienol	81, 95, **119**, 134, 163, 191, 257, 272, (290)
L9	14.59	*trans*-Abienol	81, 95, **119**, 134, 163, 191, 257, 272, (290)
L10	14.63	Unidentified abienol	81, 95, 109, **191**, 217, 234, 255, 272, (290)
P5	15.11	Pimarate	**121**, 241, 257, 301, 316
P6	15.24	Sandaracopimarate	**121**, 241, 301, 316
L19	15.45	Larixol	69, **109**, 119, 153, 187, 255, 273, 288, (306)
P12	15.62	Isopimarate	187, 227, **241**, 256, 287, 316
A5	15.67	Levopimarate	**92**, 105, **121**, 146, 187, 241, **316**
A6	15.67	Palustrate	**241**, 301, 316
L22	15.84	Lambertianate	81, **121**, 189, 330
A10	15.98	Dehydroabietate	**239**, 299, 314
P14	15.84	Pimaric acid	91, 107, **121**, 133, 241, 287, 302
L26	16.23	Larixylacetate	79, 105, **153**, 185, **255**, 270, 288, 348
P16	15.98	Sandaracopimaric acid	91, 107, **121**, 133, 241, 287, 302
P18	16.33	Isopimaric acid	91, 105, 131, 159, 187, 227, **241**, **287**, 302
A12	16.39	Abietate	185, 213, **241**, 256, 273, 316
A13	16.44	Palustric acid	91, 133, 159, 187, 213, 241, **287**, 302
A14	16.52	Levopimaric acid	**92**, 105, 131, 146, 187, 302
L32	16.74	Lambertianic acid	81, 93, 107, **121**, 147, 161, 189, 255, 316
A17	16.78	Neoabietate	121, **135**, 301, 316
A18	16.80	Dehydroabietic acid	197, **239**, 285, 300
A20	17.15	Abietic acid	105, 131, 185, 213, 241, 259, 287, **302**
A29	17.58	Neoabietic acid	91, **135**, 148, 187, 241, 287, 302
D25	19.19	Unidentified	121, 233, 267, 287, **302**, 347, 362
D26	19.32	Unidentified	91, **121**, 159, 189, 217, 271, 287, 314

Tab. 4.3 Compounds found in samples analysed in chapter 4.1.1.1, methanol and methylated methanol extracts, samples analysed with temperature program Diterpenes 1 and column A, mass spectra references see appendix

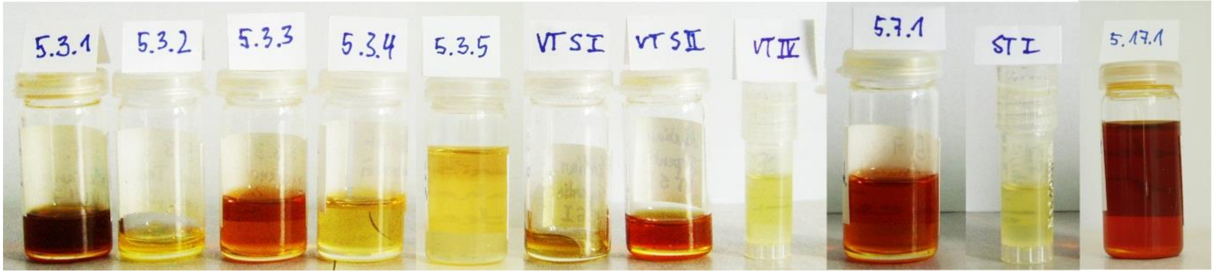


Fig. 4.4 Analysed samples of Venetian (5.3.1-5.3.5, VTSI, VTSII, VTSIV) and Strasbourg turpentines (5.7.1, STI, 5.17.1)

Commercial samples

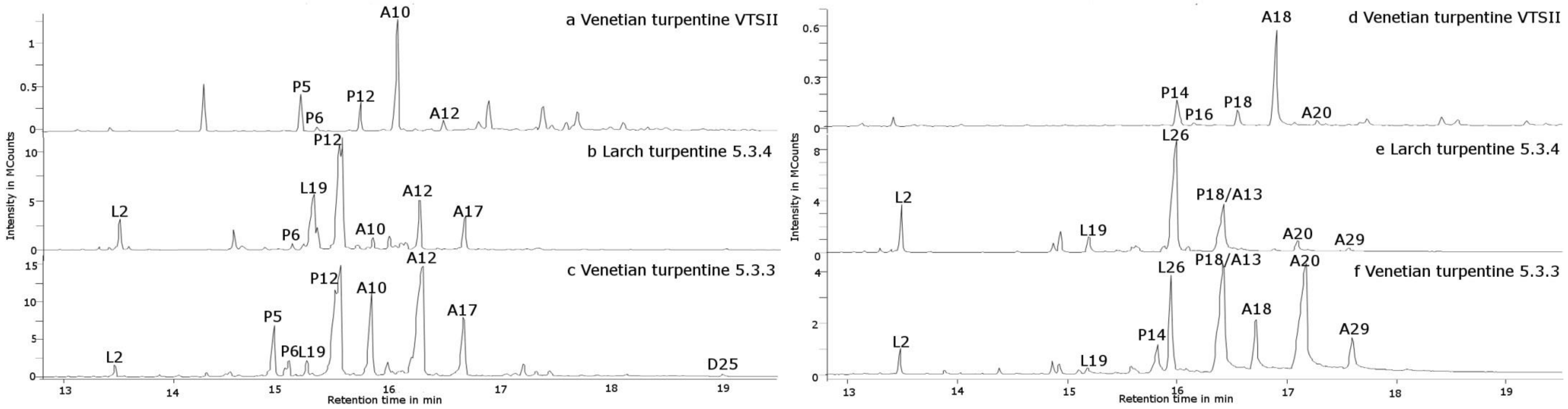
Venetian turpentine

Eight modern materials labelled as Venetian turpentine are analysed (Fig. 4.4, table 4.6). In table 4.4 the results from the analysis of commercial Venetian turpentines are summarized. The analysed samples split up into three groups, which is shown in Fig. 4.5 as examples for the conducted studies. The (methylated) methanol extracts contain pimarane and abietane acids such as sandaracopimaric, isopimaric and abietic acids together with changing amounts of dehydroabietic acid and their methylester, respectively.

The first group includes two samples (VTSII, 5.3.1). 5.3.1 is of dark brown, VTSII of brown colour (Fig. 4.4). Both materials were refilled and labelled manually as Venetian turpentine (see table 4.6). They contain in addition to the above mentioned compounds pimaric acid and its methylester, respectively. The main constituent is dehydroabietate together with small relative amounts of abietate. 5.3.1 also contains small amounts of palustrate, which are not present in VTSII (Fig. 4.5a). No epimanool, larixol and larixylacetate are found (Fig. 4.5d). Therefore, both materials are not larch, but pine resins.

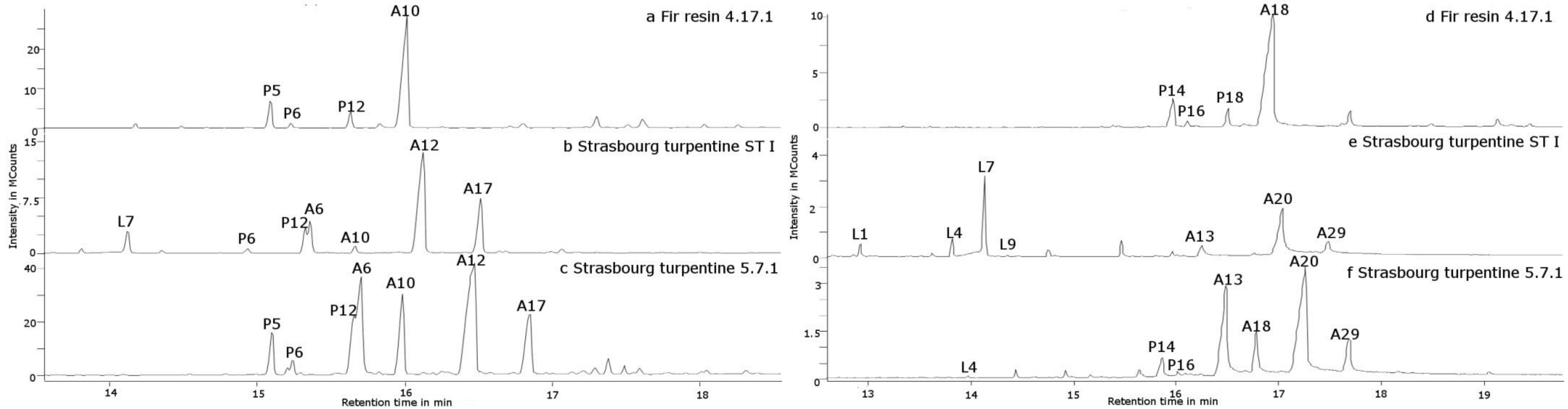
The second group includes five samples (VTSI, VTSIV, 5.3.2, 5.3.4, 5.3.5). All have a yellow colour, VTSI is somewhat darker than the other samples (Fig. 4.4). They contain in addition to the above mentioned compounds palustric, neoabietic acids and their methylester, respectively. Pimarate is not present. The main constituent is palustrate together with intermediate relative amounts of abietate and neoabietate. Dehydroabietate is present only in small relative amounts (Fig. 4.5c). That distribution is nearly identical with that found for the resin of *Larix decidua* Mill (Fig. 4.2a). Two samples (VTSI, 5.3.2) do not contain neoabietate, 5.3.2 also not palustrate (not shown). This corresponds with their age, which is higher than for the other samples (see table 4.6). The more advanced aging state results in lower amounts of palustrate and neoabietate. All samples contain epimanool, larixol, larixylacetate in high amounts (Fig. 4.5d). They are therefore pure larch turpentine.

The remaining sample 5.3.3 is a commercial Venetian turpentine from Kremer, described as a mixture of larch turpentine and colophony. It has of the same colour as VTSII (Fig. 4.4). It contains in addition to the above mentioned pimaric, palustric and neoabietic acids and their methylester, respectively. Pimarate and sandaracopimarate are present in a ratio, which is, as discussed above, typical for pine resins. The main constituents are palustrate and abietate together with intermediate relative amounts of dehydroabietate and neoabietate (Fig. 4.5b). The sample also contains epimanool, larixol and larixylacetate, however in lower amounts compared to the diterpene acids and to pure larch resin (Fig. 4.2d, Fig. 4.5e). The distribution neither resembles that of the more aged *Larix* resins (Fig. 4.2b, c, e, f) nor that of less aged Pinaceae resins (Fig. 4.1c, e). The original abietane acid composition was modified by the addition of colophony, which is composed of high relative amounts of dehydroabietic acid



Left – methylated methanol extracts, right – methanol extracts, a, d - VTSII, b, e - 5.3.4 and c, f - 5.3.3 (labels, see table 4.3)

Fig. 4.5 Gas chromatograms of commercial Venetian turpentines, diterpene section (TIC)



Left – methylated methanol extracts, right – methanol extracts, a, d - 4.17.1, b, e – ST I and c, f 5.7.1 (labels, see table 4.3)

Fig. 4.6 Gas chromatograms of commercial Strasbourg turpentines, diterpene section (TIC)

Venetian turpentine, number and label							
5.3.1, AFAD	5.3.2, Kremer	5.3.3, Kremer	5.3.4, Kremer	5.3.5, Schmincke	VTSI, AFAD	VTSII, AFAD	VTSIV, Schmincke
Venetian turpentine	Venetian turpentine	Venetian turpentine	Larch turpentine	Venetian turpentine	Venetian turpentine	Venetian turpentine (manually)	True larch turpentine
							
Marker compounds							
No	Epimanool, larixol, larixylacetate	Epimanool, larixol, larixylacetate (little)	Epimanool, larixol, larixylacetate	Epimanool, larixol, larixylacetate	Epimanool, larixol, larixylacetate	No	Epimanool, larixol, larixylacetate
Abietane acids							
Mainly DHA, few abietic	Mainly DHA, very small abietic	Mainly palustric & abietic, smaller DHA & neoabietic	Mainly palustric, smaller abietic & neoabietic	Mainly palustric, smaller abietic & neoabietic	Mainly DHA, very small abietic	Mainly DHA, few abietic	Mainly palustric, smaller abietic & neoabietic
Pimarane acids							
More pimaric then Sandarcopimaric	No pimaric	More pimaric then Sandarcopimaric	No pimaric	No pimaric	No pimaric	More pimaric then Sandarcopimaric	No pimaric
Aging markers (methylated)							
A16, A22, A28, A32	A22, A28, A32				A16, A22, A24, A28, A32	A16, A22, A28, A32	
Assignment							
Pine resin	Aged larch resin	Mixture of colophony and larch resin	Larch resin	Larch resin	Aged larch resin	Pine resin	Larch resin

Tab. 4.2 Characteristic compounds of commercial Venetian turpentines analysed in chapter 4.1.1.1; DHA – dehydroabietic acid, for the labels of the aging markers see table 4.7 in chapter 4.1.1.2

Strasburg turpentine, number and label		
 5.7.1, Kremer Strasbourg turpentine, dark from Russia	 STI, Strasbourg turpentine, Austria	 4.17.1, AFAD Fir resins
Marker compounds		
Δ13-*cis*-neoabienol	Δ13-*cis*-neoabienol, *cis*-/trans-abienols	No
Abietane acids		
Mainly palustric & abietic, smaller DHA & neoabietic	Mainly abietic, smaller palustric & neoabietic	Mainly DHA, small of abietic
Pimarane acids		
More pimaric then Sandaracopimaric acid	No pimaric acid	More pimaric then Sandaracopimaric acid
Aging markers		
A_{22}, A_{24}, A_{28}		A_{16}, A_{22}, A_{28}, A_{32}, A_{36}
Assignment		
Mixture of colophony and fir or spruce resin	Fir resin or spruce resin; probably an old product sold by Kremer until 2007	Pine resin

Tab. 4.3 Characteristic compounds of commercial Strasbourg turpentines analysed in chapter 4.1.1.1, DHA – dehydroabietic acid, for the labels of the aging markers see table 4.7 in chapter 4.1.1.2

with intermediate amounts of palustric, abietic and neoabietic acids (see chapter 4.1.1.2). As a result, the mixture contains lower amounts of dehydroabietate, compared to a pure pine resin, but higher compared to a pure larch resin. The amounts of palustrate and abietate are higher, those of labdane alcohols lower, compared to pure larch resin.

Strasbourg turpentine

Two modern materials labelled as Strasbourg turpentine (STI, 5.7.1). A semifluid resin in a glass bottle with the label “fir resin” attached is analysed as well (see table 4.6). In table 4.5 the results from the analysis of commercial Strasbourg turpentines are summarised. Fig. 4.6 shows the chromatograms of the (methylated) methanol extracts of the three samples. All of them contain mainly pimarane and abietane acids such as sandaracopimaric, isopimaric and dehydroabietic acids and their methylester, respectively.

The fir resin (4.17.1) additionally contains pimaric and small amounts of abietic acids and their methylester, respectively. Pimarate and sandaracopimarate acids are present in a ratio, which is, as discussed above, typical for pine resin. Dehydroabietate is the most prominent constituent (Fig. 4.6a). The distribution of the abietane acids is typical for an advanced isomerisation process as it is discussed above. The composition of this material is nearly identical with that of the samples 5.3.1 and VTSII (Fig. 4.5a, d). It is also of a dark brown colour (Fig. 4.4).

The light yellow Strasbourg turpentine (STI, Fig. 4.4) additionally contains palustric, abietic and neoabietic acids and their methylester, respectively. Pimarate is not present. The main constituent is abietate together with intermediate relative amounts of palustrate and neo-

Label	Description	Picture	Sampled; date, description
5.3.1	Venetian Turpentine, VK 1977, AFAD material collection		June 2008; dark brown and very liquid resin, intense smell of pine
5.3.2	Venetian Turpentine, H. Klein Dresden, AFAD material collection, the paper indicates the first half of the 20th century		June 2008; dark yellow very viscous resin, faintmedical smell
5.3.3	Venetian Turpentine, Kremer (#62010), 2008, mixture of larch and colophony, AFAD material collection		June 2008; pale brown and very liquid resin; transparent; intense smell of pine, medical scent somewhat fainter than that of 5.3.2
5.3.4	Larch Turpentine, Kremer (#62000), 2008, AFAD material collection		May 2008; light yellow and liquid resin; transparent; strong smell of pine
5.3.5	Venetian Turpentine, Schmincke (#50073), 2009, AFAD material collection		May 2009; light yellow and viscous resin; medical resinous smell, for the analysis dried up drops from the cap were sampled
VTSI	Venetian Turpentine, H. Neisch & Co, Dresden (1873-1970?), Ulrich Schießl		April 2008: light yellow and transparent resin; viscous with a dried up surface layer, smell of pine like 5.3.1
VTSII	Venetian Turpentine, labelled manually bottle originally filled with painting materials, AFAD material collection		April 2008; brown transparent semiliquid resin; resinous medical smell
VTSIV	"True larch turpentine", Schmincke (#50073), Laboratory of the Saxon State Authority for the Conservation of Monuments, 2008		July 2008; light yellow, transparent and viscous resin
5.7.1	Strasbourg Turpentine, dark, from Russia, Kremer (#62040), 2008, contains colophony		June 2008; brown and transparent resin; liquid after purchase, became viscous and crystalized within one year; medical smell stronger than 5.3.2
ST I	Strasbourg Turpentine, Austria, Laboratory of the Saxon State Office for the Conservation of Monuments, 2008		July 2008; probably an older product sold by Kremer before the middle of 2007 (#62044); light yellow, transparent and viscous resin; strong smell of pine
4.17.1	„Fir resin", State Office for the Conservation of Monuments Halle		12.02.2009; brown and transparent semiliquid resin; strong resinous medical smell

Tab. 4.4 Description of commercial turpentine reference samples analysed in chapter 4.1.1.1

abietate. It contains only small relative amounts of dehydroabietate (Fig. 4.6c). It contains epimanoyloxide, Δ13-*cis*-neoabienol, high amounts of *cis*- and low of *trans*-abienol (Fig. 4.6f). Δ13-*cis*-neoabienol is found above only in *Picea* resins, notable that from *Picea abies* and *P. pungens* (Fig. 4.1e). The absence of pimaric acid and the presence of epimanoyloxide and *cis*-abienol in STI, however, point to an *Abies* resin. Because no iso-abienol and abienol are present, which are found in both *Abies alba* samples (Fig. 4.3a) and due to the presence of Δ13-*cis*-neoabienol the material may be obtained from a *Picea* species, which does not contain pimaric acid (see table 2.2).

The brown Russian Strasbourg turpentine (5.7.1, Fig. 4.4) additionally contains pimaric, palustric, abietic and neoabietic acids and their methylester, respectively. Pimarate and sandaracopimarate are present in a ratio, which is, as discussed above, typical for pine resins. The main constituents are palustrate and abietate together with intermediate relative amounts of dehydroabietate and neoabietate (Fig. 4.6b). Very small amounts of Δ13-*cis*-neoabienol are present (Fig. 4.6e). The composition of the abietane acids is nearly identical to that of the sample 5.3.3 (Fig. 4.5b, e), a Venetian turpentine made from larch resin and colophony. According to the supplier the Russian Strasbourg turpentine is no mixture, but the safety data sheet, however, lists colophony as a constituent together with 70% resinous balsam (Kremer 2008). The presence of Δ13-*cis*-neoabienol points to a *Picea* resin, but the ratio of pimaric and sandaracopimaric acids indicates a pine resin. The ratio may be modified by the addition of colophony made from pine. In that case, 5.7.1 is a mixture of the resin used for STI (Strasbourg turpentine) with colophony.

4.1.1.2 Aging by heat and light

Colophony and Burgundy pitch

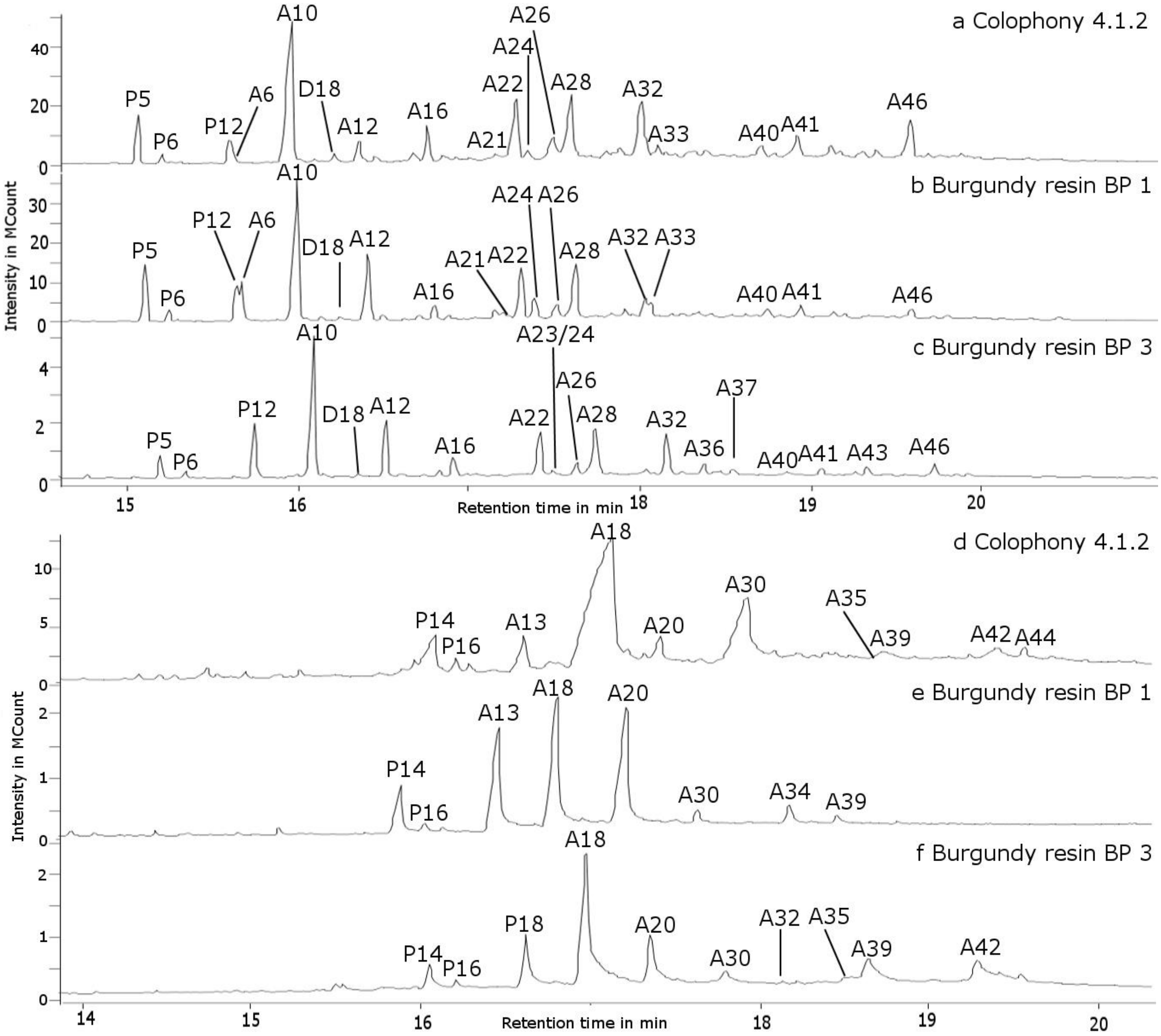
For the investigation three samples of commercial colophony and three of Burgundy resin are analysed (4.1.1, 4.1.2, 4.1.7, BP1-3). All samples are described in table 4.8.

In Fig. 4.7a, d, the chromatograms of the (methylated) methanol extracts of colophony (4.1.2) as examples for these analyses are shown. The sample contains low amounts of unmodified pimarane and abietane acids (P5, P6, P12, A6, A12), the most prominent constituent is dehydroabietate together with its C-7 and C-15 oxygenated derivatives: 7-methoxy-, 7-hydroxy-, 15-hydroxy-, 7-oxo- and 7-oxo-15-hydroxydehydroabietate (A16, A22, A30, A32, A46) and compound A41 (Fig. 4.7a). Other constituents are 12-methoxy-podocarpa-8,9,12-trien-15-oate (D18), the compounds A21, A24, A26, A31 and A33. In the methanol extract pimaric, sandaracopimaric, palustric, abietic and dehydroabietic acids are present, together with 7-methoxy-, 7-hydroxy- and 15-hydroxy- and 7-oxo-dehydroabietic acids and compound A44 (Fig. 4.7d).

Fig. 4.7b, e shows the chromatograms of the (methylated) methanol extracts of commercial Burgundy pitch from Kremer (BP1). The main constituent is dehydroabietate, together with pimarate, isopimarate, palustrate, abietate, 7-hydroxy- (A22) and 7-methoxy-dehydroabietate (A30). Other constituents are sandaracopimarate, the compounds A16, A21, A24, A26, A31, A33, A41 and A46 (Fig. 4.7b). Aging markers are 7-methoxy- and 15-hydroxy-dehydroabietic acids and compound A34 (Fig. 4.7e). The chromatogram of another Burgundy pitch purchased from Eggebrecht (BP2) is identical (not shown). The (methylated) methanol extracts of a Burgundy pitch from another collection (BP3), where it was stored about 50 years, are shown in Fig. 4.7c, f. It does not contain palustrate, the compounds A31 and A33, but a 15-methoxy-dehydroabietate (A23), compound A36, 15-methoxy-tetradehydroabietate

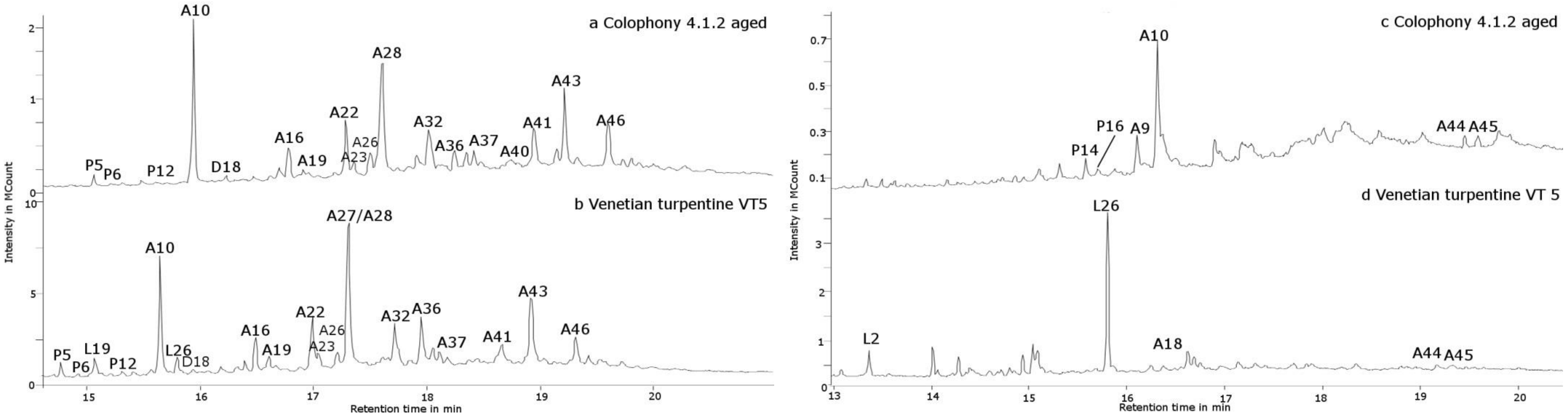
(A37) and compound A43 (Fig. 4.7c). In the methanol extract also no palustric acid is present, but higher relative amounts of 7-hydroxy- and 15-hydroxy- as well as 7-oxo-dehydroabietic acids compared to the other samples. Also small amounts of 7-oxo-dehydroabietate are present (Fig. 4.7f).

In all samples, unmodified pimarane and abietane acids are still present, in the two samples of fresh Burgundy pitch (BP1, BP2) in significant amounts. The compositions of colophony and Burgundy pitch are comparable. Compared to the fresh botanical samples, neoabietic acid is missing, and the amounts of palustric and abietic acids are decreased. Despite no detailed information about the production process of Burgundy pitch are found, this chemical composition indicates a gentle melting process as described by traders (Scents of the Earth 2012). The main reactions are isomerisation and dehydrogenation together with the formation of intermediate amounts of C-7 and C-15 oxygenated abietane acids from oxidations state 3 to 5 (see Fig. 2.4). The formation of these compounds is widely known from literature (see chapter 2.1.1). It is noticeable, that the older Burgundy pitch (BP3) does not contain palustric acid but other compounds (A23, A36, A37 and A43), which are present neither in colophony nor in the fresh purchased Burgundy resins. In the case, those compounds were produced during the storage, they are probably light aging markers.



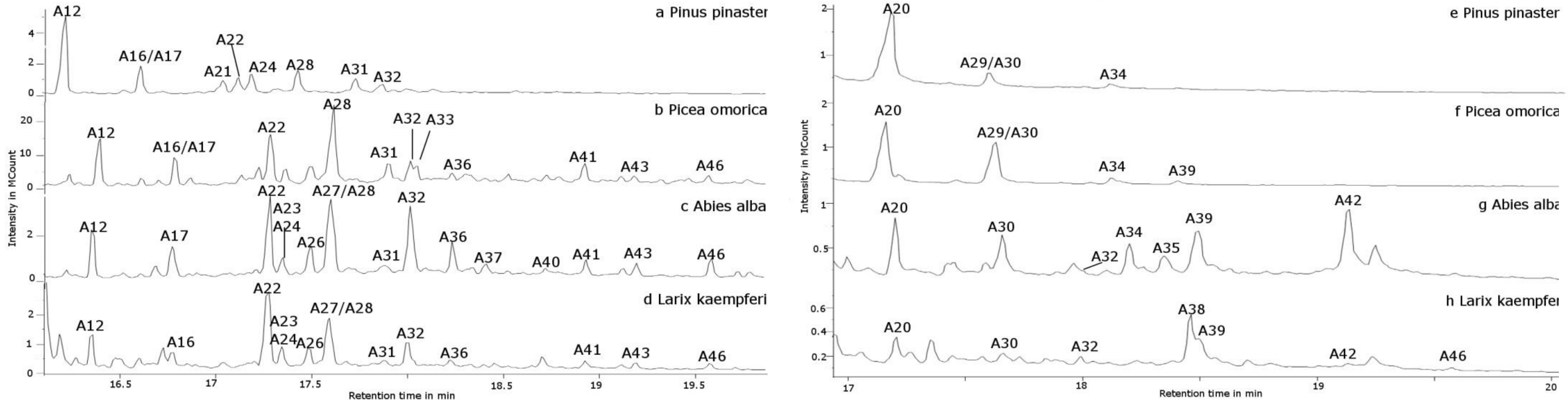
Top (a - c) methylated methanol extracts, bottom (d – f) methanol extracts, a, d – colophony 4.1.2, b, e – Burgundy resin BP1 and c, f – Burgundy resin BP3 (labels, see table 4.7)

Fig. 4.7 Gas chromatograms of different products of Pinaceae resins, diterpene section (TIC)



Left – methylated methanol extract, right – methanol extracts, a, c - Colophony 4.1.2 aged and b, d - Venetian turpentine VT5 (labels, 1see table 4.7)

Fig. 4.8 Gas chromatograms of light aged Pinaceae resins, diterpene section (TIC)



Left – methylated methanol extract, right – methanol extract, a, e - Pinus pinaster*, b, f -* Picea omorica *, c, g -* Abies alb*a and d, h -* Larix kaempferi *(labels, see table 4.7)*

Fig. 4.9 Gas chromatograms of Pinaceae resins, diterpene section (TIC)

Label	t_R	Name	Main mass fragments
L$_2$	13.36	Epimanool	**81**, 95, 137, 257, 272, (290)
P$_5$	15.11	Pimarate	**121**, 241, 257, 301, 316
P$_6$	15.24	Sandaracopimarate	**121**, 241, 301, 316
L$_{19}$	15.45	Larixol	69, **109**, 119, 153, 187, 255, 273, 288, (306)
P$_{12}$	15.62	Isopimarate	187, 227, **241**, 256, 287, 316
A$_5$	15.67	Levopimarate	**92**, 105, **121**, 146, 187, 241, **316**
A$_6$	15.67	Palustrate	**241**, 301, 316
A$_{10}$	15.98	Dehydroabietate	**239**, 299, 314
P$_{14}$	15.84	Pimaric acid	91, 107, **121**, 133, 241, 287, 302
L$_{26}$	15.79	Larixylacetate	79, 105, **153**, 185, **255**, 270, 288, 348
P$_{16}$	15.98	Sandaracopimaric acid	91, 107, **121**, 133, 241, 287, 302
D$_{18}$	16.07	12-methoxy-podocarpa-8,9,12-trien-15-oate	159, 173, **227**, 239, 287, 302
P$_{18}$	16.33	Isopimaric acid	91, 105, 131, 159, 187, 227, **241**, **287**, 302
A$_{12}$	16.39	Abietate	185, 213, **241**, 256, 273, 316
A$_{13}$	16.44	Palustric acid	91, 133, 159, 187, 213, 241, **287**, 302
A$_{14}$	16.52	Levopimaric acid	**92**, 105, 131, 146, 187, 302
A$_{16}$	16.79	7-methoxy-dehydroabietate	195, **237**, 253, 312, 344
A$_{17}$	16.78	neoabietate	121, **135**, 301, 316
A$_{18}$	16.72	Dehydroabietic acid	197, **239**, 285, 300
A$_{19}$	17.04	7-methoxy-Δ6(7)-dehydrodehydroabietate	209, 227, **267**, 283, 327, 342
A$_{20}$	17.15	Abietic acid	105, 31, 185, 213, 241, 259, 287, **302**
A$_{21}$	17.21	Unidentified oxygenated abietane acid	227, **269**, 329, 344
A$_{22}$	17.18	7-hydroxy-dehydroabietate	121, 195, **237**, 253, 297, 312, 330
A$_{23}$	17.30	15-methoxy-dehydroabietate isomer	237, 269, 313, **329**, 344
A$_{24}$	17.30	Oxygenated 7,13,15-abietatrien18-oate	121, 183, 239, **254**, 299, 314, 315, 329, 330
A$_{26}$	17.48	Unidentified abietane	163, 195, **237**, 255, 287, 312, 330
A$_{27}$	17.65	Δ16-demethyl-7-oxo-dehydroabietate (proposed)	155, 197, 211, 239, **253**, 299, 313, 314
A$_{28}$	17.66	15-hydroxy-dehydroabietate	255, 273, **315**, 330
A$_{29}$	17.67	Neoabietic acid	91, **135**, 148, 187, 241, 287, 302
A$_{30}$	17.66	7-methoxy-dehydroabietic acid (proposed)	181, 195, **237**, 283, 297, 315, 330
A$_{31}$	17.73	Unidentified, oxidised abietane	107, 147, 229, 239, **289**, 331, 346
A$_{32}$	18.00	7-oxo-dehydroabietate	187, 211, **253**, 269, 296, 328
A$_{33}$	18.06	Unidentified	121, 199, 229, **241**, 257, 272, 289, 317, 332
A$_{34}$	18.19	Unidentified	91, 134, 185, 239, 254, 285, **300**
A$_{35}$	18.35	7-hydroxy-dehydroabietic acid	145, 185, 195, **237**, 273, 299, 316
A$_{36}$	18.38	Unidentified (di)hydroxy-dehydroabietate	181, 195, 211, **249**, 264, 309, 324, 342
A$_{37}$	18.41	15-hydroxy-Δ6(7)-dehydrodehydroabietate (proposed)	213, 237, 251, **267**, 311, 327, 342
A$_{38}$	18.46	Unidentified abietane	**187**, 225, 267, 285, 300

Label	tR	Name	Main mass fragments
A39	18.49	15-hydroxy-dehydroabietic acid	131, 197, 237, 255, 283, **301**, 316
A40		7-oxo-Δ15(16)-dehydro-dehydroabietate	211, **251**, 266, 294, 326
A41	18.91	Unidentified aging marker	195, 211, **253**, 313, 328, **331**
A42	19.13	7-oxo-dehydroabietic acid	211, **253**, 299, 314
A43	19.38	Unidentified methoxy-dehydroabietate	59, 156, 212, 251, 255, 269, 311, **315**, 329, 343, 358
A44	19.46	Unidentified abietane	209, 239, 251, 253, **266**, 282, 310
A46	19.55	7-oxo-15-hydroxy-dehydroabietate	187, 269, **329**, (344)

Tab. 4.5 Compounds found in samples analysed in chapter 4.1.1.2, methanol and methylated methanol extracts, samples analysed with temperature program Diterpenes 1 and column A, mass spectra references see appendix

Concerning the botanical origin of Burgundy pitch, all analysed samples contain more pimarate than sandaracopimarate (Fig. 4.7b, c). In Burgundy resin from Kremer and Eggebrecht (4.17.1) iso-abienol and small amounts of Δ13-cis-neoabienol are present, in the older sample (PP3) the compound D10 (not shown). Iso-abienol is reported for the resin of *Pinus pinaster* Ait. (see table 2.2), but it is not found in this work. Δ13-cis-neoabienol is found in the resin of *Picea abies* (Fig. 4.1d), and a commercial Strasbourg turpentine (Fig. 4.6d), the latter loosely attributed to *Abies alba* or the resin of a *Picea* species, which does not contain pimaric acid (see chapter 4.1.4). The descriptions given by the supplier are confusing. In German the product is labelled Burgunderharz, Burgunderpech or Fichtenharz both by Kremer and Eggebrecht, obtained from the Burgundertanne *Picea abies*. In the English translation supplied by Kremer the material is labelled as Burgundy resin or colophony of the European pine (Kremer 2011). Even though this may be a mistranslation, the botanical origin of commercial available Burgundy pitch is more likely a pine resin than a spruce.

Light aging of Pinaceae resins

In Fig. 4.8 the chromatograms of the (methylated) methanol extracts from light aged colophony and Venetian turpentine are shown. Both were painted on chalk ground, the colophony was dissolved in ethanol before. The plate was stored indoors for 12 years, where it was exposed to light and air.

Both samples contain pimarate and sandaracopimarate in a ratio (Fig. 4.8a, b), which is, as discussed in chapter 4.1.1.1, typical for pine resins (Fig. 4.1). Colophony is made mainly from pine resins, but it cannot be ruled out that the samples were from a different botanical origin. The Venetian turpentine was purchased from Talens. It contains lower amounts of epimanool and larixylacetate, larixol is absent (Fig. 4.8d). The supplier gives no information about an addition of colophony, as it is done in the case of the Venetian turpentine from Kremer (chapter 4.1.1.1. Fig. 4.5c, f), but the (unaged) material contain pimaric acid as well (Osete-Cortina, Doménech-Carbó 2005). Pimaric acid was found in the resin of some American and Japanese *Larix* species (Mills 1973), which are, however, not known to be used for the production of commercial Venice turpentine. Therefore, the presence of pimaric acid indicates the addition of a pine resin or colophony. The original composition of the Venetian turpentine is not known, therefore the stability of the ratio of pimaric and sandaracopimaric acid remains open. Both acids, however, are visible also in strongly aged materials.

In both samples no unmodified abietane acids are present. The most prominent constituents are dehydroabietate, 15-hydroxy-dehydroabietate and compound A43. Other compounds present in significant amounts are 7-methoxy-, 7-hydroxy-, 7-oxo-, 7-oxo-15-hydroxy-dehydroabietate and compound A36 as well as low relative amounts of compounds D18 and A19, 15-methoxy-dehydroabietate (A23), compound A26, 15-methoxy-tetradehydroabietate (A37) and compound A41.

The compounds A27, A36, A37 and A43 are not present in unaged colophony (Fig. 4.7a). Compound A27 has a mass spectrum very similar to that of 7-oxo-dehydroabietate. The main fragmentation for 7-oxo-dehydroabietate (A32) (MW 328) is $[M\text{-}CH_3\text{-}HCOOCH_3]^+$ at m/z 253. Side reactions are the elimination of methanol (m/z 296) and water from $[M\text{-}CH_3]^+$ (m/z 278). In A27 (MW 314) the main reaction is $[M\text{-}H^{\cdot}\text{-}HCOOCH_3]^+$ at m/z 253 and $[M\text{-}CH_3]^+$ at m/z 299 followed by the loss of the carboxyl group $[M\text{-}CH_3\text{-}HCOOCH_3]^+$ at m/z 239. The loss of an electron $[M\text{-}H^{\cdot}]^+$ stabilizes the mesomerism of the aromatic ring. Such a fragmentation pattern is not found for any of the other oxygenated abietane acids, which indicates that the missing methyl group was part of the propyl group. No such compounds are reported. A27 is present in this work only in (light) aged samples, wherefore an artifact formed during sample preparation or measurement is unlikely.

Compound A36 is not yet identified, but its mass spectrum resembles that of 7-methoxy-Δ6(7),15(16)-dehydro-dehydroabietate (Pastorova et al. 1997). The molecular ion is 342 instead of 340, which indicates only one double bond present. However, the $[M\text{-}H_2O]^+$ peak at m/z 324 is quite prominent, which points to a hydroxyl and not a methoxy group. The molecular ion at m/z 342 indicates a second hydroxyl group. The elimination of water is followed by the splitting of a methyl group and the carboxyl group resulting in the main peak at m/z 249. A small peak is present at m/z 291, which results from the second hydroxyl group ($[M\text{-}H_2O\text{-}CH_3\text{-}H_2O]^+$). The mass spectra of dihydroxy-dehydroabietates published by van den Berg et al. (van den Berg et al. 2000) originate from their methoxylated derivatives. Therefore, the identity of compound A36 remains open. It is nevertheless an oxygenated abietane acid.

The mass spectrum of compound A37 is nearly identical to that of compound A19, the latter identified based on literature data as 7-methoxy-Δ6(7)-dehydrodehydroabietate (van den Berg et al. 2000), probably the methoxyether of 7-oxo-dehydroabietate. The online derivatisation with trimethylammoniumhydroxide followed in a methoxylation of 7-oxo-dehydroabietate resulted in an additional double bond at Δ6(7) (ibd.). The compound A19 may the natural C-7 methoxyether of tetradehydroabietate considering that a methoxylation with TMSH is not reported in literature (chapter 3.1.2). Compound A37 possesses an additional peak for $[M\text{-}CH_3OH]$ and $[M\text{-}CH_3O^{\cdot}]^+$ at m/z 310 and 311, which indicates a methoxy group at C-15. A37 would be 15-methoxy-tetradehydroabietate then.

Compound A43 is not identified. The main peak at m/z 311 results from $[M\text{-}CH_3\text{-}CH_3OH]^+$, which indicates a methoxy group.

Compound A23, which is also present in the older Burgundy resin (BP3) (Fig. 4.7c), is identified as a 15-methoxy-dehydroabietate (van den Berg et al. 2000). It is not present in the methanol extract, but several other methylated abietane derivatives (A28, A32, A46), which indicates a natural methylation occurring in minor amounts. As discussed above, TMSH methylates hydroxyl groups only in traces, if at all. All discussed mass spectra are shown in the appendix.

In summary, the possible aging markers A27, A36, A37 and A43 are demethylated, dehydrogenated and hydroxyl- or methoxy-abietane acids. A37 is present only in samples, were A19 is also found. The additional endocyclic double bond may result from a process occurred during oxidation as suggested by literature data (Koller et al. 1998; Weser et al. 1998), but may also originate from a dehydrogenation followed by oxidation. Another compound, A40, which was identified as 7-oxo-Δ15(16)-tetradehydroabietate (Pastorova et al. 1997), is found in some of the aged samples. Endo- and exocyclic double bonds are therefore formed on different pathways. According to literature (van den Berg et al. 2000), hydroxy-derivatives of dehydroabietic acid are light sensitive, which would explain the formation of other higher oxygenated, dehydrogenated and demethylated compounds. Another difference between the unaged colophony, Burgundy resin and the light aged samples is that the latter contain slightly higher relative amounts of C-15 oxygenated dehydroabietic acids, while in colophony and Burgundy resin oxygenated abietane acids are present in equal amounts.

Fig. 4.9 shows the partial chromatograms of the (methylated) methanol extracts from *Pinus sylvestris*, *Picea omorica*, *Abies alba* and *Larix kaempferi*. All botanical resins were exposed some time outdoors to light and air before sampling. All botanical samples are described in table 4.1 in chapter 4.1.1.1. The composition of abietane and pimarane acids of these samples is reported in chapter 4.1.1.1.

Label	Description	Picture	Sampling: date; description
4.1.1	Colophony, Binneweg, 1970, AFAD material collection		December 2007, January 2009; odourless, dark brown and opaque resin, solid and brittle
4.1.2	Colophony, Bleck, between 1970 and 1972, AFAD material collection		December 2007, January 2009; yellow powder with a sour smell, solid and brittle
4.1.7	Colophony, Bode museum, 1978, AFAD material collection		December 2007, January 2009; odourless dark brown and transparent resin, solid and brittle
BP1	Burgundy pitch, Kremer (#60320), 2008, Burgunderharz or Burgunderpech from Picea abies (German), Burgundy resin or colophony of the European pine (English)		June 2008, October 2008; light yellow and transparent solid resin; nearly odourless, smell somewhat like colophony (sour)
BP2	Burgundy pitch, Eggebrecht (#100700), 2006, Burgunderharz (Fichtenharz) (German)		June 2008, October 2008; light yellow and transparent resin; nearly odourless, smell somewhat like colophony (sour)
BP3	Burgundy pitch, old sample from MMA, maybe from Amend Chemical or Kremer, about 50 years old, Vaclav Pitthard		May 2009; light brown and opaque resin; odourless
VT5	Venetian turpentine, Talens, painted on chalk ground, indoor aged for about 12 years		August 2008; about 1 mg sample was scraped with a scalpel from the plate
4.1.2 aged	Colophony 4.1.2 dissolved in ethanol, painted on chalk ground, indoor aged for about 12 years		April 2009; about 0.8 mg sample was scraped with a scalpel from the plate

Tab. 4.6 Description of reference samples analysed in chapter 4.1.1.2

In the methylated methanol extract of the resins from *Pinus pinaster* main aging markers are the compounds A16, A22, A24 and A30, in that of *Picea omorica* compounds A22 and A30 (Fig. 4.9a, b). Other constituents are the compounds D18, A21, A23, A26, A32, A33, A41 and A46. The resin of *Abies alba* contains in addition the compounds A27, A36, A37 and A43 (Fig. 4.9c). These compounds are also (partly) present in the resin of *Picea omorica* and *Larix kaempferi* (Fig. 4.9b-d). The compounds A_{27}, A_{36}, A_{37} and A_{43} are present in all of light aged samples.

In the methanol extracts all resins contain 7-methoxy-dehydroabietic acid, 15-hydroxy-dehydroabietic acid (4.9e-h), those of *Pinus pinaster*, *Picea omorica* and *Abies alba* also compound A34 (Fig. 4.9e-g). The resin of *Abies alba* contains in addition also 7-hydroxy- and 7-oxo-dehydroabietic acids (Fig. 4.9g). The resin of *Larix kaempferi* contains 7-hydroxy-, 7-oxo-dehydroabietate and compound A38 (Fig. 4.9h). It is noticeable that the resin of *Larix kaempferi* contains lower relative amounts of aging compounds compared to the other *Larix* resins, even though it was sampled as a dried up exudate from the bark similar to that of *Abies alba* (table 4.1).

The light aged botanical samples contain apart from the characteristic C-7 and C-15 oxygenated and dehydrogenated abietane acids the light aging markers A27, A36, A37 and A43.

4.1.2 Cupressaceae - Sandarac

Three reliable botanical samples from *Tetraclinis articulata* Mast. and *Juniperus communis* L. are investigated together with sandarac labelled materials. All samples are described in table 4.11, the results are summarised in table 4.9. The aim of the chapter is to identify phytochemical markers of the Sandarac cypress.

Botanical samples

Two samples of *Tetraclinis articulata* Mast. (TADD, TABD) and one of *Juniperus communis* L. (JC) are analysed. In the methanol extracts of the resin of *Tetraclinis articulata* (TADD, TABD) (Fig. 4.11a, b), main compounds are compound Ph4, totarol, ferruginol, compound Ph16, hinokinol and in TADD also compounds Ph4, Ph15 and sugiol. Apart from two isomeric communic (L23, L28) and sandaracopimaric acids, high amounts of 12-acetoxy-sandaracopimarate (P21) are present, together with smaller amounts of acetoxy-sandaracopimarate (P20), compound D22 and isopimaric acid. Both samples contain more totarol than ferruginol and only small amounts of sugiol. The main compound in the methanol extract of the resin of *Juniperus communis* (Fig. 4.11c)are totarol, ferruginol and compound Ph6, together with smaller amounts of the compounds Ph8, Ph10, Ph11, Ph14, Ph15 and sugiol. The sample contains high amounts of the compounds L23, L28 and sandaracopimaric acid.

In the methylated methanol extract of TADD and TABD (Fig. 4.11d, e), mainly *cis*- and *trans*-communate, sandaracopimarate, hydroxy-sandaracopimarate (P19) and 12-acetoxy-sandaracopimarate (P20) are present. Other constituents are methoxy-ferruginol, -totarol and –sandaracopimarate (P17), the compounds D13, L20 and isopimarate. The methylated methanol extract of JC (Fig. 4.11f) contains methoxy-ferruginol, -totarol and -sugiol with high amounts of *cis*- and *trans*-communates and the compounds D13 and L47.

In the methanol extract treated with oxalic acid of TADD and TABD (Fig. 4.12a, b) totarol, ferruginol, sugiol, compound P21, dehydroabietic acid and dehydroabietate are present, in that of JC (Fig. 4.12c) totarol, ferruginol, callitrisate and dehydroabietate. All extracts contain a wide range of unidentified compounds (not labelled), which are not present in the untreated extracts.

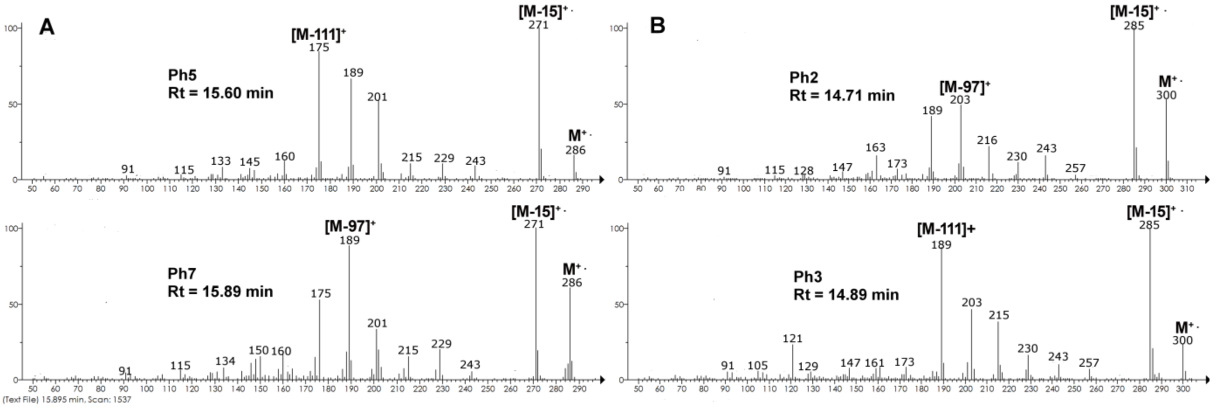
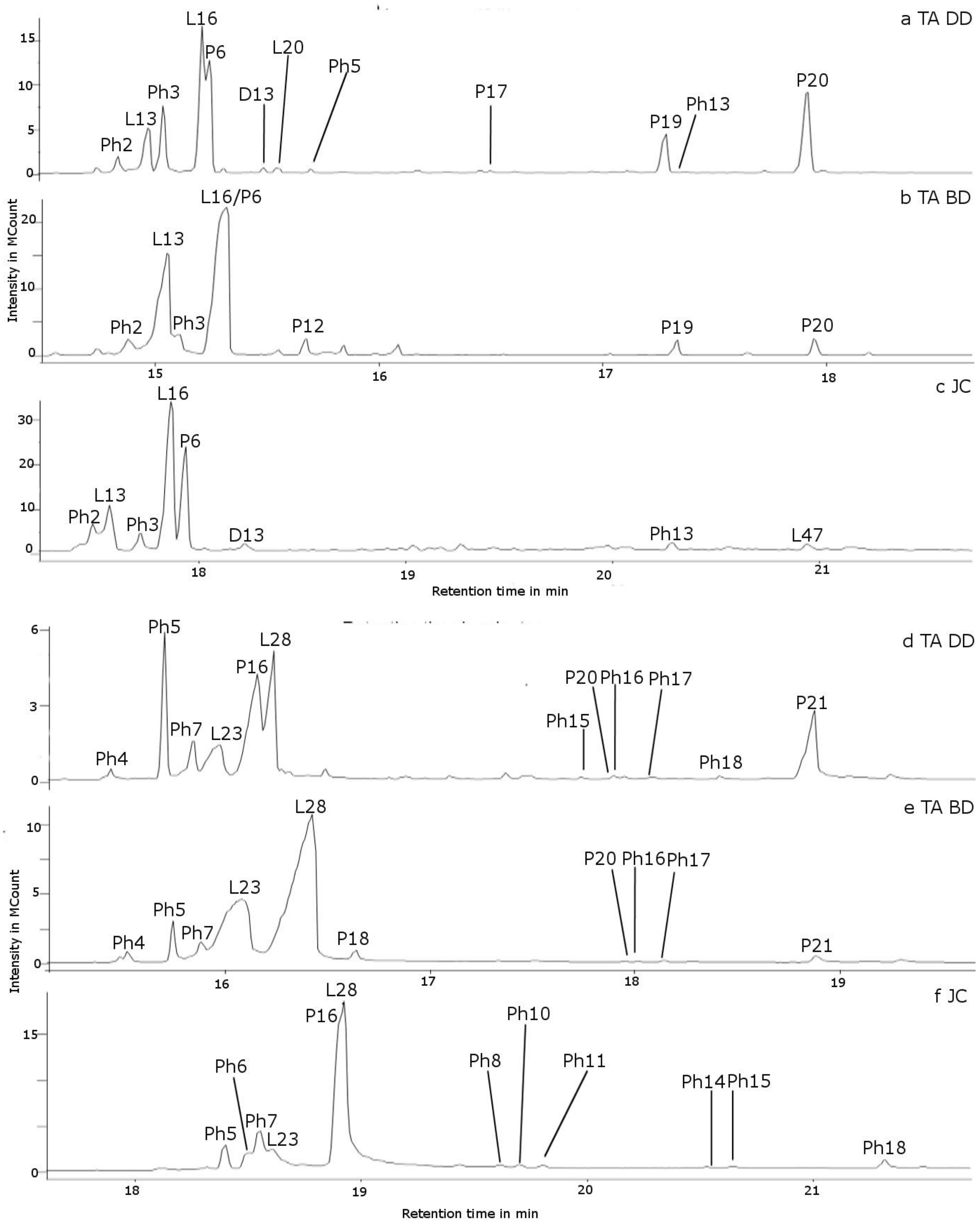


Fig. 4.10 Mass spectra of totarol (Ph5) and ferruginol (Ph7) (A) and methoxy-ferruginol (Ph2) and –totarol (Ph3) (B) with retention time and main fragmentation characteristics (Enzell, Wahlberg 1969)

The elution order of methoxy-totarol (Ph3) and -ferruginol (Ph2) is reversed to the order reported in literature for totarol (Ph5) and ferruginol (Ph7) (Koller et al. 1997) and also to the order found in the methanol extracts (Fig. 4.11). Mass spectra are published only for totarol and ferruginol (Enzell, Wahlberg 1969). The described fragmentation indicates a more intense $[M\text{-}15]^+$ and $[M\text{-}97]^+$ ion for ferruginol, while totarol possesses a more intense $[M\text{-}111]^+$ peak (shown in Fig. 4.10a for own mass spectra). A similar fragmentation pattern is observed for the compounds Ph2 and Ph3 present in the methylated methanol extracts (Fig. 4.10b), which, however, elute in reversed order compared to their not methylated precursors. The relative intensities of Ph2 and Ph3 show that the methylation capacity of TMSH under the applied conditions for hydroxyl groups is low. Resulting methoxyether are presnt only in small amounts. However, Ph3 and Ph2 are present in the same ratio as Ph5 and Ph7.

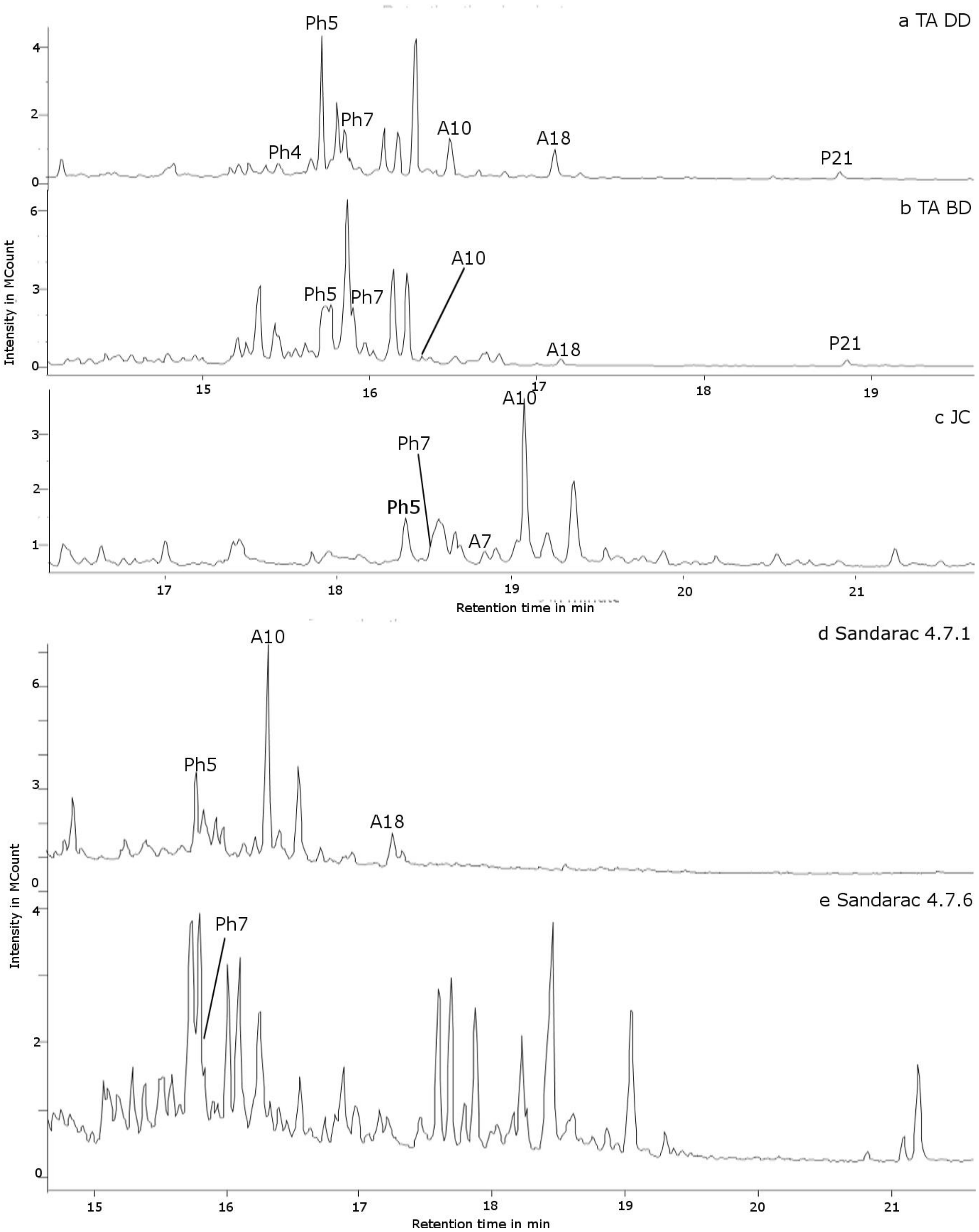
The identification of the compounds P17 and P19 is supported by the same considerations. P17 is identified by literature data as methoxy-sandaracopimarate, where characteristic ions for a hydroxy form of sandaracopimaric acid at m/z 121 and 346 are published without a detailed mass spectrum (van Keulen 2009). Assuming that only one hydroxyl group is present, the peak at m/z 346 is the molecular ion of methoxy-sandaracopimarate. Van Keulen used TMAH as a methylation reagent, which is known to methylate hydroxyl groups more easily than TMSH. A more intense peak eluting at 17.30 minutes with a base peak at m/z 121 and molecular ion at m/z 332 is therefore identified as hydroxy-sandaracopimarate (P19).

The relative amounts of sandaracopimaric and communic acids are the result of aging processes. Sandarac resins possess a polymeric part, which is formed from polymerised labdanes, mainly communic acids and communol (van den Berg et al. 2002). Due to the sample preparation used here, only free acids are dissolved. Due to increasing polymerisation, the relative amounts of communic acid decrease over time and sandaracopimaric acid becomes more prominent in the methanol extract. Both, the resins from Tetraclinis articulate (TADD) and *Juniperus communis*, were taken directly from the bark, and contain lower amounts of communic acids in relation to sandaracopimaric acid. In contrast, in the other sample from Tetraclinis articulate (TABD), which was taken from a cut tree, sandaracopimaric acid is only difficult to identify, because it coelutes with *trans*-communic acid. Apart from that and somewhat higher amounts of phenolic abietatrienes in TADD, the resins from *Tetraclinis articulata* show only slight differences. The principal reason for that is that the Sandarac cypress shows only traumatic resin production (Langenheim 2003: 382), which is why a constitutive resin, which would be composed different, is not exuded.



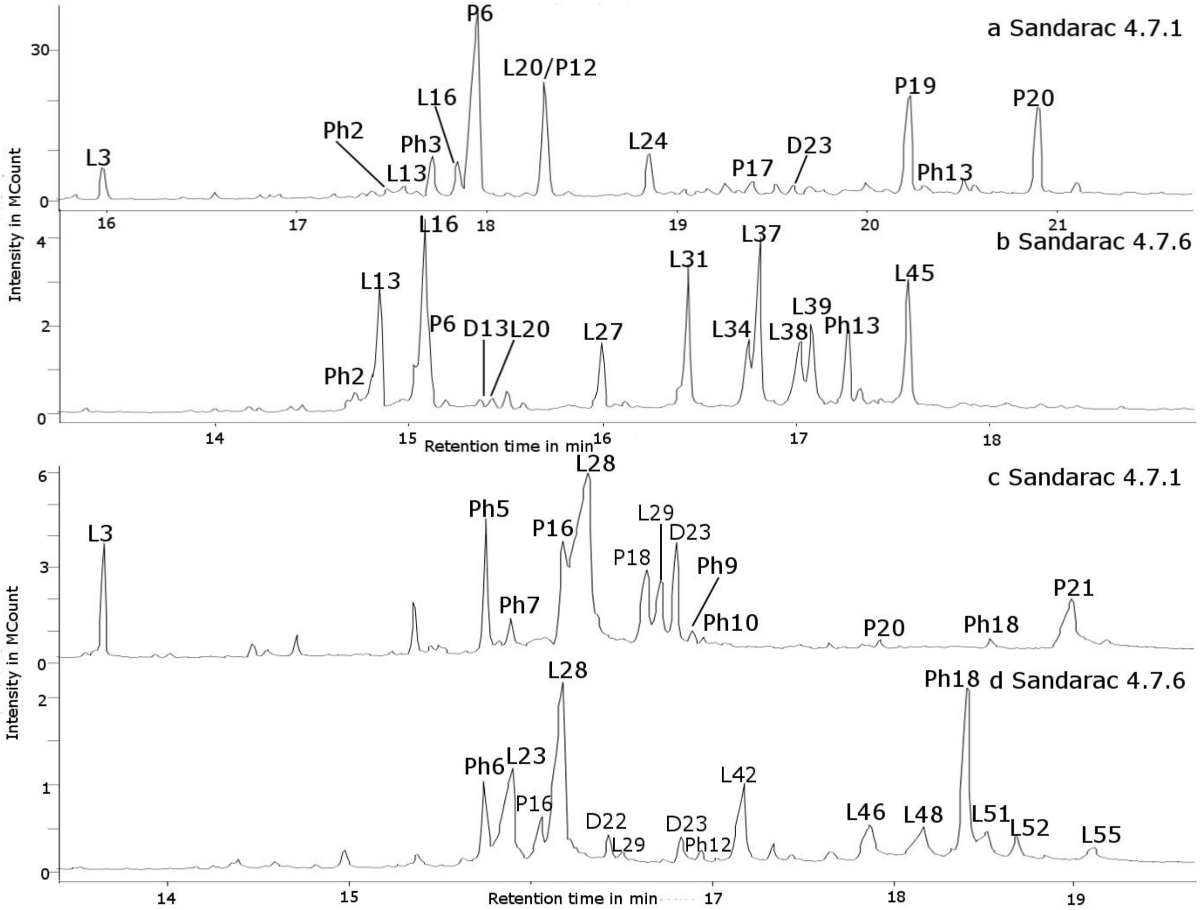
Top (a - c) methylated methanol extracts, bottom (d – f) methanol extract, a, d – resin of Tetraclinis articulata *TADD, b, e -* Tetraclinis articulata *TABD and c, f -* Juniperus communis *JC (labels, see table 4.10)*

Fig. 4.11 Gas chromatogram of the resins from *Tetraclinis articulata* (Vahl) Mast., *Juniperus communis* L., diterpene section (TIC)



Methanol extracts treated with oxalic acid, a – resin of *Tetraclinis articulata TADD, b - Tetraclinis articulata TABD and c - Juniperus communis JC as well as d - sandarac 4.7.1 and e - sandarac 4.7.6 (labels, see table 4.10)*

Fig. 4.12 Gas chromatograms of the resins from *Tetraclinis articulata* (Vahl) Mast., *Juniperus communis* L. and commercial sandarac resin, diterpene section (TIC)



Top (a, b) methylated methanol extracts, bottom (c, d) methanol extracts, a, c - sandarac 4.7.1 and b, d - sandarac 4.7.6 (labels, see table 4.10)

Fig. 4.13 Gas chromatograms of commerical sandarac resins, diterpene section (TIC)

		Group I	Group II
	Samples	4.7.1, 4.7.4, TADD, TABD, JC	4.7.2, 4.7.5, 4.7.6, BlaD7
Methanol extract	Totarol/ferruginol	More totarol	More ferruginol
	Sugiol	Small amounts	High amounts
	Manool	Yes (not in TADD, TABD)	None
	Other typical constituents	12-acetoxy-sandaracopimaric acid + ME	Isocupressic, agathic acids
Methylated methanol extract	Phenols	Mainly totarol	Mainly ferruginol or Ph6
	Sugiol	Small amounts	High amounts
	Other typical compounds	Hydroxy-, methoxy- & 12-acetoxy-sandaracopimarate (not in JC)	Isocupressate, agathate, L38, occ. L34, L37
Oxalic acid	Abietanes	Dehydroabietic acid + ME	No abietane compounds

Tab. 4.7 Characteristic compounds of reference samples analysed in chapter 4.1.2

Label	t_{R1}	t_{R2}	Name	Main mass fragments
L3	13.65	15.99	Manool	**81**, 107, 121, 137, 161, 189, 229, 257, 272, 290
Ph1	14.75		Methoxyether of phenolic abietatriene (Ph6)	189, 203, 215, 243, **285**, 300
Ph2	14.84	17.48	Methoxyether of ferruginol	189, 203, 215, 243, **285**, 300
L13	14.87	17.57	*cis*-Communate	79, **121**, 175, 241, 301, 316
Ph3	15.05	17.71	Methoxyether of totarol	**189**, 203, 215, **285**, 300
L16	15.22	17.86	*tran*s-Communic acid	79, 119, 175, **241**, 316
P6	15.25	17.93	Sandaracopimarate	**121**, 241, 301, 316
Ph4	15.44		Unidentified phenolic abietatriene	175, 189, 201, **271**, 286
D13	15.49	18.21	Unidentified diterpenoate, ME of D22	95, 119, **175**, 235, 330
L20	15.55	18.28	Unidentified labdane acid, ME of L29 (see also chapter 4.1.3)	**121**, 189, 241, 287, 301, 316
P12	15.60	18.31	Isopimarate	187, 227, **241**, 256, 287, 316
Ph5	15.69	18.39	Totarol	175, 189, 201, 253, **271**, 286
Ph6	15.69	18.50	Unidentified phenolic abietatriene	159, 185, **202**, 213, 227, 269, 284
Ph7	15.85	18.55	Ferruginol	175, **189**, 201, 253, **271**, 286
L23	15.80	18.61	*cis*-Communic acid	**79**, 107, **119**, 175, 241, 287, 302
A7		18.71	Callitrisate	225, **239**, 285, 299, 314
L24		18.84	Probably communol	**81**, 93, 107, 119, 133, 147, 161, 175, 189, 257, 273, 288
L27	15.99		Unidentified labdane acid, ME	79, 93, **121**, 161, 221, 290, 318, 350
P16	16.00	18.88	Sandaracopimaric acid	91, 107, **121**, 133, 241, 287, 302
L28	16.23	18.92	*trans*-Communic acid	**79**, 119, 175, 241, 287, 302
A10	16.26		Dehydroabietate	**239**, 299, 314
D22	16.50	19.35	Unidentified sandarac marker	**95**, 119, 133, 175, 220, 316
P17	16.57	19.39	Methoxyether of sandaracopimarate	91, 105, **121**, 159, 213, 239, 289, 299, 346
P18	16.64		Isopimaric acid	95, 119, 145, 187, **241**, 273, 287, 302
L29	16.50		Unidentified labdane acid	81, 93, 107, **121**, 133, 159, 187, 241, 287, 302
L31	16.43		Isocupressate	79, 93, 107, **121**, 241, 257, 301, 316, 333, 334
Ph8	16.69	19.63	Unidentified phenol	197, 203, 215, **267**, 285, 300
L34	16.75		Imbricatoloate	79, 93, 107, **121**, 161, 276, 304, 336
L37	16.79	19.78	Dihydroagathate, diME	79, 93, **121**, 161, 221, 235, 304, 364
L38	17.02		Unidentified labdenoate, ME of L48	79, 93, 107, **121**, 189, 241, 257, 301, 319, 334
D23	16.79		Unidentified sandarac marker	79, 93, **107**, 119, 135, 161, 187, 255, 315, 330
Ph9	16.80		Abieta-8,11,13-triene-one	197, **267**, 285, 300
Ph10	16.79	19.69	Unidentified phenolic abietatriene	157, 199, **227**, 269, 284, 302

Commerical samples

For that investigation six modern materials labelled as sandarac are analysed. They are taken mainly from the AFAD reference collection, two were purchased from German suppliers (see table 4.11).

In the methanol extracts of commercial sandarac samples (4.7.1, 4.7.6; Fig. 4.13a, b) communic (L23, L28), sandaracopimaric acids and compound L29 are present. The sample 4.7.1 in addition contains compounds D23, the sample 4.7.6 compound D22, both reported as sandarac markers even without an identification (Dietemann 2007; van den Berg et al. 1999). Apart from that, reference materials are found to diverge into two groups (see table 4.9). Sample 4.7.1 (Fig. 4.13a), which covers samples from group I, contains high amounts of manool, totarol and small amounts of sugiol in addition to the above mentioned compounds.

Label	t_{R1}	t_{R2}	Name	Main mass fragments
Ph11		19.80	Unidentified phenolic abietatriene	157, 173, 199, 215, 243, **269**, 285, 300
Ph12	16.86		Totarolone	215, 243, 257, **285**, 300
L39	17.08		Unidentified hydroxy-labdanoate	79, 93, 105, **121**, 161, 273, 289, 316, 348
A18	17.09		Dehydroabietic acid	**239,** 285**,** 300
L42	17.17		Isocupressic acid	79, 93, 107, **121**, 161, 207, 241, 287, 302, 320
P19	17.30	20.20	Hydroxy-form of sandaracopimarate	91, 105, **121**, 239, 255, 299, 314, 332
Ph13	17.27	20.28	Methoxyether of sugiol	177, 219, 257, **299**, 314
L45	17.51	20.58	Agathate, diME	81, 93, 107, **121**, 189, 301, 347, 362
Ph14		20.54	Unidentified phenolic abietatriene	213, 243, **285**, 300
Ph15	17.58	20.65	Unidentified phenolic abietatriene	201, 213, 243, **285**, 299, 300
L46	17.87		Imbricatoloic acid	81, 93, 107, **121**, 161, 221, 276, 304, 322
P10	17.90	20.89	12-acetoxy-sandaracopimarate	93, 105, **121**, 131, 239, 255, 299, 314, (374)
L47		20.94	Unidentified labdan-19-oate	91, 105, **121**, 133, 175, 241, 301, 314, 333
Ph16	18.01		Unidentified phenolic abietatriene	175, 227, **269**, 287, 302
Ph17	18.10		Hinokinol	199, 227, **269**, 302
L48	18.19		Unidentified labdenoic acid	79, 93, 107, 121, 133, 147, 189, **241**, 259, 287, 302, 305, 320
Ph18	18.42	22.33	Sugiol	203, 217, 243, **285**, 300
P21	18.86		12-acetoxy-sandaracopimaric acid (proposed)	91, 119, **134**, 157, 185, 239, 285, 300, 360
L51	18.51		Dihydroagathic acid (proposed)	79, 93, 107, **121**, 161, 175, 290, 300, 318, 336
L52	18.67		Unidentified labdane acid	**82**, 93, 107, 121, 189, 211, 235, 301, (334)
L55	19.09		Unidentified labdanoic acid	**82**, 93, 107, 121, 136, 161, 189, 288, 298, 319, 341

Tab. 4.8 Compounds found in samples analysed in chapter 4.1.2, methanol and methylated methanol extracts, samples analysed with temperature program Diterpenes 1, t_{R1} = retention time of samples analysed with column A, t_{R2} = retention time of samples analysed with column B; mass spectra references see appendix

Other constituents are Ph8, isopimaric and 12-acetoxy-sandaracopimaric acid. Sample 4.7.6 (Fig. 4.13b), which covers samples from group II, contains high amounts of sugiol, compound Ph6 and ferruginol together with compound Ph12, isocupressic, imbricatoloic acid, compound L48, dihydroagathic acid and compounds L52 and L55.

In the methylated methanol extract of sandarac references 4.7.1 and 4.7.6 (Fig. 4.13c, d) methoxy-ferruginol, -totarol and –sugiol as well as *cis*-, *trans*-communate and sandaracopimarate are present. Sandarac from group I additionally contains high amounts of hydroxy-, methoxy- and 12-acetoxy-sandaracopimarate, compound L20 and isopimarate (Fig. 4.13c), sandarac from group II the compound L27, isocupressate, compounds L38 and L39, dimethylagathate and in some samples also the dihydro-derivatives of isocupressate and agathate (L34, L37). None of such compounds are found in group I.

Isopimaric acid, which is present in high amounts in same samples from group I, is a possible aging marker (Scalarone et al. 2003b). It is derived from sandaracopimaric acid by isomerisa-

Label	Description	Picture	Sampling: date, description
4.7.1	Sandarac, VK 1977, AFAD material collection		December 2007; fragments from the bottom of the container
4.7.2	Sandarac, Dr. Bleck, AFAD material collection		December 2007; small orange pieces with a powered surface
4.7.4	Sandarac, AFAD material collection		December 2007; small yellow pieces with a powdered surface
4.7.5	Sandarac, AFAD material collection		December 2007; small light yellow pieces with a powdered surface
4.7.6	Gum Sandarac, pure moroccan, Kremer (#60100), 2008		January 2008; light yellow pieces with a powdered surface
BlaD7	Gummi Sandarac, moroccan tears, Eggebrecht (# 10-1900), 2.05.2006		March 2008; light yellow pieces with a powdered surface
TA DD	*Tetraclinis articulata*, Conservatory of the Botanical Garden, TU Dresden, small shrub		17.02.2009; small light yellow and cloudy drop, taken from the bark, about 3 g
TA BD	*Tetraclinis articulata*., tree from the Botanical Garden, FU Berlin, Berlin-Dahlem, listed 2004, origin Marocco		12.02.2009; yellowish to whitish drops, odourless, sticky, taken from the cutting area of the branches (pouring out between bark and heart wood), about 3.3 g
JC	*Juniperus communis*, tree from Bergianska trädgården, Botanical Garden of Strockholm		17.09.2009; small yellowish drops, brittle and cloudy, taken from the bark, stored in paper until analysis in 2011

Tab. 4.9 Description of sandarac reference samples and botanical reference samples analysed in chapter 4.1.2

tion (ibid.). It is, however, also present in the relatively fresh sample TABD (Fig. 4.11b). The unidentified labdane acid L29 and its methylester L20 are reported for several sandarac and Kauri copal resins (van den Berg et al. 2002). They are present in conifer copals analysed in this work as well (see chapter 4.1.3). The samples have different shades of yellow (see table 4.11), which however does not correspond with the differing compositions of group I and II.

The main difference between the two groups is the presence of oxygenated sandaracopimaric acids in group I, which are due to their absence in group II no aging marker, and the presence of several C-13 and C-19 oxygenated labdane acids such as agathic and cupressic acids in group II. The latter are widely reported for sandarac resins (Scalarone et al. 2003; Scalarone et al. 2003b), but are not part of the resin from *Tetraclinis articulata* nor *Juniperus communis* analysed above. The resin of *Juniperus communis* does not contain oxygenated sandaracopimaric acids, which may serve as phytochemical markers for true sandarac. It is, however, significant that sandarac resins from group I are of nearly identical composition than the resin of *Tetraclinis articulata*. From the present data, it is impossible to identify the origin of the additional C-13 and C-19 labdane acids in group II.

4.1.3 Araucariaceae – Coniferous copals

This chapter presents analyses of Araucariaceae resins from the genera *Araucaria* and *Agathis* (Manila and Kauri copal). All samples are described in table 4.13. The aim of the chapter is the gain a data profile for Araucariaceae resins (see also chapter 4.2.2 and 4.3.2).

***Araucaria angustifolia* resin**

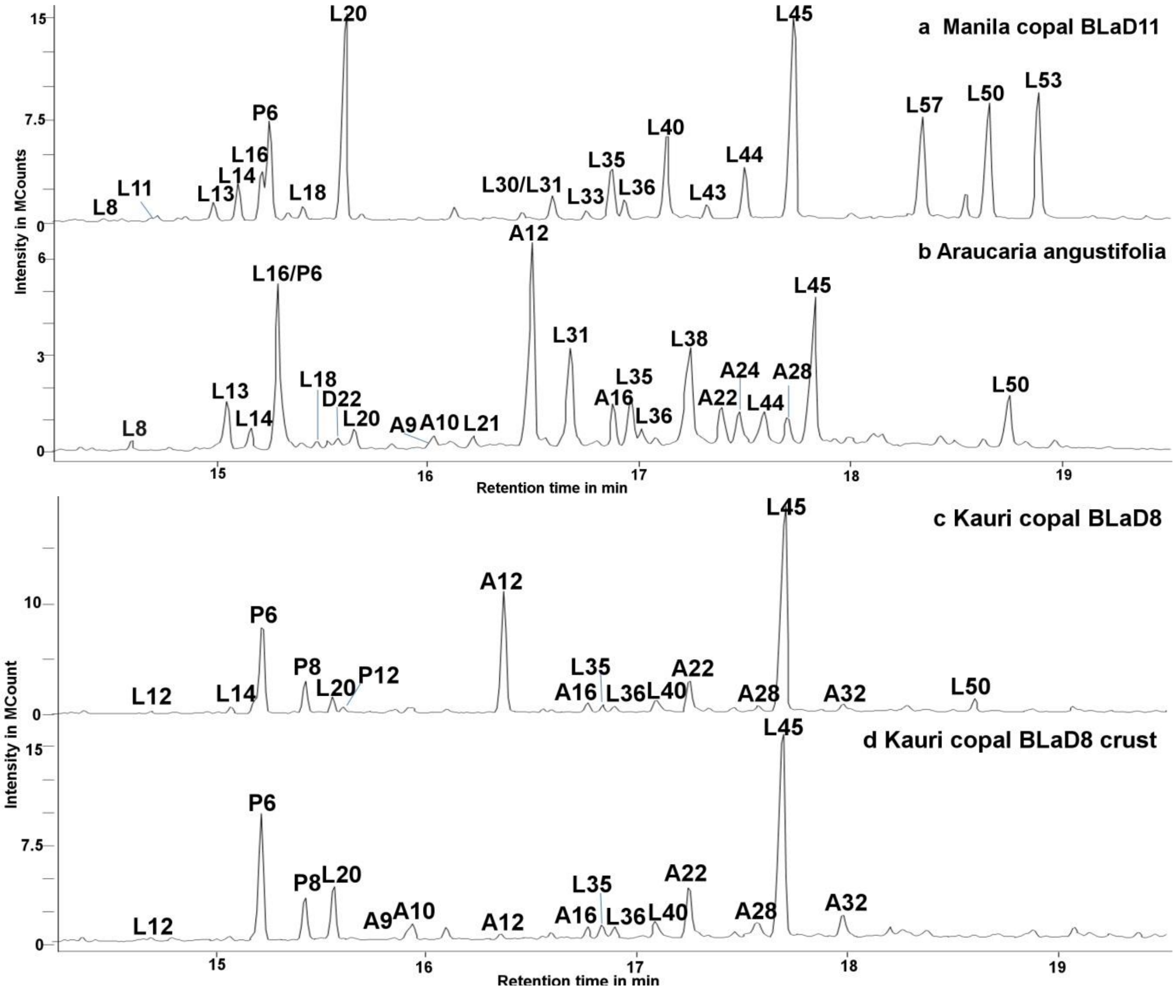
For this investigation a sample of *Araucaria angustifolia* Kuntze is investigated. In the methylated methanol extract of the resin from *Araucaria angustifolia* (Fig. 4.14b) *cis*- and *trans*-communates, sandarcopimarate, compounds D22, L20, dehydroabietate, abietate, isocupressate, compound L38, agathalate, dimethyl-agathate and several dimethylated dicarboxylic acids (L35, L36) are present. Other constituents are small amounts of several abietane aging markers, A16, A22, A24, A28 (see chapter 4.1.1.2). Several of the constituents (L31, L38, D22) are also present in sandarac references, mainly in those, which belongs to group II. In the literature a prevalence of *Araucaria* resins for C-19 oxygenated labdanes is reported (Cox et al. 2007), which is also found in this study.

Manila and Kauri copals (*Agathis* species)

For lack of reliable botanical samples from the genus Agathis, four samples of Manila copal and three samples of Kauri copal are analysed. Manila copal is ascribed to *A. dammara* (Lamb.) Rich., Kauri copal to *A. australis* (D. Don) Steud. (see also chapter 2.1.3). In the methylated methanol extract of Manila copal (BLaD11; Fig. 4.14a) *cis*- and *trans*-communates, sandaracopimarate, compound L20, agathalate, dimethylagathate, several-dimethylated dicarboxylic acids (L35, L36, L40, L43), agatholate, compound L50 and acetoxy-agatholate are present. Two degradation products of agathic acid, the compounds L14 and L18 (19-norlabda-8(20)3-dien-15-oates), are also present. Compound L30 is very likely a further degradation product of agathic acid, as reported by Scalarone et al. as 19-norlabda-4,8(20),13-trien-15-oate (Scalarone et al. 2003a; cf. also Chiavari et al. 2008). All samples labelled as Manila copal and the sample of dark copal resin (BLaD13) show a similar composition (see table 4.13). Compound L20 is present in high amounts in two modern Manila resins purchased from Eggebrecht (BLaD11, BLaD13), but not in two older samples from the AFAD collection (4.4.8, 4.4.9). In the literature, it is reported only for Kauri copal and sandarac (van den Berg et al. 2002). It is present in sandarac analysed in this work as well (see chapter 4.1.2).

In the methylated methanol extract of Kauri copal (BLaD8; Fig. 4.14c) sandaracopimarate, compound L20, isopimarate, dehydroabietate, abietate, agathate, several dimethylated dicarboxylic acids (L35, L36, L40, L43) and compound L50 are present. Other constituents are small amounts of several abietane aging markers, A16, A22, A24 and A32 (see chapter 4.1.1.2). In the white crust (Fig. 4.14d) no isopimarate, communates, abietate and L50 are present. Compound L20 is present in slightly higher amounts than in the interior. The absence of isopimaric acid is in contrast to its reference as an aging marker (Scalarone et al. 2003b). The other Kauri copal (BLaD14) does not contain compound L20. A sample labelled Sambao copal (4.4.7) shows the same composition (see table 4.13)

The main markers to distinguish Kauri from Manila copal are the absence of communic acids, compounds L44, L49 and L53 and the presence of abietane compounds and their aging markers in Kauri copal.



Methylated methanol extracts, top: a - Manila copal BLaD11, b - Araucaria angustifolia, bottom: c - Kauri copal BLaD8 interior and d- Kauri copal BLaD8 crust (labels, see table 4.12)

Fig. 4 14 Gas chromatograms of Araucariaceae resins, diterpene section (TIC)

Label	t_R	Name	Main mass fragments
L8	14.47	Unidentified labdane	79, 93, 105, **121**, 139, 159, 220, 246
L12	14.68	Unidentified labdane	79, **93**, 105, 121, 33, 161, 189, 241, 246, 259, 274
L12	14.69	Unidentified labdane	81, **91**, 107, 121, 133, 147, 161, 243, 257, 271, 286
L13	14.98	*cis*-Communate	79, **121**, 175, 241, 301, 316
L14	15.09	19-norlabda-8(20),3-dien-15-oate	81, 95, 107, 135, 191, 207, 215, 229, 257, **289**, 304
L16	15.20	*trans*-Communate	79, 119, 175, **241**, 316
P6	15.22	Sandaracopimarate	**121**, 241, 301, 316
L18	15.39	Isomer of L14	**81**, 95, 107, 121, 135, 147, 189, 289, 304
D22	15.58	Unidentified	**95**, 119, 133, 175, 220, 316
P8	15.44	Sandaracopimarol	81, 91, 107, 121, 133, 147, 161, **257**, 273, 288
L20	15.59	Unidentified (see chapter 4.1.2)	**121**, 188, 241, 287, 301, 316
P12	15.61	Isopimarate	187, 227, **241**, 256, 287, 316
L21	15.68	Unidentified labdane	81, 93, 107, **121**, 159, 173, 188, 213, 274, 290
A9	15.91	Didehydroabietate	197, **237**, 312
A10	15.93	Dehydroabietate	**239**, 299, 314
A12	16.40	Abietate	185, 213, **241**, 256, 273, 316
L30	16.58	19-norlabda-4,8(20),13-trien-15-oate	81, 93, 121, **211**, 227, 287, 302
L31	16.67	Isocupressate	79, 93, 107, **121**, 241, 257, 301, 316, 333, 334
L33	16.74	Unidentified	79, 93, **107**, 119, 135, 161, 187, 255, 257, 302, 315, 330
A16	16.77	7-methoxy-dehydroabietate	195, **237**, 253, 312, 344
L35	16.86	Unidentified dicarboxylic labdane acid, diME	79, 93, 107, **121**, 175, 201, 211, 227, 287, 303, 315, 347, 362
L36	16.92	Unidentified dicarboxylic labdane acid, diME	79, 93, 107, **121**, 161, 189, 221, 287, 302, 347, 362
L40	17.12	Unidentified dicarboxylic labdane acid, diME	79, 93, 107, **121**, 189, 287, 302, 347, (362)
L38	17.24	Unidentified labdenoate	79, 93, 107, **121**, 189, 241, 257, 301, 319, 334
L43	17.31	Unidentified dicarboxylic labdane acid, diME	79, 93, 107, **121**, 175, 201, 211, 288, 303, 347, 362
A22	17.39	7-hydroxy-dehydroabietate	121, 195, **237**, 253, 297, 312, 330
A24	17.30	Oxygenated 7,13,15-abietatrien18-oate	91, 117, 121, 183,197, 239, **254**, 267, 299, 314, 329
A28	17.69	15-hydroxy-dehydroabietate	255, 273, **315**, 330
L44	17.49	Agathalate	79, 93, **107**, 121, 133, 147, 201, 229, 239, 289, 303, 314, 332
L45	17.75	Agathate, dimethylester	81, 93, 107, **121**, 189, 211, 227, 249, 287, 302, 347, 362
A32	17.98	7-oxo-dehydroabietate	187, 211, **253**, 269, 296, 328
L49	18.34	Agatholate	81, 93, **107**, 121, 243, 271, 303, 319, 334
L50	18.63	Unidentified labdane	79, 93, **107**, 119, 147, 237, 253, 315, 331, 346
L53	18.87	Acetoxy-agatholate	79, 93, **107**, 135, 147, 241, 301, 316, 329, 344, 361, (376)

Tab. 4.10 Compounds found in samples analysed in chapter 4.1.3, methylated methanol extracts, all samples analysed with temperature program Diterpenes 1 and column A, mass spectra references see appendix

Label	Description	Picture	Sampling: date, description
4.4.8	Manila Copal, medium hard, Dr. Rehbaum, 1978, F. 200°C, AFAD material collection		14.10.2008; irregular orange pieces, transparent with dirt included
4.4.9	Manila Copal, dark, Dr. Rehbaum, 1978, F. 110°C, AFAD material collection		14.10.2008; yellow to brown irregular pieces, opaque, with dirt included
BlaD 11	Gum Copal Manila, medium lumps, Eggebrecht, 2006 (#*101170*)		14.10.2008; light yellow to citron pieces, opaque, with dirt included
BlaD 13	Copal resin, dark, Eggebrecht, 2006 (#*101120/101130*)		05.11.2008; grey and brownish pieces, opaque and weathered surface, scraped material was powdered
4.4.7	Sambao Copal, Dr. Rehbaum, AFAD material collection		05.11.2008; light yellow and opaque piece, scraped material was powdered
BlaD 8	Copal, Kauri, Eggebrecht, 2006 (#*101310/101320*)		09.10.2008; yellow irregular pieces, opaque white crust and transparent interior, crust and interior sampled separately
BlaD 14	Kauri Copal, Fa. Hammerl, Christian Gruber		09.04.2008; sampled light brown to orange weathered pieces, opaque, material contains also light yellow to whitish weathered and opaque piece and grey pieces, which consists of a grew ash-like powder
AA BD	*Araucaria angustifolia* (Bertol.) Kuntze, tree from Argentinia, listed 2008, Botanical Garden Berlin-Dahlem		11.02.2009; yellow and white, granulous drops, odourless, sticky and viscous, became greasy inside the vial, taken from the cut area between bark and heartwood, about 9.3 mg

Tab. 4.11 Description of reference samples analysed in chapter 4.1.3

4.1.4 Discussion

As discussed in chapter 2.5, conifer resins from different families are clearly distinguishable by the primary appearance of different compound classes or single compounds from these classes: abietane acids (Pinaceae), sandaracopimaric and communic acids, phenolic abietatrienes (Cupressaceae) and sandaracopimaric and labdane acids (Araucariaceae). Beside these predominant constituents, every family shows a typical profile of minor components, which in turn makes it additional possible to distinguish resins from different genera.

Pinaceae resins can be distinguished by the presence of pimaric acid and marker compounds such as abienols (*Picea* and *Abies*), labdane alcohols (*Larix*) and labdane acids (some species of *Pinus*). Pimaric acid proved to be a good marker for adulterations of commercial materials such as Venetian and Strasbourg turpentine, because both *Larix* and *Abies alba* Mill. resins do not contain that compound and it is stable also in aged materials. A comparison of the results from this work and literature data reveals some *Picea* resins which do not contain pimaric, and *Larix* resins which contain pimaric acid (table 2.2). The reported *Picea* resins were obtained from the bark and the cone, a harvesting method commonly applied for *Abies* (blisters) and *Larix* resins. Pimaric acid is a compound of the sapwood, and *Picea* and *Pinus* resins usually are exuded from the primary and secondary xylem (Langenheim 2003: 114-119). But all Pinaceae genera may also produce resins in the cortex and the cambium (ibid.). Therefore, *Picea* (and *Pinus*) resins obtained from other parts than the sapwood would probably not contain pimaric acid.

This is different with *Larix* resins, because several species were found to contain pimaric acid even though they were obtained from the heartwood (table 2.2, Mills 1973). The grouping suggested by Mills indicates mainly American species and *L. kaempferi* to contain small amounts of pimaric acid and no larixol and larixylacetate. Instead they contain cembrol and *iso*-cembrol. European species such as *L. decidua* and *L. gmelinii* contain no or only traces of pimaric acid and high amounts of larixol and larixylacetate, while the third group containing *L. pendula* and *L. x marschlinsii* (listed as *L. x eurolepis*) contains traces of pimaric and intermediate amounts of larixol and larixylacetate (Mills 1973). This would make materials obtained from European larches well distinguishable from other Pinaceae. However, the composition of *L. kaempferi* found in this work differs from the compositions reported by Mills. This indicates it is part of the European larch group. One may argue that the sample analysed here was obtained from the sapwood, but this was the case with *L. gmelinii* as well, which does show a similar composition to that published by Mills.

Concerning the non-acidic markers, *Larix* resins contain high amounts of larixol and epimanool and *Abies* epimanool, high amounts of abienol and *cis*-abienol and lower of iso-, *trans*-abienol and L10. The resins of *Picea abies* Karst. and *P. pungens* Englm. contain cembrene, *iso*-cembrol, Δ13-*cis*-neoabienol and *cis*- and *trans*-abienol (table 4.2), that of *P. omorica* Purk. epimanool, *iso*-abienol, abienol, high amounts of *cis*-abienol and lower of *trans*-abienol. *cis*-abienol is present both in *Abies* and in *Picea* resins, but the composition of other abienols (*iso*-abienol, abienol, Δ13-*cis*-neoabienol, *trans*-abienol, D8, D10, L10) and non-acidic diterpenes such as cembrene, cembrol and epimanoyloxide is different. The composition of the resin of *Picea omorica* was clearly different from that of *P. abies* and *P. pungens*. The analysis of commercial reference samples demonstrated that the data profiles are still incomplete. Δ13-*cis*-neoabienol – present in *P. abies* and *P. pungens* but not in *Abies alba* – is, however, found in modern Strasbourg turpentine attributed to *Abies alba* and in modern Burgundy pitch, obtained reportedly from *Picea abies* but attributed by the ratio of pimaric and sandaracopimaric acid to pine resin.

The aim of the investigation of Burgundy pitch was to characterize a typical composition and draw conclusions about its botanical origin and production procedure. The investigated samples are derived from pine species and are composed very similar to colophony. Main characteristics are the presence of unisomerised abietane acids (palustric and abietic acids) and relatively uniformely distributed amounts of oxygenated abietane acids from oxidation states 3 to 5 (see Fig. 2.4). Colophony is produced at temperatures between 150 and 180°C (Falbe, Regnitz 1995). Considering the aging state of Burgundy pitch and the fact that the main process during heating is isomerisation, the materials may be heated or melted at low temperatures. This gives rise to the questions whether modern descriptions of Burgundy resin melted in the sun may be correct (Scents of the Earth 2012).

Aged Pinaceae resins show a very complex composition, and there are still several unidentified compounds, which complicates the interpretation. Several compounds are identified as light aging markers (A27, A36, A37 and A43), the main process seemingly was the formation of additional double bonds. Light aged materials also contain higher amounts of C-15 oxygenated abietane acids.

Main constituents of **sandarac** called resins are the diterpene phenolic abietatrienes ferruginol, totarol and sugiol, together with high amounts of sandaracopimaric and isomers of communic acids. From literature data it is known that the combined presence of communic and sandaracopimaric acids and phenols is typical for other resins from the Cupressaceae as well (Mangoni, Belardini 1967; Hegnauer 2001: 493; Cox et al. 2007). Cupressaceae resins from *Tetraclinis articulata* Mast. and *Juniperus communis* L. can be distinguished by the presence of oxygenated sandaracopimaric acids, which are present in high amounts in the resin of *Tetraclinis articulata* Mast. Results indicate that the presence of hydroxy- and acetoxy-sandaracopimaric acid is exclusive to the genus *Tetraclinis*. The presence of the phenolic abietatrienes is not sufficient for an unambiguous identification of true sandarac. High amounts of sandaracopimaric, communic and phenolic abietatrienes such as totarol, ferruginol, sugiol but also hinokinol and several others are present in both resins. Additionally, sandaracopimaric and communic acids are also present in some Araucariaceae resins from *Agathis* and *Araucaria*, even though no phenolic abietatrienes are visible.

Commercial sandarac partically shows the composition of *Tetraclinis articulata*, and partly lacks the phytochemical markers and contains high amounts of C-15 and C-19 oxygenated labdane acids such as agathic and cupressic acids. They are reported as typical constituents of sandarac (Scalarone et al. 2003; Scalarone et al. 2003b), but are not present in the resins of *Tetraclinis articulata* Mast. and *Juniperus communis* L.. Several of those acids are present in Araucariaceae resins as well, even though in a different composition, which supports the assumption of a chemotaxonomical connection. From the present data, the origin of these labdane acids, however, remains open. The commercial sandarac references clearly diverge into two groups: Samples, which do not contain the mentioned labdane acids, contain hydroxy- and 12-acetoxy-sandaracopimaric acids, dehydroabietic acids and a differing composition of phenolic abietrienes and the other way around.

Araucariaceae resins are well distinguishable from other conifer resins and, when labeled as copal, from other legume and triterpene copals (see chapter 4.2.2 and 4.3.2). They contain high amounts of sandaracopimaric and labdane acids, Kauri copals (*Agathis australis* Steud) and *Araucaria* resins also abietane acids and their aging products. The present investigation shows a phytochemical connection to Cupressaceae resins, in particular to some of the commercial sandarac materials: sandaracopimaric, communic acids, compound D22 and labdane acids such as agathic, isocupressic acids and the compounds L20 and L38.

4.2. Angiosperm Resins I - Fabales

The chapter covers resins from Angiosperm family *Fabacaea*, order Fabales. It was not possible to obtain botanical samples, therefore the analyses are based on samples selected according to their terminology rather their botanical classification. A chemotaxonomical attribution is given by literature data (chapter 2.2), Copaiba balsam from *Copaifera* species (chapter 4.2.1), legume copals from *Guibourtia*, *Tessmania* and *Daniellia* species (chapter 4.2.2) and Balsam of Peru and Tolu from *Myroxylon balsamum* Harms varieties (chapter 4.2.3). The chapter does not focus on chemotaxonomical correlations between the different genera in contrast to chapter 4.1 but rather to supplement the data profiles of the investigated resins. The harvesting methods and trading details of these non-European resins are partially unknown or poorly documented, which is why a possible influence of these parameters on the chemical composition of a material of a particular name have to be kept in mind for the interpretation of the chemical data.

4.2.1 Copaifera – Copaiba balsam

Seven reference samples labelled Copaiba, Kopaivabalsam or Balsamum Copaive are investigated in order in order to gain a more complete picture of the differences between the species used for the production of the material. The references originate from the AFAD collection or were purchased for this work. All samples are described in table 4.14. Table 4.16 summarizes the results from the analyses.

The methylated methanol extract of Copaiba balsam purchased in 2008 (BLaD5) is shown in Fig. 4.15. The older materials 5.1.4 and 5.1.5 from the AFAD collection show a similar composition (see table 4.14). Main compounds in the sesquiterpene fraction are β-caryophyllene together with lower amounts of α-copaene, trans-α-bergamotene, α-humulene, γ-muurolene, δ-cadinene. In the diterpene fraction high amounts of copalate together with lower amounts of eperuate, labda-8-en-15-oate, kovalenate, hardwickiate, hydroxy- and acetoxy-copalate and 12-acetoxy-hardwickiate are present. Other constituents are compound eL2, kaur-16-en-15-oate and dimethylagathate. This composition corresponds with the type A reported in the literature (see tables 2.3, 4.16). Additionally, high amounts of pimarate and abietane acids such as pimaric, sandaracopimarate, isopimarate, palustrate, dehydroabietate, abietate and neoabietate, their aging markers (A24, A28, A32), are present.

The methylated methanol extract of Copaiba balsam 5.1.6 is shown in Fig. 4.16. The materials 5.1.1 and 5.1.2 show a similar composition. Main compounds in the sesquiterpene fraction are trans-α-bergamotene, β-selinene, β-bisabolene and caryophyllene oxide together with lower amounts of α-copaene and β-elemene. In sample 5.1.1 also β-caryophyllene is present (not shown). In the diterpene fraction high amounts of kaur-16-en-19-oate, kauran-19-oate, copalate and polyalthate and lower of eperuate, labda-8-en-15-oate, labdanoate, cativate, compound eL17, hardwickiate and dimethyl-ent-pinifolate are present. Other constituents are hydroxy- and acetoxy-copalate and 12-acetoxy-hardwickiate. They are present in varying but low amounts. This composition corresponds with the type B reported in the literature (see tables 2.3, 4.16). Additionally, small amounts of pimarane and abietane acids such as pimaric, sandaracopimarate, isopimarate, dehydroabietate as well as their aging markers (A24, A28, A32) are present. In contrary to the type A, no unisomerised abietane acids such as palustrate, abietate and neoabietate are found. Pimarane acids are minor constituents, while the relative amounts of dehydroabietate change. All samples of this type show a somewhat darker, brownish, colour compared to those of the type A (5.1.4, 5.1.5, BLaD5; see table 4.14).

The methylated methanol extract of Copaiba balsam 5.1.3 is shown in Fig. 4.17. Main compounds in the sesquiterpene fraction are caryophyllene oxide together with intermediate amounts of α-copaene, β-elemene, δ-selinene, β-caryophyllene, trans-α-bergamotene, γ-muurolene, β-selinene and β-bisabolene. Small amounts of α-humulene, the compounds S11 and S13 are also present. Some of these compounds are not found in any of the other investigated samples, such as δ-selinene, S11 and S13, but the other constituents are a mixture of the typical compounds of the two compositions types A and B. In the diterpene fraction high amounts of daniellate together with intermediate amounts of compound eL30, labda-8-en-15-oate, cativate, copalate, compound eL17, kovalenate and hardwickiate are present. Other constituents are eperuate, kaur-16-en-19-oate, polyalthic and 12-acetoxy-hardwickiate. 5.1.3 also contains dihydro- and Δ8-dihydroagathate, pimarate, sandaracopimarate, isopimarate and high amounts of abietate.

Abietane and pimarane compounds are chemotaxonomical uncharacteristic for resins from Fabaceae. As mentioned in the literature, these compounds originate from an adulteration

Label	Description	Picture	Sampling: date, description
5.1.1	Copaiba, AFAD material collection		April 2008: dark brown and transparent liquid with a medical smell, quickly dried up after sampling
5.1.2	Copaiva-Balsam, Vormelker, AFAD material collection		April 2008; dark brown and transparent liquid with a medical smell
5.1.3	Copaiva-Balsam, Emil Geller Nachfahren Dresden, AFAD material collection		April 2008; dark brown and transparent liquid with a medical smell, very viscous to solid (dried up)
5.1.4	Copaiba, CB Kassel, AFAD material collection		April 2008; dark brown and transparent liquid with a medical smell, solid to very viscous (dried up), sampled in solid lumps
5.1.5	Balsamum Copaive, 1977, AFAD material collection		April 2008; semi-liquid, clear and transparent upper layer of yellow colour, whitish, crystalline and opaque layer below of dark yellow colour, medical smell
5.1.6	Copaiva-Balsam, AFAD material collection		April 2008; dark brown and transparent liquid with a medical smell, very viscous to solid, brittle surface
BlaD 5	Copaiba balsam, naturally clarified, Eggebrecht, purchased in 2008, Christian Gruber		2008; light yellow, clear and transparent liquid with a medical smell, darkens with time

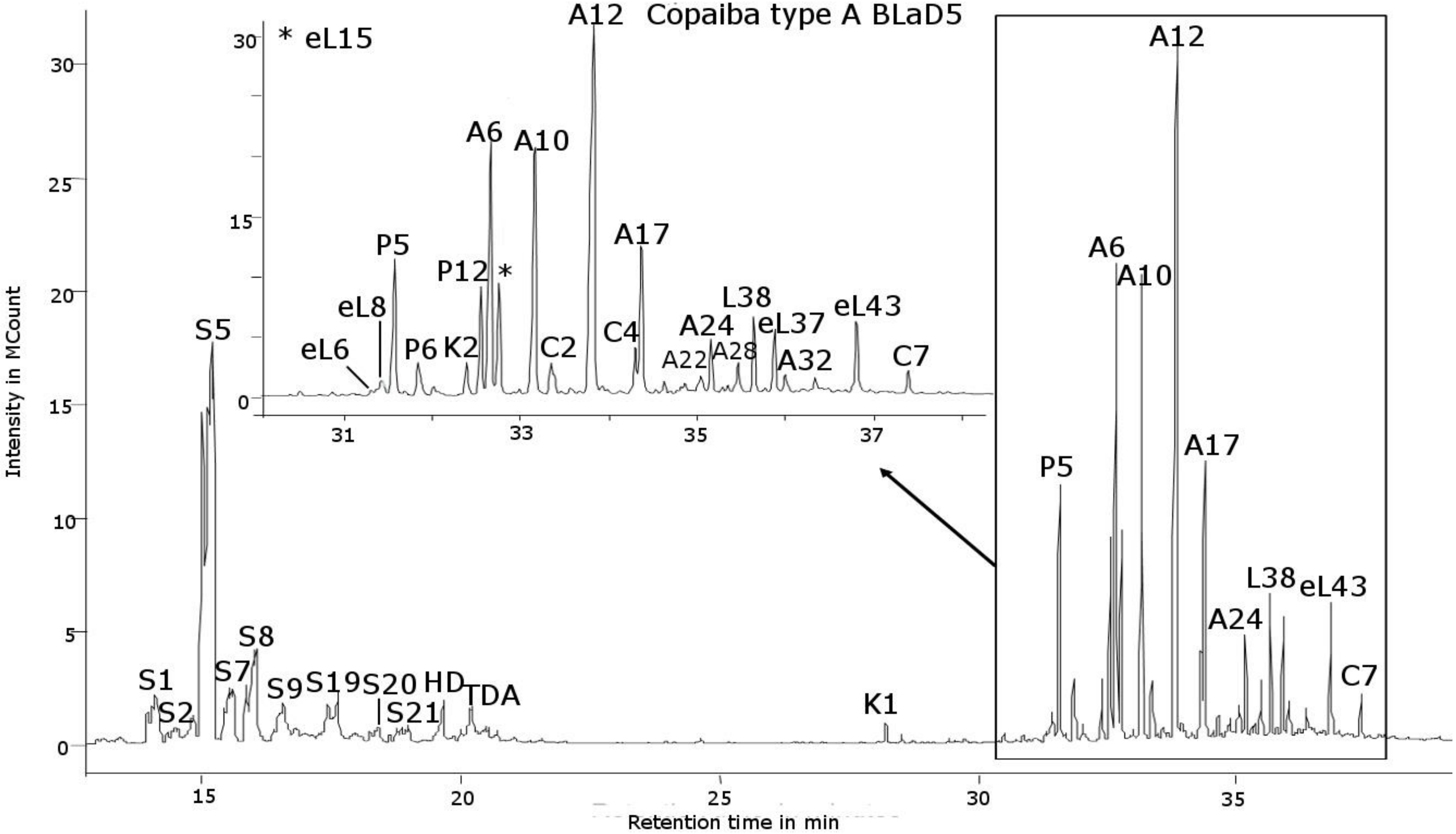
Tab. 4.12 Description of reference samples analysed in chapter 4.2.1

with conifer resin or colophony (van der Werf et al. 2000; Langenheim 2003: 395). They are found here in all of the investigated samples in changing amounts, in much higher amounts in samples of the type A than in samples of the type B. Samples of the type B do also not contain unisomerised abietane acids, which indicates colophony was used rather than pine resin for adulteration.

The results from both composition types are summarised in table 4.16. Marker compounds for the type A are γ-muurolene, δ-cadinene and kovalenic acid, for the type B β-selinene, β-bisabolene, kauran-19-oic and polyalthic acid. α-Humulene is found only in the type A, but literature data suggest that it is present in a wide range of *Copaifera* resins belonging to both composition types (table 2.3). Ent-pinifolic acid is found in this work only in the type B, but it is reported also for the type A (van der Werf et al. 2000). It is evident that characteristic marker compounds are only present in small amounts, while the main constituents (S5, S7, S21, eL15, K2, C4) are found in high amounts in both types. Also some other compounds (eL6, eL37, eL43, C7) are present in smaller amounts in both types. The two composition types differ in the relative amounts of marker compounds, however. For example, typical high amounts of kaur-16-en-19-oic, kauran-19-oic, polyalthic and hardwickiic acid appear together in samples of the type B. β-caryophyllene is present in high amounts together with small amounts of α-bergamotene only in samples of the type A, while it is the other way around in samples of the type B. The results are mainly consistent with published data (chapter 2.2, table 2.3).

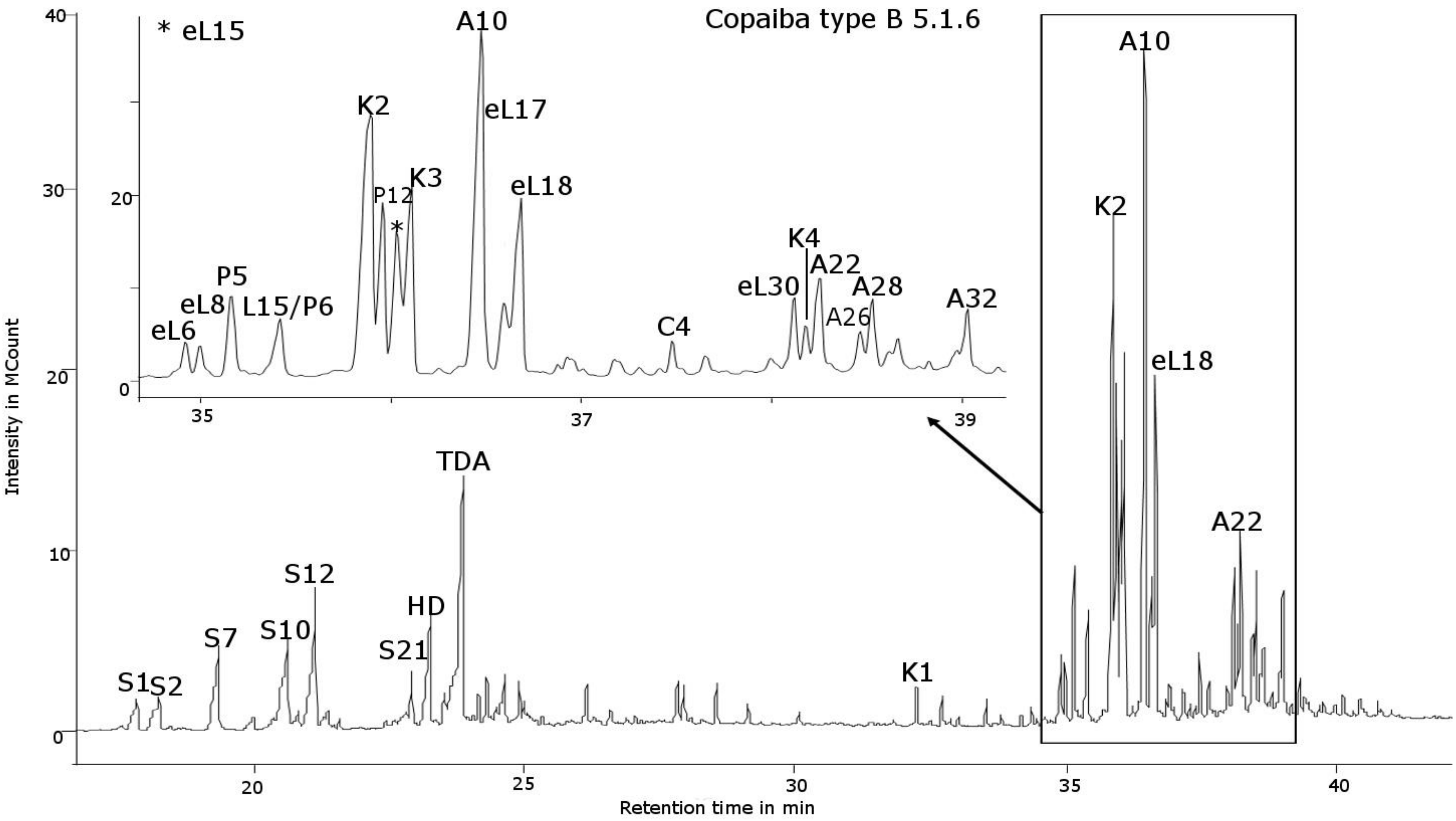
The composition of sample 5.1.3 does not correspond to one of the two types. The presence of kovalenic and polyalthic acids indicates the type A as well as the absence of kaur-19-oic and ent-pinifolic acids. But compound eL17 is found only in samples of the type B. Additionally, daniellic acid is present, which is not found in any of the other samples. Daniellic acid is reported for the resin of *Daniellia oliveri* Hutch. & Dalziel, which also contain oliveric acid, the 13β-epimer of ent-pinifolic acid. Mass spectra of stereoisomers are in general very similar and differ mainly in the intensity of the peaks. Epimanool, the 13α-epimer of manool, is present in Pinaceae resins (chapter 4.1.1.1), manool in sandarac (chapter 4.1.2). The 13α-epimer elutes somewhat earlier than the 13β-epimer. eL30 elutes at the same retention time in 513 and 516, which indicates that it is the same stereoisomer, ent-pinifolate. If not both epimers are present or the stereochemistry was investigated with other methods than those used in this work, it is impossible to determine for sure, which epimer is present. Because ent-pinifolic acid is reported as a typical constituent of Copaiba balsam (van der Werf et al. 2000), eL30 is identified as ent-pinifolate. eL30 is also present only in minor amounts here, while oliveric acid reported to be is present in higher amounts in the resin of *Daniellia oliveri*.

Also, the sesquiterpene fraction of 5.1.3 contain marker from both types (S9, S10, S12). It somewhat resembles the reported composition of the sesquiterpene fraction of the resin from *Copaifera reticulata* Ducke (table 2.3). Herrero-Jáuregui et al. analysed several different samples of this resin. The constituents with the most constant presence and amounts are β-elemene, trans-α-bergamotene, β- and α-selinene and β-bisabolene (Herrero-Jáuregui et al. 2011). Because no investigation of its diterpene fraction is found, the botanical origin of 5.1.3 remains open.



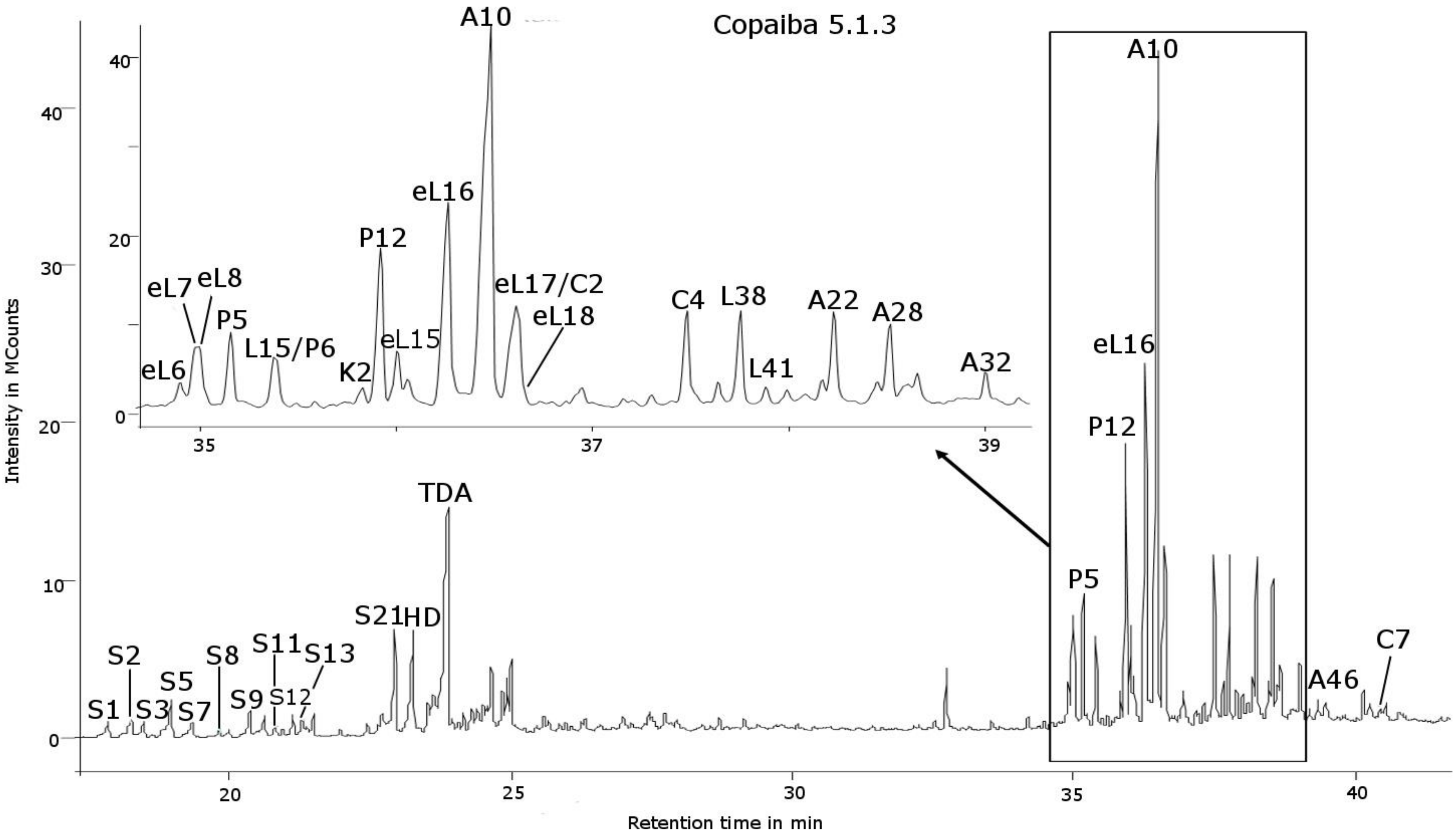
Methylated methanol extract (labels, see table 4.15)

Fig. 4.15 Gas chromatogram of Copaiba balsam BLaD5 (type A), sesqui- and diterpene section (TIC)



Methylated methanol extract (labels, see table 4.15)

Fig. 4.16 Gas chromatogram of Copaiba balsam 5.1.6 (type B), sesqui- and diterpene section (TIC)



Methylated methanol extract (labels, see table 4.15)

Fig. 4.17 Gas chromatogram of Copaiba balsam 5.1.3, sesqui- and diterpene section (TIC)

Label	t_{R1}	t_{R2}	Name	Main mass fragments
S1	14.17	17.83	α-Copaene	91, **105**, 119, 161, 204
S2	14.51	18.23	β-Elemene	79, **93**, 105, 119, 147, 161, 189, 204
S3		18.45	δ-Selinene	91, 105, 119, 133, 161, 189, **204**
S4			Cyperene	79, 91, 105, 119, 133, 161, 189, **204**
S5	15.19	18.96	*Trans*-β-caryophyllene	79, **91**, 93, 105, 133, 161, 204
S7	15.61	19.33	*Trans*-α-bergamotene	79, 93, **119**, 204
S8	16.06	19.80	α-Humulene	79, 80, **93**, 105, 121, 204
S9	16.59	20.37	γ-Muurolene	91, 105, 119, **161**, 204
S10		20.61	β-Selinene	**79**, 93, 105, 119, 133, 161, 189, 204
S11			Probably valencene	79, 93, **105**, 119, 161, 189, 204
S12		21.11	β-Bisabolene	67, 79, **93**, 119, 161, 204
S13		21.28	Unidentified	79, 91, 105, 119, **161**, 189, 204
S19	17.62		δ-Cadinene	91, 105, 119, **161**, 204
S20	18.40		Unidentified	67, 79, **93**, 105, 121, 161, 189, 204
S21	19.01	22.93	Caryophyllene oxide	**79**, 91, 93, 105, 220
K1	28.51		Ent-kaur-16-ene	79, 91, **105**, 119, 213, 229, 257, 272
eL2	31.29		Unidentified labdane acid, ME	81, 95, 107, **121**, 135, 217, 244, 303, 318
eL6	31.40	34.90	Eperuate	**81**, **95**, 121, 137, 177, 191, 305, 320
eL7		34.97	Unidentified labdane acid, ME	79, 95, 107, **121**, 161, 191, 215, 262, 277, 305, 322
eL8		34.99	Labda-8-en-15-oate	**95**, 107, 121, 191, 277, 305, 320
eL10	31.68		Labdanate	67, 81, 95, 109, **123**, 257, 275, 307, 322
P5	31.54	35.15	Pimarate	**121**, 241, 257, 301, 316
P6	31.84	35.35	Sandaracopimarate	**121**, 241, 301, 316
L15	31.96	35.40	Cativate	79, 93, **107**, 122, 149, 191, 305, 320
K2	32.37	35.82	Kaur-16-en-19-oate	91, 131, 187, 213, **241**, 257, 273, 301, 316
P12	32.54	35.92	Isopimarate	187, 227, **241**, 256, 287, 316
A6	32.64		Palustrate	**241**, 301, 316
eL15	32.75	35.99	Copalate	**81**, 95, 114, 121, 137, 243, 271, **303**, 318
K3		36.09	Kauran-19-oate	81, 93, 109, 123, 149, 243, **259**, 286, 303, 318
eL16		36.26	Daniellate	81, **121**, 189, 239, 330
A10	33.13	36.46	Dehydroabietate	**239**, 299, 314
eL17		36.57	Probably ent-labda-13-en-8-ol-15-oate	81, **109**, 135, 161, 189, **204**, 243, 271, 303, 318, (336)
C2	33.33	36.61	Kovalenate	95, 107, 120, **189**, 243, 253, 303, 318
eL18		36.69	Polyalthate	81, **121**, 189, 255, 330
A12	33.75		Abietate	185, 213, **241**, 256, 273, 316
C4	34.28	37.48	Hardwickiate	96, **139**, 175, 203, 219, 235, 283, 299, 330
L38		37.74	Dihydroagathate, diME	**121**, 161, 304, 364
A17	34.36		Neoabietate	121, **135**, 301, 316
L41		37.88	Δ8-Dihydroagathate, diME, see chapter 4.2.2	119, **175**, 235, 257, 289, 304, 364
eL30		38.11	Ent-pinifolate, diME	93, **121**, 161, 235, 304, 332, 364

Label	t_{R1}	t_{R2}	Name	Main mass fragments
K4		38.16	Probably an oxygenated kaurane	229, **255**, 289, 315, 330
A22	35.03	38.22	7-Hydroxy-dehydroabietate	121, 195, **237**, 253, 297, 312, 330
A24	35.14		Oxygenated 7,13,15-abietatrien18-oate	121, 183, 239, **254**, 299, 314, 315, 329, 330
A26	35.33		Unidentified abietane	163, 195, **237**, 255, 287, 330
A28	(35.46)	38.52	15-Hydroxy-dehydroabietate	255, 273, **315**, 330
L45	35.64		Agathate, diME	81, 93, 107, **121**, 189, 301, 347, 362
eL37	35.86		Hydroxy-copalate	93, **107**, 119, 135, 175, 203, 225, 241, 269, 273, 301, 316, 319, (334)
A32	35.99	39.01	7-Oxo-dehydroabietate	187, 211, **253**, 269, 296, 328
A36		39.32	Unidentified hydroxy-dehydroabietate	181, 195, 211, **249**, 264, 309, 324
eL43	36.79		Acetoxy-copalate	93, 107, 119, 135, 147, 175, 203, 225, 241, 269, 273, **301**, 316, (362)
C7	37.38	40.43	12-Acetoxy-hardwickiate	81, 139, 173, 187, 201, **219**, 233, 281, 296, 328, 357, 408
A46			7-Oxo-15-hydroxy-dehydroabietate	187, 269, **329**, (344)

Tab. 4.13 Compounds found in samples analysed in chapter 4.2.1, methylated methanol extracts, samples analysed with temperature program Diterpenes 2, t_{R1} = retention time of samples analysed with column A, t_{R2} = retention time of samples analysed with column B, mass spectra references see appendix

	BlaD5, 5.1.4, 5.1.5	5.1.1, 5.1.2, 5.1.6
Attributed to	*C. multijuga, C. cearensis*	*C. duckei, C. guyanensis, C. langsdorfii*
Sesquiterpenes		
Main	trans-β-caryophyllene	caryophyllene oxide, trans-α-bergamotene, β-bisabolene
Minor	α-copaene, trans-α-bergamotene, α-humulene, γ-muurolene, δ-cadinene	α-copaene, trans-β-caryophyllene, β-selinene
Labdanes		
Main	copalic acid	kaur-16-en-19-oic, kauran-19-oic, copalic, eL17, polyalthic, hardwickiic acids
Minor	eperuic, kovalenic, hardwickiic acids	eperuic, labdanic acids
Occ.	kaur-16-en-19-oic acid (minor)	cativic, ent-pinifolic acids (see text)
Misc.	agathic acid, hydroxy- & acetoxy-copalic acid, acetoxy-hardwickiic acid	
Pimaranes and Abietanes		
	pimaric, sandaracopimaric, isopimaric acid	pimaric, isopimaric acid
	dehydroabietic, abietic, neoabietic acid	dehydroabietic acid

Tab. 4.14 Characteristic compounds of Copaiba balsam reference samples

4.2.2 Legume copals

Six samples attributed by their name to legume copals, which according to literature may originate from the genera *Hymenaea* (Africa, America), *Guibourtia, Tessmania* and *Daniellia* (America), are investigated. The aim is to gain a more complete picture of the chemical composition of legume copals, of which no systematic investigation is found. All samples are described in table 4.17.

Congo copal

The methylated methanol extract of Congo copal (4.4.10; Fig. 4.19a) is characterised by high amounts of eperuate and ent-labda-8-en-15-oate together with smaller amounts of kovalenate, ent-labdanolate (eL20) and oxygenated ent-labdan-15-oates such as eL33, eL34 and eL40. Minor constituents are epimanool, compound eL1, iso-ozate, compound eL4, cativate, compound eL12, copalate, the compounds D16, D20 and eL22, dimethyl-ent-pinifolate and compound eL32. Iso-ozate, which is present only in traces, coelutes with compound eL4. The other Congo copal (BLaD12) also contains C1, an unidentified compound with a mass spectrum resembling that of kovalenate (not shown). Compound D16 is reported by van den Berg et al. for Congo copal without identification (van den Berg et al. 2002).

For several of these compounds, no reference mass spectra are found. Typical fragmentation reactions of ent-labdane acids are shown in Fig. 4.18, based on Enzell and Ryhage, Domenech-Carbo et al. and own considerations (Enzell, Ryhage 1964; Domenech-Carbo et al. 2009). Main differentiation characteristics are the position of the double bond and the position of the carboxyl group at C-15 or C-18. All discussed mass spectra are given in the appendix.

If the double bond is exocyclic or no double bond is present, the fragmentation proceeds as shown in Fig. 4.18a and 4.18b. The reaction in Fig. 4.18b is characteristic for ent-labda-8(20)-en-18-oic acids, and results in a prominent peak at m/z 121, which is not found for ent-labdanes with a carboxyl group at C-15. Ent-labdanes are mainly oxygenated at C-15, but single compounds have a carboxyl group at C-18 (see Fig. 2.8). C-19 oxygenation is reported occasionally for guamáic and polyalthic acids and for additional hydroxyl and carbonyl groups (Mills, White 1999: 104; Domenech-Carbo et al. 2009). While Hugel et al. report hydroxyl groups at position C-18 for the resin of *Hymenaea verrucosa* Gaertn., Domenech-Carbo et al. report a variety of 19-hydroxy-ent-labden-15-oic acids (Hugel et al. 1966; Domenech-Carbo et al. 2009). Because it is not possible to determine the exact position here, in the following a related functional group is set on C-18, where C-19 may also be possible.

In the case of an endocyclic double bond, fragmentation as shown in Fig. 4.18a is not present. This is the case for cativate (Δ7(8)), L17 and L41 (Δ8(9)). The elimination of the side chain (Fig. 4.18c) is a characteristic reaction for a Δ8(20) (exocyclic) and of high intense for a endocyclic (Δ7(8), Δ8(9)) double bonds, when the fragmentation as in Fig. 4.18a is hindered (see also discussion under 'Other copals' below). When the double bond is located in the side chain, an alternative fragmentation is observed, as shown in Fig. 4.18d.

The mass spectrum of ent-labdanolate is given by Enzell and Ryhage and somewhat differently by Pinto et al. (Enzell, Ryhage 1964; Pinto et al. 2000). The compound eL20 is identified as ent-labdanolate by its mass spectrum, which is similar to that of Pinto et al. Characteristic peaks are at m/z 177, 123, 109 and 101. After the elimination of water from C-8 and that of the side chain (Fig. 4.18c) the resulting fragment at m/z 177 is further decomposed as shown in Fig. 4.18e, which results in the peaks at m/z 123 and 109. This fragmentation is typical for a Δ7(8) double bond, which is formed after the elimination of water from C-8. The origin of the main peak at m/z 101 is not clear. Compound eL22 shows a similar mass spectrum, whereas it is probably the 8β-isomer of ent-labdanolate.

Compound eL12 has a base peak at m/z 121, which is typical for C-18 (or C-19) oxygenation (Enzell, Ryhage 1964). The fragment results from a fragmentation similar to that in Δ8(20)-ent-labdenes with further elimination of the functional group (Fig. 4.18b) (see also 'Sierra Leone copal' below).

The compound eL32 shows a peak for [M-28] at m/z 304, which indicates a carbonyl group and a compound with two double bonds. The peaks at m/z 203 and a low intense one at m/z 187 indicate a fragmentation of the side chain (Fig. 4.18c). However, the peaks at m/z 235 and 175 are very typical peaks for a carboxyl group located at C-18 together with endocyclic double bonds, which prevent a fragmentation of the ring B as shown in Fig. 4.18a. The peak at m/z 139 in contrast suggests a fragmentation as shown in Fig. 4.18e. The position of the carbonyl group therefore stays unclear.

Compounds eL33, eL34 and eL40 are oxygenated ent-labden-15-oates. Compound eL33 is discussed in the next paragraph about Sierra Leone copal, where it is the main constituent. Compound eL34 (MW 334) has peaks at m/z 303 ($[M-OCH_3]^+$) and 287 ($[M-CH_3-CH_3OH]^+$), followed by the loss of water (m/z 269). This indicates a hydroxyl group, which is sterically hindered. The main peak at m/z 205 results from the fragmentation of the side chain, followed by the loss of water (Fig. 4.18c), the fragmentation of ring B (Fig. 4.18a, b) is visible at m/z 149, 135 and 121, both indicating a Δ8(20) double bond. Due to the molecular ion at m/z 334, the compound must have two double bonds. The second one is probably located in rng A, because a fragmentation such as shown in Fig. 4.18d is not observed, and an endocyclic double bond in ring B would have prevented its fragmentation.

Label	Description	Picture	Sampling: date, description
4.4.10	Kongo Copal, light, Dr. Rehbaum, 1978, AFAD material collection		Oktober 2008: very brittle orange and opaque pieces with black inclusions, powdered surface
BlaD 12	Gum Copal Kongo, hard, Eggebrecht, 2006 *(#101300, Gum animae*)		November 2008: orange and brown pieces, opaque crust, transparent interior with inclusions
4.4.3	Copal, Sierra Leone, Dr. Bleck, AFAD material collection		November 2008: light yellow and transparent, powdered surface
4.4.12	Copal, Sierra Leone, AFAD material collection		November 2008: brittle light yellow and opaque pieces, powdered surface
4.4.4	Gum Copal, americ. , AFAD material collection		November 2008: yellow and brownish opaque pieces
C 1	Zansibar Copal, also 'goose-like' copal, Bern, Ulrich Schießl		Oktober 2008: light yellow, opaque pieces with knobs on the surface

Tab. 4.15 Description of references samples analysed in chapter 4.2.2

Compound eL40 (MW 354) shows peaks for the elimination of CH_3OH followed by the loss of water (m/z 322, 304). The base peak at m/z 189 results from the elimination of water from C-8, followed by the fragmentation of the side chain (m/z 207) and further loss of water from C-18. The mass spectrum additionally shows small peaks at m/z 177, 123 and 109 as well as 101, which are typical for a hydroxyl group located at C-8 (see eL20 above). eL40 is ent-labda-8,18-diol-15-oate.

Sierra Leone copal

The methylated methanol extract of Sierra Leone copal 4.4.3 (Fig. 4.19b) is characterised by high amounts of the compounds eL29, eL31 and eL33, together with intermediate amounts of the compounds eL21, eL24, eL25 and eL27. Other constituents of Sierra Leone copal 4.4.3 are epimanool, compounds eL4 and eL5, eperuate, cativate, compound eL12, copalate, compound eL19 and ent-pinifolate, compounds eL4, L15 and eL15 are present only in traces. The other Sierra Leone copal (4.4.12) contains mainly the compounds eL24 and eL33 and only small amounts of the other compounds, instead small amounts of iso-ozate, daniellate and ent-labdanolate are present (not shown; see table 4.17).

For the main constituents no reference mass spectra are found. Fragmentation reactions of ent-labdanes are shown in Fig. 4.18 and discussed in the paragraph about ‘Congo copal’. All discussed mass spectra are given in the appendix. The main constituents are oxygenated

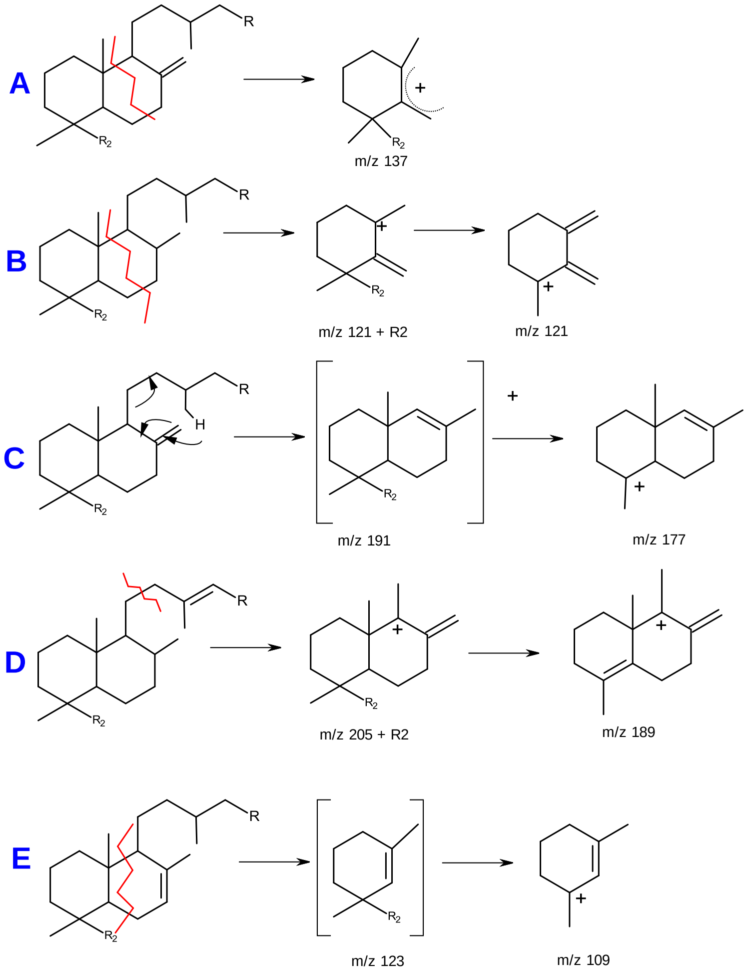
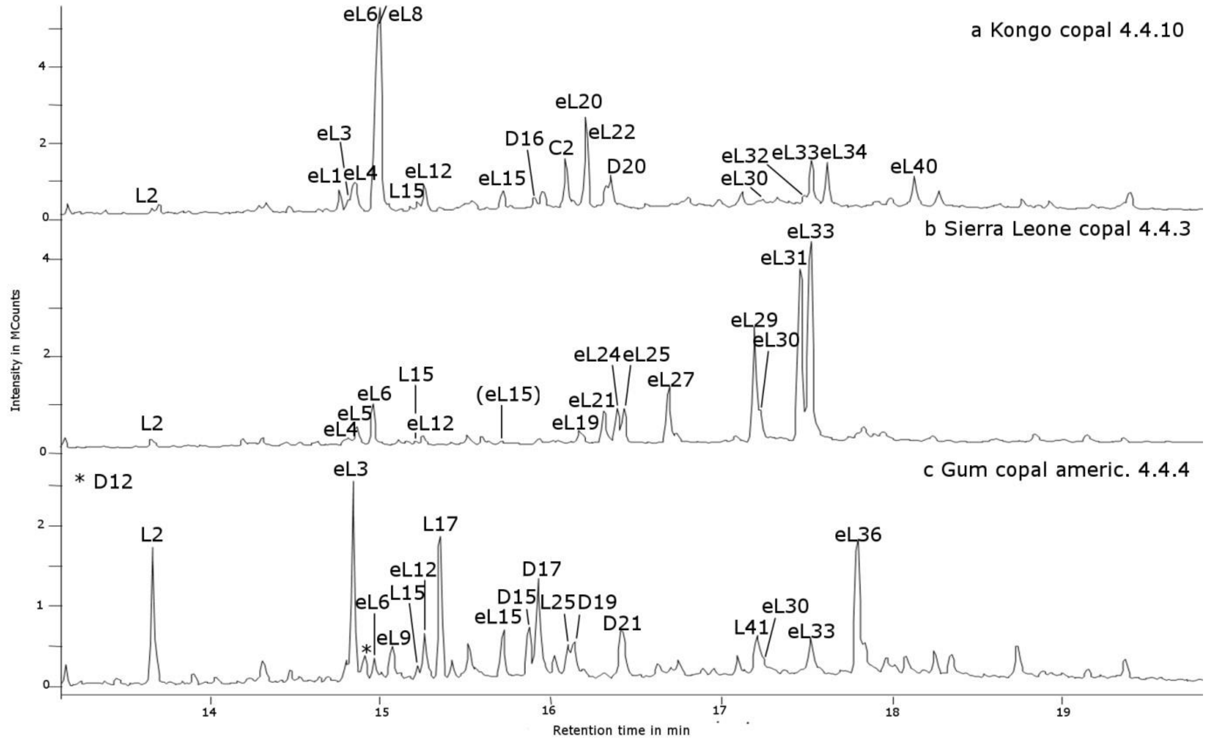


Fig. 4.18 Fragmentation reactions of ent-labdanes (based on Enzell, Ryhage 1964; Domenech-Carbo et al. 2009)



Methylated methanol extracts, a - Kongo copal 4.4.10, b - Sierra Leone copal 4.4.3 and c - Gum copal americanum 4.4.4 (labels, see table 4.18)

Fig. 4.19 Gas chromatograms of legume copals, diterpene section (TIC)

ent-labdane acids: nor-ent-labdanes (eL19, eL27), oxygenated ent-labdanes (eL21, eL31), 18-hydroxy- and methoxy-ent-labda-8(20)-en-15-oate (eL24, eL33) and hydroxy-ent-labden-18-oates (eL25, eL29). Methoxy-compounds are very likely artefacts of the sample preparation (see chapter 3.1.2).

eL19 is a nor-ent-labdane with the molecular ion at m/z 292. It shows a typical peak at m/z 123, which is found by Domenech-Carbo et al. for nor-ent-labdanes (Domenech-Carbo et al. 2009), and no elimination of an oxygen containing functional group. It is also present in the unmethylated methanol extract (not shown), therefore no carboxyl group is present. The peaks at m/z 191, 177 and 137 all result from fragmentation as shown in Fig. 4.18a. eL19 is therefore 19-nor-ent-labda-8(20)-ene.

Compounds eL21 and eL31 possess peaks for $[M-CH_2OH]^+$ and $[M-H_2O]^+$ from the loss of a methoxy and hydroxyl group, respectively. The peak for $[M-45]^+$, probably from the elimination of ethanol, is prominent for eL21 and smaller for eL31. eL31 is also present in the unmethylated methanol extract (not shown). Its mass spectrum does not show a peak from the elimination of the carboxyl group. The molecular ion is at m/z 308, the peaks at m/z 195, 177 and 163 result from the elimination of the side chain (Fig. 4.18c).

The elimination of ethanol from the whole molecule and of water and methanol from the peak at m/z 195 indicate a hydroxyl group at C-15. eL31 is 15,18-dihydroxy-ent-labane. eL21 has a small peak at m/z 259, which probably results from $[M-45-H_2O]^+$. Due to the sterical hinderness of this fragmentation, the eliminations of $[M-CH_3OH]^+$ and $[M-CH_3OCH_2]^+$ result from the methoxy group at C-15. eL21 is 15-methoxy-18-hydroxy-ent-labdane.

Compound eL24 is identified by published data as 19-methoxy-ent-labd-8(20)-en-15-oate (Domenech-Carbo et al. 2009, without identification at van den Berg et al. 2002). Typical peaks results from the loss of methanol (m/z 318) and ethanol ($[M-45]^+$, m/z 305). The peaks

Label	t$_R$	Name	Main mass fragments
L2	13.66	Epimanool	**81**, 95, 107, 121, 137, 163, 257, 272, (290)
eL1	14.76	Endocyclic ent-labden-15-oate	95, 107, 121, **191**, 277, 305, 320
eL3	14.83	Iso-ozate	93, 107, **121,** 187, **241**, 257, 301, 316
eL4	14.84	Unidentified ent-labdane acid, ME	**95**, 109, 135, 191, 257, 275, 301, 317
eL5	14.86	Unidentified ent-labdane	**81**, 95, 121, 137, 177, 191, 277, 292, 305, (320)
D12	14.89	Unknown diterpene acid	93, 133, **173**, **188**, 203, 241
eL6	14.95	Eperuate	81, **95**, 107, 121, 137, 177, 191, **305**, 320
eL8	15.00	Ent-ent-labda-8-en-15-oate	**95**, 107, 121, **191**, 277, 289, 305, 320
eL9	15.11	Unidentified ent-labdan-diol	**93**, 107, 257, 273, 288, (306)
L15	15.21	Cativate	95, **107**, 122, 191, 289, 305, 320
eL12	15.25	Ent-labda-18-oate	79, **121**, 161, 215, 231, 247, 262, 275, 290, 322
L17	15.33	Probably rearranged labdane (Fig. 4.20)	105, 119, 133, **175**, 203, 235, 257, 316
eL15	15.71	Copalate	**81**, 95, 114, 121, 137, 243, 271, 303, 318
D15	15.85	Unidentified diterpene acid	133, 173, **188**, 203, 241, 330
D16	15.89	Unidentified diterpene	107, 119, 138, **189**, 207, 305, 321, 336
D17	15.91	Probably ent-labda-8(20)-en-15,18-diol	95, 119, 133, **161**, 189, 207, 257
C2	16.08	Kovalenate	95, 107, 120, **189**, 243, 253, 303, 318
L25	16.09	Labda-13-en-8-ol-15-oate	81, 109, 114, 135, 161, 189, **204**, 303, 318, 336
D19	16.12	Unidentified	81, 107, **121**, 161, 189, 257, 273, 330
eL19	16.16	19-Nor-ent-labda-8(20)-ene	81, **95**, 109, 123, 177, 277, 292
eL20	16.21	Ent-labda-8-ol-15-oate (ent-labdanolate)	81, **101**, 109, 121, 123, 177, 235, 305, 320, 338
eL21	16.31	15-Methoxy-18-hydroxy-ent-labdane	81, 95, 121, 149, 195, **277**, 290, 307, 322
eL22	16.32	Unidentified ent-labdane acid, ME, probably 8β-labdanolate	81, 93, 95, 101, **109**, 123, 161, 189, 217, 303, 318, 336
D20	16.35	Unidentified ent-labdane	95, 109, 135, **191**, 207, 289, 305, (320)
eL24	16.38	18-methoxy-ent-labda-8(20)-en-15-oate	93, 107, 121, 175, 223, **305**, 318, 335, 350
D21	16.40	Unidentified diterpene	81, **93**, 107, 119, 133, 187, 220, 257, 305, 320
eL25	16.42	15-Methoxy-ent-labd-8(20)-en-18-oate	**121**, 161, 235, 290, 303, 318, 335, 350
eL27	16.69	18-Hydroxy-nor-ent-labda-13(14)-en-15-oate (proposed)	**81**, 95, 107, 121, 135, 163, 277, 291, 304, 322
eL29	17.19	Hydroxy-ent-labda-8(20)en-18-oate	**121**, 161, 253, 276, 289, 304, 318, 336
L41	17.19	Δ8-Dihydroagathate, diME	95, 107, 121, 175, 203, **235**, 257, 289, 304, 349, 364
eL30	17.23	Ent-pinifolate, diME	**121**, 161, 235, 304, 322, 364
eL31	17.45	15,18-Dihydroxy -ent-labane	81, 95, 121, 149, 263, **277**, 290, 308
eL32	17.48	Oxo-ent-labda-13(14)-dien-15-oate	107, 139, 175, 203, 235, 286, 304, **332**
eL33	17.52	18-hydroxy-ent-labda-8(20)-en-15-oate	81, 107, 121, 135, 175, 223, 291, **305**, 318, 336
eL34	17.62	Hydroxy-ent-labda-8(20)- diene-15-oate	121, 135, **205**, 287, 303, 319, 334
eL36	17.79	18-hydroxy-ent-labda-7(8)-en-15-oate	95, **107**, 122, 149, 189, 207, 291, 305, 318, 336
eL40	18.13	Ent-labda-8,18-diol-15-oate (proposed)	95, 137, 163, **189**, 207, 304, 322, 354

Tab. 4.16 Compounds found in samples analysed in chapter 4.2.2, methylated methanol extracts, samples analysed with temperature program Diterpenes 1 and column A, mass spectra references see appendix

at m/z 121, 135 and 149 result from a fragmentation as shown in Fig. 4.18a. According to literature, the peak at m/z 223 originates from the elimination of the side chain (Fig. 4.18c) followed by the elimination of the methoxy group yielding m/z 175 (Domenech-Carbo et al. 2009). The original hydroxyl-form is eL33, which corresponds in fragmentation patterns, retention time and relative amounts (for the methoxy ether of hydroxyl groups yielded by TMSH see chapter 3.1.2). In the mass spectrum of eL33 peaks for $[M-H_2O]^+$, $[M-CH_2OH]^+$, the fragmentation of the side chain at m/z 223 and 191 indicate a carboxyl group at C-15, hydroxyl group at C-18 and a Δ8(20) double bond. Fragmentation as shown in Fig. 4.18a gives m/z 149, 135 and 121.

Compound eL25 (MW 350) is a methoxy-ent-labden-18-oate, the fragmentation pattern of C-18 oxygenated labdane acids is discussed in the paragraph about Congo copals above. The same fragmentation pattern with an additional peak at $[M-H_2O]^+$ is observed for compound eL29 (MW 336), which is the hydroxy-form of eL25. The double very likely is located at Δ8(20) due to peaks at m/z 235 and 175 (Fig. 4.18c). Small peaks are visible at mz 243 and 258 resulting from a fragmentation of the side chain as shown in Fig. 4.18d. The double bond at Δ13(14) is a result of the elimination of methanol from C-15. The two compounds elute very close together, therefore a double bond isomerisation is possible.

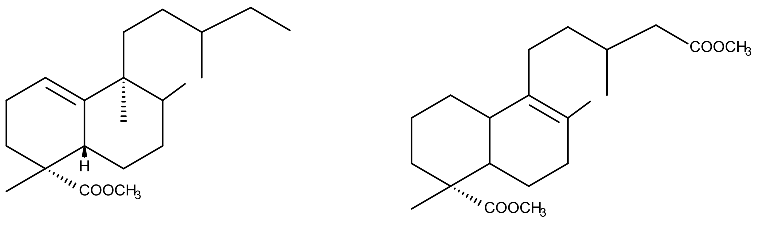
The fragmentation pattern of eL27 is not totally clear. It has peaks for $[M-H_2O]^+$ and $[M-CH_2OH]^+$ and $[M-CH_3OCH_2]^+$. It is not present in the unmethylated methanol extract, and the peaks at m/z 209, 177 and 163 very likely result from a fragmentation as shown in Fig. 4.18d. This indicates a double bond at Δ13(14) and a carboxyl group at C-15. Due to its molecular ion at m/z 322 eL27 is probably a 18-hydroxy-nor-ent-labda-13(14)-en-15-oate, whereby the exact position of the lost methyl group is not known.

Other copals

The methylated methanol extract of Gum copal americanum (4.4.4; Fig. 4.19c) is characterised by high amounts of iso-ozate, the compounds L17, D17 and eL36. Lower amounts of the compounds eL9, eL12, copalate, compound D15, labda-13-en-8-ol-15-oate (L25), compounds D19, D21, L41 and eL33 are present. Other compounds are D12, eperuate, cativate and dimethyl-ent-pinifolate. The compounds D12 and D15 have similar mass spectra, but were not identified. Compound D17 possesses no carboxyl group, because it elutes at the same retention time in the unmethylated methanol extract (not shown), it is identified by referencing the literature as labda-8(20)-en-15,18-diol (Hugel et al. 1966). The Zansibar copal C1 is composed similar with higher amounts of the compounds eL9, copalate and eL33. It additionally contains a compound with a mass spectrum very similar to dimethylagathate, probably the enantiomeric dimethyl-guamáate (Cunningham et al. 1973). According to Cunningham et al., compound L25 is labda-13-en-8-ol-15-oate, no ent-labdane but the enantiomeric form, found as a major compound in the trunk resin of *Hymenaea courbaril* (Cunningham et al. 1974). In Copaiba balsam the entantiomer is present (eL17; chapter 4.1.2).

All discussed mass spectra are given in the appendix. Compound eL36 (MW 336) shows typical peaks at $[M-H_2O]^+$, $[M-CH_2OH]^+$ and [M-45] and m/z 207 and further loss of water at m/z 189 due to the loss of the side chain (Fig. 4.18c). This indicates a hydroxyl group at position C-18. Fragmentation as shown in Fig. 4.18e at m/z 122 and 109 is typical for Δ7(8) double bond. It is therefore the Δ7(8) isomer of 18-hydroxy-ent-labden-15-oate.

The mass spectrum of compound L41 indicates a dicarboxylic acid (MW 364), where the elimination of the side chain as main fragmentation reaction leads to the fragments at m/z 235 and 175 (Fig. 4.18c). As discussed under 'Congo copals', the lack of the typical fragmentation as shown in Fig. 4.18a indicates an endocyclic double bond. In compounds with a Δ8(20) double bond, for example ent-pinifolic acid, peaks at m/z 235 and 175 are of low intensity while m/z 161 and 121 resulting from fragmentation 4.18a are much more intense. The mass spectrum of L41 is nearly identical with the published mass spectrum of Δ8-dihydroagathate, a double bond isomer of pinifolate (Mills et al. 1984/85; Fig. 4.20). L41 is present in Baltic amber at the same retention time (see chapter 4.4.1). Baltic amber does not contain ent-labdanes, therefore compound L41 may be the enantiomeric labda-8(9)-en-15,18-dioate. On the other hand, a rearranged labdane, as found in the seed pod resin of *H. courbaril*, with a double bond at C-10 and the methyl group moved from C-10 to C-9, possesses a similar mass spectrum (Khoo, Oehlschlager 1973). This is supported by the high amounts of L25 in Gum copal americanum 4.4.4, which is reported as a major compound in *H. courbaril* (Cunningham et al. 1974). The rearranged labdane possesses only one carboxyl group (Fig. 4.20), wherefore it is probably identical with L17, which has a mass spectrum similar to L41 and a molecular weight of 316.



Rearranged labdane

Dihydro-Δ8-agathic acid

Fig. 4.20 Possible structures of compound L17 and L41 (mass spectra see table 4.18 and appendix)

Summary

The Congo copals analysed are dominated by ent-labda-8(20)-en-15-oic acids, isomers thereof, ent-labdan-8-ol-15-oic and kovalenic acids. Compounds with additional functional groups at C-18 are present in lower amounts. Typical compounds are eperuic, ent-labd-8-en-15-oic, kovalenic, labdanolic, D20 and 18-oxygenated ent-labdane and ent-labdene acids (eL32, eL33, eL34, eL40). The Sierra Leone copals analysed show a different composition, dominated by hydroxylated and methoxylated ent-labdanes and ent-labdane acids. Additionally, nor-ent-labdanes and ent-labda-8(20)-en-18-oic acids are present. Eperuic and copalic acid are present only in small amounts, the latter only in traces, which is reported to be typical for Sierra Leone copal (White, Kirby 2001).

Gum copal americanum and Zansibar copal are composed similar. They contain high amounts of epimanool, iso-ozic acid, 18-hydroxy-ent-labda-7(8)-en-15-oic acid and two rearranged labdanes (L17, L41), lower of eperuic, copalic, labda-13-en-8-ol-15-oic acid (L25) and eL33 are present. The presence of L25, rearranged labdanes and guamáic acid points to *Hymenaea* as does the nomenclature. Rearranged labdanes (L17, L41) are reported for Hym*enaea courbaril*, high amounts of epimanool for *Hymenaea verrucosa* and guamáic acid for the Amazonian species *Hymenaea oblongifolia*. Diterpene American copals are mainly derived from tropical American *Hymenaea* species, and Zansibar copal is known to be obtained from *Hymenaea verrucosa* Gaertn. (chapter 2.2). Several of the present compounds could not be identified. It is also known from the literature that the composition of *Hymenaea* resins varies widely within the genus (Cunningham et al. 1973), therefore the present data supplement the data profiles of *Hymenaea* resins without any general conclusion derivable.

4.2.3 *Myroxylon* – Balsam of Tolu and Peru

In this chapter two samples of Balsam of Peru and two samples of Balsam of Tolu are investigated. All samples are described in table 4.19. The aim of the chapter is to determine typical constituents of those *Myroxylon* resins and evaluate mass spectrometric data.

Balsam of Peru

The methanol extract of Balsam of Peru (5.2.2; Fig 4.22) contains high amounts of benzylbenzoate and benzylcinnamate together with smaller amounts of free benzoic and cinnamic acids, *trans*-nerolidol, cinnamylbenzoate and cinnamylcinnamate. Cinnamylcinnamate is not present in the older sample from the AFAD reference collection (5.2.1; not shown). Other constituents are cinnamyl and coniferyl alcohol, vanillin, benzoate and cinnamate. In the methylated methanol extract (Fig. 4.24a) benzyl alcohol and its methylether, dihydrocinnamyl alcohol and methoxy-ferulate are present. Because they are not methylated, phenylpropanoid esters are discriminated with TMSH used. Benzyl alcohol is not present in the methanol extract, because a different column with lower retention times was used (see chapter 3.1.3).

In the diterpene section of the methanol extract a variety of unidentified phenylpropanoid esters elute (PP23-PP24, PP26-PP34). Mass spectra of benzyl-, cinnamyl- and other alcohols with benzoic, cinnamic and ferulic acid have been presented in the NIST database and in the literature (Pastorova 1997: 76, 77; Bankova et al. 1989). Esters of coniferyl and p-coumaryl alcohol and ferulic and p-coumaric acids are more difficult to find. These compounds possess hydroxyl groups, which may be methylated depending on the derivatisation agent used. In other investigations they were examined mainly as their trimethylsilylated form (Pastorova 1997: 69-89; Modugno et al. 2006a; Hovaneissian et al. 2008). Silylation of hydroxyl groups has been proven to be more easier than methylation, but mass spectra of trimethylsilylated compounds differ from that of the methylated compounds and are therefore of limited value for this work. Pastorova presented the elution order of some compounds (Pastorova 1997: 74f). In order to identify some of the unknown compounds, the respective mass spectra are evaluated. Identification is achieved mainly by comparison of typical peaks of the methylesters of benzoic, cinnamic and ferulic acids and corresponding alcohols from known mass spectra (Fig. 4.21). The main fragmentation is the cleavage of the ester bond resulting in the formation of a radical from the alcohol. The remaining cation is further decomposed (Fig. 4.21, red cleavage). Characteristic fragments for the acids are benzoate at m/z 105, cinnamate at m/z 131 and 103 and ferulate at m/z 177, 150 and 145. In the literature m/z 193 is also mentioned (Bankova et al. 1989).

A second fragmentation reaction is a McLafferty rearrangement of the whole molecule involving the alkyl group, which is typical for higher alcohols (GDC 2009). It results in the formation of alkene radicals, which are further fragmented (Fig. 4.19, black cleavage). Characteristic fragments for the alcohols are benzyl alcohol at m/z 91, cinnamyl alcohol at m/z 115 and coniferyl alcohol at m/z 163. Dihydro-coniferyl alcohol, which is mentioned in the literature as a component of benzoate and cinnamate esters (Hausen et al. 1995; Hausen 2001), would have an additional peak at m/z 137. The remaining cation undergoes further fragmentation, which results in small but characteristic peaks for benzoate at m/z 105, cinnamate at m/z 107 and ferulate at m/z 193 (Fig. 4.21).

Another McLafferty rearrangement is typical for aldehydes and results in the elimination of water and carbon monoxide. Typical fragments are $[M-18]^+$ and $[M-28]^+$ (Pastorova 1997: 76-81). Another peak characteristic for acrylic cinnamate is present at $[M-46]^+$ resulting from the elimination of formic acid. It should not be found in benzoates (ibid.). Applied on ferulates and p-coumarates, which should also undergo that reaction, it is found in the present data as a double peak at [M-46/45], while the $[M-45]^+$ ion results from the elimination of the ethoxy radical.

Label	Description	Picture	Sampling: date, description
5.2.1	Peru Balsam, AFAD material collection		20.02.2009; semi-liquid black liquid with a smell of vanilla, dried out
5.2.2	Perubalsam nat. Ph. Eur. 5, Eggebrecht (#181000), 2008		25.02.2009; semi-liquid black brownish liquid with a smell of vanilla
5.6.1	Tolu Balsam, AFAD material collection		17.02.2009; soft brown reddish pieces with a smell of vanilla
5.6.2	Tolubalsam solid BP 2003/Ph. Eur. 5, Eggebrecht (#181400), 2008		17.02.2009; dark brown and glittering, very viscous and soft, consistence does not change with time, smell of vanilla and spices

Tab. 4.17 Description of reference samples analysed in chapter 4.2.3

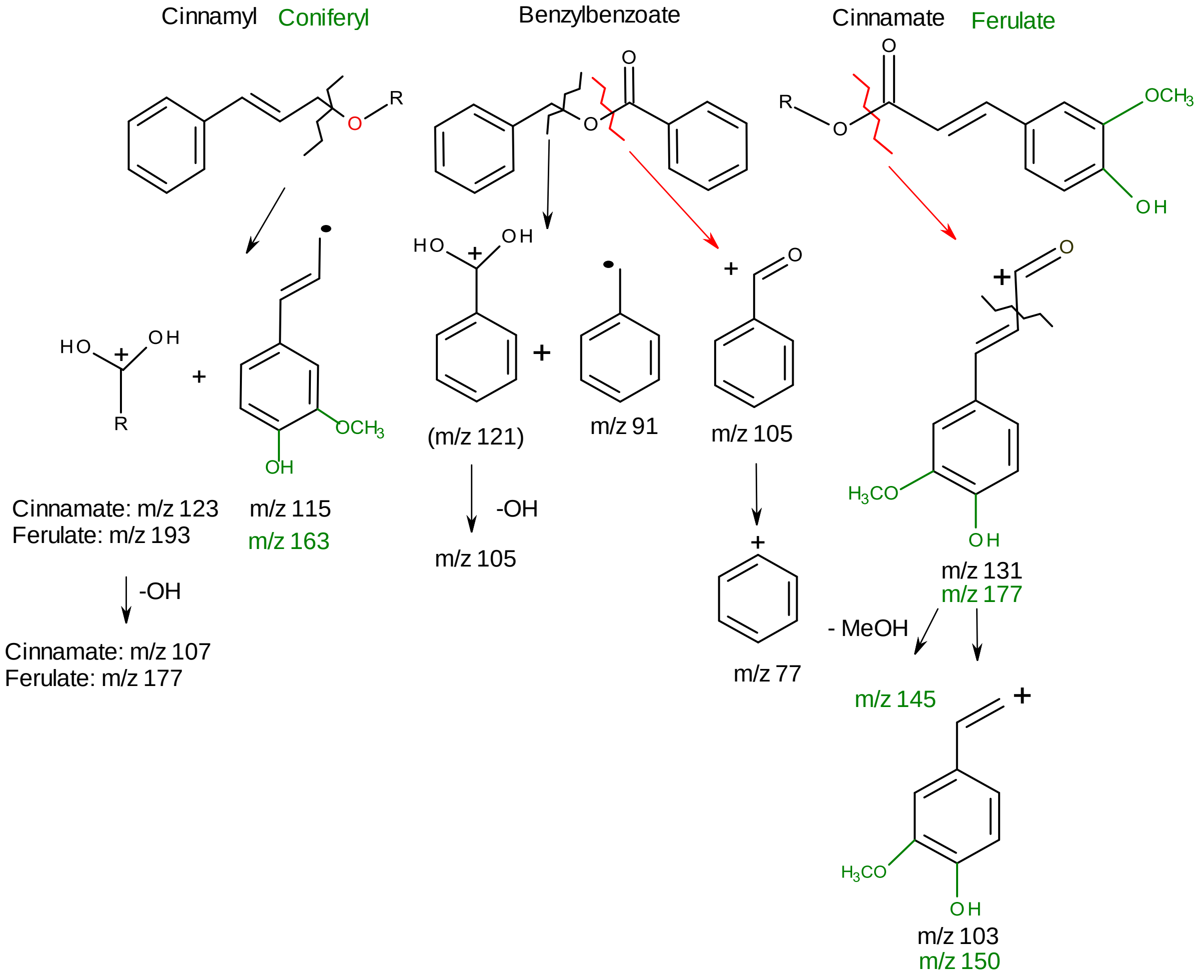


Fig. 4.21 Fragmentation reactions of esterified phenylpropanoids

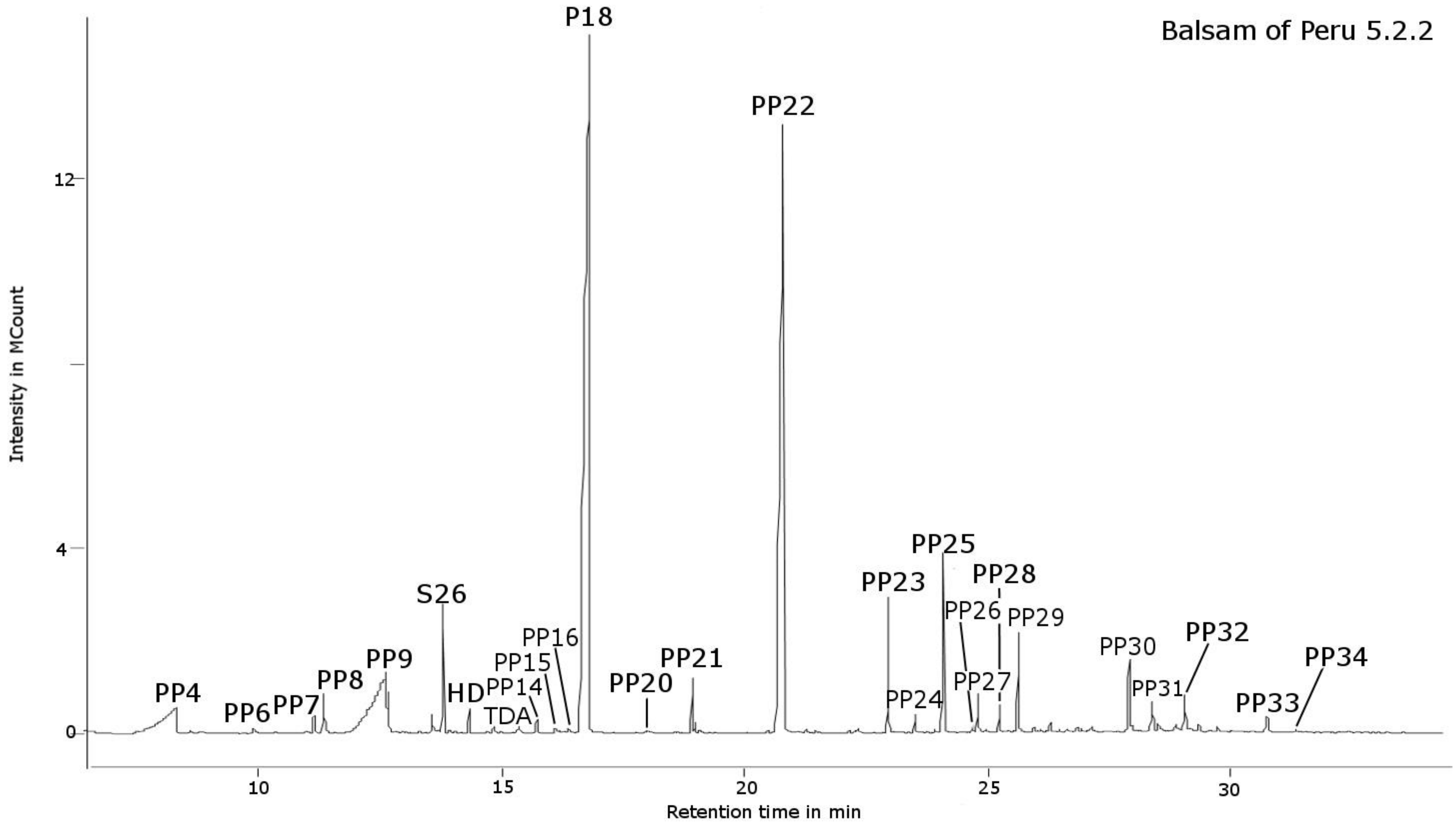
Label	t_R	MW	Proposed identification	Typical mass fragments (acid)	Typical mass fragments (alcohol)
PP23	22.96	(268)	Probably dihydrocinnamyl dihydrocinnamate, NIST: 3-phenylpropyl-3-phenylpropanoate	117, 118	103, 131, 147
PP24	23.51	284	Benzylferulate	145, 150, 161, 177, 207	91, 193, [M-18] at 266
PP26	24.68	254	Benzyl-p-coumarate	119, 147 [M-46/45] at 208/209	91, [M-18] at 236
PP27	24.80	300	Methyl-dihydroconiferylbenzoate	77, 105	137, 150, 163
PP28	25.23	284	Probably coniferylbenzoate	77, 105	163, 179?
PP29	25.63	284	Isobenzylferulate	145, 150, 161, 177, 207	91, 105, 193, [M-18] at 266
PP30	27.89	326	Methyl-dihydroconiferylcinnamate	103, 131	137, 150, 163
PP31	28.39	310	Cinnamate	103, 131, [M-45] at 265	
PP32	29.06	312	Unidentified	115, 139, 175, 188, 297, 312	
PP33	30.74	324	Probably methyl-dihydroconiferylcinnamate	103, 131	137, 150, 163
PP34	31.35	358	Cinnamate, dihydroconiferyl derivative	[M-46], [M-31], 131	137, 151, 163

Tab. 4.18 Phenylpropanoid esters in Balsam of Peru, retention times refer to Fig. 4.22; main mass fragments are given in table 4.21

PP24 and PP29 show typical peaks for ferulic acid (m/z 145, 150, 177, 193,) and benzyl alcohol (m/z 91, [M-18]). Despite being reported only for Balsam of Tolu (Wahlberg et al. 1971), PP24 and PP29 are identified as (iso-)benzylferulate. Also p-coumaric acid is not reported for *Myroxylon* resins, characteristic peaks would be at m/z 147 and 119. Compound PP26 shows such peaks, together with a base peak at m/z 91 and high intense peaks at m/z 236 [M-18]$^+$ and 209 [M-45]$^+$. Therefore, it is identified as benzyl-p-coumarate. PP27 shows peaks for benzoic acid (m/z 77, 105), PP30 for cinnamic acid (m/z 103, 131). Both constituents possess characteristic peaks at m/z 137, 150 and 163. The latter is reported by Bankova et al. for 3,4-dihydroxy-cinnamate (caffeates), and m/z 137 and 150 are characteristic fragments of (dihydro-)coniferyl alcohol and the corresponding acid, 3-methoxy-4-hydroxy-cinnamic acid (ferulic acid). PP27 and PP30 are (dihydro-)coniferylbenzoate and –cinnamate, respectively. The corresponding molecular weight should be 284 and 310 for dihydro-coniferyl alcohols, in fact it is 16 Da higher in both cases. The alcohol may be 3,4-methoxy-dihydro-cinnamyl alcohol then. Dihydro-coniferyl benzoate and –cinnamate are reported as constituents of Balsam of Peru (Hausen et al. 1995; Hausen 2001). PP28 is probably coniferyl benzoate, which is reported for Balsam of Peru as a typical but instable compound (Hausen et al. 1995). It possesses typical peaks for benzoic acid (m/z 77, 105) and coniferyl alcohol (m/z 163), but the peak at m/z 179 points to ferulic acid. Benzylferulate however would have a prominent peak at m/z 91, which is not the case. The remaining compounds could not be identified. For PP23 the NIST database suggests 3-phenylpropyl-3-phenylpropanoate, which would be dihydrocinnamyl dihydrocinnamte. PP31, PP33 and PP34 show peaks for cinnamic acid, but the identity of the alcohol is not clear. Both, PP33 and PP34 have small peaks at m/z 137 and 163, which points to another dihydro-coniferyl derivative.

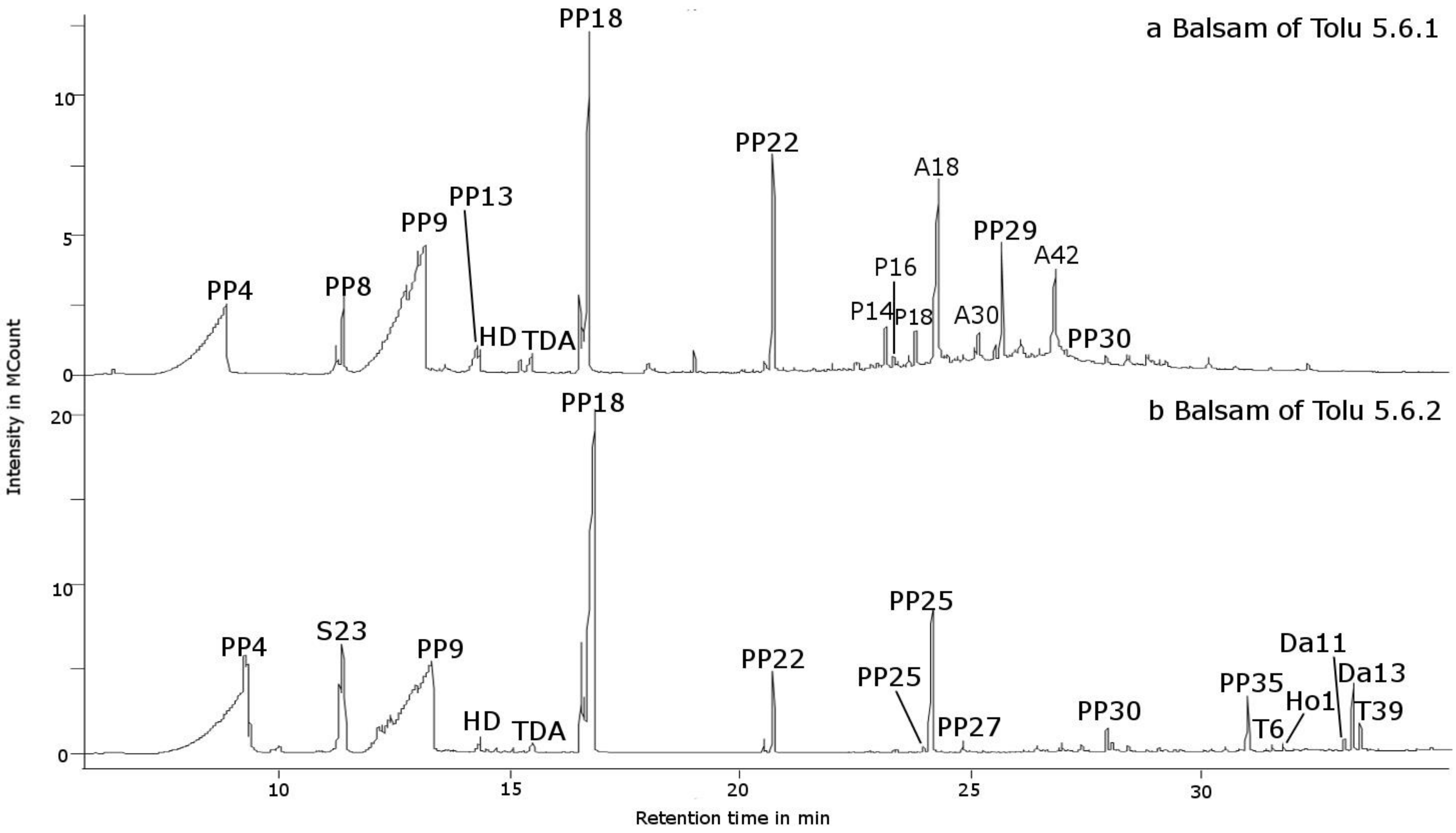
Balsam of Tolu

In the methanol extracts of Balsam of Tolu (5.6.2; Fig. 4.23b) high amounts of benzylbenzoate, benzylcinnamate, cinnamylcinnamate, free benzoic and cinnamic acids are present, together with lower amounts of cinnamal, cinnamyl alcohol and eudesamin. Another Balsam of Tolu (5.6.1; Fig. 4.23a) contains higher amounts of benzylcinnamate and additionally vanillic acid, but no cinnamylcinnamate, cinnamyl alcohol, any other cinnamyl esters but pimarane and abietane acids (P14, P16, P18, A18, A30, A32, A42). Neither of them contains cinnamylbenzoate, which is mentioned in the literature only for Balsam of Tolu but is found here only in the Balsam of Peru samples (see above). Sample 5.6.1 is adulterated with colophony. When compared to the Balsam of Peru samples investigated above, Balsam of Tolu (5.6.2) differs in containing cinnamal, S23, S24, S25, no cinnamylbenzoate and several triterpenes such as T6, Ho1, Da11 and Da13 (Fig. 4.22b). In the methylated methanol extract additionally oleanonate, oleanolate, 3-oxo-6β-hydroxy-olean-12-en-28-oate and sumaresinolate are present (Fig. 4.23b).



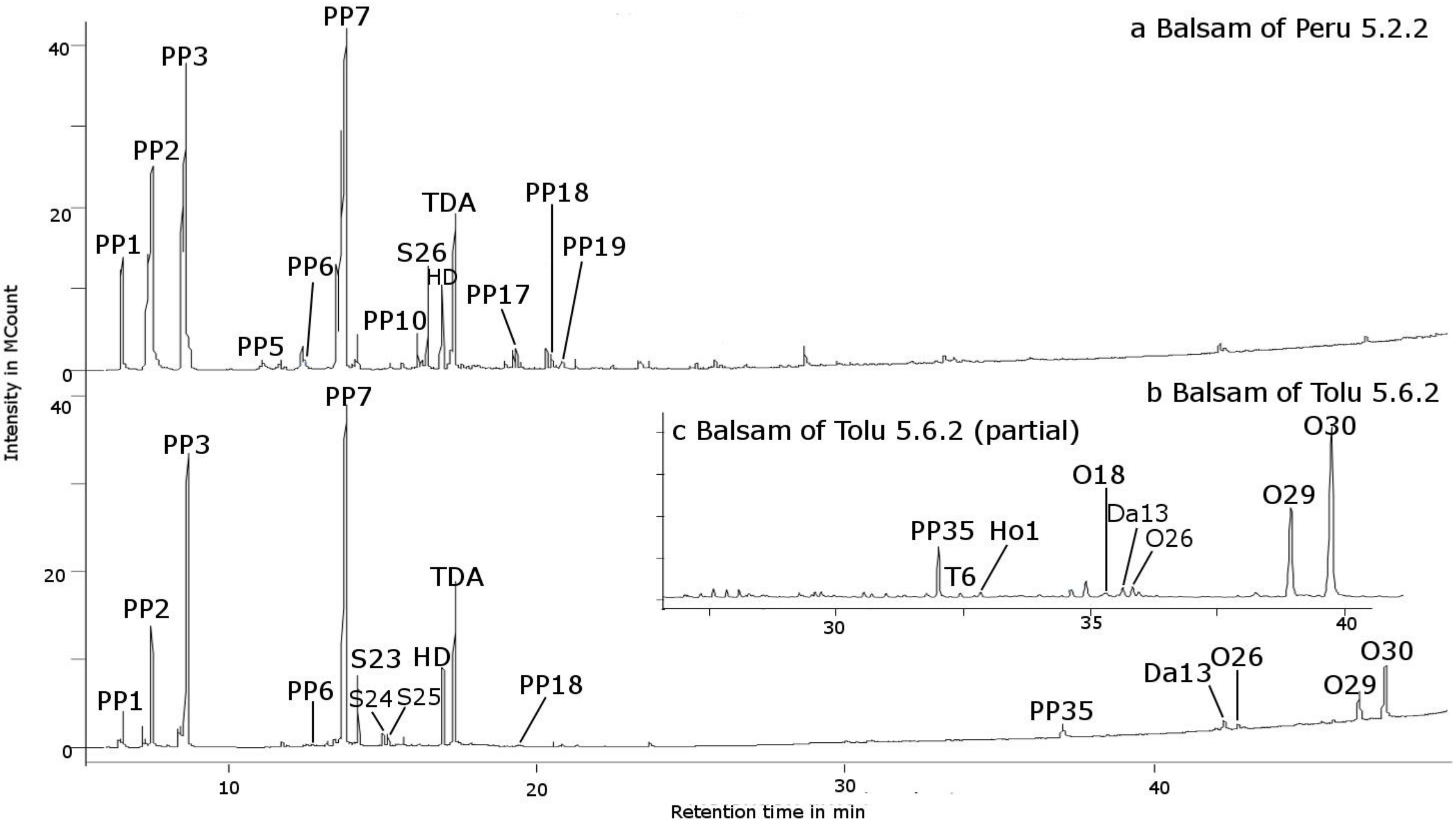
Methanol extract (labels, see table 4.21)

Fig. 4.22 Gas chromatogram of Balsam of Peru 5.2.2, mono-, sesqui- and diterpene section (TIC)



Methanol extracts, a - Tolu balsam 5.6.1 and b - Tolubalsam 5.6.2 (labels, see table 4.21)

Fig. 4.23 Gas chromatograms of Balsam of Tolu, mono-, sesqui-, di- and triterpene section (TIC)



Methylated methanol extracts, a - Perubalsam 5.2.2, b - Tolubalsam 5.6.2 and c - Tolubalsam 5.6.2 triterpene section (labels, see table 4.21)

Fig. 4.24 Gas chromatograms of Balsam of Peru and Tolu, mono-, sesqui-, di- and triterpene section (TIC)

Label	t_{R1}	t_{R2}	Name	Main mass fragments
PP1		6.50	Benzyl methyl ether	77, **91**, 121, 122
PP2		7.50	Benzyl alcohol	77, **79**, 91, 108
PP3	6.43	8.57	Benzoate	51, 77, **105**, 135, 136
PP4	8.24		Benzoic acid	51, 77, **105**, 122
PP5		11.11	Benzenepropanol (dihydrocinnamyl alcohol)	77, 91, 92, **117,** 118, 136
PP6	9.93	12.39	Cinnamyl alcohol	77, 78, 91, **92**, 105, 115, 134
PP7	11.13	13.73	Cinnamate	51, 77, 103, **131**, 162
S23	11.37	14.18	Cadina-3,9-diene (β-cadinene)	91, **105**, 119, 133, 147, 161, 189, **204**
PP8	11.33		Vanillin	81, 109, 123, **151**, 152
PP9	12.59		Cinnamic acid	77, 91, 103, 131, **147**, 148
S24		14.99	Unidentified sesquiterpene	79, **91**, 105, 119, 133, 147, 161, 189, 204
S25		15.15	Unidentified sesquiterpene	91, **105**, 107, 119, 133, 147, 161, 189, 204
PP10		16.13	Isomer of PP17	146, 165, **177**, 181, 193, 208
S26	13.79	16.44	*trans*-Nerolidol	67, 79, 81, **93**, 107, 121, 161, (222)
PP13	14.29		Vanillic acid	57, 71, 97, 125, 153, **168**
PP14	15.71		Methoxyeugenol	77, 91, 103, 119, 131, 162, **194**
PP15	16.09		Dihydroferulic acid	94, 122, **137**, 196
PP16	16.37		Coniferyl alcohol	77, 91, 124, **137**, 180
PP17		19.93	1,2-Dimethoxy-4-(3-methoxy-1-propenyl)benzene	77, 103, 131, 145, 146, **177**, 181, 208
PP18	16.72	19.31	Benzylbenzoate	77,91, **105**, 167, 194, 212
PP19		20.77	3,4-Dimethoxy-cinnamate	91, 147, 191, 207, **222**
PP20	17.98		Ferulic acid	77, 105, 133, 179, **194**
PP21	18.92		Cinnamylbenzoate	77, **91**, 103, 115, 131, 147, 178, 192, 220, 238
PP22	20.74	23.34	Benzylcinnamate	77, 91, 103, 115, 131, **192**, 220, 238
PP23	22.96		3-Phenylpropyl-3-phenylpropanoate	77, 91, 103, **117**, 118, 131, 280
P14	23.16		Pimaric acid	91, 107, **121**, 133, 241, 287, 302
P16	23.32		Sandaracopimaric acid	91, 107, **121**, 133, 241, 287, 302
PP24	23.51		Benzylferulate	**91**, 145, 150, 161, 177, 207, 239, 266, 284
P18	23.79		Isopimaric acid	91, 105, 131, 159, 187, 227, **241**, **287**, 302
PP25	24.12		Cinnamylcinnamate	77, 103, 115, 117, **131**, 219, 264
A18	24.29		Dehydroabietic acid	197, **239**, 285, 300
PP26	24.68		Benzyl-p-coumarate	**91**, 120, 147, 208, 209, 236, 254
PP27	24.80		Methyl-dihydroconiferylbenzoate	77, 105, **137**, 150, 163, 300
A30	25.15		7-methoxy-dehydroabietic acid (proposed)	181, 195, **237**, 283, 298, 315, 330
PP28	25.23		Unidentified phenylpropanoid	77, **105**, 131, 179, 284
A32	25.53		7-oxo-dehydroabietate	187, 211, **253**, 269, 296, 328
PP29	25.63		Isobenzylferulate	91, 145, 150, 161, 177, 207, 239, 266, **284**
A42	26.82		7-oxo-dehydroabietic acid	211, **253**, 299, 314
PP30	27.89		Methyl-dihydroconiferylcinnamate	103, **131**, 137, 150, 189, 326
PP31	28.39		Unidentifed phenylpropanoid	103, **131**, 265, 298, 310

Label	t_{R1}	t_{R2}	Name	Main mass fragments
PP32	29.06		Unidentified phenylpropanoid	139, 175, 189, **312**
PP33	30.74		Unidentified phenylpropanoid	103, 131, 137, 163, **324**
PP34	31.35		Unidentified phenylpropanoid	131, 137, **151**, 163, 312, 327, **358**
PP35	31.77	37.03	Eudesamin	151, **165**, 177, 355, 386
T6	32.19		Unidentified	**93**, 109, 189, 205, 313, 381, 409, 424
Ho1	32.59		22-Hydroxy-hopanone	**93**, 107, 121, 189, 205, 311, 355, 424
Da11	34.92	42.01	20,24-Epoxy-25-hydroxy-dammaran-3-one	107, 125, **143**, 161, 175, 205, 381, 399, 411, 443, (458)
O18	34.93	42.16	Oleanonate	133, 189, **203**, 262, 393, 409, 468
Da13	35.29	42.24	Hydroxydammarenone	68, 81, 95, **109**, 205, 298, 311, 355, 409, 424, (442)
O26	35.43	42.73	18α-Oleanonate	119, 133, 189, **203**, 262, 393, 453, (468)
T39	35.58		Unidentified triterpene	**79**, 95, 105, 119, 147, 189, 205, 395, 409, 423, 438
O29	38.42	46.63	3-Oxo-6β-hydroxy-olean-12-en-28-oate	133, 189, **203**, 262, 391, 407, 466, 466, 484
O30	39.17	47.47	Sumaresinolate	133, 189, **203**, 262, 425, 449, 468, 486

Tab. 4.19 Compounds found in samples analysed in chapter 4.2.3, methanol and methylated methanol extracts, all samples are analysed with temperature program Triterpenes 1, t_{R1} = retention time of samples analysed on column A, sample 5.6.2 in Fig. 4.23 with Triterpenes 3, which changes the t_{R1} of T6 (31.52), Ho1 (31.46), Da11 (33.07), Da13 (33.25) and T39 (33.43), t_{R2} = retention time of samples analysed on column B, mass spectra references see appendix

4.2.4 Discussion

Fabaceae resins containing ent-labdanes can be divided into soft and hard resins. The hardness is the result of the proportion of sesquiterpenes and polymerizable labdanes.

Copaifera resins, in particular **Copaiba balsams** from different species thereof, are composed of a complex mixture of sesquiterpenes and diterpenes with ent-labdane (main), clerodanes and kaurane structures. The results obtained here are mostly consistent with published data (chapter 2.2, table 2.3) concerning the two types A and B and their chemical composition (see table 4.16). Differences are the presence of cativic, kovalenic, ent-pinifolic and hydroxy- and acetoxy-copalic acids: cativic and ent-pinifolic acid are reported for both types, while they are found in this work only in the type B. Literature data suggest that they are not always present, which would make them possible phytochemical differentiation marker. Kovalenic acid is reported for the resins of *C. multijuga* Hayne and *C. cearensis* Ducke (Braga et al. 1998; Pinto et al. 2000; Sant'Anna et al. 2007). The two species are assigned to the type A without findings of kovalenic acid by van der Werf et al. (van der Werf et al. 2000). It is present here in all three samples of the type A, and is therefore taken as a typical marker for the type A. Hydroxy- and acetoxy-copalic acids are reported only occasionally in literature, but more than traces mainly for the type A (Delle Monache et al. 1969; Delle Monache et al. 1970; Cascon, Gilbert 2000; van der Werf et al. 2000). It is found here in the type A samples as well. However, two samples of the type B, which show a comparatively small adulteration with pine resin, also contain significant amounts of hydroxy- and acetoxy-copalic acids. It remains open, whether these compounds are of phytochemical significance or merely oxidation products of the original constituents. Finally, a third type, which is probably identical with the resin of *Copaifera reticulata* Ducke, is identified, the diterpene composition of which is not reported until now. Because it is not possible to determine which of the two 13-epimers, ent-pinifolic and oliveric acid, is present, it is also possible that the sample originates from *Danillia oliveri* Hutch. & Dalziel, the botanical source of African copaiba (Langenheim 2003: 395).

These consistent findings of two chemically distinguishable groups is remarkable, considering the wide range of species mentioned in the literature. This indicates either a very stable chemical composition within the genus or the use of only few or one species for the Copaiba balsam exported to Europe. The latter is supported by the fact that the samples van den Werf et al. analysed, originated mainly from the 1990ies and belonged to the type A. In contrary, the reference samples analysed in this work, originate from the older AFAD collection, belong mostly to the type B. Resins of the type A are attributed to *C. multijuga* Hayne, which is mentioned as the main source for modern Cobaiba balsam (Sant'Anna et al. 2007). Resins of the type B are attributed to different species (*C. duckei* Dwyer, *G. guyanensis* Desf. and *C. cearensis* Ducke), wherefore the reports about changing species over time may not be based only on growing taxonomical knowledge. Furthermore, the harvesting of *Copaifera* resins from tropical forest trees requires knowledge of the place and the ecological system, which is not transmitted by the harvesters. Therefore, the chemical consistency within the different types may be caused by restricted import regarding possible species for the production of Copaiba balsam.

It was not possible to obtain botanical samples from the resins of the genera *Daniellia*, *Tessmania*, *Guibourtia*, the botanical sources of African **legume copals**, or of African *Copaifera* species and South American *Hymenaea* resins. Reliable botanical samples of endemic trees such as Pinaceae resins are available in Central Europe more easily than resins from tropical plants. Additionally, there is a particular lack of knowledge about the specific species used for the harvesting of these resins, which made it impossible within the scope of this work to find a chemotaxonomical significant number of botanical samples for this group of resins.

The composition of these genera is basically known, and several samples analysed for this work, which are labelled as copals, were attributed to that group by their chemical composition and terminology. Compounds, which were widely found, are iso-ozic, eperuic, eL12, copalic, cativic, ent-pinifolic and 18-hydroxy-labda-8(20)-en-15-oic acids. Ent-labdanes oxygenated at C-18 (or C-19, see discussion under 'Congo copals') are found on a regular basis but in changing amounts, in Congo copals and *Hymenaea* resins also C-8 oxygenated labdanolates. Apart from that, the composition is very different but constant within a terminology based group. As reported in the literature (Mills, White 1999: 104) Sierra Leone copal can be easily distinguished from the other copals. Congo copals analysed in this work show a consistent composition as well, which resembles what has been reported in the literature for some *Hymenaea* resins (Cunningham et al. 1973; Cunningham et al. 1974; Doménech-Carbó et al. 2009). Clerodanes such as kovalenic acid, for example, are reported for *Hymenaea* resins and Congo copal, but are found here only in the Congo copal samples. However, Congo copal is reported to be very variably composed (Mills, White 1999: 104). A possible explanation for these findings is that such copal resins are sorted out before export in a similar way as suggested above for Copaiba balsam. It is unlikely that within a terminology and not botanical based group all possible botanical (table 2.4) are equally distributed.

Soft Copaiba resins and hard Fabaceae copals are easily distinguishable. Until now no kauranes are reported in the literature for legume copals (see chapter 2.2). *Copaifera* resins labelled Copaiba balsam contain a significant sesquiterpene fraction, which is analysed here in detail. And high amounts of polyalthic and hardwickiic acid are markers for *Copaifera* resins as well. Legume copals, in turn, contain higher amounts of (C-18-)oxygenated ent-labdanes and acids, which are present in *Copaifera* resins only in traces. A wide range of compounds reported in the literature for these resins, such as iso-ozic, eperuic, labda-8-en-15-oic, copalic, cativic, D16, kovalenic, labdanolic, labda-13-en-8-ol-15-oic, ent-pinifolic, 18-methoxlabda-8(20)-en-15-oic (see chapter 2.2), are identified. Others are probably identical with reported compounds (L17, L41, D17, eL22, guamáic acid), and a third group is characterised by the evaluation of its mass spectra (eL12, eL19, eL21, eL25, eL29, eL31, eL32, eL33, eL34, eL36 and eL40). Several authors identified various ent-labda-8(20),13-dienes in African copals and a Brazilian *Hymenaea* resin (van den Berg et al. 2002; Domenech-Carbo et al. 2009). No such compounds were found in the study presented here. 18-acetoxy-ent-labda-8(20)-en-15-oic acid and several compounds found by van den Berg et al. for African copals are not found as well (van den Berg et al. 2002).

Myroxylon resins are of a different composition. In the case of Balsam of Peru, the results obtained in the analyses are largely consistent with published data. The evaluation of mass spectra revealed several phenylpropanoid esters, which are, in part, mentioned without mass spectral data as constituents of Balsam of Peru and Tolu. In the case of Balsam of Tolu only the characteristic triterpene fraction serves as a differentiation criteria, because the composition of the phenylpropanoid compounds proved to be very similar to that of Balsam of Peru samples. Differences between Balsam of Peru and Tolu, found in this work, differ from those reported in literature. Because one of the two samples of Balsam of Tolu probably is a Balsam of Tolu adulterated with colophony and due to the botanical closeness of the two varieties, this is probably the result of too few investigated samples.

4.3. Angiosperm resins II - Sapindales

In this chapter Angiosperm resins from the families Anacardiaceae (*Pistacia*) and Burseraceae are investigated. The investigation of *Pistacia* resins focusses on the differences between different samples and species. Due to the lack of botanical samples for the wide range of Burseraceae resins, reference materials have had to be selected based on their terminology rather than their botanical classification. Literature data suggest a highly variable chemical composition (chapter 2.3). The focus of the investigation of Burseraceae resins lays on the connection between chemical composition and terminology. Based on these considerations, the investigation aims to provide a more detailed picture of the chemical composition of triterpene resins from Sapindales.

4.3.1 Anacardiaceae – *Pistacia* resins

Several reference samples from the genus *Pistacia* are analysed in order to identify phytochemical markers, including several mastic samples in different aging states, a sample of the resin from *Pistacia terebinthus* L. and a Bombay mastic from *Pistacia khinjuk* Stocks or *P. atlantica* Desf. subsp. *cabulica* Rech. F. (formerly *P. cabulica* Stocks) originating from Afghanistan and Baluchistan (Tschirch 1935: 369; Hocking 1958). Pistacia turpentine is not in trade anymore and was not found in collections. All samples are described in table 4.22.

Methanol extract – neutral part

In the methanol extracts of mastic reference samples (Fig. 4.25a-d), main compounds are nor-β-amyrone, tirucallol, an olean-17-ene (O12), β-amyrin, 28-nor-olean-17-en-3-one, 3,8-dihydroxy-polypoda-13,17,21-triene and oleanonic aldehyde. Other constituents are T1, 28-norolean-12,17-dien-3-one, T3, La1, tirucallone, T13, T16, 17β-hydroxy-28-norolean-12-en-3-one, 20,24-epoxy-25-hydroxy-dammaran-3-one, T34, T36, T47 and T59. The compounds Da5 and T1 elute at 28.67 and 28.95 minutes and are not shown in Fig. 4.25.

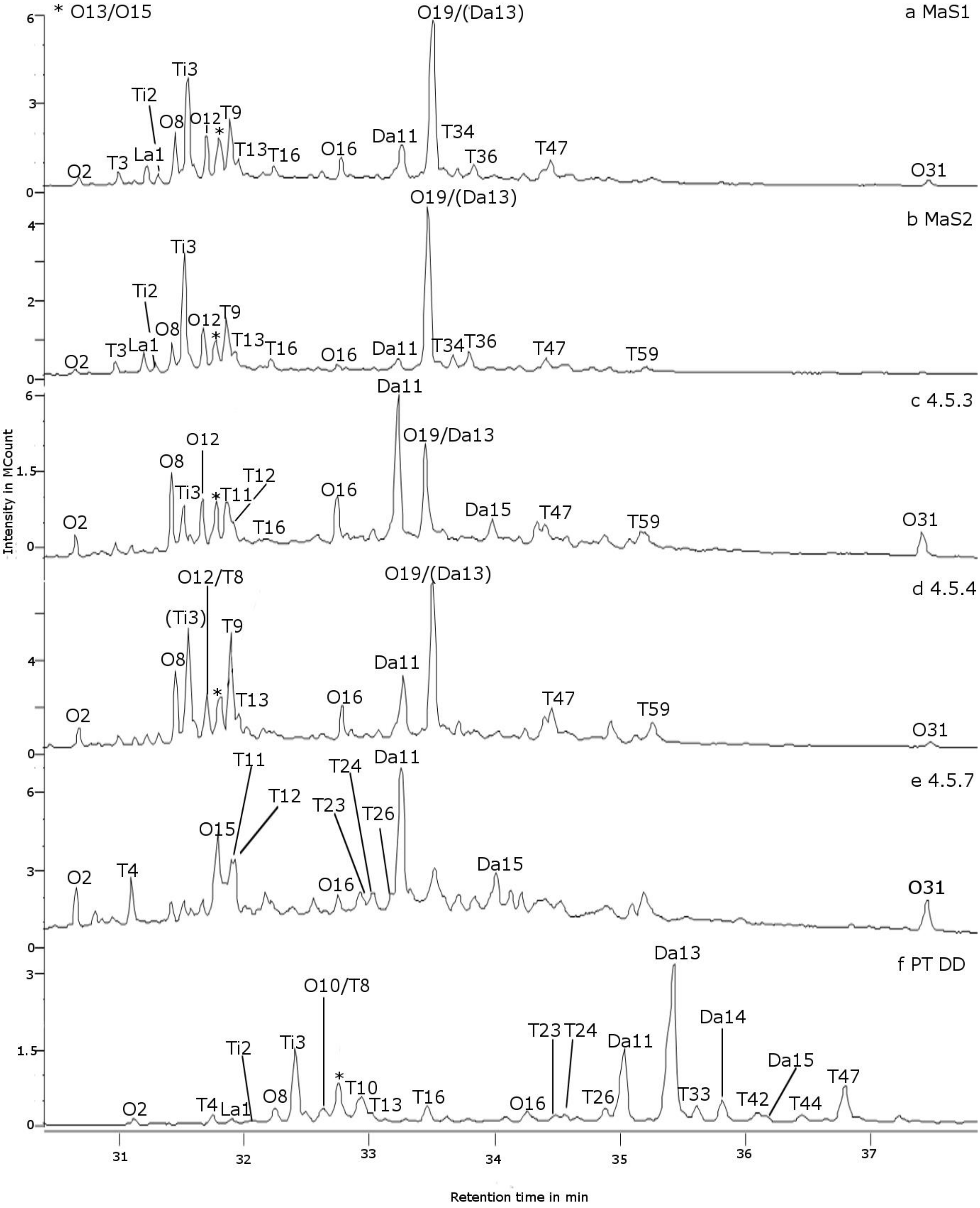
The fresh samples (MaS1, Ma2I) contain only very small amounts of hydroxy-dammarenone (Da13), which is present in the older samples from the AFAD reference collection (4.5.3, 4.5.4) in intermediate amounts. These more aged materials contain high amounts of 20,24-epoxy-25-hydroxy-dammaran-3-one (Da11) and higher amounts of 28-nor-olean-17-en-3-one (O15) than β-amyrin (O13). Both contain small amounts of hexakisnor-dammaran-3,20-dione (Da5), in 4.5.3 additional there is also 3-oxo-25,26,27-trisnordammarano-20,24-lactone (Da15) present.

The main compounds in the methanol extract of Bombay mastic (Fig. 4.25e) are 28-norolean-17-en-3-one, T11, T12 and 20,24-epoxy-25-hydroxy-dammaran-3-one. Other constituents are 28-norolean-12,17-dien-3-one, T4, nor-β-amyrone, 17β-hydroxy-28-norolean-12-en-3-one, T23, T24, T26 and 3-oxo-trinordammarano-20,24-lactone. The composition is dominated by aging compounds, none of the characteristic major compounds of fresh mastic are present (tirucallol, oleanonic aldehyde, hydroxy-dammarenone).

The main compounds in the methanol extract of the resin of *P. terebinthus* (PTDD, Fig. 4.25f) are tirucallol, β-amyrin, T10, T16, 20,24-epoxy-25-hydroxy-dammaran-3-one and hydroxy-dammarenone. Other constituents are hexakisnor-dammaran-3,0-dione, T1, T4, La1, Ti2, nor-β-amyrone, β-amyrone, T8, 28-norolean-17-en-3-one, 3,8-dihydroxy-polypoda-13,17,21-triene, T13, 17β-hydroxy-28-norolean-12-en-3-one, T23, T24, T26, T33, Da14 (hydroxy-dammarenol), T42, Da15, T44, T47 and T53. No oleanonic aldehyde is present.

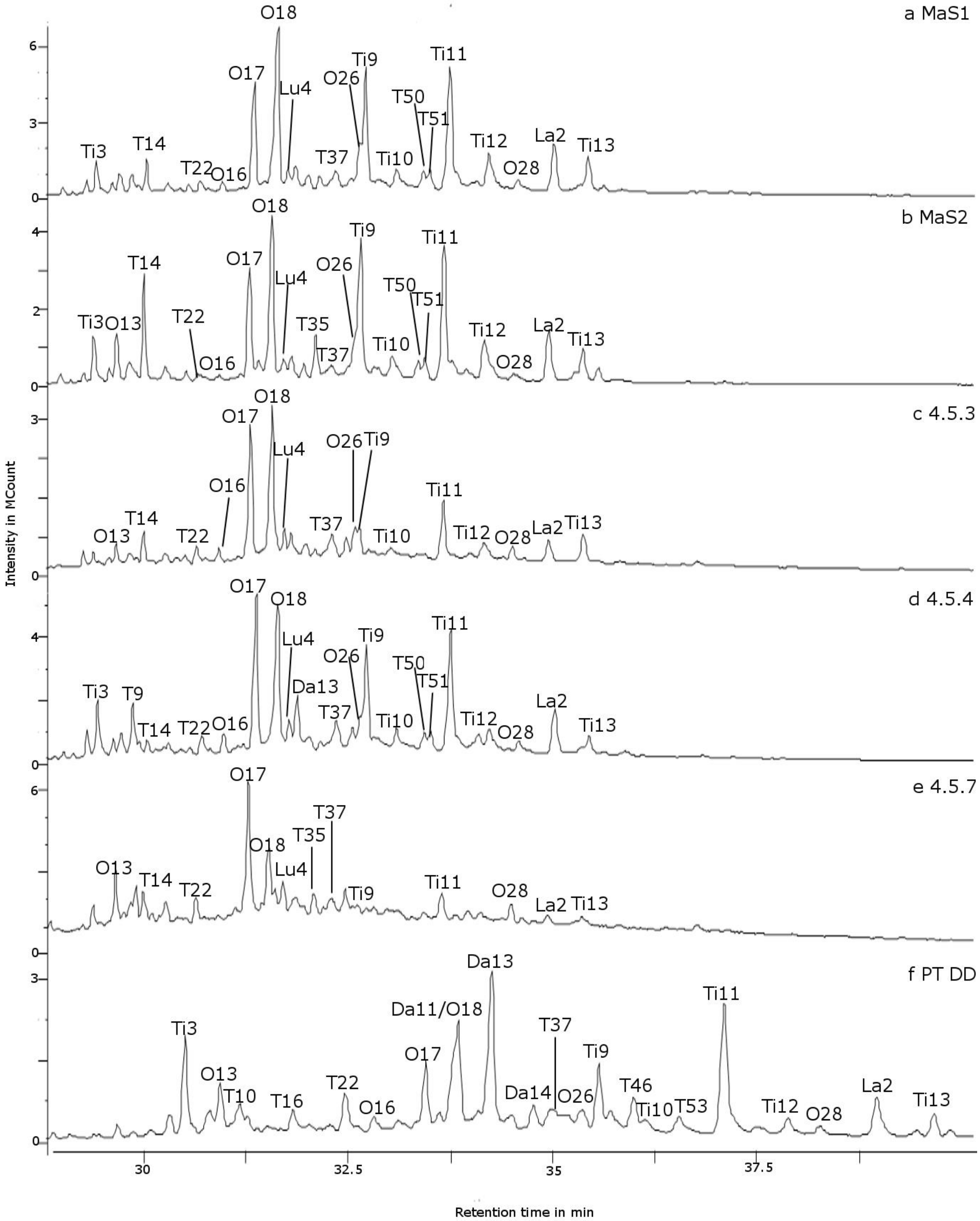
Label	Description	Picture	Sampling: date, description
4.5.1	Mastic, AFAD material collection		24.06.2011; light yellow to white little pieces, transparent
4.5.2	Mastic, VK 1977, AFAD material collection		24.06.2011; light yellow and transparent little pieces with small inclusions of dirt
4.5.3	Mastic, Prof. Schulze, AFAD material collection		December 2008; orange to brown, inside transparent little pieces, odourless, brittle, cloudy crust
4.5.4	Mastic, Vormelker, 1910, AFAD material collection		December 2008: light yellow to dark orange little pieces, odourless, solid, during sampling somewhat tenacious, inside transparent, cloudy crust
4.5.5	Mastic, VK 1977, AFAD material collection		24.06.2011; light yellow to dark orange little pieces, solid and transparent
4.5.7	Bombay-Mastic		January 2009; orange to brown very little pieces, faint resinous smell, brittle, transparent, thin cloudy crust
4.5.8	Mastic, Vormelker, AFAD material collection		01.07.2011; light yellow little pieces, transparent
Ma S 1	Gum Mastic, Kremer (#6005), date unknown, U. Schießl		December 2008; light yellow little piece, solid, brittle and transparent, fragrant minty smell, stored in a brown glass bottle
Ma S 2	chewing Mastic, marketplace in Athen, december 2006, U. Schießl		December 2008; irregular light yellow pieces, brittle and transparent, cloudy surface, smell similar to MaS1 but stronger, somewhat softer than MaS1
PT DD	*Pistacia Terebinthus* L., conservatory of the Botanical Garden TU Dresden		17.02.2009; light yellow and cloudy resin frop taken from the cutting area of a small branch, crusty, viscous and tenacious, shrub stored in glass house

Tab. 4.20 Description of reference samples analysed in chapter 4.3.1



Methanol extracts, a - Mastic MaS1, b- -MaS2, c – 4.5.3, d – 4.5.4, e - Bombay mastic 4.5.7 and f - resin of Pistacia terebinthus PTDD (labels, see table 4.23)

Fig. 4.25 Gas chromatograms of Pistacia reference samples, triterpene section (TIC)



Methylated methanol extracts, a - Mastic MaS1, b – MaS2, c – 4.5.3, d – 4.5.4, e - Bombay mastic 4.5.7 and f - resin of Pistacia terebinthus (labels, see table 4.23)

Fig. 4.26 Gas chromatograms of Pistacia reference samples II, triterpene section (TIC)

Label	t_{R1}	t_{R2}	Name	Main mass fragments
Da5	28.67	28.79	Hexakisnor-dammaran-3,20-dione	95, 135, 205, 273, 297, **315**, 325, 340, 358
T1	28.95	29.05	Unidentified triterpene	95, 135, 189, 207, **299**, 317, 327, 342, 360
O1	30.42		3,4-Seco-28-norolean-12-en-3-	81, 119, 175, 189, **204**, 243, 355, 427, 442
O2	30.68	31.14	28-Norolean-12,17-dien-3-one	81, 119, 189, 207, 229, 269, 393, **408**
T3	30.99		Unidentified triterpene	107, 159, 257, 365, 383, **409**, 424
T4		31.74	Unidentified triterpene	91, 119, 159, 255, 391, 409, **424**
La1	31.22	31.84	Lanosterol	95, 187, 241, 259, **393, 411**, 426
T5		31.99	Unidentified triterpene	**93**, 107, 121, 147, 205, 257, 311, 355, 409,
Ti2	31.32	32.05	Tirucallone	109, 245, 257, 391, **409**, 424
O8	31.42	32.24	Nor-β-amyrone	79, 105, 175, 189, **204**, 395, 410
Ti3	31.52	32.41	Tirucallol	95, 241, 259, **393**, 411, 426
T7	31.60	32.49	Unidentified triterpene	119, 213, 257, 297, 311, 365, 383, 393, **409**, 424
O10		32.59	β-Amyrone	203, 218, 424
O12	31.67		Olean-17-ene-one	105, **163**, 175, 190, 395, 408, 424
T8		32.63	Unidentified triterpene	**93**, 107, 119, 175, **189**, 207, 297, 383, 393, 408, 426
O13	31.79	32.74	β-Amyrin	189, **203**, 218, 393, 411, 426
O15	31.82	32.79	28-Norolean-17-en-3-one	95, **163**, 175, 191, 377, 395, 410
T9	31.88	32.93	3,8-Dihydroxy-polypoda-13,17,21-triene	**81**, 107, 147, 175, 190, 203, 393, 408, 426, 444
T10		32.93	Unidentified triterpene	81, 105, 119, 173, 189, 241, 259, **393**, 411, 426
T11	31.89		Unidentified triterpene	239, 295, 391, **406**, 424
T12	31.92		Unidentified triterpene	93, 121, 147, 175, **205**, 245, 313, 391, 409,
T13	31.95		Unidentified triterpene	**93**, 121, 163, 189, 203, 313, 410, 426
T14	32.01		Unidentified triterpene	81, 119, 133, 189, **203**, 262, 440, 468, 500
T15	32.21	33.40	Unidentified triterpene	119, 151, 189, **219**, 391, 423, 467, 482
T16	32.21	33.45	Unidentified triterpene	95, 109, 241, 259, **393, 411**, 426
T18	32.44		Unidentified triterpene	133, 189, **203**, 219, 262, 467, 482
T22	32.56	33.97	Unidentified triterpene	133, 187, 239, 299, 392, 406, **466**
O16	32.77	34.31	17β-Hydroxy-28-norolean-12-en-3-one	91, 105, 132, 146, 173, 187, **202**, 393, 408, (426)
T23		34.47	Unidentified triterpene	95, 107, 121, 133, **189**, 207, 393, 408, **426**
T24		34.56	Unidentified triterpene	132, 146, 187, **202**, 379, 393, 408, 426
O17	33.08	34.64	Moronate	119, 173, **189**, 203, 248, 262, 409, 468
T26		34.88	Unidentified triterpene	93, 121, 255, 273, 407, 423, **438**
O18	33.31	34.98	Oleanonate	133, 189, **203**, 262, 393, 409, 468
Da11	33.25	35.03	20,24-Epoxy-25-hydroxy-dammaran-3-one	107, 125, **143**, 161, 175, 205, 381, 399, 411, 443, (458)
Lu4	33.37		3-Oxo-lup-20(29)-en-28-oate	119, 133, 173, **189**, 203, 249, 262, 393, 409,
O19	33.49		Oleanonic aldehyde	105, 133, 175, **203**, 232, 311, 355, 409, 424, 438
Da13		35.42	Hydroxy-dammarenone (3-oxo-20-hydroxy-dammar-24-ene)	68, 81, 95, **109**, 205, 298, 311, 355, 409, 424, (442)
O20	33.60	35.45	Oleanolate	133, 189, **203**, 262, 395, 411, (470)
T33		35.61	Unidentified triterpene	67, **82**, 95, 135, 205, 245, 323, **341**, 359
T34	33.66		Unidentified triterpene	81, **107**, 133, **203**, 395, 409, 424, 438
T35	33.68		Unidentified triterpene	95, 161, 175, 201, 217, 249, 381, **413**, 453,

Label	t_{R1}	t_{R2}	Name	Main mass fragments
Da14		35.81	Hydroxy-dammarenol (3,20-dihydroxydammar-24-ene)	95, **109**, 135, 189, 207, 300, 313, 339, 357, 426, (444)
T36	33.79		Unidentified triterpene	105, 133, 175, 189, **203**, 232, 422, 440
T37	33.88	35.87	Unidentified triterpene	119, **189**, 203, 219, 248, 262, 424, 438, 467, 482
T42		36.09	Unidentified triterpene	135, 175, 232, 273, 327, 407, **425**, 440
O26	34.11	36.22	18α-Oleanonate	119, 133, 189, **203**, 262, 393, 453, (468)
Da15		36.31	3-Oxo-25,26,27-trisnordammarano-24,20-lactone	81, 95, 99, 107, 121, 135, **205**, 287, 315, 396, 414
Ti9	34.17	36.35	Isomasticadienoate	95, 121, 159, 189, 257, 393, 403, 421, 435,
T44		36.45	Unidentified triterpene	95, 149, **205**, 409, 424, 453
T46		36.57	Unidentified triterpene	81, 105, 133, 173, **203**, 421, 436, 453, 468
Ti10	34.44		Epi-isomasticadienoloate	241, 378, 396, 406, 424, **437**, 455, 470
T47	34.44	36.79	Unidentified triterpene	105, 133, **203**, 391, 409, 422, 440
T50	34.73		Unidentified triterpene	131, 159, 201, 215, 393, 408, **421**, 452
T51	34.79		Unidentified triterpene	131, 173, 203, 215, 393, **421**, 437, 452
T53		37.34	Unidentified triterpene	109, 133, **203**, 393, 409, 421, 438
Ti11	34.99		Masticadienoate	95, 121, 159, 187, 257, 393, 403, 421, 435,
T58		37.92	Unidentified triterpene	95 133, **203**, 409, 447, 479, 494
T59	35.21		Unidentified triterpene	95, 107, 121, 133, 147, 189, **203**, 245, 409, 440
Ti12	35.34	38.19	Acetoxy-isomasticadienolate	95, 187, 377, 405, 422, **437**, 453, 497, 512
O28	35.65		11-Oxo-oleanonate	119, 189, **217**, **257**, 276, 317, 407, 423, 435,
La2	36.02	39.08	Lanost-8-en-ol-oate	95, 173, 301, 341, 427, 449, **467**, 482
Ti13	36.34	39.59	Acetoxy-masticadienolate	95, 187, 377, 406, **437**, 497, (512)
T62	36.45		Unidentified triterpene	95, 159, 203, 301, 407, 435, 449, **467**, 482
O31	37.45		Oxo-oleanane	119, 147, 175, 189, 204, **217**, 233, 365, 407, 422, 435, 453, 468

Tab. 4.21 Compounds found in samples analysed in chapter 4.3.1, methanol and methylated methanol extract,t_{Rt1} = retention time of samples analysed with temperature program Triterpenes 2 and column A, t_{R2} = retention time of samples analysed with temperature program Triterpenes 1 and column A, mass spectra references see appendix

Main compounds of the fresh materials (MaS1, MaS2) are original compounds (see table 2.5), but small amounts of aging markers are already present. Low amounts of hydroxy-dammarenone correspond with low amounts of its aging products (Da5, Da11, Da15) and the other way around. Hydroxy-dammarenone, which is present in high amounts in traditionally harvested mastic, was found absent in mastic collected with a chemically aided harvesting method (Assimopoulou, Papageorgiou 2005a). Therefore, the low initial amounts of hydroxy-dammarenone in MaS1 and MaS2 are probably the result of changed harvesting practices.

The composition of Bombay mastic is surprising. Tirucallanes and dammaranes, originally present (see table 2.5), completely disappeared, remaining constituents are oxygenated nor-oleananes and degradation products of dammaranes (see Fig. 2.11, 2.12). Despite being stored under the same conditions, the other mastic samples from the AFAD reference collection show a much less advanced aging state. Also it is known that Bombay mastic is darker and less transparent then the yellow and bright mastic from *P. lentiscus* L., no investigation about its (original) composition is found. It is therefore not possible to determine the reason for the advanced aging state of the Bombay mastic.

The composition of the resin of *P. terebinthus* (PT DD) is very similar to the mastic reference samples, both regarding original and aging compounds. Also the relative amounts of the major constituents are the same, which correspond to the results from the mastic samples.

Remarkable differences are high amounts of hydroxy-dammarenone and the absence of oleanonic aldehyde. As discussed above, hydroxy-dammareone may be a marker for the harvesting method, while the reason for its absence in resin harvested with the aid of chemicals is unknown. The sample of PT DD was due to pathological wounding, which assumingly approaches natural harvested mastic (see also chapter 2.3.1). However, two samples of *P. terebinthus* L. var. Chia analysed by the same authors did not contain hydroxy-dammarenone but oleanonic aldehyde (Assimopoulou, Papageorgiou 2005b). The mass spectrum and elution order of hydroxy-dammarenone in this investigation do not agree with that of the same compound published in the former investigation of the resin from *P. lentiscus* var. Chia and data published by other authors (van der Doelen 1999: 159; Dietemann 2003: 110, 142; Assimopoulou, Papageorgiou 2005a; Assimopoulou, Papageorgiou 2005b). Also, the presence of hydroxy-dammarenone in traditional harvested resin from P. terebinthus var. Chia may be a misidentification, the presence of this compound cannot be excluded for sure. This is in opposition to the results obtained in this work, as well as the absence of oleanonic aldehyde, which was found by Assimopoulou and Papageorgiou in the resin of *P. terebinthus* var. Chia. (Assimopoulou, Papageorgiou 2005b). It is however true, that some of the intermediates of the oleanane aging process (see Fig. 2.12) such as O12, nor-β-amyrone and 28-norolean-17-en-3-one are also absent or present only in low amounts in PT DD.

A possible explanation for the differences is that they are the result of aging. PT DD was exuded indoors and analysed shortly after sampling. Dammaranes may have been protected from degradation. In aged samples, however, dammarane degradation products such as Da5, Da11 and Da15 provide the main information about the amounts original present. Da5, Da11 and Da15 are all present in significant amounts in the sample 4.5.3, Da11 also in the other mastic samples (Fig. 4.25a-d). This, however, does not explain the – considering the presence and amounts of dammaranes – differing aging state of 4.5.3 and 4.5.4 (Fig. 4.25c,d). The absence of oleanonic aldehyde is surprising, because it is reported as an intermediate of the aging process and precursor of oleanonic acid (Marner et al. 1991; Fig. 2.13), which is present in all samples (Fig. 4.26, see below). Nor-β-amyrone and 28-norolean-17-en-3-one are end products of the proposed aging mechanism (Fig. 2.13), O12 may be another intermediate or an original consitutent. Because there are a number of unidentified compounds, the data only suggests lower original amounts of oleananes in the resin of *P. terebinthus* than in that of *P. lentiscus* L.

Other differences to the mastic samples are the presence of the compounds T4, T10, T26, T33 and T53. T4 and T26 are also present in Bombay mastic. From the present data, it is not possible to determine whether that is of environmental, botanical or harvesting origin.

Methylated methanol extract - acidic part

The main compound in the methylated methanol extract of the mastic reference samples (Fig. 4.26a-d) are moronate, oleanonate, 18α-oleanonate and (iso-)masticadienonates. Other compounds, which are not present in the methanol extracts, are 3,4-seco-28-norolean-12-en-3-oate, T14, T15 and T22 as well 3-oxo-lup-20(29)-en-28-oate, oleanolate, T35, T37, epi-isomasticadienolate, T50, T51, acetoxy-(iso-)masticadienolates, 11-oxo-oleanonate, a lanost-

8-en-ol-oate (La2) and T62. All samples are composed nearly identically, also with regard to the relative amounts of the compounds. The samples 4.5.3 and 4.5.4 contain somewhat higher amounts of hydroxy-dammarenone, which corresponds to the results from the neutral fraction. MaS2 contains relatively high amounts of the unidentified compound T14.

In the methylated methanol extract of Bombay mastic (Fig. 4.26e), main compounds are moronate and oleanonate. Other compounds are T14, T22, 3-oxo-lup-20(29)-en-28-oate, T35, T37, (iso-)masticadienonates, 11-oxo-oleanonate, lanost-8-en-ol-oate (La2) and acetoxy-masticadienolate. While Bombay mastic neither contains oleanonic aldehyde, not any other original oleanane neutral compound, nor hydroxy-dammarenone (see above), the aging profile of the acidic fraction corresponds with aging reactions reported in the literature for (light and air) aged mastic resin (low stability of tirucallanes particular of the Δ-7(8)-isomer and higher stability of oleananes, particular of moronic acid, see chapter 2.3.1).

In the methylated methanol extract of the resin of *P. terebinthus* (Fig. 4.26f), main compounds are moronate, oleanonate, hydroxy-dammarenone and (iso-)masticadienonates. Other constituents are T22, 20,24-epoxy-25-hydroxy-dammaran-3-one, oleanolate, hydroxy-dammarenol, T37, 18α-oleanolate, T46, epi-isomasticadienoate, T53, acetoxy-(iso-)masticadienolates, 11-oxo-oleanonate, lanost-8-en-ol-oate (La2) and T62. Apart from the high relative amounts of hydroxy-dammaranone and the lower amounts of isomasticadienonate it is composed identically to the mastic references.

In the front part of the chromatogram several of the compounds identified in the methanol extract are visible, even though their intensity and resolution are better without derivatisation. The discrimination however differs for the different neutral compounds, olean-17-ene derivatives (O12, O15) and 3,8-dihydroxy-polypoda-13,17,21-triene show a significant lower intensity than tirucallol and β-amyrin compared to the intensities in the methanol extract.

4.3.2 Burseraceae – Elemi, copal and others

Several reference samples from Burseraceae are investigated including elemis, American copals, anime, tacamahaca and African copals (table 2.6). They are presented depending on their geographical origin derived from their name. All samples are described in table 4.28 at the end of the chapter. The chapter aims to broaden the data from phytochemical literature and to achieve a more detailed picture of chemical composition of Burseraceae resins.

Manila and Indonesian elemi

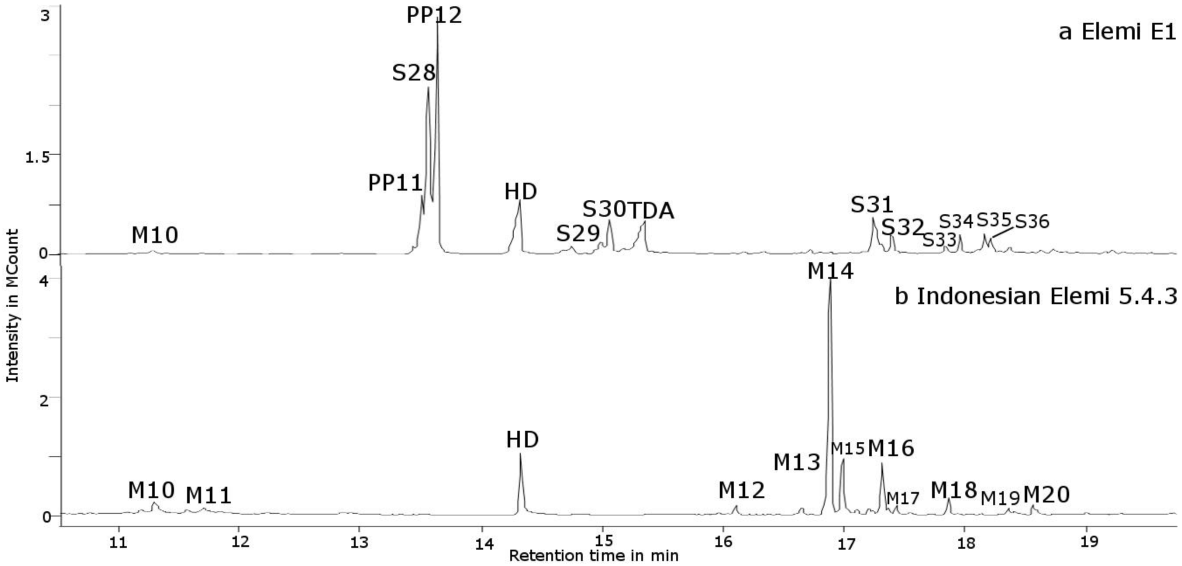
For the investigation five Manila elemis and one Indonesian elemi are analysed (compare table 4.28). They originate from different reference collections. The volatile fraction of the investigated samples is composed differently between the samples. All elemi labelled samples, apart from Indonesian elemi (5.4.3), contain high amounts of elemol, elemicin and lower amounts of γ- and β-eudesmol (Fig. 4.27a). Several unidentified compounds assigned by their mass spectra to eudesmol (S29, S30, S31, S32-S36) are present. Indonesian elemi contains high amounts of different dimers of α-phellandrene (M12-M20) (Fig. 4.27b).

Identification and elution order

Main compounds of the methanol extract of the analysed elemis are the epimers of olean-12-en-ol and urs-12-en-ol (α- and β-amyrin) (Fig. 4.28, Fig. 4.30). Published mass spectra of α- and β-amyrin show a base peak at m/z 218 and intense ions at m/z 189 and 203. These result from a retro-Diels-Alder-reaction in ring C and the loss of water from fragment b (Fig.

Label	t_R	Name	Main mass fragments
M10	11.34	Unidentified	**71**, 79, 91, 100, 109, **111**, 126, 137, 147, 178
M11	11.72	Unidentified	55, 69, **98**, **111**, 126, 168
PP11	13.51	Elemicin	79, 105, 133, 165, 177, 193, **208**
S27	13.60	Elemol	59, 67, 79, **93**, 107, 119, 133, 161, 189, 204, (222)
PP12	13.67	Isoelemicin	79, 91, 105, 133, 165, 177, 193, **208**
S28	14.76	γ-eudesmol	59, 81, 91, 105, 119, 133, 147, **161**, **189**, 204, 222
S29	15.08	β-eudesmol	**59**, 79, 81, 93, 107, 121, 149, 161, 189, 204, 222
M12	16.10	α-phellandrene dimer	77, **92, 93**, 105, 119, 136, 159, 165?, 183?, 205?, (272)
M13	16.83	α-phellandrene dimer	77, 92, **93**, 105, 119, 136, 159, (272)
M14	16.91	α-phellandrene dimer	77, 92, **93**, 105, 119, 136, 157, 165, 227, 272
M15	16.99	α-phellandrene dimer	77, 92, **93**, 105, 119, 136,(272)
S30	17.25	Unidentified sesquiterpene	**59**, 79, 81, 93, 107, 121, 149, 161, 189, 204, 222
M16	17.33	α-phellandrene dimer	77, 92, **93**, 119, 136, 229, 257, 272
S31	17.43	Unidentified sesquiterpene	79, 93, 119, 146, **159**, 187, 202, 220
M17	17.44	α-phellandrene dimer	77, 92, 93, 105, 119, 136, 183?, 185?, 272
S32	17.85	Unidentified sesquiterpene	79, 93, 105, 119, 133, **159**, 187, 202, 220
M18	17.86	α-phellandrene dimer	81, **92**, 105, 119, 137?, 145?, 173?, 185?, 228, 257, 272
S33	17.98	Unidentified sesquiterpene	59, 91, 105, 119, 131, **159**, 187, 202, 220
S34	18.19	Unidentified sesquiterpene	59, **93**, 105, 121, 147, 159, 177, 187, 202, 220
S35	18.24	Unidentified sesquiterpene	**59**, 79, 91, 105, 119, 147, 162, 177, 187, 202, 220
M19	18.36	α-phellandrene dimer	77, 92, **93**, 105, 121, 136,
M20	18.56	α-phellandrene dimer	77, 92, **93**, 105, 119, 136, 157

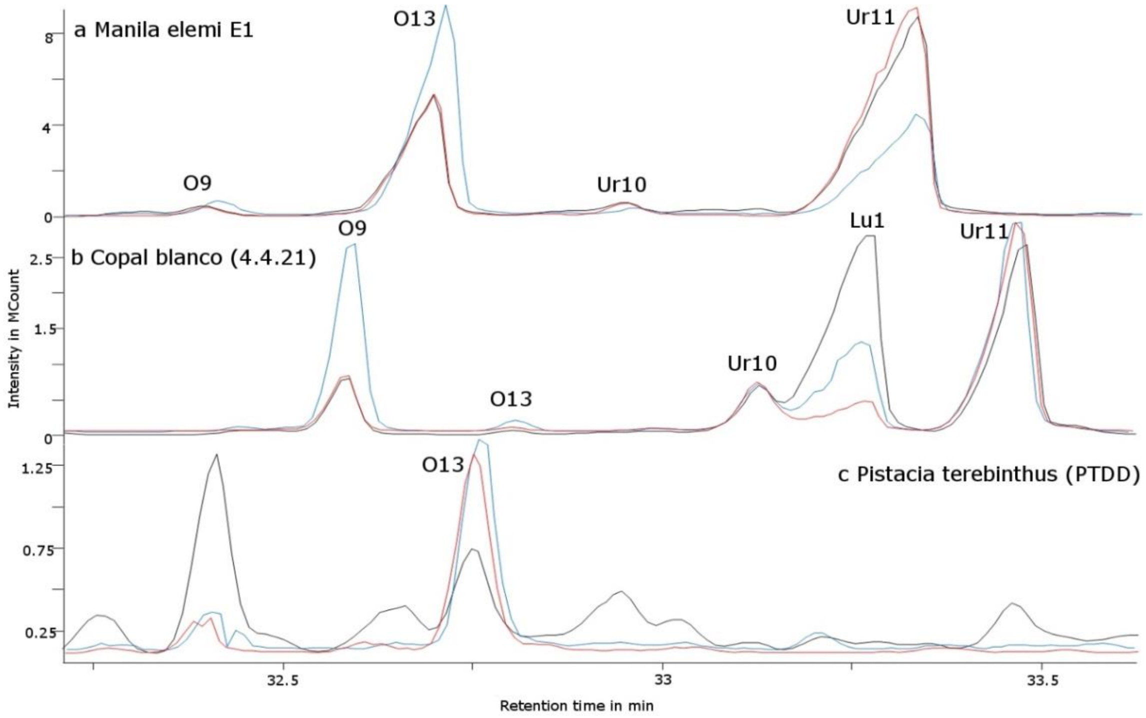
Tab. 4 22 Compounds found in samples analysed in chapter 4.3.2 (Asian elemis, volatile fraction), methanol extracts, samples analysed with temperature program Triterpenes 1 and column A, mass spectra references see appendix



Methanol extracts, a - Elemi E1 and b - Indonesian elemi 5.4.3 (labels, see table 4.24)

Fig. 4.27 Gas chromatograms of elemi resins from the reference collection, sesquiterpene fraction (TIC)

4.29). According to literature data, for β-amyrin the peak at m/z 203 is higher than the one at m/z 189, for α-amyrin it is the other way around (Shiojima et al. 1992; de la Cruz-Canizares et al. 2005; Modugno et al. 2006b). The mass spectra of their trimethylsilyl derivatives are similar (Bauer et al. 2004; Stacey et al. 2006). Fragment b, which is normally present only in minor amounts, is more common for ursanes than for oleananes. Mass spectra differing from that fragmentation pattern are reported only for trimethylsilylated samples analysed with an ion trap mass spectrometer. The mass spectra of the oleananes (olean-12-en-3α-ol and olean-12-en-3β-ol) possess a base peak at m/z 203, that of the ursanes (urs-12-en-3α-ol and urs-12-en-3β-ol) one at m/z 218 (Mathe et al. 2004). According to Budzikiewicz et al., the loss of a methyl group from fragment a is less pronounced (Budzikiewicz et al. 1963). However, due to the fact that mass spectra with a base peak at m/z 218 for all constitutions are reported only for a quadrupole mass spectrometer, the differing mass spectra reported by Mathe et al. very likely result from the use of an ion trap mass spectrometer, as it was used for this work, too. In that case, the compound class (oleanane or ursane) is probably of greater influence on the fragmentation of fragment a.



Methanol extracts, a - Elemi E1, b- Prontium copal blanco 4.4.21and c - resin of Pistacia terebinthus L. PTDD (labels, see table 4.25)

Fig. 4.28 Partial gas chromatograms of reference samples analysed in chapter 4.3, triterpene section (TIC - black, EIC at m/z 218 - red, EIC at m/z 203 – blue)

The compounds O9 and O13 possess a base peak at m/z 203, followed by compounds Ur10 and Ur11 with a base peak at m/z 218. The peak at m/z 189 is of similar intensity for both constitutions, only the loss of the methyl group from fragment a is higher for the first two compounds (Fig. 4.28). This is the case for all elemi reference samples and Prontium copals (see section below; Fig. 4.30, 4.33). Additionally, compound O13 is present in the resin of *Pistacia terebinthus* L. (Fig 4.28c) and all mastic samples investigated in this work (chapter 4.3.1). According to the literature, *Pistacia* resins contain no ursane compounds but only oleananes (chapter 2.3.1). β-amyrin is reported for these resins as an original constituent (table 2.5). Compound O13 would be olean-12-en-3β-ol (β-amyrin) then. Because the configuration at the C-3 has no effect on the fragmentation of fragment a, O9, which also possesses a base peak at m/z 203, is the corresponding 3α-epimer (olean-12-en-3α-ol). Ur10 and Ur11, the mass spectra of which correspond with those reported in the literature, are hence urs-12-en-3α-ol and urs-12-en-3β-ol (α-amyrin).

This, however, does not match with the published elution order, which is olean-12-en-3α-ol, urs-12-en-3α-ol, olean-12-en-3β-ol (β-amyrin), urs-12-en-3β-ol (α-amyrin), irrespective of the reported mass spectra (Mathe et al. 2004; Stacey et al. 2006). However, the presence of compound O13 in *Pistacia* resins, the corresponding elution order and the discussed fragmentation characteristics indicate an oleanane as the second eluting compound. Based on these considerations, an alternating elution order of oleananes and ursanes, as reported by several authors (see above), would be coupled with a different fragmentation.

The elution order of O9, O13, Ur10 and Ur11 is constant for all samples analysed in this work. The same elution order for oleananes and ursane is found for the corresponding 9(11),12-dienes and 3,16-diols (O5, O6, Ur5, Ur7, O21, O25, Ur19, Ur22). Additionally, for Mexican copals (see below) the prevalence of the 3α-epimers reported in the literature was recovered, which indicates that the identification is correct. Otherwise the reported relative amounts would be different. Both observations indicate that the elution order found here is not based on a misidentification but is truly different from that reported in the literature.

A likely reason for this phenomenon is the use of different derivatisation agents. A reagent, which methylates hydroxyl groups more easily than TMSH (see chapter 3.1.2), may influence the elution order, which is dependent on the on the polarity of the molecule. The differing fragmentation characteristics - configuration is more important – may be caused by the ion trap mass spectrometer. There are, however, no indications for any of the mentioned parameters in literature.

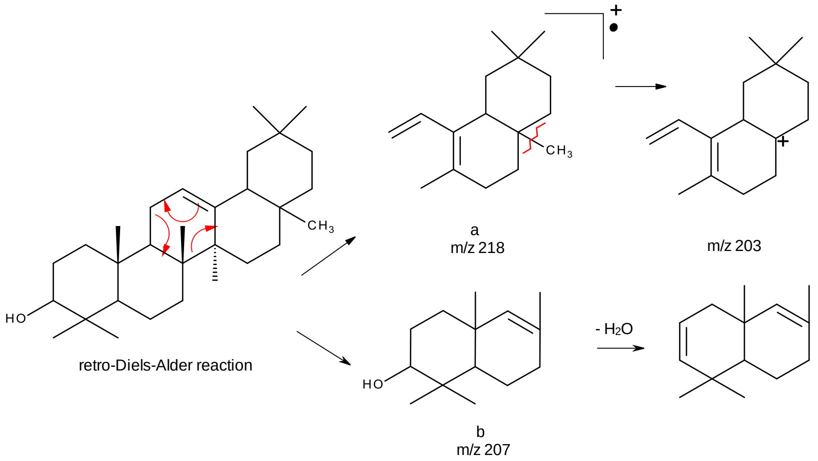


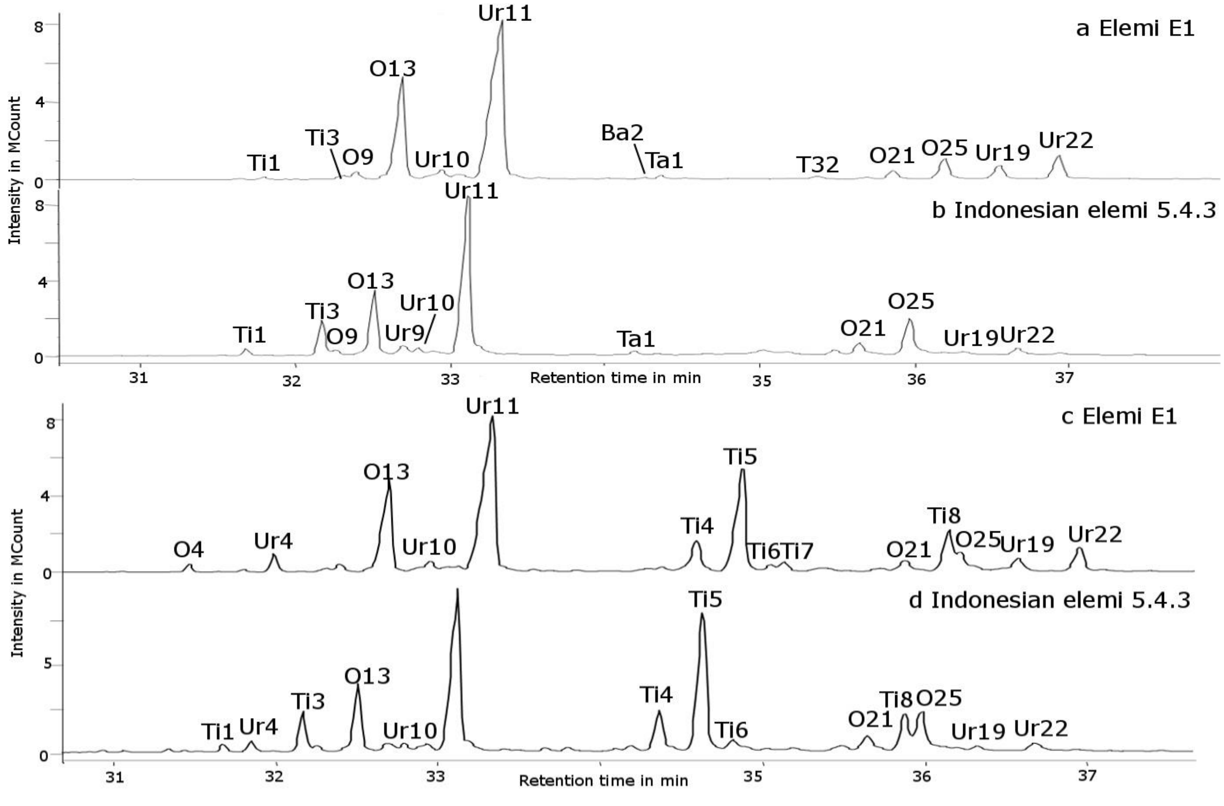
Fig. 4.29 Fragmentation of pentacyclic triterpenes (Budzierkiewicz et al. 1963), the figure shows olean-12-en-3-ol, in the case of ursanes the methyl groups are located at C-18 and C-19

Composition

In Fig. 4.30a. c exemplary the chromatograms of a Manila elemi are shown (E1; Fig. 4.30a). Main compounds of the methanol extract are β- and α-amyrin, together with smaller amounts their 3α-epimers, maniladiol and brein and their isomers (O21, Ur19). The other Manila elemis (5.4.1, 5.4.2, BLaD1; see table 4.28) are composed identical. Indonesian elemi (Fig. 4.30b) is composed similarly with somewhat higher amounts of tirucallol (Fig. 4.30b), in the crust α-amyrone is present (not shown).

In the methylated methanol extract of Manila elemi (Fig. 4.30c) several tirucallanes are present: Ti4, Ti5, Ti6, Ti7 and Ti8. In the methylated methanol extract of Indonesian elemi (Fig. 4.30d) only Ti4, Ti5, Ti6 and Ti8 are found, not Ti7. In the black crust the relative amounts of tirucallol, the elemolic and elemonic acids are slightly decreased (not shown).

The mass spectra of (unmethylated) α- and β-elemolic acids are reported by Tessier et al. (Tessier et al. 1982). The authors report the elimination of a methyl groups followed by the loss of water leading to the base peak at m/z 423 for both, 3α-hydroxytirucall-8,24-dien-21-oic acid and its Δ-7-isomer. Afterwards the carboxyl group and the side chain are lost leading to peaks at m/z 377 and 281. In the compounds Ti5, Ti6 and Ti8, the first two fragmentations are present at m/z 455 and 437 (base peak), the latter two fragmentations at the same m/z values (see table 4.25). The mass spectra also resembles that of 3α-hydroxytirucall-8,24-dien-21-oate (Liu, Abreu 2006), apart from a base peak at m/z 149, which is not present in the compounds found here. According to Cotterell et al. high amounts of this compound should be present in Manila elemi, together with smaller of the 3β-isomer of α-elemolic acid (Cotterell et al. 1970). Ti5, Ti6 and Ti8 have a hydroxytirucalladien-21-oic structure. Therefore, Ti5 is α-elemonate and Ti8 β-elemonate. Ti6 has a similar mass spectrum, but could not be identified for certain.



Top (a – b)methanol extracts, bottom (c – d) methylated methanol extracts, a, c - Elemi E1 and b, d - Indonesian elemi 5.4.3 (labels, see table 4.25)

Fig. 4.30 Gas chromatograms of Asian elemis from the reference collection, triterpene fraction (TIC)

The mass spectrum of compound Ti4 resembles that of 3-oxo-tirucall-7,24-dien-21-oic acid reported by Tessier et al. (Tessier et al. 1982). The base peak is caused by the loss of the methyl group followed by the elimination of the carboxyl group leading to a peak at m/z 393 for both the methylated and not methylated compound. The base peak of compound Ti4 is at m/z 453 with the molecular ion at m/z 468. Additionally, Tessier reports a peak at m/z 297 (Tessier et al. 1982). It arises from the cleavage of the side chain from the $[M-CH_3]^+$ ion. The ion [M-CH$_3$-CO]$^+$ at m/z 421 is typical for compounds with a carbonyl group. This leads to the conclusion that the compound is 3-oxo-tirucalla-7,24-dien-21-oate (elemonate).

Label	t$_R$	Name	Main mass fragments
O4	31.46	3β-Methoxy-olean-12-ene	81, 95, 107, 189, **203**, 218, 393, 408, 425, 440
O6	31.65	Olean-9(11),12-dien-3β-ol	95, 119, 159, 255, 355, 391, 409, **424**
Ti1	31.79	Hydroxy-Δ8-tirucallene	95, 241, 259, **393**, 411, 426
Ur4	31.98	3β-Methoxy-urs-12-ene	119, 147, 161, 189, 203, **218**, 393, 408, 425, 440
Ur7	32.16	Urs-9(11),12-dien-3β-ol	159, 255, 295, 391, 409, **424**
Ti3	32.31	Tirucallol	81, 95, 187, 241, 259, 311, **393**, 411, 426
O9	32.38	Olean-12-en-3α-ol (epi-β-amyrin)	95, 107, 119, 175 189, **203**, 218, 393, 411, 426
O13	32.68	Olean-12-en-3β-ol (β-amyrin)	95, 119, 175, 189, **203**, 218, 393, 411, 426
Ur9	32.73	α-amyrone	107, 147, 189, 203, **218**, 409, 424
Ur10	32.94	Urs-12-en-3α-ol (epi-α-amyrin)	107, 147, 189, 203, **218**, 393, 411, 426
Lu1	33.24	Epi-lupeol	107, 135, **189**, 203, 207, 218, 229, 257, 393, 411, 426
Ur11	33.30	Urs-12-en-3β-ol (α-amyrin)	107, 147, 189, 203, **218**, 393, 408, 411, 426
T17	33.55	Unidentified acetoxy-triterpene	93, 107, 175, **189**, 203, 218, 297, 393, 408, 453, 468
Ba2	34.25	Baurenol	95, **229**, 241, 247, 393, 411, 426
Ta1	34.37	Taraxasterol	93, 107, 121, 175, **189**, 207, 229, 393, 408, 426
Ur13	34.58	Urs-12-en-3β-acetate	79, 119, 147, 189, 203, **218**, 408, 453, 468
Ti4	34.58	Elemonate (proposed)	189, 257, 297, 311, 393, 421, **453**, 468
Ti5	34.86	3α-hydroxytirucall-8,24-dien-21-oate (α-elemolate) (proposed)	187, 281, 299, 377, 405, **437**, 455, 470
Ti6	35.03	Unidentified hydroxytirucalladien-21-oate	119, 187, 241, 281, 299, 377, 405, **437**, 455, 470
Ti7	35.13	3α-acetoxytirucalla-dien-21-oic acid (proposed)	187, 281, 377, 405, **437**, 453, 497, 512
T30	35.30	Unidentified	67, 107, 121, **189**, 203, 377, 392, 395, 410
T32	35.38	Unidentified	95, **109**, 135, 189, 207, 300, 313, 407, 426, 454
O21	35.85	Isomer of maniladiol	175, 190, 201, **216**, 219, 234, 391, 409, 424, 442
O23	35.86	11-oxo-olean-12-en-3α-ol	**135**, 175, 217, 232, 273, 287, 407, 425, 440
T40	36.00	Unidentified	67, **109**, 121, 147, 189, 203, 297, 339, 355, 468
T41	36.07	11-oxo derivative of amyrin	**135**, 232, 273, 395, 410, 423, 438
Ti8	36.13	3α-hydroxy-7,24-dien-21-oate (β-elemolate) (proposed)	187, 282, 378, 406, **437**, 455, 470
O25	36.20	Maniladiol	148, 160, 190, 201, **216**, 219, 234, 409, 424, 442
Ur18	36.36	11-oxo-urs-12-en-3α-ol	105, **135**, 149, 175, 232, 273, 407, 425, 440
Ur19	36.56	Isomer of brein	110, 151, 190, 219, **234**, 391, 409, 424, 442
Ur20	36.68	11-oxo-urs-12-en-3β-ol (11-oxo-α-amyrin)	**135**, 175, 232, 273, 407, 425, 440
Ur22	36.92	Brein	110, 151, 191, 207, 219, **234**, 409, 424, 442

Tab. 4.23 Compounds found in samples analysed in chapter 4.3.2 (elemi, Mexican copal, triterpene section), methanol and methylated methanol extracts, samples analysed with temperature program Triterpenes 1 and column A, mass spectra references see appendix

The related compound is reported to be present in Manila elemi (Argay et al. 1997). The base peak of compound Ti7 is at m/z 437, which is caused by the $[M\text{-}CH_3\text{-}AcOH]^+$ ion. This is typical for acetoxy-compounds. Compound Ti7 is therefore 3α-acetoxytirucall-8,24-dien-21-oic acid, which is reported by Cotterell et al. to be present in Manila elemi (Cotterell et al. 1970).

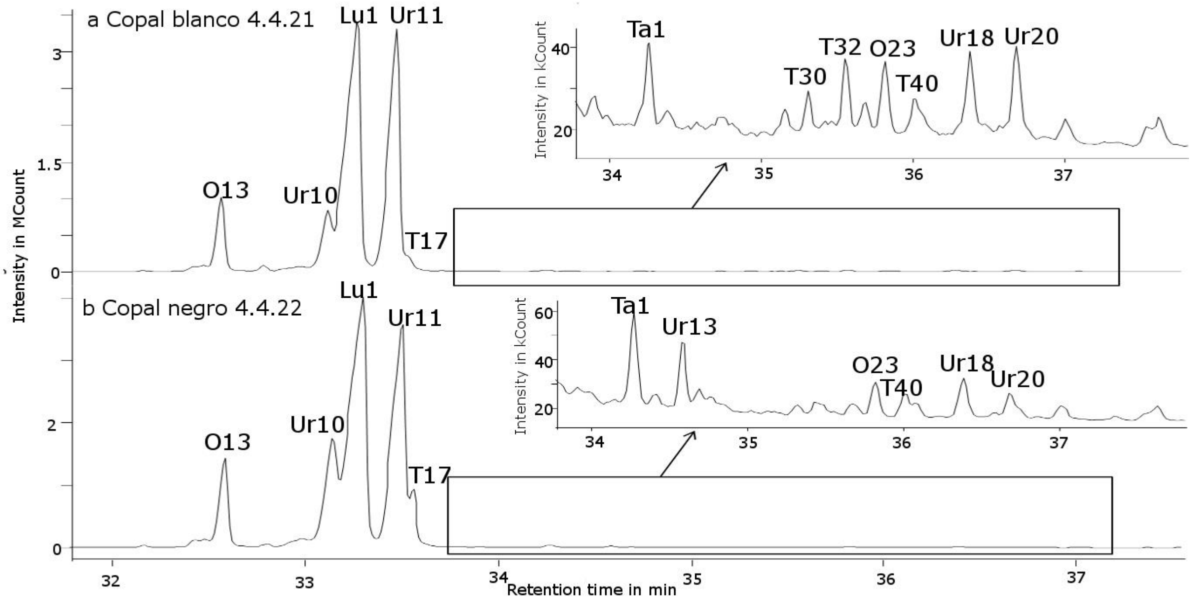
Prontium copals

The two Mexican copals were purchased from Eggebrecht (see table 4.28). They are labelled as Prontium Copal blanco and Prontium Copal negro (4.4.21, 4.4.22). In the sesquiterpene fraction small amounts of caryophyllene and caryophyllene oxide, in Copal blanco also two dimers of α-phellandrene are present (not shown).

Identification of Lu1

Main constituents of both materials are α-amyrin and compound Lu1 (Fig. 4.31a, b). For the identification of the amyrins see section 'Manila and Indonesian elemi' above. Compound Lu1 is reported by several authors for *Bursera* resins (see Fig. 2.14b, c). Common characteristics are similar mass spectra and elution before α-amyrin. In a Mexican *Bursera* resin the related compound elutes between β- and α- amyrin and is identified as hop-22(29)-en-3β-ol (de la Cruz-Canizares et al. 2005). In another Mexican resin it elutes between the 3α- and 3β-epimers and is identified as lupeol. Another (unidentified) compound with a base peak at m/z 189 elutes between β- and α-amyrin (Stacey et al. 2006).

The mass spectrum of Lu1 is very similar to that of lupeol, which is reported for American copal resins (and the chemotaxonomical related genera *Boswellia* and *Commiphora*; Peraza-Sánchez et al. 1995; Mathe et al. 2004; Basar 2005: 148; Stacey et al. 2006). According to literature, epi-lupeol elutes shortly after the 3α-epimers of α- and β-amyrin and lupeol after α-amyrin (Itoh et al. 1982; Mathe et al. 2004). In this work, apart from Lu1, Lu2 und Lu3 are found (in Angola copal AS07; see Fig. 4.33 in section 'Kongo and Angola copals' below). Lu3 has a mass spectrum similar to that of lupeol and elutes after α-amyrin (Fig. 4.33a, b; table 4.27). Similar to the 3-epimers of α- and β-amyrin, epi-lupeol elute earlier than the 3β-



Methanol extracts, a - Copal blanco 4.4.21 and b - Copal negro 4.4.22 (labels, see table 4.25)

Fig. 4.31 Gas chromatograms of commercial Prontium copals (Mexico), triterpene fraction (TIC) epimer lupeol. Then Lu1 is epi-lupeol and Lu3 lupeol, while Lu2 has the mass spectrum of lupenone (Bauer et al. 2004; NIST 2005). Lu1 corresponds to the 'lupeol' found by Stacey et al. (Fig. 2.14c). Lu1 elutes after 3α-epi-α-amyrin as reported by Itoh et al., only the elution order of β-amyrin is different (see also paragraph 'Manila and Indonesian elemi' above). Hop-22(29)-en-3β-ol found by de la Cruz-Canizares (Fig. 2.14b) is probably the same compound as the one reported by Stacey et al. (both with a base peak at m/z 189) (Itoh et al. 1982; de la Cruz-Canizares et al. 2003).

Composition

In the methanol extract of the Mexican copals (4.4.21, 4.4.22; Fig. 4.31a, b) main compounds in both samples are α-amyrin and epi-lupeol with smaller amounts of (3-epi-)β-amyrin, taraxasterol, compounds T32 and T40 and several compounds related to 11-oxo-derivatives of α- and β-amyrins (O23, T41, Ur18, Ur20). According to their relative amounts, elution order and molecular weights the compounds O23, Ur18 and Ur20 are the 11-oxo derivatives of 3-epi-β-amyrin, 3-epi-α-amyrin and α-amyrin. The 11-oxo-derivative of β-amyrin is not found, probably because β-amyrin is present only in small amounts. The higher amounts of 3-epi-β-amyrin compared to β-amyrin correspond to similar findings by Stacey et al., who report the trimethylsilylester of 3β-hydroxy-olean-12-en-11-one and the corresponding ursane for *Bursera* related Mesoamerican copals but not for *Protium* resins (Stacey et al. 2006). In Copal negro urs-12-en-3β-acetate (Ur13) and compound T30 are present, which are not found in Copal blanco. Apart from that, the two materials are composed identically. The methylated methanol extracts of the Mexican copals do not contain any further compounds, which are not also present in the unmethylated extracts.

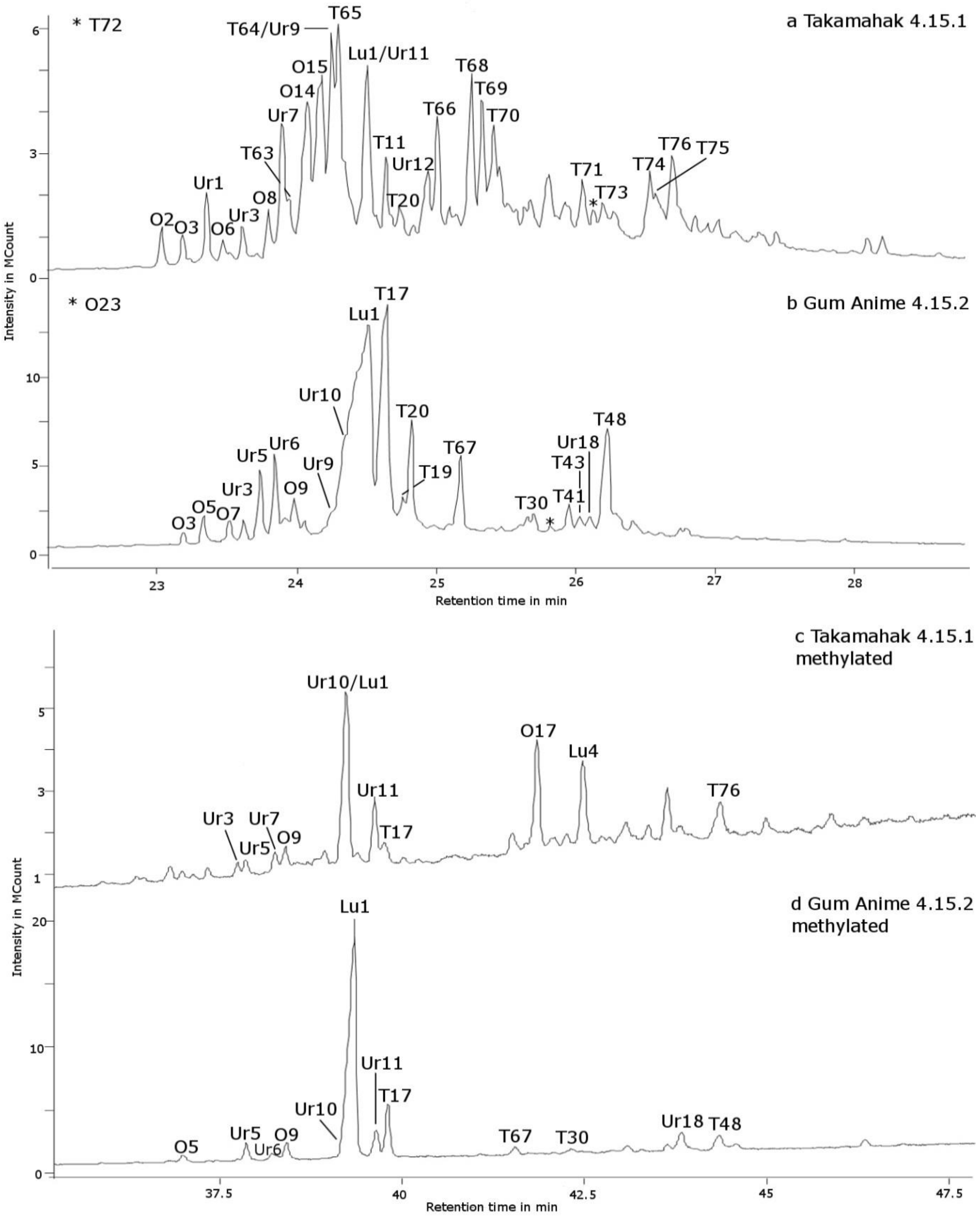
Gum anime and tacamahak

The two samples originate from the AFAD reference collection. They are labelled as Takamahak or Gummi Tacamahacae (4.15.1) and Gum Anime (4.15.2; see Tab. 4.28). The methanol extract was measured with a differing temperature program. Therefore, several compounds, which are not present in other Burseraceae resins, were numbered separately, because it was not possible to determine the exact elution order. As a consequence, the numbering is not always sequent (see appendix, compound list 'triterpenes'). In the sesquiterpene fraction both samples contain intermediate amounts of caryophyllene oxide, Gum Anime also M15 and M17 (not shown).

The methanol extract of Takamahak is of a very complex composition (Fig. 4.32a). Main constituents are urs-9(11),12-dien-3β-ol (Ur7), germanicene (O14), 28-nor-olean-17-en-3-one (O15), compounds T64 and T65, epi-lupeol, compounds T66, T68 and T69. β-amyrin coelutes with O15, α-amyrin with compound T65. The corresponding 3-epimers of the amyrins are not found. Smaller amounts of 28-nor-olean-12,17-dien-3-one (O2), olean- and urs-9(11),12-dien-3-one (O3, Ur3), olean-9(11),12-dien-3β-ol (O6), nor-β-amyrone (O8), compounds T63, T11 and Ur12 (probably a 3-acetoxy-14-nor-urs-12-ene), compounds T70, T71, and T73 – T76 are also present. In the methylated methanol extract of Takamahak (Fig. 4.32c) in addition 3-epi-α-amyrin, moronate and 3-oxo-lup-20(29)-en-28-oate are present.

The main compounds in the methanol extract of Gum Anime (Fig. 4.32b) are epi-lupeol and compound T17 together with smaller amounts of urs-9(11),12-dien-3α-ol, urs-10(11),12-dien-3-acetoxy (Ur6), 3epi-α-amyrin, compounds T20, T67 and T48. Compound T48 is probably an acetoxy-derivative of a pentacyclic triterpene such as 11-oxo-olea- or 11-oxo-urs-12-en-3-

ol, the mass spectrum of compound T67 is similar to that of lup-20(29)-en-3β-yl acetate or taraxast-20(30)-en-3β-yl acetate (Shiojima et al. 1992). Other constituents are olean- and



Top (a – b) methanol extracts, bottom (c – d) methylated methanol extracts, a, c - Gum Anime and b, d - Takamahak (labels, see table 4.26)

Fig. 4.32 Gas chromatograms of American Burseraceae resins from the reference collection, triterpene section (TIC)

Label	t_{R1}	t_{R2}	Name	Main mass fragments
O2	23.03		28-Norolean-12,17-dien-3-one	81, 119, 189, 207, 229, 269, 393, **408**
O3	23.18		Olean-9(11),12-dien-3-one	189, 255, 269, 408, **422**
Ur1	23.35		28-Nor-urs-12,17-dien-3-one	241, 269, 351, 375, 393, **408**
O5	23.33	36.98	Olean-9(11),12-dien-3α-ol	159, 189, 255, 391, 409, **424**
O6	23.46		Olean-9(11),12-dien-3β-ol	95, 119, 159, 255, 355, 391, 409, **424**
O7	23.52		Olean-10(11),12-dien-3-acetoxy	255, 295, 391, 424, 451, **466**
Ur3	23.62	37.75	Urs-9(11),12-dien-3-one	133, 159, 255, 269, 311, 389, 408, **422**
Ur5	23.73	37.87	Urs-9(11),12-dien-3α-ol	159, 255, (395), 391, 409, **424**
O8	23.79		Nor-β-amyrone	79, 105, 175, 189, **204**, 395, 410
Ur6	23.84	38.21	Urs-10(11),12-dien-3-acetoxy	255, 295, 391, 424, 451, **466**
Ur7	23.91	38.26	Urs-9(11),12-dien-3β-ol	159, 255, 295, 391, 409, **424**
T63	23.94		Unidentified	177, 189, 257, 311, 391, **409**, 424, 437, 452
O9	23.98	38.41	Olean-12-en-3α-ol (epi-β-amyrin)	95, 107, 119, 175 189, **203**, 218, 393, 411, 426
O14	24.07		Germanicene (olean-18-ene)	105, 134, 175, 191, **204**, 395, 410
O15	24.18		28-Norolean-17-en-3-one	95, **163**, 175, 191, 377, 395, 410
T64	24.24		Unidentified	105, 119, 173, 189, 203, 218, 257, **393**, 408
Ur9	24.39		α-Amyrone	107, 147, 189, 203, **218**, 409, 424
Ur10	24.28	39.17	Urs-12-en-3α-ol (epi-α-amyrin)	107, 147, 189, 203, **218**, 393, 411, 426
T65	24.29		Unidentified	107, 189, **205**, 218, 245, 313, 391, 406, 409, 424
Lu1	24.50	39.35	Epi-lupeol	107, 135, **189**, 203, 207, 218, 257, 393, 411, 426
Ur11	24.50	39.65	Urs-12-en-3β-ol (α-amyrin)	107, 147, 189, 203, **218**, 393, 408, 411, 426
T11	24.63		Unidentified, see chapter 4.3.1	239, 295, 321, 391, **406**, 424
T17	24.63	39.80	Unidentified acetoxy-triterpene	107, 175, **189**, 203, 216, 297, 393, 408, 453, 468
T19	24.76		Unidentified	107, 147, 189, 203, **218**, 393, 408, 426, 439, 454
T20	24.82		Unidentified	107, 147, **189**, 203, 216, 229, 393, 408, 439, 454
Ur12	24.94		3-acetoxy-14-nor-urs-12-ene	105, 134, 147, 175, 189, **204**, 439, 454
T66	25.00		Unidentified	132, 163, 175, 191, **202**, 393, 408, 454
T67	25.17	41.55	Acetoxy-triterpene	121, **189**, 203, 218, 229, 297, 393, 408, 453, 468
O17		41.86	Moronate	119, 173, **189**, 203, 248, 262, 409, 468
T68	25.25		Unidentified	175, 189, 202, 365, 393, **408**, 426
T69	25.32		Unidentified	117, 132, **202**, 393, **408**
T70	25.41		Unidentified	107, 173, 189, 202, 205, 393, **408**, 426
T30	25.70	42.33	Unidentified	67, 107, 121, **189**, 203, 377, 392, 395, 410
Lu4		42.48	3-Oxo-lup-20(29)-en-28-oate	119, 133, 173, **189**, 203, 249, 262, 393, 409, 437, 453, 468
O23	25.82		11-oxo-olean-12-en-3α-ol	**135**, 175, 217, 232, 273, 287, 407, 425, 440
T41	25.95		11-oxo derivative of amyrin	**135**, 232, 273, 395, 410, 423, 438
T43	26.02		Unidentified	**135**, 175, 232, 273, 407, 422, 482
T71	26.04		Unidentified	107, 147, 163, 175, **189**, 349, 377, 410, 452
Ur18	26.09	43.82	11-oxo-urs-12-en-3α-ol	105, **135**, 149, 175, 232, 273, 407, 425, 440
T72	26.12		Unidentified	117, 132, **202**, 377, 393, 437, 452
T73	26.19		Unidentified	135, 159, 189, **203**, 232, 273, 407, 452, 470
T48	26.23	44.37	Unidentified oxygenated oleanane	**135**, 175, 232, 273, 383, 407, 422, 482
T74	26.53		Unidentified	105, 147, 189, **203**, 205, 409, 422, 468
T75	26.57		Unidentified	133, **203**, 205, 216, 407, 414, 422, 468
T76	26.69		Unidentified	107, 137, **189**, 203, 205, 216, 409, 424, 437, 452

Tab. 4.24 Compounds found in samples analysed in chapter 4.3.2 (anime and takamahak), methanol and methylated methanol extracts, t_{R1} - analysed with temperature program Diterpenes 1 and column A, t_{R2} - analysed with temperature program Triterpenes 3 and column B, mass spectra references see appendix

urs-9(11),12-dien-3-one (O3, Ur3), olean- and urs-9(11,12-dien-3α-ol (O5, Ur5), olean- and urs-10(11),12-dien-3-acecoxy (O7, Ur6), 3epi-β-amyrin (O9), α-amyrone, compounds T19, T30 and T41, another acetoxy-derivative of 11-oxo-olean- or urs-12-ene (T43) and the 11-oxo-derivatives of 3α-epimers of α-and β-amyrin (O23, Ur18). In the methylated methanol extract (Fig. 4.32d) in addition α-amyrin is visible coeluting with compound T17.

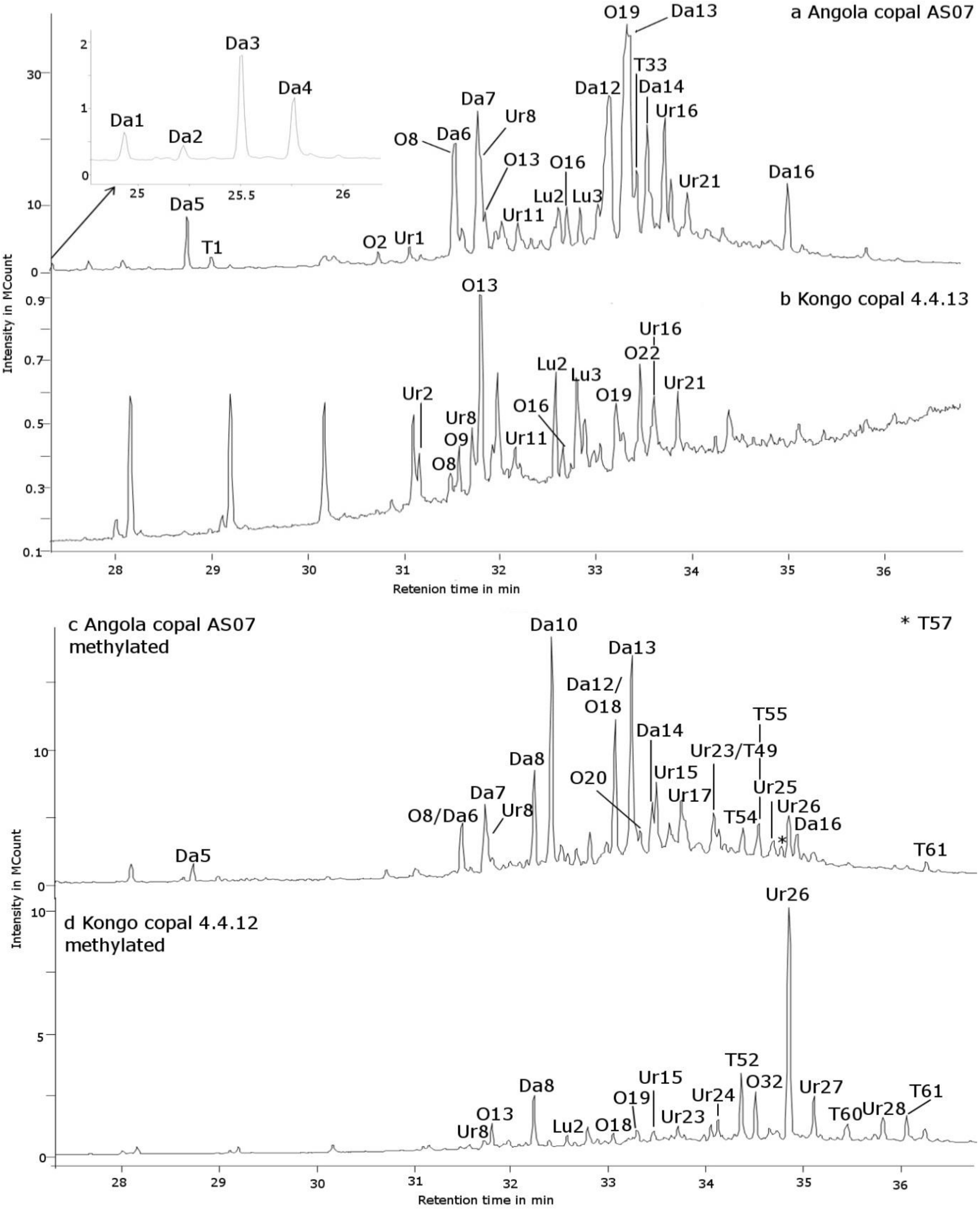
Takamahak contains mainly α-amyrin and its corresponding aging markers (Ur3, Ur7), while the presence of β-amyrin is visible through the presence of its aging marker O6, O8 and O15. The coelution of O13 (β-amyrin) and O15 is also observed for mastic reference samples (see Fig. 4.25). In contrast, Gum Anime mainly contains the 3-α-epimers and their corresponding aging markers (O3, O5, Ur3, Ur5, O23, Ur18). 11-oxo-derivatives of the amyrins derived from their present epimers are found only in Gum Anime. Takamahak, in contrast, contains several additional decarboxylated aging compounds (O2, Ur1, O8, O15, Ur12). The decarboxylation and oxidation of functional groups is reported mainly for *Pistacia* resins such as mastic (chapter 2.3.1 and 4.3.1). As with Mexican copals, Burseraceae resins mainly show the formation of keto groups and additional double bonds, while C-16 oxygenated amyrin derivatives are not present.

Kongo and Angola copal

The Kongo copal (4.4.13) originates from the AFAD reference collection, the Angola copal (AS07) was supplied by Anja Schönemann (see table 4.28). In the methanol extract of the Angola copal AS07 (Fig. 4.33a) main compounds are nor-β-amyrone, dammaradienone, dammaradienol, nor-α-amyrone, 20,24-epoxy-25-hydroxy-dammaran-3-one, hydroxy-dammarenone, hydroxy-dammardienol, oleanonic aldehyde and ursonic aldehyde. Other constituents are several mansubianes (Da1-Da4), hexakisnor-dammaran-3,20-dione, β- and α-amyrin, lupenone, 17β-hydroxy-28-norolean-12-en-3-one, lupeol, compound T33, ursolic aldehyde and compound Da16. Small amounts of compound T1, 28-nor- and 28-nor-urs-12,17-dien-3-one and compound Ur1 are also present. The methylated methanol extract (4.33b) in addition contains 20,24-epoxy-25-hydroxy-3,4-seco-damaren-3-oate, dammarenolate as well as smaller amounts of oleanonate, ursonate, 3-acetoxy-ursolate, several unidentified ursanes (Ur23, Ur25, Ur26) and other triterpenes compounds (T49, T54, T55, T57, T61).

In the methanol extract of the Kongo copal (Fig. 4.33b) main compounds are β-amyrin, lupenone, lupeol, oleanonic, oleanolic and ursolic aldehyde. Other constituents are urs-9(11),12-dien-3α-ol, nor-β-amyrone, epi-β-amyrin, nor-α-amyrone, α-amyrin, 17β- hydroxy-28-norolean-12-en-3-one and 11-oxo-olean-12-en-3α-ol. The methylated methanol extract (Fig. 4.33d) in addition contains 20,24-epoxy-25-hydroxy-3,4-seco-damaren-3-oate and Ur26 as well as smaller amounts of oleanonate, ursonate, several unidentified ursanes (Ur23, Ur24, Ur27, Ur28), oleanane (O32) and other triterpene compounds (T52, T60, T61).

Despite some similarities in their chemical composition, such as the presence of oleanane and ursane aldehydes and acids, lupanes and as α- and β-amyrins, the two African copals show clear differences. The Angola copal contains high amounts of dammarane compounds, only small amounts of α- and β-amyrin and several unidentified triterpenes, which are attributed to ursane and other triterpenes acids (Ur23, Ur25, Ur26, T49, T54, T55, T57, T61). The Kongo copal, which was poorly soluble in methanol, lacks dammaranes nearly completely and contains much higher amounts of amyrins, lupanes as well as oleanane and ursane aldehydes and acids, together with several unidentified compounds from the oleanane, ursane and triterpene class (Ur23, Ur24, Ur27, Ur28, O32, T52, T60, T61).



a to b – methylated methanol extracts, c to d – methanol extracts, a, c - Angola copal AS07 and b, d - Kongo copal 4.4.13 (labels, see table 4.27)

Fig. 4. 33 Gas chromatograms of African copals from the reference collection, triterpene section (TIC)

Label	t_R	Name	Main mass fragments
Da1	24.93	Mansumbione	**95**, 108, 121, 163, 205, 299, 314
Da2	25.22	Mansumbinol	93, 108, 147, **190**, 203, 207, 383, 301, 316
Da3	25.51	Mansumbiane	95, 108, 189, **205**, 301, 316
Da4	25.76	Mansumbiane	95, 108, 119, 175, **189**, 207, 285, 300
Da5	28.75	Hexakisnor-dammaran-3,20-dione	95, 135, 205, 273, 297, **315**, 325, 340, 358
T1	28.99	Unidentified	95, 135, 189, 207, **299**, 317, 327, 342, 360
O2	30.73	28-Nor-olean-12,17-dien-3-one	81, 119, 189, 207, 229, 269, 393, **408**
Ur1	31.05	28-Nor-urs-12,17-dien-3-one	241, 269, 351, 375, 393, **408**
Ur2	31.15	Urs-9(11),12-dien-3α-ol	159, 255, (395), 391, 409, **424**
O8	31.49	Nor-β-amyrone	105, 161, 175, 189, **204**, 395, 410
Da6	31.54	Dammaradienone	109, 161, 175, 189, **205**, 218, 245, 313, 381, 409, 424
O9	31.59	Olean-12-en-3α-ol (epi-β-amyrin)	95, 107, 119, 175 189, **203**, 218, 393, 411, 426
Da7	31.77	Dammaradienol	93, 161, 175, **189**, 207, 315, 408, 426
Ur8	31.81	Nor-α-amyrone	105, 134, 175, 189, **204**, 313, 395, 410
O13	31.85	β-Amyrin (olean-12-en-3β-ol)	189, **203**, 218, 393, 411, 426
Ur11	32.18	α-Amyrin	107, 147, 189, 203, **218**, 393, 408, 411, 426
Da8	32.23	20,24-epoxy-25-hydroxy-3,4-seco-dammaren-3-oate (proposed)	107, 125, **143**, 371, 397, 411, 429, 473, (488)
Da10	32.41	Dammarenolate	81, 95, **109**, 149, 175, 215, 303, 343, 385, 411, 454
Lu2	32.60	Lupenone	107, 121, 147, 189, **205**, 313, 355, 409, 424
O16	32.69	17β-Hydroxy-28-norolean-12-en-3-one	132, 187, **202**, 393, 408, (426)
Lu3	32.83	Lupeol	95, 107, 121,133, **189**, 207, 257, 393, 408, 426
D12	33.05	20,24-epoxy-25-hydroxy-dammaran-3-one	107, 125, **143**, 161, 175, 205, 381, 399, (458)
O18	33.07	Oleanonate	133, 189, **203**, 262, 393, 409, 468
O19	33.20	Oleanonic aldehyde	117, 189, **203**, 410, 424, 438
Da13	33.31	Hydroxy-dammarenone	68, 81, 95, **109**, 205, 298, 311, 355, 409, 424, (442)
O20	33.32	Oleanolate	133, 189, **203**, 262, 395, 411, (470)
T33	33.38	Unidentified, see also chapter 4.3.1	**82**, 135, 187, 205, **341**, 359, 438
Da14	33.45	Hydroxy-dammarenol	95, **109**, 135, 189, 207, 300, 313, 339, 357, 426, (444)
O22	33.45	Oleanolic aldehyde	105, 133, 175, **203**, 232, 311, 355, 409, 424, 440
Ur15	33.49	Ursonate	133, 189, **203**, 262, 393, 408, 453, 468
O23	33.56	11-oxo-olean-12-en-3α-ol	**135**, 175, 217, 232, 273, 287, 407, 425, 440
Ur16	33.71	Ursonic aldehyde	133, **203**, 396, 414, 438
Ur17	33.73	3-acetoxy-ursolate	133, 189, **203**, 262, 452, 512
Ur21	33.94	Ursolic aldehyde	133, **203**, 409, 422, 440
Ur23	34.05	Unidentified ursonate	133, **203**, 262, 409, 440, 498
T49	34.07	Unidentified, see also chapter 4.3.1	109, 133, 203, 262, 325, 341, 369, **421**, 437, 452
Ur24	34.12	Unidentified ursonate	133, **203**, 262, 440
T52	34.35	Unidentified	239, 371, 437, 496, **528**
T54	34.37	Unidentified	133, 203, 247, 436, **496**, 528
O32	34.51	Unidentified oleanane acid	133, **203**, 262, 421, 467, 480, 498
T55	34.53	Unidentified	131, **145**, 159, 187, 203, 215, 393, 408, 421, 542
Ur25	34.68	Acetoxy-ursanoate	**133**, 165, 187, **203**, 219, 233, 262, 407, 422, 435, 450, 467, 482
T57	34.77	Unidentified	131, **145**, 215, 246, 423, 454
Ur26	34.84	Unidentified ursanoate	133, **203**, 262, 435, 467, 480, 498
Da16	34.98	Unidentified	95, 149, **189**, 205, 369, 383, 409, 424, 452

Label	t_R	Name	Main mass fragments
Ur27	35.10	Unidentified ursane	133, **203**, 262, 435, 467, 480
T60	35.44	Unidentified	133, **203**, 262, 467, 498
Ur28	35.81	Unidentified ursane	133, **203**, 262, 456, 498
T61	36.06	Unidentified	119, 161, 189, 248, 257, 317, 407, 449, **467**, 486, 499, 512, 544

Tab. 4.25 Compounds found in samples analysed in chapter 4.3.2 (Kongo and Angola copal), methanol and methylated methanol extracts, samples analysed with temperature program Triterpenes 3 and column A, mass spectra references see appendix

Label	Description	Picture	Sampling: date, description
5.4.1	Elemi, AFAD material collection		Jan. 2009; a soft and tenacious resin in glass bottle, yellow and polluted with dirt, resinous smell
5.4.2	Elemi, AFAD material collection		Jan. 2009; mostly dried up irregular pieces, which were originally tenacious, pungent medical smell; small fragments from the bottom of the container were sampled
5.4.3	Elemi, indonesian, dark & hard, Eggebrecht (#220610)		Jan. 2009; hard and brown crust, interior light yellow and somewhat tenacious, crust polluted with bark, crust and interior sampled separately
BlaD 1	Gum Elemi, soft and white, Eggebrecht, 2006 *(#220600, Manila Elemi*)		Jan. 2009; light yellow, opaque tenacious mass with some dried up pieces
E1	Elemi, viscous, Kremer, before 2000, Nanke Schellmann		Jan. 2009; dried up yellow pieces with only little dirt included
4.4.21	Copal Prontium Mexico, Copal blanco, light, Eggebrecht, 2008 (#220560)		19.05.09; light yellow to citrona hard, brittle and transparent pieces, resinous smell, inside transparent with a cloudy crust
4.4.22	Copal Prontium Mexico, Copal negro, dark, Eggebrecht, 2008 (#220570)		19.05.09; smell brown to yellow pieces with a resinous smell, opaque
4.15.1	Takamahak, formerly Gummi Tacamahacae, AFAD material collection		21.02.2008; irregular pieces of reddish brown to brown colour, surface opaque similar to 4.4.22, small fragments from the bottom of the container were sampled
4.15.2	Gummi Anime, AFAD material collection		21.02.2008: irregular pieces of grey to reddish brown colour, crust similar to ash or stone crust
4.4.13	Kongo Copal, 1978, AFAD material collection		15.10.08; orange longish pieces, completely opaque
AS07	Angola Copal, Kremer, Anja Schönemann		Dec. 2008; one transparent and clear yellow piece

Tab. 4.26 Description of reference samples analysed in chapter 4.3.2

Summary

The sesquiterpene fraction of (Manila) elemi is highly characteristic for the resin of *Canarium luzonicum* A. Gray. The absence of (iso-)elemicin, elemol and eudesmol indicates another *Canarium* species as it is the case with the analysed Indonesian elemi. The triterpene fraction of different Asian elemi resins is, in contrast, nearly identical. Typical compounds of Asian elemi (*Canarium* resins) resins are high amounts of β- and α-amyrin, low of the 3α-epimers, high amounts of tirucallane acids and lower of maniladiol, breine and their epimers (O21, O25, Ur19, Ur22). Traces of taraxasterol are also present in some materials.

The Mexican copals show the typical low volatile fraction of hard copal resins. Typical compounds are epi-lupeol, epi-β-amyrin and α-amyrin. They are distinguishable from Asian elemis by the low amounts of β-amyrin, the lack of tirucallane acids, maniladiol and brein but high amounts of epi-lupeol. Based on these results and literature data, it seems likely that they originate from a *Bursera* instead of a *Protium* species (see chapter 2.3.2). This identification is uncertain, however, as limited information is available from the literature and also from own analyses. 11-oxo derivatives of amyrins, such as O23, O24, Ur18, Ur20, T41, T43**,** are reported for *Canarium* and *Protium* resins only occasionally, while C-16 oxygenated derivatives such as O21, O25, Ur19, Ur22 seems to be absent in *Bursera* resins. It is not clear from literature data whether amyrins oxygenated at C-11 are aging or original compounds.

The composition of Gum Anime is similar to that of the Mexican copals, although there are several additional (unidentified) compounds, in particular T19, T20, T67, T43 and T48. All three resins share the prevalence for 3α-epimers, in particular 3epi-β-amyrin, and the presence of epi-lupeol, T17 and 11-oxo-derivatives of the amyrins (O23, T41, Ur18, Ur20, T43, T48). The absence of tirucallane acids, maniladiol and brein and the relative amounts of the amyrins and their epimers indicate a *Bursera* resin as well, which is, however, different from those used for Copal blanco and Copal negro.

The composition of Takamahak is uncharacteristic for Burseraceae resins as described in chapter 2.3.2 from the genera *Canarium*, *Protium*, *Bursera*, *Boswellia* and *Commiphora*. Characteristic constituents are germanicene, α-amyrin and its aging compounds (Ur3, Ur7, Ur12), lower of β-amyrin and its aging compounds (O3, O6, O8), several nor-oleananes (O2, O15, O8), epi-lupeol and several unidentified triterpene compounds (T64, T65, T66, T68 and T69). The presence of moronic and 3-oxo-lupenoic acids in the methylated extract and several aging compounds indicate a chemotaxonomical connection to *Pistacia* resins instead.

The two African copals are composed slightly differently, but show more common constituents compared to the other samples analysed in this chapter. They contain oleanane and ursane aldehydes and acids, lupanes, amyrins and several unidentified oleanane and particularly ursane acids (Ur23, Ur24, Ur25, Ur26, Ur27, Ur28, O32, T49, T52, T54, T55, T57, T60, T61). Oxygenated dammaranes called mansubianes, α- and β-amyrin, lupenone and lupeol are characteristic constituents of some *Commiphora* resins, even though no resin with a composition like that of AS07 is reported in the literature (see chapter 2.3.2). *Boswellia* resins mainly contain boswellic acids, but other resins from that genus consisting mainly of lupanes and amyrins are also reported (Basar 2005: 148). In the resin of *Boswellia frereana* dammaranes are present (Fattorusso et al. 1985), even though its composition is somewhat different from that of Kongo copal and clearly from that of AS07. According to literature data, high amounts of β-amyrin are in general uncharacteristic for *Boswellia* resins. Therefore, the Kongo copal probably originates from a *Boswellia* or from a *Commiphora* species, the Angola copal from a differing *Commiphora* species.

4.3.3 Discussion

Main compounds in Sapindales are tetra- and pentacyclic triterpenes with an ursane, oleanane, lupane, tirucallane or dammarane skeleton. Apart from that, families differ very much, both in the number of materials in use and their chemical composition and aging characteristics.

The present investigation of ***Pistacia* resins**, particularily mastic, aimed mainly the identification of chemotaxonomical markers. Different *Pistacia* resins show a consistent acidic fraction, main differences are found in the neutral fraction. The observable composition of the neutral fraction is altered when a methylation reagent is used, because olean-17-enes are discriminated compared to tirucallanes and olean-12-enes. Main differences between mastic (*Pistacia lentiscus* L.) and *P. terebinthus* L. are lower initial amounts of oleananes in *P. terebinthus*, which results in the absence of oleanonic aldehyde, and the presence of several unidentified compounds (T4, T10, T26, T33), which are partly present in aged Bombay mastic, too. The present data do not allow to determine whether they are of botanical or environmental origin. In literature, seco-28-norolean-12-en-3oic acid, 18α-oleanonic acid, morolic aldehyde and dammaradienol are reported as markers for *P. terebinthus* var. *Chia*, because these compounds were not present in the resin of *P. lentiscus* var. *Chia* (Assimopoulou, Papageorgiou 2005a; Assimopoulou, Papageorgiou 2005b). This is not found in this work, 18α-oleanonic acid is present in mastic as well, morolic aldehyde and dammaradienol are not present in any of the investigated samples. Seco-28-norolean-12-en-3oic acid is an aging product, its presence is therefore of low phytochemical significance. It is found in this work in several of the mastic samples. In sum, the compositions published by Assimopoulou and Papageorgiou for *P. lentiscus* var. *Chia* and *P. terebinthus* var. *Chia* considerable differ from those found in this work.

While from the genus *Pistacia* mainly mastic is still in use, **Burseraceae resins** can be found in various forms from all over the world. This variety of resins and their differing properties are reflected by the reference samples analysed in this work. They show highly varying compositions, as expected from the literature (see chapter 2.3.2). The main aim of the study, to gain a differentiation profile for the genera and the names of the materials, is only partially achieved. This is the result of a limited number of reference samples with a very different chemical composition, and on the other hand the lack of botanical samples. Reliable botanical samples of endemic trees such as Pinaceae resins are available in Central Europe more easily than resins from tropical plants, also because of the involvement of three continents (Asia, Africa, America). Additionally, the various forms of materials in use and lacking knowledge about the botanical origin of these materials, made it impossible within the scope of this study to find a chemotaxonomical significant number of botanical samples for this group of resins. In case a botanical identification was given in chapter 4.3.2, it is based on comparison of the present data and phytochemical data from literature (see chapter 2.3.2). Own data presented in this work only illuminate the connection of the chemical composition and terminology.

The following differentiation is based on data obtained in this work and (phyto)chemical data from the literature (chapter 2.2): American hard (copal) resins can be distinguished from Asian or African triterpene copals by the presence of amyrins, with low amounts of β-amyrin and higher of 3α-β-amyrin, lupanes such as epi-lupeol and 11-oxo derivatives of amyrins. Additionally, oxygenated non-acidic oleananes, ursanes, taraxastanes and lupanes may be present. If the origin of a material is known, *Bursera* resins will be distinguishable were good, because the genus is restricted to America. If not, the typical non-acidic composition of *Bursera* resins still differs enough from other Burseraceae resins to allow a reasonable assumption. The triterpene fraction of the copal from *Protium copal* Englm., which is not investigated so far, may be composed similar to American soft *Protium* resins. It would be well distinguishable from other American *Bursera* copals, provided that the geographical origin of the related material is known.

Due to the similarities in chemical compositions reported in the literature, *Canarium* and *Protium* resins seem to be undistinguishable by their triterpene fraction up to the present moment. This includes certain problems in the differentiation of Asian elemis not obtained from *Canarium luzonicum* A. Gray. and reclassified Asian *Protium* species (for example *P. serratum* Englm., originally *Bursera serrata* Wallich ex Colebrooke) Tirucallane acids and C-16 oxygenated amyrins are good indicators for both, *Canarium* and *Protium* resins.

For a more detailed differentiation, it is necessary to investigate the volatile fraction. This was not done in this work, because apart from the Asian elemis no other samples could be attributed to *Canarium* or *Protium* species, the only genera within the Burseraceae reported to yield a reliable volatile fraction. Literature data, however, indicates that *Protium* and *Canarium* are distinguishable by their volatile fraction (Khalid 1983; Marinach et al. 2004; Chiavari et al. 2008; Siani et al. 1999; Ramos et al. 2000; Machado et al. 2003; Siani et al. 2004; Pontes et al. 2007; Rüdiger et al. 2007). Additionally, Case et al. distinguished several Mexican copals by their mono- or sesquiterpene fraction, a copal blanco to *Bursera bipinnata* and a copal negro to *Protium copal*, whereas the *Bursera* species possessed a more prominent sesquiterpene and the *Protium* species a more prominent monoterpene fraction (Case et al. 2003). At least, the latter corresponds to phytochemical data on the volatile fraction of soft *Protium* resins. However, a Mexican copal attributed to *Bursera cuneata* Englm. showed a prominent monoterpene fraction as well. The copal additionally contained a compound identified by the authors as hop-22(29)-en-3ß-ol (de la Cruz-Caňizares et al. 2005), which is equated in this work with epi-lupeol (Lu1), which is in turn a marker for *Bursera* resins. In the literature, only friedelan-3-one, taraxastandiol and taraxastanonol are mentioned as additional constituents of *Protium* resins, all of them eluting after α-amyrin (Itoh et al. 1982). This supports the assignment of the samples analysed by de la Cruz-Caňizares et al. to a *Bursera* species. In this case, however, the differentiation of American *Bursera* and *Protium* copals by their mono- and sesquiterpene fraction, respectively, as reported by Case et al., does not work.

African *Commiphora* copals investigated here consist of oleanane and ursane acids, α- and β-amyrin and their aging compounds, lupanes and sometimes high amounts of dammaranes. Therefore, African triterpene hard resins with a different composition from *Boswellia* and *Commiphora* may aso be composed differently compared to American *Bursera* species. The assumption however needs further investigation.

Soft (elemi) resins are more difficult to distinguish, because of the unknown composition of African *Canarium* resins, the use of different Asian *Canarium* species as sources of soft elemi resins and, in particular, the use of the term for *Protium* resins.

4.4 Fossil resins

This chapter contains the results from the investigation of fossil resins, in particular Baltic amber. Fossil resins contain a macromolecular polymer, the monomeric constituents of which are generally used as a basis for their classification. For their investigation a pyrolytic sample pretreatment is necessary. In this work, however, a consistent sample preparation is used based on solvent extraction (see chapter 3.1.2). The aim was to analyse all samples taken from the Vigani Cabinet with the same sample preparation. Additionally, amber is reported to contain a soluble part of up to 30% of the resin, which possesses a characteristic composition. In this chapter the solubility of a Baltic amber from Poland in different solvents is compared. The investigation aims to show whether the results from these extracts are applicable for the analysis of Baltic amber.

4.4.1 Baltic amber

A sample of Baltic amber purchased in 2007 in Poland at the Baltic Sea coast is analysed. It consisted of small different coloured pieces in a plastic bag, sold for medical purpose at the market in Kołobrzeg, Poland. It is separated into yellow (4.3.6a) and brown lumps (4.3.6b; table 4.29). As shown in Fig. 3.1 (chapter 3.1.2) the following solvents are used: isooctane, methanol, a mixture of methanol and chloroform and dichloromethane. The former three are adopted from the solvent extraction scheme described in chapter 3.1.2 (Koller, Baumer 2000; Baumer et al. 2009), dichloromethane is mentioned in literature as a suitable solvent for amber (Czechowski et al. 1996).

Solvent extracts without methylation

Both samples (4.3.6a, 4.3.6b) are dissolved in different solvents and heated. The results are shown in table 4.30. The extract yields are low in both cases. 4.3.6a dissolves best in dichloromethane, 4.3.6b in methanol. Heating does not improve the extract yields.

In the sesquiterpene region of the methanol-chloroform extract of 4.3.6a (Fig. 4.34a) dihydro-ar-curcumene, 1,5,6-trimethyl- and 1,1,5,6-tetramethyl-1,2,3,4-tetrahydro-naphthalene, calamenene, cadina-1(10),6,8-triene, palustrol and several unidentified compounds are present. Small amounts of fenchyl- and (iso-)bornylsuccinic acid are present and several (nor-)abietatrienes (A1, A2, A3). In the diterpene region Δ8-isopimaric acid, Δ8-pimaric, dihydro-Δ8-isopimaric acid, dehydroabietol and dehydroabietic acid together with lower amounts of

Label	Description	Picture	Sampling: date, description
4.3.6a	Bursztyn, 2007, purchased in Kołobrzeg, Poland		After purchase stored in a brown glass bottle, in July 2008 yellow lumps were sorted out and powdered coarsly
4.3.6b	Bursztyn, 2007, purchased in Kołobrzeg, Poland		After purchase stored in a brown glass bottle, in April 2009 brown lumos were sorted out and powdered coarsly

Tab. 4.27 Description of reference samples analysed in chapter 4.4.1

sandaracopimaric and abietic acid are present. Additionally, difenchyl-, di(iso-)bornyl- and fenchylbornylsuccinates are present. (Iso-)bornyl esters of pimaradien- and pimara-ene acids are present together with (iso-)bornyl-(dehydro-)abietates (Fig. 4.34; Fig. 4.36). No free succinic acid is found. However, the monoterpene region is not analysed due to a long solvent delay.

The dichloromethane extract of 4.3.6a (Fig. 4.34b) is nearly identical to its methanol-chloroform extract. Due to a different temperature program, the monoterpene region is partially acquired. It contains p- and m-cymenes, fenchol, camphor and borneol, the latter in high amounts. Between 16 and 28 minutes a homologous series of n-alkanes elutes (Fig. 4.35). Main peaks of the mass spectra are at m/z 57, 71, 85, 97, 111, 125, 139, 153, 167, 181 and 195. Such a phenomenon is reported by Czechowski et al. (shown at the EIC at m/z 71) and ascribed to degraded lipid biomass materials (Czechowski et al. 1996).

The brown sample 4.3.6b is poorly soluble, only the methanol extract shows a sufficient intensity and resolution for evaluation. The mono- and sesquiterpene fraction of 4.3.6b is identical to that of 4.3.6a, apart from the monoterpanyl succinic acids and monoterpanyl pimarane and abietane acids, which are not present. Instead the natural methylester 1,2,3,4-tetrahydro-1,5,6-trimethyl-1-naphthalenecarboxylate (D5) is present (not shown; for D5 see Fig. 4.39). In the diterpene region of the methanol extract of 4.3.6b (Fig. 4.36a) main compounds are Δ8-isopimaric acid, sandaracopimaric acid, dehydroabietol, isopimaric acid, dehydroabietic acid together with lower amounts of dihydro-Δ8-isopimaric acid. No Δ8-pimaric acid is present such as in 436a. Abietic acid is not present and dehydroabietic acid is decomposed during heating (Fig. 4.37b). Instead several additional compounds are present: P2, U4, U6, A15, U11. The extract was heated for 30 minutes at 40°C (Fig. 4.36a), while longer heating for 24 hours caused a degradation of a significant number of constituents (Fig. 4.36b).

Methylated solvent extracts

The methanol extracts of 4.3.6b are heated for different times and methylated thereafter. The resolution and intensity is better for the extract, which was heated for 24 hours. This stands in contrast to the results found for the unmethylated methanol extracts (Fig. 4.37). The extracts of methanol-chloroform and dichloromethane are evaporated to dryness and the TMSH-solution is added (see chapter 3.1.2). That concentration step results in a good intensity.

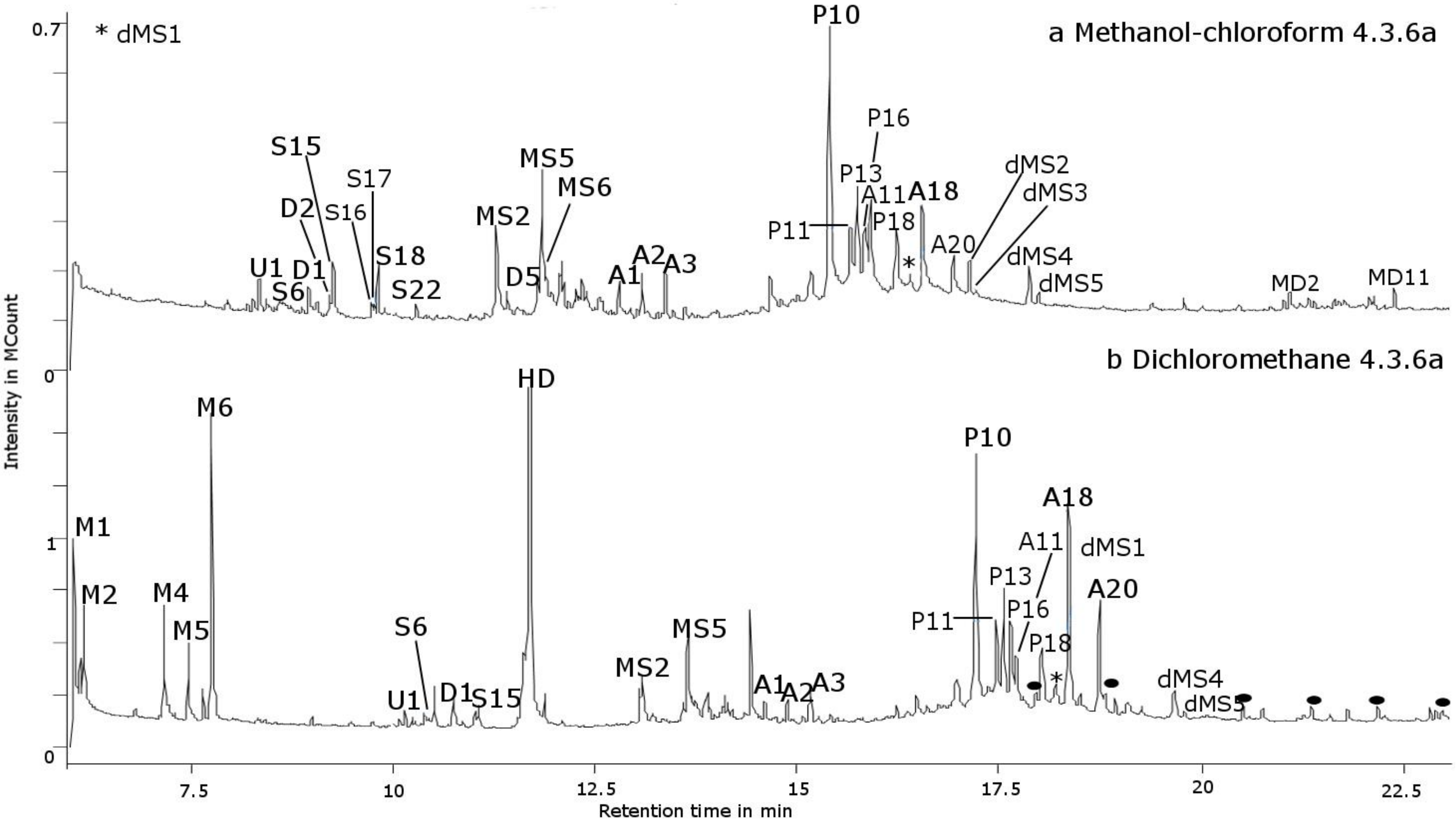
Fig. 4.39 shows the methylated methanol-chloroform and dichloromethane extracts of 4.3.6b. The mono- and sesquiterpene fraction is less dominant than in the unmethylated extracts, but apart from some missing compounds identical to that of 4.3.6a (Fig. 4.34). Dimethylsuccinate is not found, but small amounts of monoterpanyl succinates are present (MS1, MS3, MS4). Naphthalene derivatives and (nor-)abietatrienes are present only in small amount.

In the diterpene section Δ8-isopimarate, sandaracopimarate, isopimarate, dihydro-Δ8-isopimarate, dehydroabietate, abietate and dihydro-Δ8-agathate (L41) are present. Other compounds are 13-methylpodocarpatrien-18-oate, 5β-dehydroabietate, pimaradienol (P2), compound U2, Δ-8-pimarate and compound U4. Compounds P2, U4 and the unmethylated derivative of U2 (U7) are present in the methanol extracts (Fig. 4.36), where Δ8-pimaric and abietic acids are present with non-acidic compounds (P2, U4).

Dimonoterpanyl succinates are not found, and monoterpanyl diterpenoates are present only in traces (Fig. 4.38). They are not found in unmethylated extracts because of their low concentration. They became visible after a concentration step was included in the sample preparation. Only the compounds MD2, MD4, MD8 and MD11 are present. Additionally small amounts of monoterpanyl ester with compound L41 are present (ML1, ML2). L41 is a dicarboxylic acid. According to literature data it is identified as Δ8-dihydroagathate (Mills, White 1984/85). ML1 and ML2 have characteristic peaks at m/z 175, 235, 289 and 249, which originate from Δ8-dihydroagathatic acid, which is esterified with one monoterpene, probably (iso-)bornyl alcohol. The second carboxyl group is methylated by TMSH, the molecular ion is not found but the fragment [M-60]$^+$ at m/z 426 is present, which results from the elimination of the methylated carboxyl group.

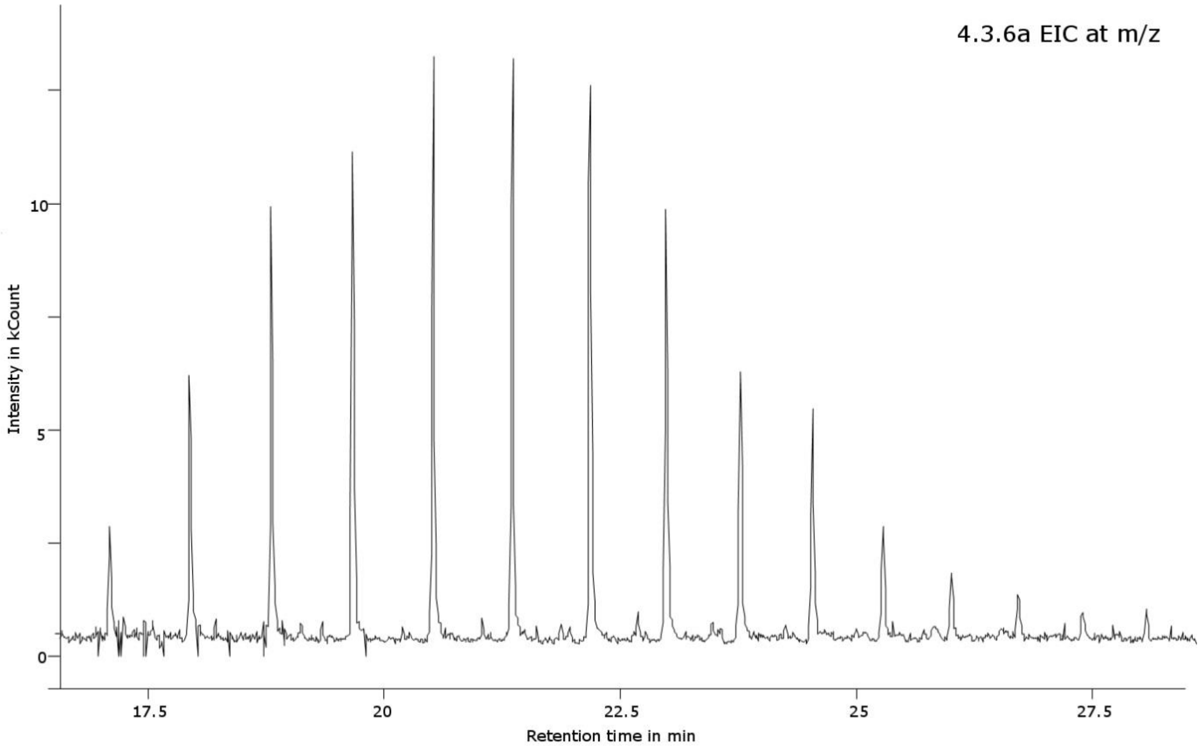
	4.3.6a yellow	4.3.6b brown	4.3.6b brown, methylated
Methanol	Low extract yield		
Methanol, heated 30 min at 40°C (Lit.)	No change	**Low extract yield**	**Low intensity**
Methanol, heated 24 h at 40°C (Lit.)		Very low extract yield, low resolution	Better intensity
CF/MeOH	Low extract yield	Very low extract yield, low resolution	With concentration good intensity
CF/MeOH, heated 30 min at 40°C	No change		
Dichloromethane	**Best intensity**	Very low extract yield	With concentration good intensity
Dichloromethane, heated 30 min at 40°C		No change	
Characteristic compounds	Homologous n-alkanes, significant amounts of various ester of succinic acid	No ester of succinic acid, small amounts of maturation products, no Δ-8-pimaric, abietic acids, additional compounds P2, U3-U7, A15, U10, U11	Only small amounts of ester of succinic acid, small amounts of maturation products, additional compounds P2, U4, 5β-dehydroabietate, U2, L41

Tab. 4.28 Solvent extract yields of Baltic amber and characteristic compounds thereof, best intensities are marked in bold, extracts presented in the form of chromatograms are highlighted in green



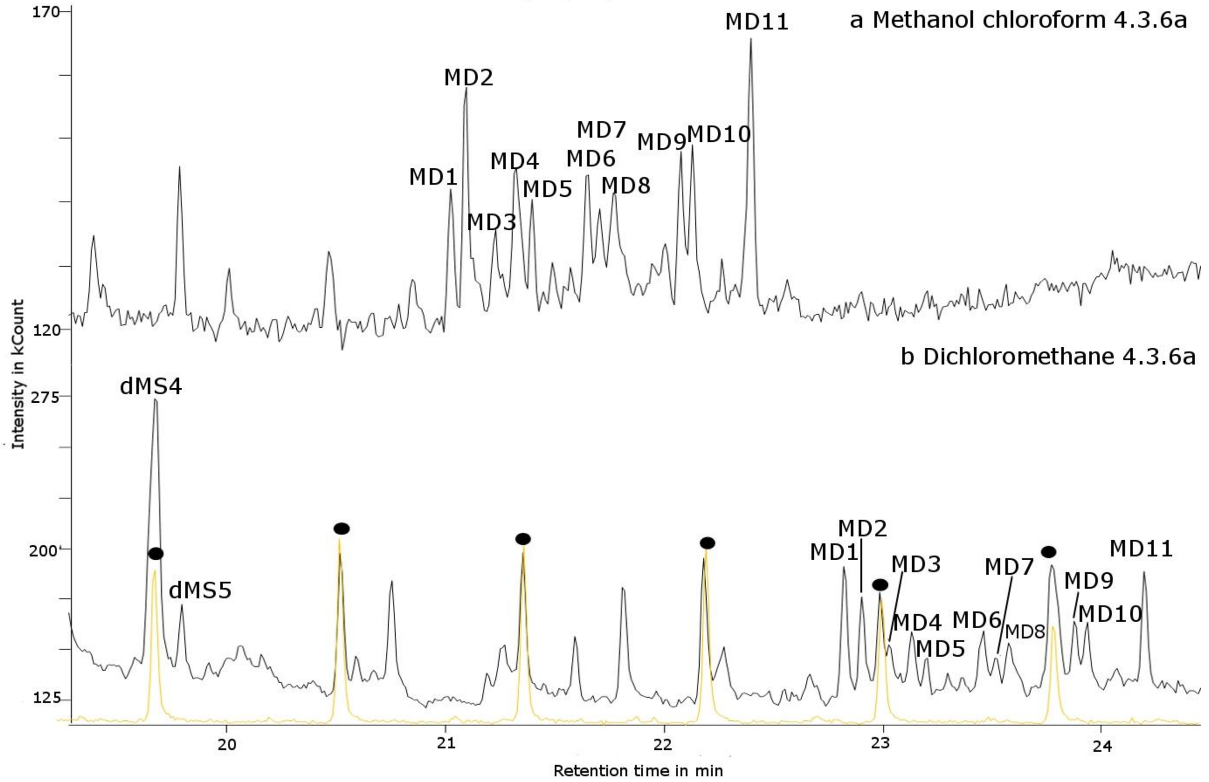
a - methanol-chloroform extract and b - dichloromethane extract, peaks of the homologous series (Fig. 4.35) are marked with a dot, a partial chromatogram from 19.5 min on is given in Fig. 4.37 (labels, see table 4.31)

Fig. 4.34 Gas chromatogram of Baltic amber 4.3.6a yellow pieces, mono-, sesqui- and diterpene section (TIC)



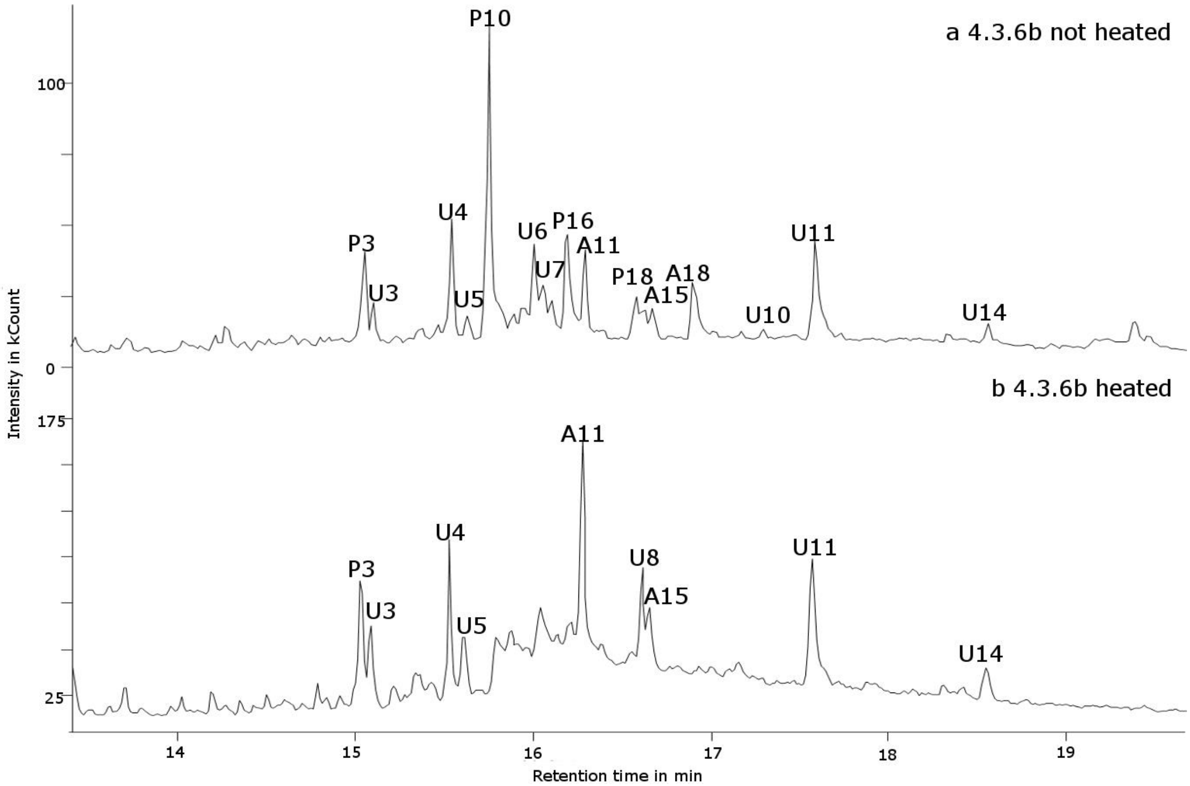
Dichloromethane extract

Fig. 4.35 Extracted ion chromatogram of Baltic amber 4.3.6a yellow pieces at m/z 71 (cf. Czechowski et al. 1996)



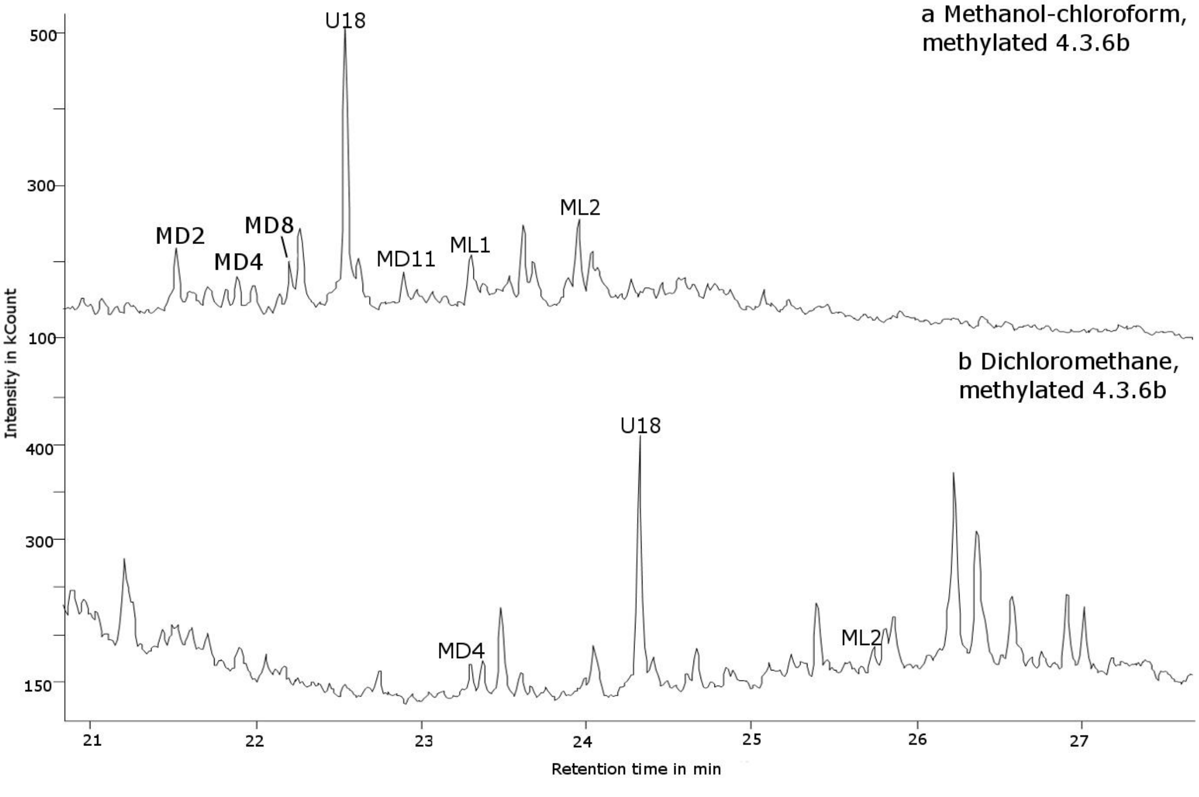
a - methanol-chloroform extract and b - dichloromethane extract, peaks of the homologous series are marked with a dot (labels, see table 4.31)

Fig. 4. 36 Partial gas chromatogram of Baltic amber 4.3.6a yellow pieces, diterpene section (TIC, yellow line - EIC at m/z 71)



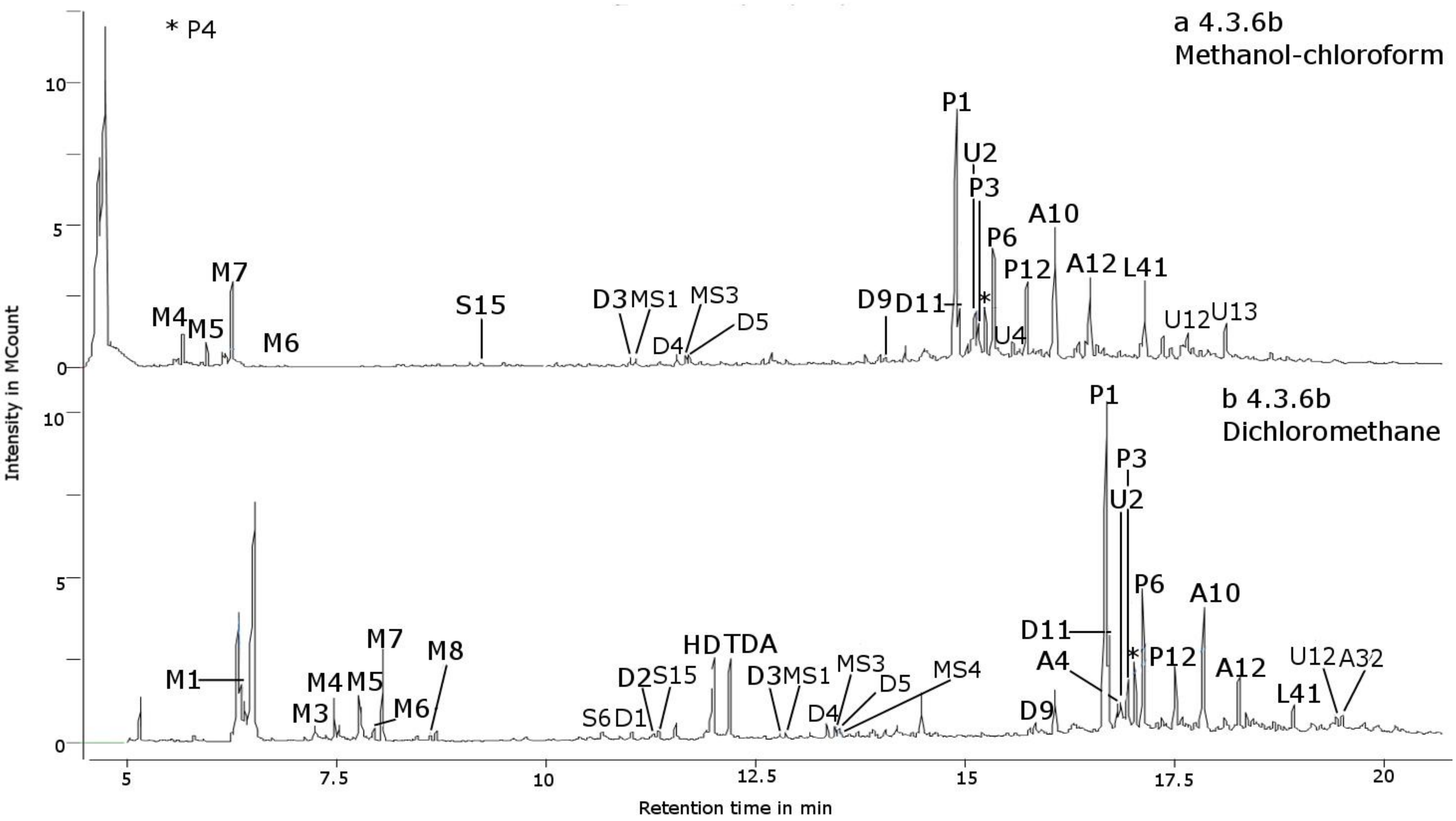
a - methanol extract heated for 30 min at 40°C and b - methanol extract heated for 24 h at 40°C (labels, see table 4.31)

Fig. 4.38 Partial gas chromatogram of Baltic amber 4.3.6b brown pieces, influence of the sample preparation, diterpene region (TIC)



a - methylated methanol-chloroform extract and b - methylated dichloromethane extract (labels, see table 4.31)

Fig. 4.37 Partial gas chromatograms of Baltic amber 4.3.6b brown pieces, diterpene section (TIC)



a - methylated methanol-chloroform extract and b - methylated dichloromethane extract (labels, see table 4.31)

Fig. 4.39 Gas chromatogram of Baltic amber 4.3.6b brown pieces, mono-, sesqui- and diterpene section (TIC)

Label	t_{R1}	t_{R2}	Name	Main mass fragments
M1		6.06	p-Cymene	53, 77, 91, **119**, 134
M2		6.18	m-Cymene	53, 77, 91, **119**, 134
M3		6.81	l-Fenchone	53, 69, **81**, 109, 152
M4	5.67	7.17	Fenchol	55, 67, 80, **81**, 93, 107, 121, 154
M5	5.92	7.47	Camphor(+)	55, 67, 81, **95**, 108, 137, 152
M6	6.15	7.65	Isoborneol	55, 67, 79, **95**, 121, (154)
M7	6.25	7.76	Borneol	55, 67, 79, **95**, 121, (154)
M8		8.32	Bornylformate	67, 93, **95**, 121, 136, (182)
U1	8.35	10.16		55, 67, **82**, 93, 95, 107, 121, 133, 161, 189, 207,222
S6	8.60	10.39	Dihydro-ar-curcumene	91, 105, **119**, 179, 204
D1	8.95	10.76	1,5,6-Trimethyl-1,2,3,4-tetrahydro -naphthalene	91, 115, 128, 131, 145, **159**, 174
D2	9.22	11.02	1,1,5,6-Tetramethyl-1,2,3,4-tetrahydro-naphthalene	119, 131, 145, 159, **173**, 188
S15	9.26	11.06	Calamenene	91, 115, 129, 144, **159**, 174, 187, 202
S16	9.74			55, 82, 95, **111**, 123, 161, 179, 189, 204, 220
S17	9.78		Cadina-1(10),6,8-triene	83, 131, 145, 159, **187**, 202
S18	9.83		Palustrol	55, 67, 82, 93, **111**, 123, 133, 151, 161, 179, 204, 207, 222
D3	11.02	12.81		91, 115, 128, 131, 143, 145, 158, **173**, 186
MS1	11.07	12.87	Fenchylsuccinate	55, 81, 87, **115**, 121, 136, 153, (268)
S22	10.29			67, 83, 95, 123, 161, **207**, 222
MS2	11.28	13.08	Fenchylsuccinic acid	55, 80, **81**, 93, 101, 121, 136, 173, (254)
D4	11.55	13.10	1,2,3,4-Tetrahydro-1,5,6-trimethyl-1-naphthalenecarboxylate	91, 115, 128, 145, 158, **173,** 185, 232
MS3	11.66	13.46	Bornylsuccinate	55, 81, 93, 95, 108, **115**, 121, 136, 153, (268)
D5	11.41	13.22		67, 79, 95, 107, 119, 135, **191**, 207, 222
MS4		13.52	Isobornylsuccinate	55, 81, 93, 95, 108, **115**, 121, 136, 153, (268)
MS5	11.84	13.65	Bornylsuccinic acid	55, 67, 80, 93, **95**, 108, 121, 136, 154, 236, (254)
MS6	11.90	13.69	Isobornylsuccinic acid	55, 67, 93, **95**, 108, 11, 136, 175, 231, (254)
A1	12.79	14.59	18-Norabietatriene	117, 129, **159**,185, **241**, 256
A2	13.08	14.87	19-Norabietatriene	117, 129, **159**,185, **241**, 256
A3	13.38	15.16	Abietatriene	67, 79, 93, 107, 121, 159, 173, 185, 237, **255**, (270)
D9	14.03	15.84	10,18-bisnorabieta-5,7,9(10,11,13)-pentaene	55, 67, 91, 96, 165, 181, 195, **223**, 238
P1	14.86	16.69	Δ8-Isopimarate	91, 131, 185, **241**, 257, 269, 301, 316
D11	14.89	16.73	13-Methylpodocarpatrien-18-oate	91, 131, 145, 155, **211**, 227, 241, 271, 287, 301, 316
A4	15.04	16.83	5β-Dehydroabietate	91, 143, 157, 183, 211, **239**, 255, 273, 299, 314
P2	15.05	16.86	Pimaradienol	105, **131**, 145, 155, 185, 225, 243, 288
U2	15.13		Unidentified acid, ME of U7	79, 119, **175**, 189, 235, 245, 279, 304
U3	15.11		Unidentified	67, 81, 107, 119, 177, **243**, 261, 279

Label	t_{R1}	t_{R2}	Name	Main mass fragments
P3	15.15	16.96	Δ8-Pimarate	105, 185, **241**, 257, 269, 301, 316
P4	15.21	17.04	Dihydro-Δ8-isopimarate	91, 187, **243**, 259, 271, 303, 318
P6	15.30	17.13	Sandaracopimarate	79, 91, **121**, 241, 257, 301, 316
U4	15.54		Unidentified	79, **95**, 105, 119, **189**, 207, 245, 302
U5	15.63		Unidentified	105, 119, **133**, 175, 187, 213, 288
P10	15.39	17.21	Δ8-isopimaric acid	91, 105, 185, **241**, 269, 287, 302
P11	15.66	17.49	Δ8-pimaric acid	91, 105, 159, 185, 241, 269, **287**, 302
U6	16.01		Unidentified	91, 105, 119, 133, **173**, 189, 221, 229, 287, 302
U7	16.05		Unidentified acid	79, **107**, 121, 153, **175**, 235, 290
P12	15.69	17.52	Isopimarate	91, 105, 121, 187, 201, 227, **241**, 256, 257, 287, 301, 316
P13	15.74	17.55	Dihydro-Δ8-isopimaric acid	91, 105, 133, 159, 187, 243, 271, **289**, 304
A11	15.91	17.72	Dehydroabietol	117, 159, 173, 185, 211, **253**, 271, 286
A10	16.02	17.86	Dehydroabietate	197, **239**, 299, 314
P16	15.84	17.65	Sandaracopimaric acid	79, 91, 105, **121**, 133, 241, 287, 302
P18	16.24	18.03	Isopimaric acid	91, 105, 159, 187, **241**, 287, 302
A12	16.45	18.28	Abietate	91, 105, 121, 185, 213, **241**, 256, 316
U8	16.61		Unidentified	**91**, 107, 133, 185, 227, 241, 255, 288
A15	16.67		Tetradehydroabietic acid (didehydroabietic acid)	165, 195, **237**, 302
dMS1	16.39		Difenchylsuccinate	67, **81**, 95, 121, 137, (390)
A18	16.55	18.36	Dehydroabietic acid	197, **239**, 285, 300
A20	16.94	18.75	Abietic acid	91, 105, 131, 213, 241, 259, 287, 302
L41	17.13	18.92	Dihydro-Δ8-agathate, diME	79, 105, 119, **175**, 203, **235**, 257, 289, 304, 349, 364
U10	17.29		Unidentified	105, 131, **159**, 239, 259, 302
U11	17.58		Unidentified	55, 67, 81, **95**, 107, 119, 135, 161, 189, 207, 277
dMS2	17.13	18.94	Fenchylisobornylsuccinate	67, **81**, 95, 121, 137, 390
dMS3	17.21		Fenchylbornylsuccinate	67, **81**, 95, 121, 137, (390)
U12	17.63	19.44	Unidentified	81, **95**, 121, 189, 207, 229, 291, 305
A32	17.69	19.51	7-Oxo-dehydroabietate	187, 211, **253**, 269, 296, 328
dMS4	17.88	19.68	Dibornylsuccinate	57, 67, **81**, 95, 121, 137, (390)
dMS5	17.98	19.78	Diisobornylsuccinate or Bornylisobornylsuccinate	57, 67, **81**, 95, 121, 137, (390)
U13	18.06		Unidentified	91, 133, **189**, 249, 303
U14	18.55		Unidentified	117, 128, **187**, 225, 267, 285, 300
MD1	21.02	22.81	Bornylisopimara-8,15-diene-18-oate	**81**, 95, 137, 175, 241, 287, 301, 396, 438
MD2	21.09	22.89	Isobornylisopimara-8,15-dien-18-oate	**81**, 95, 137, 175, 241, 287, 301, 396, 438
MD3	21.23	23.02	See MD7	**81**, 95, 137, 215, 229, 275, 289, 301
MD4	21.32	23.13	Isobornylpimar-9(11)-en-18-oate	**81**, 137, 177, 193, 243, 271, 287, 289, 303, 377, (440)
MD5	21.39	23.20	Isobornylpimar-7-en-18-oate	**81**, 137, 177, 193, 243, 257, 271, 289, 303, 440

Label	t_{R1}	t_{R2}	Name	Main mass fragments
MD6	21.64	23.45	(Iso-)Bornylpimaradiene-18-oate	**81**, 95, 137, 229, 275, 289, 301, 417, 438
MD7	21.71	23.52	See MD3	**81**, 95, 137, 229, 257, 275, 289, 301, 377, 438
MD8	21.77	23.57	(Iso-)Bornylpimaradiene-18-oate	**81**, 95, 137, 255, 301, 350, 410, 438
MD9	22.08	23.88	Bornyldehydroabietate	**81**, 95, 137, 173, 239, 285, 299, 436
U18	22.54	24.33	Di- or polymeric matrix constituent	105, **133**, 257, 375, 435, 450
MD10	22.13	23.94	Isobornyldehydroabietate	81, 137, 173, 239, 285, 299, 436
MD11	22.39	24.19	Isobornylabietate	81, 173, 255, **301**, 438
ML1	23.29		Monoterpanylester of dihydro-Δ8-agathate	**81**, 95, 137, 175, 235, 271, 289, 331, 349, 426, (486)
ML2	23.95	25.74	Monoterpanylester of dihydro-Δ8-agathate	**81**, 95, 137, 175, 235, 271, 289, 349, 426, (486)

Tab. 4.29 Compounds found in samples analysed in chapter 4.4.1, t_{R1} – methanol and methanol-chloroform extracts, analysed with temperature program Diterpenes1; t_{R2} – dichloromethane extracts, analysed with temperature program Diterpenes 3, mass spectra references see appendix

4.4.2 Discussion

The analyses show that Baltic amber can be investigated by its solvent extracts. The chemical composition found here corresponds very well with published data. The only difference is the absence of succinic acid, which is a marker for Baltic amber. However, in all solvent extracts even though sometimes only small amounts of succinates are present. The presence and amounts of oxygenated monoterpenes (M1 – M7) is characteristic for Baltic amber as well, even though there are other fossil resins loosely attributed to extinct coniferous species, which contain these compounds (Mills, White 1984/85).

From a methodological point of view, the soluble fraction of amber is dissolved all used solvents with few changes yielding chromatograms of low intensity. The solubility of the different coloured pieces slightly differs, the yellow pieces (4.3.6a) are soluble the best in methanol-chloroform and dichloromethane, the brown pieces (4.3.6b) in methanol. Heating the methanol extract improves the intensity in a limited way, for the brown pieces a degradation of the diterpene composition is observed. For the methanol-chloroform and dichloromethane extracts no improvement by heating is found. The concentration step, however, yields chromatograms with a good intensity and resolution. Because TMSH is available as a methanol-solution some loss may occur. Particularly for the methanol-chloroform extract, this is, however, of less importance, because the methanol and methanol-chloroform extracts are nearly identical, only the relative amounts of the constituents differ.

The two differently coloured samples show only little differences in their chemical composition. The brown pieces contain lower amounts of Δ8-pimaric and abietic acids, instead 5β-dehydroabietate and other compounds (P2, U2, U4, L41) are present. Monoterpanyl succinates and –diterpenoates, which are marker for Baltic amber as well, are also present in small amounts. Dimonoterpanyl succinates are absent. The yellow pieces contain, in contrast, a homologous series of n-alkanes and higher amounts of compounds derived from the maturation process such as (nor-)abietatrienes and naphthalenes.

Baltic amber is reported to show a very stable composition with only few quantitative changes. Monoterpanyl succinates and diterpenoates and (nor-)abietatrienes and naphthalenes are products of the maturation. The lower amounts of Δ8-pimaric and abietic acids, present in the brown pieces, are indications for a less advanced maturation. Therefore, the different composition may be the result of a different maturation state.

On the other hand, the diagenetic formation of monoterpanyl esters is reported to take place in an early stage of maturation and to result in relatively uniform amounts of these compounds (Czechowski et al. 1996). The authors report that the solubility is connected to the polymerisation state, the level of which is not necessarily an indication for the maturation level (Czechowski et al. 1996). Higher polymerised ambers were significantly less well soluble in a methanol-chloroform mixture and their reflectance in turn was higher (which means they were darker). This may be an explanation for the differing solubility of the two samples analysed in this work. Therefore, the two different coloured pieces from the purchased Baltic amber are probaly in a different polymerisation state, which is higher for the darker pieces.

4.5 Summary and research deficits

The following paragraphs summarize the results of the analyses presented in the section 4.1 to 4.4, discussing the key findings in the context of the examination of the samples from the Vigani Cabinet, which will be presented in chapter 5, and pointing to open questions for future research.

Conifer resins

Conifer resins are widely used and the main aim of the investigation is to identify the various materials and detect adulterations. The results of this study facilitate this approach, because a wide range of marker molecules were identified.

What is known? In which way does this knowledge serve the investigation of the materials from the Vigani Cabinet?

- Pimaric acid is a compound commonly found in softwood resin, which make its absence characteristic for the blister resin of *Abies alba* Mill. Additionally, it serves as a marker compound for adulterations with pine resin.
- Neutral compounds such as abienols (*Picea* and *Abies*), labdane alcohols (*Larix*) and labdane acids (some species of *Pinus*) allow a differentiation of the different genera of Pinaceae resins.
- *Picea abies* Karst. the European spruce is not the botanical source of modern Burgundy pitch. In particular for non-European materials of that name, *Pinus* species must be taken into account as possible source of Burgundy pitch. Differences in the composition of modern Burgundy pitches result from the aging processes and are no botanical markers.
- The analysis of the composition of *Tetraclinis articulata* Mast. and *Juniperus communis* L. revealed marker compounds for true sandarac. A wide range of commercial reference samples analysed in the literature and in this work, however show a differing composition, not only lacking the markers but also containing additional compounds more characteristic for other genera of the Cupressaceae and even families of conifers. The advantage of the analysis of modern reference materials is thus limited.

What has yet to be investigated?

- The typical abienols found in *Abies* and *Picea* resins in connection with the absence of pimaric acid found in this study is partially in contradiction to literature data. In order to learn whether the place of exudation has a significant influence on the composition and therefore the detection of adulterations, an investigation of resins exuded from different parts of the trees would be necessary.
- The investigation of modern commercial materials labelled Venice and Strasbourg turpentine confirmed the importance of pimaric acid as a marker for the differentiation of the genera. However, the composition of neutral labdanes was not that clear. Apart from differing findings within the genus *Picea*, commercial materials others than larch resin were difficult to assign to a species or even genus based on the presence or absence of such neutral labdanes. *Abies* resin not, as usually, obtained from blisters, but from the sapwood probably contains pimaric acid. Then, identification

ought to be based on the composition of the neutral labdanes. The commercial Strasbourg turpentine analysed in this work could not be unequivocally attributed to the resin of *Abies alba* Mill. (obtained as a drop from the bark), because the composition of labdanes was different from that of the resin from the Silver fir. This may indicate that Strasbourg turpentine is not made in any case from *Abies alba* Mill. or there is an unknown phytochemical variation in the compositions of the resin from blisters and from naturally exuded drops from the bark.

- In the study indications are found that larch resins show a slower aging process compared to resins from other genera of the Pinaceae. This has to be investigated in more detail, together with the stability of the ratio of pimaric and sandaracopimaric acids.
- The production process of Burgundy pitch is still unknown, from the present chemical data it is also impossible to tell, whether the materials were heated or only melted, because the analysed Burgundy pitch samples are composed nearly identically to colophony. Burgundy pitch or resin is not easy to find, further investigation may be affected by the lack of systematic data as well.
- Are 12-acetoxy- and hydroxy-sandaracopimaric acids exclusive for the genus *Tetraclinis*? Is a differentiation between *Tetraclinis* and *Cupressus* resins possible?
- The origin of the differing composition of commercial sandarac samples may be botanical, which mainly points to other species from *Cupressus*, or environmental, which includes influences through climate, harvesting, exudation or treatment after the harvest. Additionally, common compounds of *Araucaria* resins and some commercial sandarac resins need further investigation. Such an investigation will support a clear differentiation for mixed samples (conifer copals and sandarac).

Fabaceae resins

Fabacaeae resins originate from non-European regions of the world, and the knowledge about their botanical origin, harvesting and trading is, therefore, limited. Because systematic chemotaxonomic studies are not easy to realize due to the lack of reliable botanical samples, the investigation of commercial materials together with known chemotaxanomical data provides a basis for the investigation of unknown materials.

What is known? In which way does this knowledge serve the investigation of the materials from the Vigani Cabinet?

- The different types of Copaiba balsam reported in the literature are recovered for the reference samples analysed here. There are only minor differences, which may be caused by environmental influences on the resin production or differing botanical sources not reported in the literature until now. The phytochemical profile shown in table 2.3 completed by own chemical data serves as a good basis to identify unknown materials and their potential botanical origin.
- All in all, the chemical composition of different types is remarkably consistent, which very likely originates from export restrictions, for example because the resins of some species are used only on the internal market. Lacking knowledge about this trade complicates the evaluation of the chemical analyses of *Copaifera* resins.

- Additionally, a third type, of which only the sesquiterpene fraction was reported until now, is characterized. It originates from *Copaifera reticulata Ducke* or *Daniellia oliveri* Hutch. & Dalziel.
- Modern Copaiba balsam are frequently adulterated mostly with colophony and pine resin, which partly complicates the investigation of trace constituents.
- The investigation of a selection of legume copals yields new insights into the composition of the different groups and the connection of chemical composition and terminology. It is possible to distinguish legume copals from other Fabaceae based on these data, and partly also from each other. Because African legume copals, apart from Zansibar copal, originate mainly from the African East coast and connected regions, the presented chemical composition would allow a geographical assignment.
- Balsam of Peru and Tolu examined in this study show some remarkable differences compared to the (consistent) chemical composition of both reported in the literature, in particular the absence of cinnamylbenzoate in Balsam of Tolu is surprising. Also several compounds found in the references are not reported in the literature. Based on the present data, it will, however, be possible to identify *Myroxylon* resins. Additionally, several esterified phenylpropanoid esters have been identified by their mass spectra, which allows further insights into the chemistry of these resins.

What has yet to be investigated?

- The assumed influence of the trade of Copaiba balsams has to be investigated further by the analysis of samples, which are not exported to Europe. This would also include more botanical samples, to fill in the gap of the phytochemical profile in table 2.3.
- It is not known where the adulteration of Copaiba balsam with pine resins is maintained. Additionally, adulteration with turpentine oil is mentioned in the literature, but not found in this work.
- Because the resin of *Daniellia oliveri* Hutch. & Dalziel is also mentioned to be a copal, and because of several chemotaxonomical connections between *Copaifera* resins and legume copals, an investigation of botanical samples would be necessary.
- Only very little is known about the botanical origins, harvesting and trade of African legume copals, the chemical composition is reported only for a few selected compounds. *Hymeneae* resins are better investigated, mainly because of their common use in America. Even though the Congo copals analysed here are composed very similarly, literature suggests that they are of high chemical variety. It is not possible to distinguish them from *Hymenaea* resins as reported in the literature. Sierra Leone copal is better distinguishable from other African copals, the reason for that is unknown. The most likely reason would be the use of few selected species for its harvesting.

Sapindales

Resins from Sapindales fall into two groups, resins from *Pistacia* and from Burseracea. The former yield mastic and Pistacia turpentine, which were analysed in this work in order to distinguish the species. For the various resins from the Burseraceae, the connection of nomenclature and botanical origin is investigated regarding the geographical origin.

What is known? In which way does this knowledge serve the investigation of the materials from the Vigani Cabinet?

- The investigation of mastic reference samples and one botanical sample from *Pistacia terebinthus* L. illustrated the great similarity of the resins. Differences are found relating the presence and amounts of oleananes and dammaranes. It was not possible to clarify whether they are of botanical or environmental origin, also because the aging processes of Pistacia resins are not fully understood and the resins are - especially in the neutral part – composed of a complex mixture of partly unidentified compounds.
- From the analysis of the different Burseraceae resins a differentiation scheme is accomplished. Main differentiation criterias are the presence of amyrins, lupanes, oxygenated derivatives thereof and tirucallane acids. *Canarium* and *Protium* are distinguishable from other Burseraceae, in case the origin is known also that of *Bursera*. African *Commiphora* and *Boswellia* resins show a differing composition from both groups.

What has yet to be investigated?

- *P. atlantica* Desf. and varieties thereof are mentioned in the literature as a source of Pistacia turpentine and could not be investiged in this work. Additionally, the analysis of the volatile as well as the polymeric fraction of *Pistacia* resins may yield further insights into the chemistry of the differing species.
- Several Burseraceae resins are not investigated in literature and no reference samples could be analysed in this work. This concerns mainly African elemis from *Cana*rium species and American copals from *Protium copal* Engl. In general, Asian and American Protium resins and African Boswellia and Commiphora copals are investigatred only fragmentary.
- In mixtures or other application characteristics it may be impossible to distinguish a *Canarium* elemi from a *Protium* copal based on the present data presented in this study and in literature. For the assignment of the different African elemis and copals to certain species or even genera, a more detailed investigation of African *Boswellia*, of which mainly incense yielding species are investigated, *Commiphora* and *Canarium* would be necessary.
- The composition of tacamahaca resin is still open, the present reference sample does not originate from *Protium heptaphyllum*, the composition of which has been published.
- The Rutaceae genus *Amyris* is a possible source for Mexican elemi, too. Because the composition of *Amyris elemifera* is very similar to *Bursera* resins, further investigations would be necessary.

Fossil resins

The soluble fraction of amber was investigated in order to improve the sample preparation. The aim was to prepare the analysis of the amber samples from the Vigani Cabinet without pyrolysis.

What is known? In which way does this knowledge serve the investigation of the materials from the Vigani Cabinet?

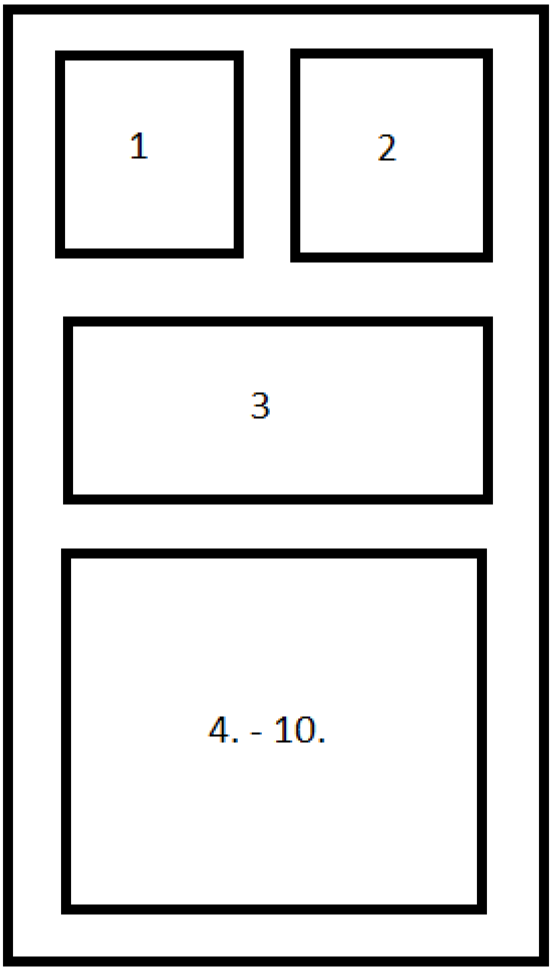
- The soluble fraction of Baltic amber is recovered and a wide range of characteristic compounds described in literature (see chapter 2.4) are identified.

What has yet to be investigated?

- The polymer fraction of Baltic amber is not acquired. For that reason infrared spectroscopy will be necessary.

5. RESULTS – RESINOUS MATERIALS FROM THE VIGANI CABINET

In the following, the results of the analysis of the materials from the Vigani Cabinet are presented as data sheets, one for each material analysed, based on the presentation in Wagner (Wagner 2007, Vol. 2, 3). These data sheets include contemporary information about terminology, origin, trade, manufacture, and properties. Based on this information, a possible chemical composition, together with marker compounds, is discussed, followed by the chemical analysis of the material from the Vigani Cabinet and a discussion of the results. Particularly with regard to the historical literature, the data sheets aim to provide an overview of all sorts and varieties of the material in question mentioned in the historical sources listed in section three, not only those, which turned out to be purchased for the Vigani Cabinet. In the case, differing historical sorts could be attributed to different materials from the Vigani Cabinet, the information are presented separately. This was the case, for example, for "Tacamahaca in tears" and "Tacamahaca sublimis", "Succinum Citrinum" and "Succinum nigrum". In all other cases the information are concentrated on one data sheet.



The data sheets contain the following elements:

1. A **picture** of the material and its sampling is shown.

2. A short **description** of the material, of its sampling and references from the works attributed to Vigani (Wagner 2007: Vol. 1, 15-22) are provided.

3. A **list of historical sources** that mention or describe the material under the name used in the Vigani Cabinet. This includes those from the fine arts, sciences and encyclopaedic works. Some references from the fine arts are taken from the compendium by Leslie Carlyle (Carlyle 2001). The selected sources concentrate on the fields associated with Vigani's work and a time period from about 1680 to 1780. The list should illuminate the contemporary scientific background of the material and does not intend to describe the published literature completely. All referenced manuscripts are listed and annotated in the appendix.

The sections 4 to 7 focuss on information from the historical sources.

4. **Terminology**: The section presents etymology and the historical use of the term. When modern literature makes a substantial contribution to etymology, the appropriate information is included.

5. **Botanical and geographical origin**: The section focusses on the botanical and geographical origin and discusses taxonomical problems. In many cases the geographical origin is con-

nected with different sorts of the same material. The main historical sources are those given in the literature list above. In some cases, it was necessary to consult sources published earlier or later.

6. **Manufacture and trade**: The harvesting and manufacture are described, in some case different sorts of the same material were produced or harvested in a different way. 95 per cent of the goods imported to England at the time of Vigani were traded through London (Wagner 2007a: 43-44), and pharmacological and chemical sources do not focus on trading details. Therefore, trading details are only given occasionally.

7. **Properties**: Detecting adulterations was mainly sense-perceptive in Vigani's time. Therefore, a variety of precise information of taste, smell, colour, density, viscosity, solubility and other properties is found in the historical sources.

In section 8 historical and modern (chemo)taxonomical information melt together, followed by the chemical analysis (section 9) and a discussion of the results (10).

8. **Possible chemical composition**: The section tries to translate the historical information into one or more chemical compositions. Based on the historical information and the modern literature (chapter 2) and own investigations (chapter 4), an overview on possible chemical compositions is given. How would a resin from the 18th century labelled in the way as it is found in the Vigani Cabinet be composed and which differentiation criteria and marker compounds are known for an unambigious identification?

9. **Chemical analysis** presents the results from the GC-MS analysis and, in the case of amber, infrared spectroscopy.

10. **Discussion**: In this section the results from the chemical analysis are discussed in relation to the phytochemical data from both literature (chapter 2) and reference analysis (chapter 4). A possible botanical origin is discussed as well as the connection between modern and historical terminology. The information from the historical sources is included into this discussion. Terminological, botanical or chemical comparisons with other materials from the Cabinet are made in this section.

5.1 Gymnosperm resins – conifer resins and products

Conifer resins originate from the families of Pinaceae, Cupressaceae and Araucariaceae. Their chemical composition is summarized in chapter 2.1. A wide range of reference samples was analysed (chapter 4.1), with the results discussed in chapter 4.1.4. Based on these data profiles, this chapter presents all materials from the Vigani Cabinet containing mainly abietane, pimarane or labdane acids.

The binominal botanical taxonomy did not exist at Vigani's time, nor did it the modern coniferous genera. The term "*Abies*" or "fir" were used for different trees, which are part of the modern genera *Picea* and *Abies*. The trees were distinguished among other things by the direction of their cones (Ray 1690: 212-3; Dale 1693: 395-6; Lemery 1721: 888; Miller 1759: Abies; Miller 1768: Abies). The German translation of pines, Kiefer, is a contracted compound of Old High German "kienforha" (Kienföhre) and is found first in the 17th century (Kluge 1883: 161; Fritz-Scheuplein 1997: 96). Consequently, the term "kiefer" is mentioned only occasionally in the consulted historical sources, "*Pinus*" trees are called "Fichte", some species also "Zirbel-Baum" (Dale 1693: 396; Lemery 1721: 879-81; Dale 1739: 303-4; Krünitz 1843: 102). The different terms are summarized in table 5.1.

Modern	Latin	English	French	German
Abies (fir)	Abies, Pinus Abies	Fir(r)	Sapin	Tanne
Picea (spruce)	Abies (major), Picea	Fir(r)	Sapin	Tanne
Pinus (pine)	Pinus	Pine, spruce, fir	Pin	Fichte
Larix (larch)	Larix	Larch	Melesse	Lärche

Tab. 5.1 Historical names of conifer trees, references see text

5.1.1 1/8 Terebin. Strasb.

Fig. 5.1 1/8 "Terebin. Strasb."

Fig. 5.2 Sampling of 1/8

Description

The glass bottle is filled with a dried-up transparent material of a brownish to reddish colour. The surface is hard and brittle with cracks and somewhat powdered.

Sampling

A sample of dried residuals of the inner wall (about 7 mg) was taken on 26 April 2007 (Fig. 4.2). The sample consisted of small friable yellow and transparent platelets with a resinous smell.

Vigani references

* MS Quns Vig. 4, folio 1, verso: as "Tereb Strass", 2 ounces at 4 pence, bottle at 1 penny

* Does not appear in LECTURE NOTES UNDATED

* Does not appear in LECTURE NOTES 1707

Contemporary literature

Fine art materials

* SALMON 1701: 859: "Strasburg Turpentine"

* SMITH 1738: 85: "Strasburg Turpentine"

* JACOBI 1800: 203: "Strasburger Terpentin"

Science

* DALE 1693: 395: "Terebinthina Argentoratense", "Strasburg Turpentine" ("*Abies Mas conis sursum spectantibus* C. B., The Silver Firr")

* JAMES 1747: 200, 453: "Terebinthina argentatorensis" or "Strasburg Turpentine" ("*Abies conis sursum spectantibus* C. B., Silver Firr")

* GEOFFROY, THICKNESSE 1749: 234-5: "Terebinthina abiegna", "Terebinthina Abietina", "Terebinthina Argentoratensis", "Strassburg Turpentine" ("*Abies conis sursum spectantibus* C. B., Silver Fir")

* HILL 1751: 709-10: "Terebinthina Argentoratensis" ("*Abies Taxi folio fructu sursum spectante* R. H")

* LEWIS 1761: 551: "Terebinthina argentoratensis", "Strasburg turpentine" ("silver & red fir")

Encyclopaedias

* CHAMBERS 1728b: 265: "Turpentine of Strasbourg"

* SAVARY DES BRÛSLONS, SAVARY 1748c: 271(2): "Terebenthine de Strasbourg"

Terminology

The origin of the term "turpentine" is described in chapter 5.1.3.

In English literature "strasburg turpentine" is mentioned from the 90ies of the 17th century on, mainly as the liquid resin of "Silver Fir(r)" also without a connection to Strasburg (Dale 1693: 395; James 1747: 200). Additionally, terms like "terebinthina argentoratense" or "terebinthina argentatorensis" can be found (Dale 1693: 395; James 1747: 453; Hill 1751: 709; Lewis 1761: 551). Chambers lists "turpentine of Strasbourg, Dautzic, etc." without any further information about the geographical and botanical origin (Chambers 1728b: 265).

In continental literature, the term "strasburg turpentine" is nearly absent until the end of the 18th century, it is only mentioned by Geoffroy (Geoffroy, Thicknesse 1743: 235). Then it appears in connection with French turpentines, which were widely distributed at this time. Their botanical source is the "red fir" (Hahnemann 1799: 432; Jacobi: 1800 203; Krünitz 1843: 104).

Botanical and geographical origin

Most authors mention "*Abies conis sursum spectantibus* C.B. " or "Abies *Taxi folio fructu sursum spectante*" ("Silver Firr") as the botanical source of "strasburg turpentine" (Dale 1693: 395; James 1747: 453; Hill 1751: 70; Geoffroy, Thicknesse 1743: 235), others the "Silver and Red Fir" (Lewis 1761: 551; Hahnemann 1799: 432; Krünitz 1843: 104). While the first volume of Krünitz' *Oekonomische Encyklopaedie* from 1773 (lemma Abies) mentions that only the "silver fir" ("*Abies taxifolio, fructu sursum spectante*") yields turpentine, in volume 182 from 1843 (lemma Terpentin) the "red fir" is listed as a source ("*Pinus abies* L.") (Krünitz 1773: 77; Krünitz 1843: 104). The botanical term "fir" in contemporary sources is used for two different species (see also table 5.1), which are distinguished by their cones as follows.

1. The "Silver Fir": "*Abies conis sursum spectantibus* C.B.", also called "A*bies taxifolio fructu sursum spectante* R.H.", "*Abies Alba*" or "*Abies F(o)emina* J. B." (Bauhin 1623: 505[6]; Ray 1690: 212; Dale 1693: 395; Lemery 1721: 2; Geoffroy, Thicknesse 1749: 235). These trees were classified as "*Pinus Picea*" by Linné (Linné 1753b: 1001), which is a synonym of modern *Abies alba* Mill. described by Philip Miller in 1768 (Miller 1768: Abies). The "silver fir" or "*Abies conis sursum spectantibus*" grows in hot regions (Dale 1693: 395).

2. The "Common or Red Fir", later also "Pitch tree": "*Abies conis/fructu deorsum inflexo* P.T.", also "*Picea*", "*Abies picea*", "*Picea Major prima*" or "*Abies rubra*" (Bauhin 1623: 493; Ray 1690: 213; Dale 1693: 395; Lemery 1721: 1-3). "*Picea (major prima)*" and "*Abies rubra*" were classified by Linné as "*Pinus Abies*" (Linné 1753b: 1002), "*Abies fructu deorsum inflexo*" is mentioned by Miller as a synonym for the "*Pinus Abies*" of Linné (Miller 1759: Abies). This was changed at the end of the 19th century to *Picea abies* H. Karst. (spruces). Dale mentions that the resin from the "*Picea*" convenes with "strasburg turpentine". The tree grows rarely in the Scottish mountains (Dale 1693: 395).

Especially the first species is mentioned in continental Europe in connection with several resinous materials called "Resina (ex) abiete" or "Resina abiegna" or "Abies resina balsamica" (Manget 1687: 64, 348; Zwinger 1724: 398-9; Mappus, Ehrmann 1742: 1-2). None of these materials are called "strasburg turpentine" by them, but they are mentioned in connection with "strasburg turpentine" by other authors from the middle of the 18th century on (Geoffroy, Thicknesse 1743: 235; Hill 1751: 709-10; Lewis 1761: 551).

Manufacture and trade

The "turpentine" from the "Silver Fir" was brought to England from different parts of Germany (Hill 1751: 709; Lewis 1761: 551), and preferred to that of Venice (Chambers 1728b: 265; James 1747: 453). In later sources also the Alsace, Tyrol and Switzerland are mentioned

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[6] Bauhin lists "*Abies foemina*" and "*Abies alba sive foemina*" as a separated species (Bauhin 1623: 505).

(Mappus, Ehrmann 1742: 1-2; Hill 1751: 709; Jacobi 1800: 203). It originated from the region around Strasbourg and was traded almost entirely over Amsterdam (Geoffroy, Thicknesse 1743: 235; Savary des Brûslons, Savary 1748c: 371(2); Hill 1751: 709). Krünitz mentions a "german turpentine", which resembles "strasburg turpentine", and is brought from the Black Forest (Krünitz 1843: 106), which is probably identical with the one brought to Amsterdam. Towards the end of the 18th century it became rare in England (Lewis 1791: 295).). It seems that it was always a rare product, which was produced only in specific regions, mostly for export (Krünitz 1773: 80). By the middle of the 18th century trading routes apparently changed and it was avaiblable also in continental Europe.

In continental Europe, where the term "strasburg turpentine" was unknown until the middle of the 18th century, Manget mentions the resin of "*Abies*" (without specification) as a substitute for the original "true turpentine", also called "venice turpentine" (Manget 1687: 348, 526). Mappus and Ehrmann describe the the resin of "*Abies conis sursum spectantibus C. B.*", obtained in the Alsace was brought to Venice and reimported and called "terebinthina veneta" thereafter (Mappus, Ehrmann 1742: 1-2).

Krünitz describes the harvesting of the turpentine from the "silver fir" in North Italy and Switzerland (Alps): In spring and August farmers from North Italy traveled to Switzerland. They climbed up the trees and cut the tubercles with cornets, which gathered up the outflowing resin. The collected resin was filtered through saplings in a funnel of bark. The younger trees yielded resin of best quality (Krünitz 1773: 80). The tears of resin on the bark were also collected (Hill 1751: 709-10; Lewis 1761: 551; Krünitz 1773: 80). The flowing juice obtained from the tubercles was called "resina abiegna", "lacryma abiegna" or "oleum abietinum". It is mentioned to be the best quality (Geoffroy, Thicknesse 1743: 235; Hill 1751: 709-10; Lewis 1761: 551).

Another method was to cut out the bark from the ground up to four to five meters height around the tree in May. The resinous balsam then flew down into prepared vessels (Hill 1751: 710).

Properties

The liquid resin of "*Abies*" is described as transparent, very clear and pellucid. Its consistency is similar to that of "venice turpentine" (see chapter 5.1.3), less tenacious but thinner than "chios turpentine" (see chapter 5.1.5) (Dale 1693: 395; Hill 1751: 709; Lewis 1761: 551). It has a yellow and brown colour. When it is fresh it is white and very liquid and becomes yellowish and thicker with age. It is distinguished from "venice turpentine" by its green shade (Chambers 1728b: 240; Hill 1751: 709; Lewis 1761: 551). It has a more bitterish and less acrid taste than the other turpentines and an agreeable very fragrant lemony smell (Dale 1693: 395; Hill 1751: 709; Lewis 1761: 551; James 1747: 453). James describes a boiled sort of this turpentine: it is boiled in water until it becomes hard and brittle. In this way it becomes less detergent and more agglutinating. It is also distilled with water to produce an essential oil (James 1747: 453).

Possible chemical composition

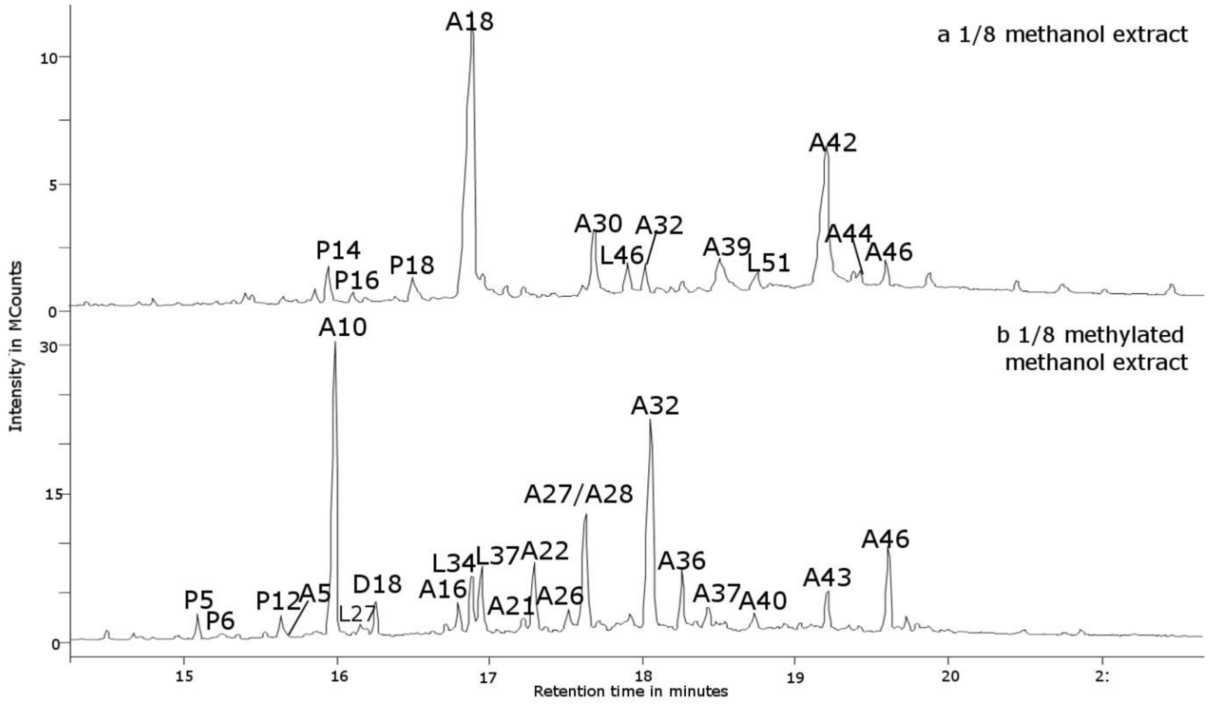
"Strasburg turpentine" was obtained from two different species of the contemporary genus "*Abies*", which are very likely the modern *Abies alba* Mill. and *Picea abies* Karst. Resins from *Abies* and *Picea* species are investigated very well. They consist of high amounts of pimarane and abietane acids as well as their aging markers and are distinguishable by their pimarane acids and several marker compounds (Mills, White 1977; Sturm 1982: 24, 25; Koller et al.

1997a; Mills, White 1999: 100-2; van den Berg et al. 2000; Scalarone et al. 2002; Breitmaier 2005: 53; see also chapter 2.1.1, table 2.2).

Several samples of *Abies alba* Mill. and *Picea* species were analysed for this investigation, with the results presented in chapters 4.1.1.1 and 4.1.1.2. Marker molecules for all genera are listed in table 4.2. That are, for *Abies alba* Mill. high amounts of *cis*-abienol and lower of abienol, *iso*- and *trans*-abienols. Other compounds present are epimanoyloxide, D8, D10 and L10. Additionally, no pimaric acid is present. In contrary, *Picea* resins contain both pimaric and sandaracopimaric acid, but always higher amounts of the latter one. In *Picea abies* Karst. and *P. pungens* Engelm. cembrene, *iso*-cembrol, Δ13-trans- and *cis*- and *trans*-abienols are present, in *P. omorica* Purk. epimanool, *iso*-abienol, abienol, *cis*- and *trans*-abienol. Even though characteristic alcoholic labdanes and other neutral diterpenes are partly present as well, the analysis of commercial reference materials (Strasbourg turpentine) showed inconsistencies, which could not be clarified within this work. Additionally, resin from *Pinus* species are reported also to contain abienols (Lange et al. 1994; Arrabal et al. 2002), even though no own data were obtained. *Pinus* species contain more pimaric than sandaracopimaric acid. Only the resin of *Pinus cembra* L. does contain specific marker molecules, namely high amounts of lambertianic acid. These findings are consistent with literature data about a section of *Pinus* resins, which do not contain pimaric acid but high amounts of labdane acids (Mills, White 1999: 101; Raldugin et al. 1976b).

Chemical analysis

In the methanol extract (Fig. 4.3a) pimaric, sandaracopimaric, isopimaric, levopimaric and dehydroabietic acids are present. No palustric, abietic and neoabietic acids are found. Aging markers are 7-methoxy-, 15-hydroxy- and 7-oxo-dehydroabietc acid as well as 7-oxo- and 7-oxo-15-hydroxy-dehydroabietate and small amounts of 7-oxo-Δ15(16)-dehydro-dehydroabietate (A40). Additionally, the two labdanes imbricatoloic acid (L46) and L51 are present, the methylester of which are found in the methylated extract.



a – methanol extract, b – methylated methanol extract (labels, see table 5.2)

Fig. 5.3 Gas chromatograms of 1/8 "Terebin. Strasb." from the Vigani Cabinet, diterpene section (TIC)

In the methylated methanol extract (Fig. 4.3b) pimarate, sandaracopimarate, isopimarate, levopimarate and dehydroabietate are present. The material contains more pimarate than sandaracopimate. The (di)methylester of L46 and L51 are according to their retention time and mass spectra present as L34, identified as imbricatoloate, and dihydroagathate (L37). L51 is dihydroagathic acid, then. Another unidentified labdane acid (L27) is present in small amounts. Main aging markers are dehydroabietate (A10) and derivatives of 7-oxo-dehydro-

Label	t_R	Name	Main mass fragments
P5	15.09	Pimarate	**121**, 241, 257, 301, 316
P6	15.24	Sandaracopimarate	**121**, 241, 301, 316
P12	15.62	Isopimarate	187, 227, **241**, 256, 287, 316
A5	15.66	Levopimarate	91, **92, 121**, 146, 187, 316
A10	15.98	Dehydroabietate	**239**, 299, 314
P14	15.94	Pimaric acid	91, 107, **121**, 133, 241, 287, 302
P16	16.10	Sandaracopimaric acid	91, 107, **121**, 133, 241, 287, 302
L27	16.16	Unidentified labdane acid, ME	79, 93, **121**, 161, 221, 290, 318, 350
D18	16.26	12-methoxy-podocarpa-8,9,12-trien-15-oate	159, 173, **227**, 239, 287, 302
P18	16.50	Isopimaric acid	91, 105, 131, 159, 187, 227, **241, 287**, 302
A14	16.88	Levopimaric acid	**92**, 105, 131, 146, 187, 302
A16	16.79	7-methoxy-dehydroabietate	195, **237**, 253, 312, 344
A18	16.72	Dehydroabietic acid	197, **239**, 285, 300
L34	16.89	Imbricatoloate	**121**, 161, 225, 276, 336
L37	16.95	Dihydroagathate, diME	79, 93, **121**, 161, 257, 304, 364
A21	17.22	Unidentified oxygenated abietane acid	227, **269**, 329, 344
A22	17.29	7-hydroxy-dehydroabietate	121, 195, **237**, 253, 297, 312, 330
A23	17.36	15-methoxy-dehydroabietate isomer	237, 269, 312, **329**, 344
A26	17.52	Unidentified	162, 195, **237**, 255, 283, 297, 330
A27	17.65	Δ16-demethyl-7-oxo-dehydroabietate (proposed)	155, 197, 211, **253**, 254, 299, 313, 314, 328
A28	17.66	15-hydroxy-dehydroabietate	255, 273, **315**, 330
A30	17.68	7-methoxy-dehydroabietic acid (proposed)	181, 195, **237**, 283, 297, 315, 330
L46	17.90	Imbricatoloic acid	81, **121**, 161, 221, 276, 322
A32	18.05	7-oxo-dehydroabietate	187, 211, **253**, 269, 296, 328
A35	18.37	7-hydroxy-dehydroabietic acid	145, 185, 195, **237**, 273, 299, 316
A36	18.26	Unidentified hydroxy-dehydroabietate, probably a dihydroxy-compound	181, 195, 211, **249**, 264, 309, 324
A37	18.42	15-methoxy-Δ6(7)-dehydro-dehydroabietate (proposed)	213, 237, 251, **267**, 311, 327, 342, 360
A39	18.50	15-hydroxy-dehydroabietic acid	131, 197, 237, 255, 283, **301**, 316
A40	18.47	7-oxo-Δ15(16)-dehydro-dehydroabietate	211, **251**, 266, 294, 326
L51	18.75	Dihydroagathic acid (proposed)	79, 93, 107, **121**, 161, 175, 290, 300, 318, 336
A42	19.19	7-oxo-dehydroabietic acid	211, **253**, 299, 314
A43	19.19	Unidentified methoxy-dehydroabietate	59, 156, 212, 251, 255, 269, 312, **315**, 329
A46	19.59	7-oxo-15-hydroxy-dehydroabietate	188, 269, **329**, (344)

Tab. 5.2 Compounds found in 1/8 “Terebin. Strasb”, sample analysed with temperature program Diterpenes 1 and column A, mass spectra references see appendix

abietic acid (A27, A32). Imbricatoloate, dihydroagathate, derivatives of 7-hydroxy- (A16, A22) and 7-oxo-15-hydroxy-dehydroabietate (A46) are present in medium amounts. Other constituents are 12-methoxy-podocarpa-8,9,12-trien-15-oate (D18), A21, 15-hydroxy-dehydroabietates (A23, A28), 15-methoxy-Δ6(7)-dehydrodehydroabietate (A37), 7-oxo-Δ15(16)-dehydro-dehydroabietate (A40) and several unidentified oxygenated aging marker (A26, A36, A43). A36 is probably a dihydroxy-dehydroabietate, A43 a methoxy-dehydroabietate, please refer to chapter 4.1.1.2. A19 is elutes at 16.93 min, but only in small amounts. It is visible only in EIC, and coelutes with L38.

Discussion

The composition is typical for resins from *Pinus* species, which contain higher relative amounts of pimaric than sandaracopimaric acid and no neutral labdane compounds as found in resins from *Abies* and *Picea*. The presence of dihydroagathic acid points to *Pinus* species from the section Pinea. Several Asian pines from the section Pinea are found to contain this compound (Coppen et al. 1993; Bambang et al. 2006; Wang 2007). For European species of this section, only small amounts of C-8 oxygenated labdanes are reported (Papajannopoulos et al. 2001; Arrabal et al. 2002). 1/8 "Terebin. Strasb." also contain two other labdane acids, imbricatoloic acid (L34) and compound L27. All three compounds are also present in 1/10 "Venice turpentine" and 1/13 "Tereb. E Chio". They were therefore obtained from a *Pinus* species, possibly from the section Pinea.

Also the remaining chemical composition of 1/8 "Terebin. Strasb." is nearly identical to that of 1/13 "Tereb. E Chio" and very similar to that of 1/10 "Venice turpentine" (chapter 5.1.3, 5.1.5). Differences between the three samples are mostly the result of differing aging processes. 1/8 "Terebin. Strasb." is in an advanced aging state, only pimarane acids are still present in significant amounts. The only not oxygenated abietane acid, levopimaric acid, is present in small amounts. Levopimaric acid (A5, A14) is an intermediate of the isomerisation process, for the formation of levopimaric acid please refer to chapter 4.1.1.1. Levopimaric acid is also present in several other conifer "turpentines" from the Vigani Cabinet, (1/9, 1/10, 1/11, 1/13). Other aging markers in 1/8 "Terebin. Strasb." are 7-hydroxy-, 7-methoxy- and 7-oxo-dehydroabietic acids and derivatives thereof. C-15 oxygenated dehydroabietic acids, 15-methoxy- and 15-hydroxy derivatives, are present only in small amounts. 15-hydroxy-dehydroabietic acid is an intermediate. According to literature it is further oxygenated to 7,15-dihydroxy-dehydroabietic acid, which is transferred to 7-oxo-15-hydroxy-dehydroabietic acid (van den Berg et al. 2000; see also Fig. 2.4). The compound A36 is very likely a dihydro-dehydroabietate for the identification please refere to chapter 4.1.1.2. It is present in 1/8 "Terebin. Strasb.", which was sampled from the dried-up material in the bottle, and in all other conifer "turpentines" sampled in the same way (1/8, 1/9, 1/13). In other samples, which were sampled from the still sticky bulk material, 15-hydroxy-dehydroabietic is more prominent, while A36 is present only in traces (1/10, 1/11a, A/23a, A/23b). For a detailed discussion please refer to chapter 5.1.4 and 5.1.6.

1/8 "Terebin. Strasb." shows a composition, which is different from that, which could be expected by its name. It is an adulteration. The origin of this adulteration is not apparent from the historical literature, but the similarities to 1/13 "Tereb. E Chio" and 1/10 "Venice turpentine" points to a common botanical and probably also geographical origin. Both, "Venice and chios turpentine" are mentioned to be adulterated with resins from were "larch", "pine" and "fir" in the "Wood of Pilatre" (Lemery 1714: 841; Lemery 1721: 1116-7). Another material from that region is called "bijon", which is old French for "poix liquide" or resin of "sapin"

(Godefroy 1881: 649). "Bijon" is also estimated to be superior than the other resins harvested in that woody region in South France (Pomet 1717: 421; Lemery 1721: 1116-7). Another resinous balsam from the area is described as a yellow, transparent juice like water obtained by cutting the tree, which becomes thicker and more yellow with aging (Pomet 1717: 423). This resembles the resinous balsam of *Abies alba* Mill., which is native to the region (Euforgen 2008). The resin, 1/8 "Terebin. Strasb." was made from, probably originated from that region, pretended to be a "fir" resin, which was called "strasbourg turpentine" in England.

5.1.2 1/9 Tereb Com

Fig. 5.4 1/9 "Tereb Com"

Fig. 5.5 Sampling of 1/9

Fig. 5.6 Sampling of 1/9 details, left - from above, right – leather cap and knot before opening

Description

The glass bottle contains a brown transparent material with a hard and brittle surface with cracks (Fig. 5.6). In the lower part a white and cloudy layer has been formed. Dried-up residues of the former fluid content remained at the inner side of the glass bottle. The leather cap was still close-fitting and the knot attached (Fig. 5.6).

Sampling

The knot and the leather cap were removed on 30 March 2009. A sample of dried residues of the inner wall was taken (Fig. 5.5). The sample consisted of small friable dark brown and transparent platelets with a sweetish smell.

Vigani references

* MS Quns V:ig. 4, folio 1, verso, as "Com Tereb", 2 ounces at 4 pence, bottle 1 penny

* Does not appear in LECTURE NOTES UNDATED

* Does not appear in lecture notes from 1707

Contemporary literature

Fine art materials

* SALMON 1701: 859: "Common Turpentine”

* POMET 1717: 427, 433: "gemeiner Terpentin"

* SMITH 1738: 83: "common Turpentine"

Science

* MANGET 1687: 526: "Terebinthina vulgaris" ("Resina Laricis")

* DALE 1693, 397: "Terebinthina communis seu vulgaris" or "Common Turpentine" ("*Pinus sylvestris* C. B.")

* POMET 1717: 423, 425-427: "Thérébinthine de Bordeaux", "Gemeiner Terpentin" (conifers)

* LEMERY 1721: 888: "grosse Terebinthine", "Terebinthine commune", "grober und gemeiner Terpentin" (conifers)

* JAMES 1747: 402, 452: "Common Turpentine" ("Mountain Pine, *Pinus Sylvestris C. B.P.*")

* GEOFFROY, THICKNESSE 1749: 236: "Terebinthina communis", "Resina Pinea", "Common Turpentine" ("pines", in France from "*Pinus sylvestris vulgaris Genevensis* J. B.")

* HILL 1751: 710-11: "Terebinthina Communis", "Common Turpentine" ("*Pinus Sylvestris* & pines in general")

* LEWIS 1761: 552: "Terebinthina Communis", "Common turpentine" ("Wild Pine, *Pinus Sylvestris C.B.*")

* LEWIS 1761: 552: "Terebinthina Communis", "Common turpentine" ("Wild Pine, *Pinus Sylvestris C.B.*")

Encyclopaedias

* SAVARY DES BRÛSLONS, SAVARY 1748b: 1428: "grosse Terebenthine", "Terebenthine commune" ("pine")

Terminology

The origin of the term "turpentine" is described in chapter 5.1.3.

In general, the term "common" was used for turpentines of lesser quality regarding their smell, taste, consistency and colour. In the 17th century, turpentines of lower quality were called "terebinthina germania" (Bauhin 1623: 500), "terebinthina vulgaris", "resina laricis" or just the resin of "fir", "pine" and "larch" (Schröder 1644: 112, 204; Manget 1685: 64; Blanckaert 1690: 616). The notation of larch turpentine as crude or common turpentine reflects the original differentiation in "true turpentine" from the "terebinth" (fine turpentine of best quality) and turpentines obtained from local sources, mainly from Pinaceae species (common turpentines of lesser quality). The "true turpentine" was no conifer resins, but was obtained from *Pistacia* species, please refer to chapter 5.1.3. Resins from "larch" and "fir", formerly considered of poor quality compared to the "true turpentine", were then used as an alternative. Consequentely, the term "terebinthina communis seu vulgaris" came in use only for turpentines from "pine" and "spruce".

Additonally to the pure resins, heated or melted products are mentioned under the same name. The terms "resin", "resinous balsam" and "pitch" (and their foreign-language equivalences) were often used synonymous (Pomet 1717: 425-31; Lemery 1721:887-8).

Botanical and geographical origin

Main sources for "common turpentines" were coniferous trees from the family of Pinaceae, in particular "pine", but also "fir" and "larch" are mentioned (Lemery 1721: 1116; Hill 1751: 710). As discussed in chapter 5.1.1, "firs" can relate to the "silver firr" and the "red or common firr", the latter being very likely a spruce.

The main botanical source of "terebinthina communis seu vulgaris" was "*Pinus Sylvestri*s C. B.", the "mountain pine" or later the "wild pine" (Dale 1693: 397; James 1747: 402; Lewis 1761: 559; James 1764: 240), German "Berg Zirbelbaum" (Dale 1739: 304), but several other "pine" species have seemingly been in use, too (Hill 1751: 710). According to Hill, the "pine tree" "is often so loaded with the Abundance and Turgescence of this Juice, as to be choak'ed by it; this is a Disease almost peculiar to the Pine, which is call'd *Taeda* when under it" (Hill 1751: 710). He added that the "pitch tree" and the "larix or venice turpentine" sometimes suffer from the disease as well (ibid.).

In some western parts of France, great amounts of coniferous resins were obtained from the native woods. Chambers mentions "turpentine of bordeaux", which is "white and thick as Honey. It does not ooze from the Tree in the Manner it is sent to us; but is properly a Composition, wherein, among other Ingredients, is a white hard Sort of Rosin called Galipot" (Chambers 1728b: 265). This is the "thérébinthine de bordeaux, de bayonne" or "terebinthine commune" mentioned by different French authors (Pomet 1717: 423-4; Lemery 1721: 887; Savary des Brûslons, Savary 1748c: 3271(2); ibid. 1748b: 1428). It was obtained from different coniferous trees mainly pines and called "barras". The fine and white sorts were called "galipot blanc", "garibot" or "encens blanc" and were melted over fire and the resulting solid material was barrelled (Pomet 1717: 425; Lemery 1721: 887; Savary des Brûslons, Savary 1748b: 1428). Later these terms mingled, as Hill mentions the upper dried parts of the issued resin from "*Pinus Sylvestris*" as "barras", which was sold as "galipot" or "white franciscence" when clean (Hill 1751: 710).

Manufacture and trade

A difference was made between resins forced to flow by scratching the bark and those who flow spontaneously. Extremely resinous trees like "pines" were thought to burst if not freed of their resinous juices (Lemery 1721: 887[4]; Lewis 1761: 552). Therefore turpentines flowing spontaneously were thought to be of better quality (Pomet 1717: 423). "Turpentines" of lesser quality were mainly used to produce melted or heated products like "pitch or tar" (Dale 1693: 397; Pomet 1717: 425-31; Lemery 1721: 887-8).

"Common turpentine" from "*Pinus sylvestris* C.B." originated from Marseilles, Toulon and "Guienne" (Geoffroy, Thicknesse 1749: 236). Lewis wrote: "the juice that issues from the trees is received in trenches made in the earth, and afterwards freed from its grosser impurities by colature through wicker baskets" (Lewis 1761: 552). A "common turpentine" obtained near Marseille flew from "pines", which were barked before, into a hole in the ground. The resinous balsam was then cleaned with a "Grocer`s Basket" (Bent 1698).

Krünitz describes the winning of resinous products from *Pinus sylvestris* L. in detail: The best harvest was made in warm regions with sandy grounds. The harvested trees were 30 to 40 years old, harvesting was from February until October. Three inch deep fingerbreadth incisions were made around the trunk beginning at the bottom. After 4 years, old marks could be used again. Around the tree, small deepenings in the ground collected the resin. Resin obtained in summer was called "térébinthine brute". In the winter a hard resin called "white pitch" was yielded. After the harvest the semiliquid resin have to be cleaned:

1. In Maransin near Bayonne a cupreous barrel of 350 pounds was bricked in a furnace with a small opening. This barrel was filled with turpentine and heated mildly until the turpentine became fluid. Afterwards it was strained through straw and bottled.

2. In the mountains "Teste de Buch", ten French miles from Bordeaux the turpentine was filled in a wooden container with small holes in its ground. In the sun the turpentine melted and flew through the holes in another container below. The product was of golden yellow colour, more fluid and valued than the other "common turpentines" (Krünitz 1843: 103-4).

"Thérébinthine de bordeaux" or "grosse terebinthine" was obtained in Bordeaux, Bayonne, Nantes and "Rouan" (Pomet 1717: 423-4; Lemery 1721: 887; Savary des Brûslons, Savary 1748c: 3271(2)). It was filled in barrels of 350 to 700 pounds (Savary des Brûslons, Savary 1748b: 1428).

Properties

"Common turpentine" is thick and lesser liquid than all other turpentines except "chios turpentine" (see chapter 5.1.5) (Dale 1693: 397; Hill 1751: 710). It is not transparent and pellu-

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[4] Lemery however also mentions the "turpentine tree" (the "terebinth, a *Pistacia* species) as very resinous, which has to be treated just like the "pitch-tree" (the "Common Firr", a spruce) to prevent it from suffocation (Lemery 1721: 1118).

cid and of a whitish and dirty brown colour (ibid.). James mentioned "common turpentine" as "the coarsest, heaviest, in Taste and Smell the most disagreeable of all sorts: It is about the Consistence of Honey, of an opake brownish white colour" (James 1764: 240). It has a disagreeable smell and an acrid, bitter und nauseous taste (Hill 1751: 710; Lewis 1761: 552). In contrary "fine turpentine" was described as white and clear, with a fine smell and of liquid consistency (Lemery 1721: 1117; Pomet 1717: 423; Lewis 1761: 552).

"Thérébinthine de bordeaux" was white and thick as honey (Chambers 1728b: 265). "Galipot" existed in two sorts, a white and clean one, "white galipot" or "encens blanc", and a dirty and dark one "encens marbré" (Pomet 1717: 425-27; Lemery 1721: 888; Savary des Brûslons, Savary 1748b: 1428). The white sort flew from the trees at good weather and was used for the production of "common turpentine". The best quality was white, clear and dry (Pomet 1717: 427; Lemery 1721: 888). The dark one was sometimes sold as "benzoin" by pedlars (Pomet 1717: 427; Savary des Brûslons, Savary 1748b: 1428).

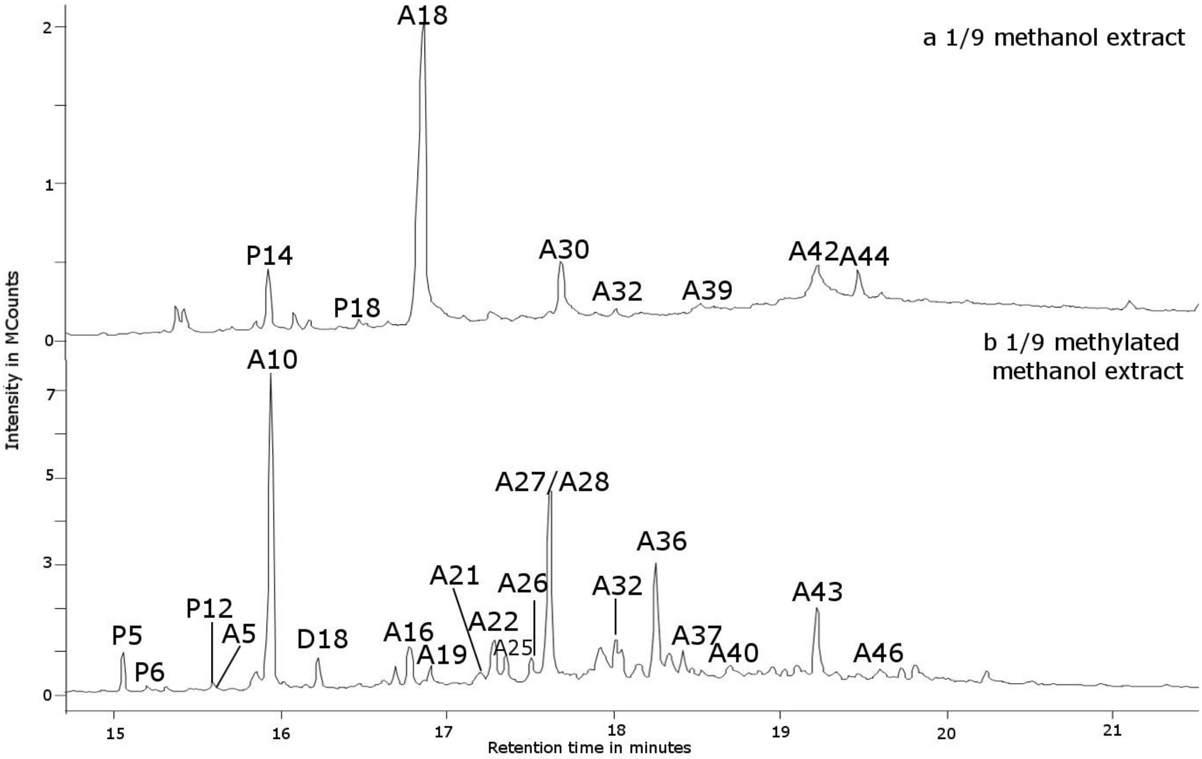
Possible chemical composition

"*Pinus Sylvestri*s C.B." was classified by Linné as *Pinus sylvestris* L. (Linné 1753b: 1000). Linné included "larch" and "fir" into the genus "*Pinus*", which meant *Abies*, *Larix* and *Picea* did not exist as a separate genus (see table 5.1). The modern genera *Larix* and *Abies* are based on the descriptions of Philipp Miller, who preferred the older distinction into different genera based on the form of the leaves in contrast to Linné (Miller 1769: Abies, Larix). Millers "Abies" still included the modern *Picea abies* Karst. (as "*Abies fructu deorsum inflexo*"). Additionally, *Abies* species do not produce high quantities of resin. For these reasons, the "firs" mentioned in connection with "common turpentine" may also refer to spruces.

Resins from Pinaceae, particularly from *Pinus* species, have been investigated very detailed and a broad variety of chemical compositions has been published (see table 2.2). They consist of high amounts of pimarane and abietane acids as well as their aging markers. The different genera of Pinaceae are distinguishable by their pimarane acids and several marker compounds (Mills, White 1999: 100-2; van den Berg et al. 2000; Scalarone et al. 2002; see also chapter 2.1.1).

Several samples of *Pinus* species were analysed for this investigation, with the results presented in chapters 4.1.1.1 and 4.1.1.2. Marker molecules for all genera are listed in table 4.2. A molecular marker for the resin of *Pinus* species is pimaric acid, which is present in all samples in higher amounts than sandaracopimaric acid. No other typical markers are present, except for the resin of *Pinus cembra* L., which contains no pimaric acid but high amounts of lambertianic acid. Additionally, the distribution of the abietane acids indicates a different original composition of the abietane and pimarane acids than for the other *Pinus* resins investigated in this work. These findings are consistent with literature data: in several *Pinus* resins, which do not contain pimaric acid, different labdane acids such as copaiferic, lambertianic, dihydroagathic and communic acid were founds (Mills, White 1999: 101; Raldugin et al. 1976b). Literature and own data suggest a high variability of the resin composition within the genus. For the composition of *Picea* resins please refer to chapter 5.1.1 (‘chemical composition’).

The absence of pimaric acid is a marker for resins from *Abies* and *Larix*, which additionally contain several other markers. *Larix* resins contain high amounts of epimanool, larixol and larixylacetate, *Abies* high amounts of *cis*-abienol and lower of abienol, *iso*- and *trans*-abienols, together with other neutral diterpenes.



a – methanol extract, b – methylated methanol extract (labels, see table 5.3)

Fig. 5.7 Gas chromatograms of 1/9 “Tereb Com” from the Vigani Cabinet, diterpene section (TIC)

Chemical analysis

In the methanol extract (Fig. 5.7a), pimaric, isopimaric and dehydroabietic acids are present. No palustric, abietic and neoabietic acids are found. Aging markers are 7-methoxy-, 15-hydroxy- and 7-oxo-dehydroabietic acid, as well as 7-oxo and 7-oxo-15-hydroxy-dehydroabietate and the unidentified abietane A44.

In the methylated methanol extract (Fig. 5.7b), pimarate, small amounts of sandaracopimarate, isopimarate and levopimarate as well as dehydroabietate are present. Main aging markers are dehydroabietate (A10) and derivatives of 7-oxo-dehydroabietate (A27, A32). Derivatives of 7-hydroxy-dehydroabietate (A16, A22), 7-oxo-15-hydroxy-dehydroabietate (A46) and unidentified aging markers (A36, A43) are present in medium amounts. A36 is probably a dihydroxy-dehydroabietate, A43 a methoxy-dehydroabietate, please refer to chapter 4.1.1.2. Other aging markers are 12-methoxy-podocarpa-8,9,12-trien-15-oate (D18), 7-methoxy- and 15-methoxy-Δ6(7)-dehydrodehydroabietate (A19, A37), 7-oxo-Δ15(16)-dehydrodehydroabie-tate (A40) and several unidentified compounds (A25, A26).

Discussion

The composition is typical for resins from *Pinus* species, which contain higher relative amounts of pimaric than sandaracopimaric acid. No further marker compounds are present. 1/9 "Tereb Com" is therefore obtained from a *Pinus* species.

The material is in an advanced aging state, only pimarane acids are still present in significant amounts. All abietane acids are isomerised and dehydrogenated to dehydroabietic acid, only small amounts of levopimaric acid are present (for levopimaric acid cf. chapter 5.1.1, 4.1.1.1). 1/9 "Tereb Com" contains high amounts of Pinaceae aging markers, particularly several derivatives of 7-oxo-dehydroabietic acid. 7-hydroxy- and 7-oxo-15-hydroxy-dehydroabietic acids are present in smaller amounts together with other aging markers (A36, A37, A43). 15-hydroxy-dehydroabietate and its methoxy derivative are present only in small amounts. For a detailed discussion please refer to chapter 5.1.1 'Discussion'.

Label	t_R	Name	Main mass fragments
P5	15.05	Pimarate	**121**, 241, 257, 301, 316
P6	15.19	Sandaracopimarate	**121**, 241, 301, 316
P12	15.59	Isopimarate	187, 227, **241**, 256, 287, 316
A5	15.63	Levopimarate	91, **92, 121**, 146, 187, 316
A10	15.94	Dehydroabietate	**239**, 299, 314
P14	15.84	Pimaric acid	91, 107, **121**, 133, 241, 287, 302
D18	16.23	12-methoxy-podocarpa-8,9,12-trien-15-oate	159, 173, **227**, 239, 287, 302
P18	16.33	Isopimaric acid	91, 105, 131, 159, 187, 227, **241, 287**, 302
A16	16.78	7-methoxy-dehydroabietate	195, **237**, 253, 312, 344
A18	16.72	Dehydroabietic acid	197, **239**, 285, 300
A19	16.90	7-methoxy-tetradehydroabietate	209, 227, **267**, 283, 327, 342
A21	17.21	Unidentified oxygenated abietane acid	227, **269**, 329, 344
A22	17.28	7-hydroxy-dehydroabietate	121, 195, **237**, 253, 297, 312, 330
A25	17.35	Unidentified oxygenated abietane	169, 211, 225, 237, **267**, 295, 327, (342)
A26	17.50	Unidentified	162, 195, **237**, 255, 283, 297, 330
A27	17.62	∆16-demethyl-7-oxo-dehydroabietate (proposed)	155, 197, 211, **253**, 299, 313, 328
A28	17.60	15-hydroxy-dehydroabietate	255, 273, **315**, 330
A30	17.69	7-methoxy-dehydroabietic acid (proposed)	181, 195, **237**, 283, 298, 330
A32	18.02	7-oxo-dehydroabietate	187, 211, **253**, 269, 296, 328
A36	18.25	Unidentified hydroxy-dehydroabietate, probably a dihydroxy-compound	181, 195, 211, **249**, 264, 309, 324
A37	18.42	15-methoxy-∆6(7)-dehydrodehydroabietate (proposed)	213, 237, 251, **267**, 311, 327, 342, 360
A39	18.49	15-hydroxy-dehydroabietic acid	131, 197, 237, 255, 283, **301**, 316
A40	18.72	7-oxo-∆15(16)-dehydro-dehydroabietate	211, **251**, 266, 294, 326
A42	19.21	7-oxo-dehydroabietic acid	211, **253**, 299, 314
A43	19.22	Unidentified methoxy-dehydroabietate	59, 156, 212, 251, 255, 269, 312, **315**, 329
A44	19.47	Unidentified abietane	209, 239, 251, 253, **266**, 282, 310
A46	19.60	7-oxo-15-hydroxy-dehydroabietate	188, 269, **329**, (344)

Tab. 5.3 Compounds found in 1/9 "Tereb Com", sample analysed with temperature program Diterpenes 1 and column A, mass spectra references see appendix

5.1.3 1/10 Venice Turpentine

Fig. 5.8 1/10 "Venice Turpentine"

Fig. 5.9 Sampling of 1/10

Fig. 5.10 Sampling of 1/10 details

Description

The glass bottle is filled with a dried-up transparent material of a brownish to reddish colour. Dried-up residues of former liquid content remained at the inner side of the wall. The surface is hard and brittle with cracks (Fig. 5.10). The leather cap was still close-fitting and the knot attached.

Sampling

The knot and the leather cap were removed on 30 March 2009. The surface cracked when touched with a scalpel. A sample of the material below the brittle surface was taken (Fig. 5.9). The sample consisted of small yellow and transparent platelets with a sweetish smell. It was somewhat sticky.

Vigani references

* MS Quns Vig. 4, folio 1, verso, as "Tereb venetiae", 2 ounces at 2 pence, bottle at 1 penny

The invoice lists two identical "Tereb venetia" in a row, most probably one for 1/10 and the other one for 1/11 (chapter 5.1.3).

* LECTURE NOTES UNDATED: 299

* LECTURE NOTES 1707: 80

Contemporary literature

Fine art materials

* SALMON 1701: 791, 835, 842, 859, 867, 869-873, 930: "Venice or Venetian Turpentine"

* SMITH 1738: 83, 93: "Venice, Venetian turpentine"

* DOSSIE 1758a: 211-4: "Venice turpentine"

* CARLYLE 2001 : ANON. 1795: 216 (asphaltum); ANON. 1808: 11, 77

Science

* BAUHIN 1623: 505: "Terebinthina Veneta" ("*Abies alba sive foemina*")

* MANGET 1687: 64, 525-6: "Terebinthina Cypria seu Veneta" ("*Terebinthus, Larix*"); 347-8: "Terebinthina Veneta" ("*Abies Alba* & *Abies rubra*")

* BLANCKAERT 1690: 616: "Terebinthina vulgaris", "Laricea" ("*Larix*")

* DALE 1693, 399: "Terebinthina veneta", "Venice Turpentine" ("*Larix Folio deciduo conifera*")

* POMET 1717: 424: "Venedischer Terpentin", "Venetianischer Terpentin"

* LEMERY 1721: 1117: "Terebinthina Veneta", "Terebinthina de Venise" ("Turpentine tree, larch, pine, fir")

* JAMES 1747: 452: "Venice Turpentine" ("*Larix*")

* GEOFFROY, THICKNESSE 1749: 230: "Terebinthina Veneta", "Larigna vel Lariceav, "Venice Turpentine" ("*Larix, folio deciduo, conifera* C. B.")

* HILL 1751: 706-7: "Terebinthina Veneta", "Venice Turpentine" ("*Larix conifera folio deciduo*")

* LEWIS 1761: 551: "Terebinthina Veneta", Venice Turpentine" ("larch, *Larix* C. B. ")

Encyclopaedias

* CHAMBERS 1728a: 265: "Turpentine of Venice"

* SAVARY DES BRÛLON, SAVARY 1748c: 370(2) "Terebenthine de Venise", "Terebenthine du bois de pilatre" ("larch, pine, fir")

Terminology

The term "terebinthina veneta" or "venice turpentine" was used for different semi-liquid resins. Originally, the "true turpentine" was obtained from the eponymous "terebinth", which is *Pistacia terebinthus* L. or another *Pistacia* species (Pliny 1855: 14:25; Pomet 1717: 419; Savary des Brûslons, Savary 1748c: 470(2)). The material was imported to Europe from the Orient and the Mediterranean over Venice (Seguier 1745: 241), and named after the trading place, a term, which became generic for a "fine turpentine" of the best quality, which not necessarily had to been traded over Venice at the time of Vigani (see also chapter 5.1.1).

The situation in Venice at the end of the 16th century is described by Mattioli: the true turpentine became rare and druggists had brought the resins from "larch" and "fir" into use instead (Merrifield 1967: ccli). The name of the original material "terebinthina" was used for these different resins and became a synonym (ibid.; Schröder 1644: 203). In the 17th century it is called "terebinthina vera" or "terebinthina cypria seu veneta" (Schröder 1644: 112; Manget 1687: 525). The source tree was still the "terebinth", a *Pistacia* species, but sometimes two sorts, from Cypria and Chios, were mentioned (Manget 1687: 525) (see also chapter 5.1.5, 5.3.2). Towards the end of the 17th century the material slowly vanished from the shops for unknown reasons and was substituted by local resins, mainly obtained from trees of the family of Pinaceae (Pomet 1717: 419; 423; Lemery 1721: 1117; Savary des Brûslons, Savary 1748c: 470(2); Geoffroy, Thicknesse 1749: 230). In the 18th century the connection between a turpentine from Venice and *Pistacia* tree is nearly absent in literature. The connection of "fine turpentine" ("terebinthina") of good quality with a particular material with certain geographical and botanical origin was no longer existent. The terminological differentiation into fine and common turpentines was in use as long as the "true turpentine" was still available. Because the former "common turpentines" from "larch" and "abies" came into use as "fine turpentines" particularly the labelling as a "common turpentine" was still in use (differentiation criteria for "fine and common turpentines" see chapter 5.1.2).

Botanical and geographical origin

In the 17th century main source was the "terebinth", later also "larch" and "fir" (Pomet 1717: 419, 423; Lemery 1721: 1117; Savary des Brûslons, Savary 1748c: 470(2); Merrifield 1967: ccli). For the botanical and geographical origin of the "terebinth"-tree see chapter 5.3.2.

According to Bauhin, "terebinthina veneta" was another name for "oleum abiegnum" obtained in Italy, which was collected from "novellis abietibus" (Bauhin 1623: 500, 505). Manget mentions a liquid "resina ex abiete" which is collected "ex tuberculis" and called wrongly "terebinthina veneta" (Manget 1687: 348). He refers to Clusius who had denoted "terebinthina vera" was unknown and the "resina abiegna" was sold for it in apothecaries (ibid.: 526). The connection of the resin from "*Abies*" with "venice turpentine" was still in use in the 18th century:

> "Abies Offic. [..] In montibus Altis Vogesi hinc inde integrae sylvae occurturi sint. Oberhalb Hoch=Andlau auf dem St. Ottilien Gebürg / und oberhalb Haslach in dem Riedecker=Thal. Ex Vomicis hujus arboris, quae illi, in superiore trunci parte adnascantur,[..] ruptis, aut pertusis terebinthina colligitur à rusticis Tyrolensibus, qui singulis annis, verno tempore illam collectam ex sylvis Alsatiae Venetias deportant, unde rursus cum aliis mercibus ad nos perducitur nomine Terebinthina Venetae [..]" (Mappus, Ehrmann 1742: 1-2)[5].

However, according to Matthioli the true resin from the "silver fir" called "olio di abezzo" was frequently adulterated with "larch resin" (Merrifield 1967: ccl), which was still in use as a "common turpentine" at the time. As discussed in chapter 5.1.1, the resin of the "silver fir" was not called "Strasburg turpentine" in continental Europe, but more or less exclusively in England. On the continent, it seems to have been used, particularly in Italy, as a substitute for the "true turpentine".

Until the end of the 17th century the term "venice turpentine" came in use for the resin from "*Larix* Offic. [..] *Folio deciduo conifera*" (Dale 1693: 399). Temporarily it was in use for both materials: "Resina Terebinthini s. Terebinthina Cypria [..] estque dublicis generis. Resina scilicet Terebinthi & Resina Laricis" (Schröder 1644: 203; Manget 1687: 525; Blanckaert 1690: 616). Several authors mention a connection to regions in Southeast France (Dauphine, Savoyen, Forez near Lyon) (Chambers 1728b: 265; Pomet 1717: 421-4; Lemery 1721: 1117; Hill 1751: 707). In the region the "terebinthina de bois de pilatre" or "thérébinthine claire" mentioned by Pomet and Lemery were produced (Pomet 1717: 421; Lemery 1721: 1116-7; Savary des Brûslons, Savary 1748c: 370(2)). Some authors mention these materials as adulterations (Pomet 1717: 424; Savary des Brûslons, Savary 1748c: 470(2)). Lemery lists "terebinthine de venise" from Dauphine obtained from "larch, pine, fir" and "resina larigna" obtained in warm regions from "*Larix folio deciduo* conifer C.B." (Lemery 1721: 616, 1117).

The "larch tree" was located in the Alps and the Pyreneans (Dale 1693: 399; Geoffroy, Thicknesse 1749: 230; Lewis 1791: 552), but it also grew commonly in English gardens (Lewis 1791: 552). Geoffroy adds "Savoy", "Grison", "Stiria", "Carinthia" and upon the "Apennine Hills" (Geoffroy, Thicknesse 1749: 230). Later, Italy, the Aegean Sea, Tyrol and the Black Forest in Germany are mentioned (Jacobi 1800: 202).

This changed in the following years. In the second part of the 18th century turpentines from South France were exclusively called "terebenthine de venise" (Geoffroy, Thicknesse 1749: 230; Hill 1751: 706; Lewis 1761: 551). Hills wrote "venice turpentine" was obtained from the "larch" and originally traded over Venice, but with the decline of the trading place, it was obtained from the "Mountains of Savoy" and some other parts of France (Hill 1751: 706). In South East France a wide range of conifer resins were produced, and the one from "Pilatre" was the most expensive (Savary des Brûslons, Savary 1748c: 372(2)). Finally, Lewis stated that the true "venice turpentine" is obtained from the "larch", "*Larix* C. B. *Pinus Larix* Linn.", which grows in the Alps and Pyreneans, but also in England (Lewis 1761: 551).

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[5] "Abies Offic. [..] in the mountains of Higher Vosges intact forest should exist, above Hoch-Andlau at the St. Ottilien mountains, and above Haslach in the Riedecker valley. From the ruptured or perforated cankers of these trees, which form in the upper part of the trunk [..], a turpentine is collected by the farmers of Tyrol, which is brought in some years during the spring from the forests of Alsace to the Venicians, and is delivered back with other goods named Venice turpentine [..]". (own translation)

Manufacture and trade

The original "true turpentine" from the "terebinth" was imported to Europe over Venice (Seguier 1745: 241), but details of the harvesting and the trade are reported only for the 17th century-product "Cyprus and Chios turpentine", please refer to chapter 5.3.2.

The "larch tree" was drilled near the ground up to the core (Jacobi 1800: 202). According to Pomet the turpentine obtained in the "Wood of Pilatre" was brought to Lyon (Pomet 1717: 423).

"Thérébinthine de bois de pilatre" or "terebentine claire" flows at great heat "du Terebinte, du Meleze, du Pin, du Sapin & de quelques autres qui croissent aux pays chauds" with or without incisions (Lemery 1714: 841). Mentioned regions are the "Dauphine", "Forest" and "Savoyen". These turpentines were obtained by incision, when the trees ceased to yield spontaneously. This naturally flowing resin, which was estimated to be superior, was called "bijon" (Pomet 1717: 421; Lemery 1721: 1116-7), which is old French for "poix liquide" or "the resin of "sapins" (Godefroy 1881: 649). For the provenance and manufacture of the resin from the "silver fir" see chapter 5.1.1.

Properties

"Venice turpentine" is described as white or yellowish clear and transparent like glass (Dale 1693: 399; Pomet 1717: 423; Lemery 1721; 1117; Chambers 1728b: 265; Geoffroy, Thicknesse 1749: 230). Chambers describes it as liquid, whitish and of the consistence of syrup (Chambers 1728b: 265). It should taste acrid and bitter, and have a pleasant and fragrant smell (Dale 1693: 399). It was mentioned as usually thinner than the other sorts, with a consistency between oil and thin honey, of clear white or pale yellowish colour, a hot pungent bitterish disagreeable taste, and a strong smell without fine aromatic flavour of the "chios turpentine" (Geoffroy, Thicknesse 1749: 230; Lewis 1761: 552; Hill 1751: 706).

Different authors warned that it was frequently adulterated with "oil of turpentine" (Chambers 1728b: 265; Pomet 1717: 423; Lewis 1761: 552) or with other coniferous resins (Pomet 1717: 424, 427; Savary des Brûslons, Savary 1748b: 1428; Dossie 1758b: 374). Pomet described a method to control the purity of "terebinthine de bois de pilatre": a piece of paper dipped in the turpentine and lighted. If the flame was black and stinking, the turpentine was adulterated with "oil". If it was pure, the paper would have a resinous smell and burn more slowly. Another method was to put a drop of turpentine on a nail. Pure turpentine stays there, mixed flows away (Pomet 1717: 423-424).

Possible chemical composition

The term "venice turpentine" is used today mainly for the resinous balsam from *Larix decidua* Mill. or mixtures thereof (mainly with colophony) (Kremer 2011). Historical information shows that it was in use in different times for different resins (resin of the "terebinth", coniferous resins from *Abies alba* Mill. and *Larix decidua* Mill.) Different coniferous resins from Southeast France are also mentioned. In that regions *Larix decidua* Mill., *Picea abies* (L.) H. Karst., *Pinus cembra* L. and *Pinus sylvestris* L. are native (Euforgen 2009; Euforgen 2008e; Euforgen 2010; Euforgen 2008b). However, the term was no generic term, all materials were named after the original trading place, because the eponymous "true turpentine" had to been substituted with local resins of similar quality.

Taking into account that adulteration is reported to occur frequently, all Pinaceae genera and one or two *Pistacia* species are possible botanical origins. *Pistacia* resins consist of triterpenes with an oleanane, dammarane, tirucallane and lupane skeleton (Mills, White 1989; Koller et al. 1997b; Serpico, White 2000; Stern et al. 2008; see also chapter 2.3.1). The chemical composition of Pistacia turpentine is discussed in chapter 5.3.2.

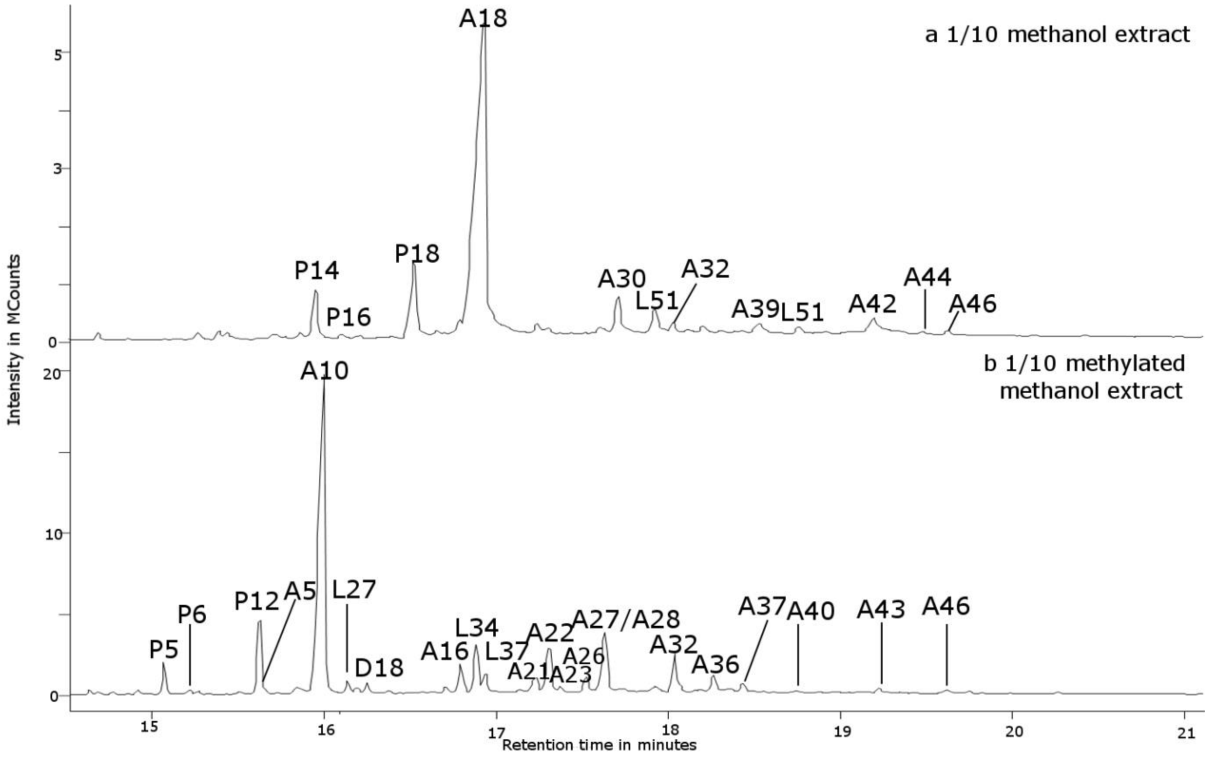
Pinaceae resins consist of abietane and pimarane acids (Mills, White 1999: 100-2; van den Berg et al. 2000; Scalarone et al. 2002; see also chapter 2.1.1). Resins from Pinaceae have been investigated very detailed and a broad variety of chemical compositions has been published (see table 2.2).

Several botanical samples from *Larix*, *Abies alba*, *Pinus* and *Picea* species as well as commercial Venice turpentines were analysed for this investigation, with the results presented in chapters 4.1.1.1 and 4.1.1.2. Marker molecules for all genera are listed in table 4.2. Molecular markers for *Larix* resins are the absence of pimaric acid and high initial amounts of epimanool, larixol and larixylacetate. Aged Venice turpentine contains lower amounts of epimanool and larixylacetate, small amounts of pimarane acids and mainly dehydroabietic and oxygenated derivatives thereof. For the composition of *Abies* and *Picea* resins please refer to chapter 5.1.1, for that of *Pinus* to chapter 5.1.2.

Chemical analysis

In the methanol extract (Fig. 5.11a), pimaric, sandaracopimaric, isopimaric and dehydroabietic acids are present. No palustric, abietic and neoabietic acids are found. Aging markers are 7-methoxy-, 7-hydroxy-, 15-hydroxy- and 7-oxo-dehydroabietic acids as well as 7-oxo and 7-oxo-15-hydroxy-dehydroabietate and A40 in small amounts. Two labdanes, imbricatoloic acid (L46) and L51, are also present, the methylester of which are found in the methylated extract.

In the methylated methanol extract (Fig. 5.11b), pimarate, sandaracopimarate, isopimarate



a – methanol extract and b –methylated methanol extract (labels, see table 5.4)

Fig. 5.11 Gas chromatograms of 1/10 “Venice turpentine” from the Vigani Cabinet, diterpene section (TIC)

Label	t_R	Name	Main mass fragments
P5	15.08	Pimarate	**121**, 241, 257, 301, 316
P6	15.22	Sandaracopimarate	**121**, 241, 301, 316
P12	15.62	Isopimarate	187, 227, **241**, 256, 287, 316
A5	15.66	Levopimarate	91, **92, 121**, 146, 187, 316
A10	15.98	Dehydroabietate	**239**, 299, 314
P14	15.95	Pimaric acid	91, 107, **121**, 133, 241, 287, 302
P16	16.11	Sandaracopimaric acid	91, 107, **121**, 133, 241, 287, 302
L27	16.14	Unidentified labdane acid, ME	79, 93, **121**, 161, 221, 290, 318, 350
D18	16.26	12-methoxy-podocarpa-8,9,12-trien-15-oate	159, 173, **227**, 239, 287, 302
P18	16.51	Isopimaric acid	91, 105, 131, 159, 187, 227, **241, 287**, 302
A18	16.91	Dehydroabietic acid	197, **239**, 285, 300
A16	16.79	7-methoxy-dehydroabietate	195, **237**, 253, 312, 344
L34	16.88	Imbricatoloate	**121**, 161, 225, 276, 336
L37	16.94	Dihydroagathate, diME	79, 93, **121**, 161, 257, 304, 364
A21	17.23	Unidentified oxygenated abietane acid	227, **269**, 329, 344
A22	17.30	7-hydroxy-dehydroabietate	121, 195, **237**, 253, 297, 312, 330
A23	17.37	15-methoxy-dehydroabietate isomer	237, 269, 312, **329**, 344
A26	17.53	Unidentified	162, 195, **237**, 255, 283, 297, 330
A27	17.64	Δ16-demethyl-7-oxo-dehydroabietate (proposed)	155, 197, 211, **253**, 299, 313, 328
A28	17.61	15-hydroxy-dehydroabietate	255, 273, **315**, 330
A30	17.71	7-methoxy-dehydroabietic acid (proposed)	181, 195, **237**, 283, 298, 330
L46	18.19	Imbricatoloic acid	81, **121**, 161, 221, 276, 304, (336)
A32	18.03	7-oxo-dehydroabietate	187, 211, **253**, 269, 296, 328
A36	18.27	Unidentified hydroxy-dehydroabietate, probably a dihydroxy-compound	181, 195, 211, **249**, 264, 309, 324
A35	18.39	7-hydroxy-dehydroabietic acid	145, 185, 195, **237**, 273, 299, 316
A37	18.44	15-methoxy-Δ6(7)-dehydro-dehydroabietate (proposed)	213, 237, 251, **267**, 311, 327, 342, 360
A39	18.54	15-hydroxy-dehydroabietic acid	131, 197, 237, 255, 283, **301**, 316
A40	18.73	Unidentified	212, **251**, 266, 294, 326
L51	18.77	Dihydroagathic acid (proposed)	79, 93, 107, **121**, 161, 175, 290, 300, 318, 336
A42	19.18	7-oxo-dehydroabietic acid	211, **253**, 299, 314
A43	19.22	Unidentified methoxy-dehydroabietate	59, 156, 212, 251, 255, 269, 312, **315**, 329
A46	19.61	7-oxo-15-hydroxy-dehydroabietate	188, 269, **329**, (344)

Tab. 5.4 Compounds found in 1/10 "Venice turpentine", sample analysed with temperature program Diterpenes 1 and column A, mass spectra references see appendix

and levopimarate as well as dehydroabietate are present. The material contains more pimarate than sandaracopimarate. The (di-)methylester of L46 and L51 are present, according to their retention time and mass spectra, as L34, identified as imbricatoloate, and dihydroagathate (L38). L51 is dihydroagathic acid, then. Another unidentified labdane acid (L27) is present in small amounts as well. The main aging marker is dehydroabietate (A10), followed by smaller amounts of several derivatives of 7-hydroxy- (A16, A22), 15-hydroxy- (A23, A28) and 7-oxo-dehydroabietate (A27, A32). Other aging marker are 12-hydroxy-podocarpa-8,9,12-trien-15-oate (D18), 15-methoxy-Δ6(7)-dehydro-dehydroabietate (A37), 7-oxo-15-hydroxy-dehydro- abietate and unidentified aging markers (A26, A36 and A43). A36 is probably a dihydroxy-dehydroabietate, A43 a methoxy-dehydroabietate, please refer to chapter 4.1.1.2. A19 elutes at 16.92 minutes, but only in small amounts. It is visible only in EIC, and coelutes with L38.

Discussion

The composition is typical for resins from *Pinus* species, which contain higher relative amounts of pimaric than sandaracopimaric acid. No marker molecules for larch or fir resins are present. The presence of dihydroagathic acid points to *Pinus* species from the section Pinea, for further details please refer to chapter 5.1.1 'Discussion'.

The chemical composition of 1/10 "Venice turpentine" is very similar to that of 1/8 "Terebin. Strasb. (chapter 5.1.1) and 1/13 "Tereb. E Chio" (chapter 5.1.5). Differences between the three samples are mostly the result of differing aging processes, because 1/10 "Venice turpentine" was taken from the bulk material, while the other two were taken from the dried-up residues in the bottles. The material is in an advanced aging state, only pimarane acids are still present in significant amounts. The only not oxygenated abietane acid, levopimaric acid, is present in small amounts (for levopimaric acid cf. chapter 5.1.1, 4.1.1.1). Other aging markers are lower amounts of Pinaceae aging markers, particularly several derivatives of 7-hydroxy-, 7-methoxy, 15-hydroxy-, 15-methoxy and 7-oxo-dehydroabietic acids. Compared to the other sample taken from the bulk material (1/11a, chapter 5.1.4), it contains relatively small amounts of the (light) aging markers A36, A37 and A43 as well as 7-oxo-15-hydroxy-dehydroabietic acid. 1/11 however shows a different aging behaviour compared to the other Pinaceae resins from the Cabinet (see chapter 5.1.4, 'Discussion'). Compared to the other samples taken from the dried-up residuals in the bottles (1/8, 1/9, 1/13), it contains very low amounts of aging markers, however the intermediate 15-hydroxy-dehydroabietic is present in significant amounts only in less aged materials. A possible dihydroxy-derivative of that compound is A36, which is present in all dried-up materials (1/8, 1/9, 1/11b, 1/13) and in small amounts in the bulk samples (1/10, 1/11a), please refer also to chapter 5.1.1. Taking into account its lower aging state, 1/10 "Venice turpentine" contains comparatively low amounts of C-15 oxygenated dehydroabietic acids (A23, A28, probably A37, A39) compared to C-7 oxygenated abietane acids (A16, A22, A30, A32, A40, A42). The preference for oxidation at the C-7 position is found for other Pinaceae samples from the Cabinet as well (chapter 5.1.1, 5.1.2, 5.1.5, 5.1.6).

1/10 "Venice turpentine" shows a composition, which is different from that, which could be expected by its name. Because another "Venice turpentine" from the Vigani Cabinet (1/11, chapter 5.1.4) contains the resin of *Larix decidua* Mill., the origin of this adulteration probably traces back to South France, where the "terebinthina de bois de pilatre" was harvested (Chambers 1728b: 265; Lemery 1721: 1117; Hill 1751: 707). In the "Wood of Pilatre" several different coniferous resins were manufactured and in particular "venice turpentine" is mentioned to be adulterated with the resins from "larch", "pine" and "fir" (Pomet 1717: 421; Lemery 1721: 616, 1116-7).

5.1.4 1/11 Venic. Turpent.

Fig. 5.13 1/11 "Venic. Turpent."

Fig. 5.12 Sampling of 1/11

Description

The glass bottle is filled with a dried-up transparent material of dark yellow to orange colour. The surface is hard and brittle with cracks. The string was found loose in the compartment.

Sampling

A sample of the material below the brittle surface was taken (1/11a; about 90 mg). It was still somewhat sticky with a slight resinous smell (Fig. 5.13). A dried-up drop from the inner side of the wall was sampled on 26 April 2007. It consisted of transparent platelets (1/11b; about 1 mg).

Vigani references

* MS Quns Vig. 4, folio 1, verso, as "Tereb venetiae", 2 ounces at 2 pence, bottle 1 penny

The invoices list two identical "Tereb venetia" in a row, most probably one for 1/10 and the other one for 1/11 (chapter 5.1.3).

* LECTURE NOTES UNDATED: 299

* LECTURE NOTES 1707: 80

Contemporary literature

See chapter 5.1.3

Terminology

See chapter 5.1.1

Botanical and geographical origin

See chapter 5.1.3

Manufacture and trade

See chapter 5.1.3

Properties

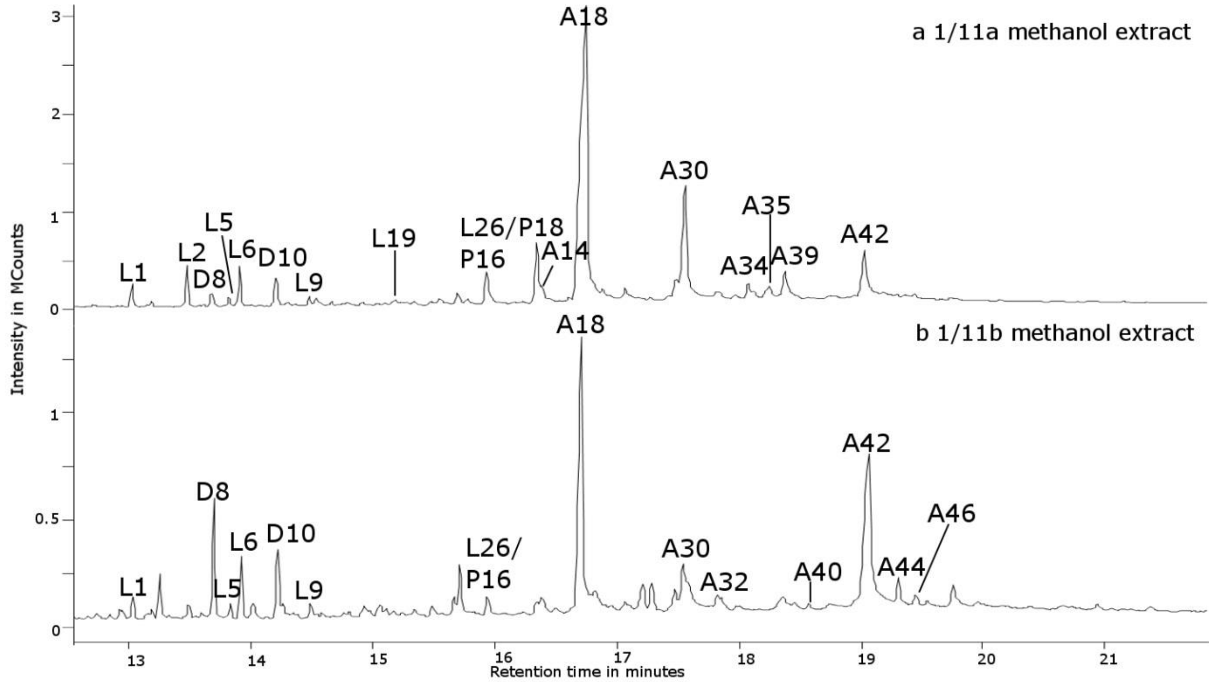
See chapter 5.1.3

Possible chemical composition

See chapter 5.1.3

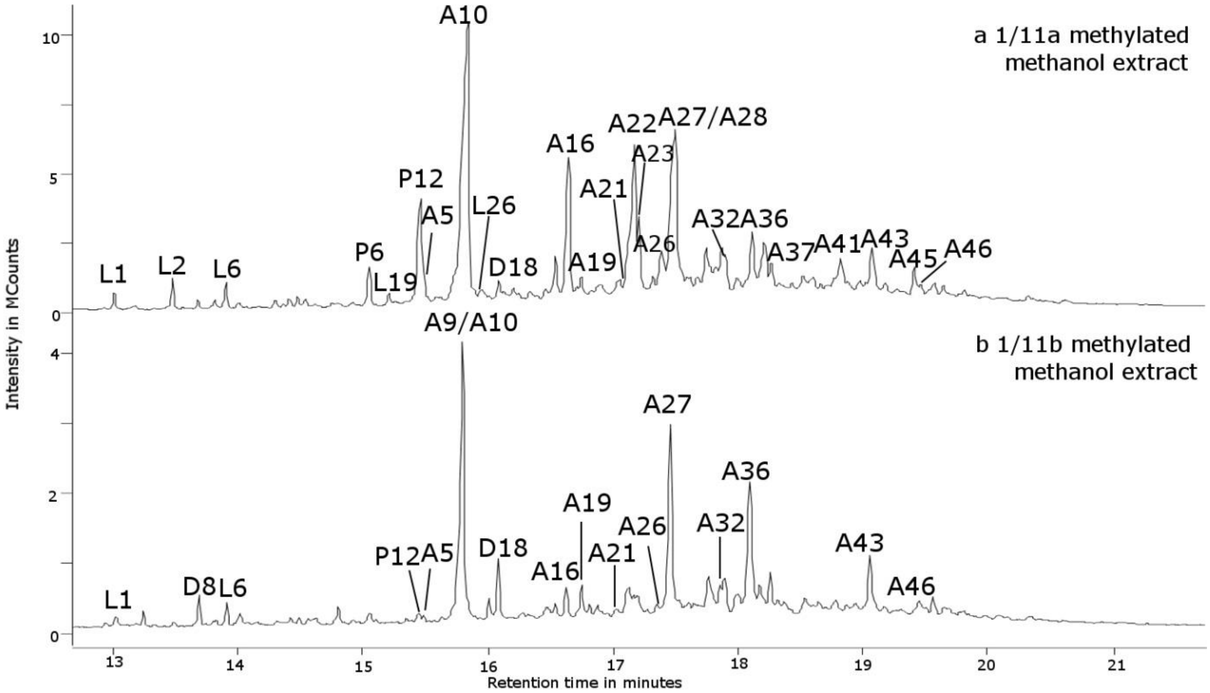
Chemical analysis

In the methanol extract (Fig. 5.14), epi-manoyloxide, epimanool, *iso*-abienol, abienol, an unidentified abienol (L10), two related diterpenes, probably also abienols (D8, D10), and larixylacetate (L26) are present. Diterpene acids are sandaracopimaric, isopimaric, levopimaric and dehydroabietic acids. No palustric, abietic and neoabietic acids are found. Larixylacetate coelutes with sandaracopimaric acid and is present in both samples in low amounts. In the bulk sample (1/11a) also traces of larixol (L19) are present.



Methanol extracts, a –bulk 1/11a, b –dried up 1/11b (labels, see table 5.5)

Fig. 5.14 Gas chromatograms of 1/11 “Venic. Turpent.” from the Vigani Cabinet, diterpene section (TIC)



Methylated methanol extract s, a – bulk 1/11a, b –dried up1/11b (labels, see table 5.5)

Fig. 5.15 Gas chromatograms of 1/11 “Venic. Turpent.” from the Vigani Cabinet II, diterpene section (TIC)

Label	t_R	Name	Main mass fragments
L1	13.01	Epimanoyloxide	81, 95, 177, 191, **257**, 275, 290
L2	13.48	Epimanool	**81**, 95, 137, 257, 272, (290)
D8	13.67	Unidentified	**67**, 81, 95, 109, 123, 135, 191, 207, 235
L5	13.82	iso-Abienol	81, 95, 109, **191**, 217, 235, 255, 272, (290)
L6	13.91	Abienol	81, 95, 109, **191**, 217, 235, 255, 272, (290)
D10	14.20	Unidentified	81, 95, **109**, 121, 161, 217, 235, 245, 278
L10	14.48	Unidentified abienol	81, 95, 109, **191**, 217, 234, 255, 272, (290)
P6	15.05	Sandaracopimarate	**121**, 241, 301, 316
L19	15.18	Larixol	69, **109**, 119, 153, 187, 255, 273, 288, (306)
P12	15.45	Isopimarate	187, 227, **241**, 256, 287, 316
A5	15.48	Levopimarate	91, **92, 121**, 146, 187, 316
A9	15.77	Tetradehydroabietate	195, **237**, 312
A10	15.79	Dehydroabietate	**239**, 299, 314
L26	15.91	Larixylacetate	79, 105, **153**, 185, 255, 270, 288, 348
P16	15.93	Sandaracopimaric acid	91, 107, **121**, 133, 241, 287, 302
D18	16.08	12-methoxy-podocarpa-8,9,12-trien-15-oate	159, 173, **227**, 239, 287, 302
P18	16.33	Isopimaric acid	91, 105, 131, 159, 187, 227, **241, 287**, 302
A14	16.38	Levopimaric acid	**92**, 105, 131, 146, 187, 302
A16	16.64	7-methoxy-dehydroabietate	195, **237**, 253, 312, 344
A18	16.74	Dehydroabietic acid	197, **239**, 285, 300
A19	16.75	7-methoxy-tetradehydroabietiate	209, 227, **267**, 283, 327, 342
A21	17.05	Unidentified oxygenated abietane acid	227, **269**, 329, 344
A22	17.16	7-hydroxy-dehydroabietate	121, 195, **237**, 253, 297, 312, 330
A23	17.19	15-methoxy-dehydroabietate isomer	237, 269, 312, **329**, 344
A26	17.38	Unidentified	162, 195, **237**, 255, 283, 297, 330
A27	17.47	∆16-demethyl-7-oxo-dehydroabietate (proposed)	155, 197, 211, **253**, 299, 313, 328
A28	17.51	15-hydroxy-dehydroabietate	255, 273, **315**, 330
A30	17.55	7-methoxy-dehydroabietic acid (proposed)	181, 195, **237**, 283, 298, 330
A32	17.87	7-oxo-dehydroabietate	187, 211, **253**, 269, 296, 328
A34	18.08	Unidentified	91, 134, 185, 239, 254, 285, **300**
A35	18.24	7-hydroxy-dehydroabietic acid	145, 185, 195, **237**, 273, 299, 316
A36	18.11	Unidentified hydroxy-dehydroabietate, probably a dihydroxy-compound	181, 195, 211, **249**, 264, 309, 324
A37	18.27	15-methoxy-∆6(7)-dehydro-dehydroabietate (proposed)	213, 237, 251, **267**, 311, 327, 342, 360
A39	18.38	15-hydroxy-dehydroabietic acid	131, 197, 237, 255, 283, **301**, 316
A40	18.57	7-oxo-∆15(16)-dehydro-dehydroabietate	211, **251**, 266, 294, 326
A41	18.82	Unidentified aging marker, oxygenated abietane	195, 211, **253**, 313, 328, 331
A42	19.03	7-oxo-dehydroabietic acid	211, **253**, 299, 314
A43	19.08	Unidentified methoxy-dehydroabietate	59, 156, 212, 251, 255, 269, 312, **315**, 329
A44	19.31	Unidentified abietane	209, 239, 251, 253, **266**, 282, 310
A45	19.41	Unidentified	185, 213, 241, 269, 284, 301, 326, **344**
A46	19.47	7-oxo-15-hydroxy-dehydroabietate	188, 269, **329**, (344)

Tab. 5.5 Compounds found in 1/11 “Venic. Turpent.”, sample analysed with temperature program Diterpenes 1 and column A, mass spectra references see appendix

In the bulk sample (1/11a) main aging markers are 7-methoxy- and 7-oxo-dehydroabietic acids, other aging compounds present are A34, 7-hydroxy- and 15-hydoxy-dehydroabietic acids (Fig. 5.14a). In the dried-up sample (1/11b) the main aging marker is 7-oxo-dehydroabietic acid, other aging compounds present are 7-methoxy-dehydroabietic acid, 7-oxo- and 7-oxo-15-hydroxy-dehydroabietate, 7-oxo-Δ15(16)-dehydro-dehydroabietate (A40) and A44 (Fig. 5.14b).

In the methylated methanol extract (Fig. 5.15) epi-manoyloxide, epimanool, abienol, sandaracopimarate, isopimarate, levopimarate and dehydroabietate are present. In the bulk sample (1/11a) larixol and traces of larixylacetate are present, in the dried-up sample (1/11b) D8.

In the bulk sample (1/11a) main aging markers are 7-hydroxy- (A16, A22) and 15-hydroxy-dehydroabietate derivatives (A23, A28). Other aging markers present in lower amounts are 7-oxo-dehydroabietate derivatives (A27, A32), A36 and A43. A36 is probably a dihydroxy-dehydroabietate, A43 a methoxy-dehydroabietate, please refer to chapter 4.1.1.2. Small amounts of 12-methoxy-podocarpa-8,9,12-trien-15-oate (D18), 7-methoxy- and 15-methoxy-Δ6(7)-dehydro-dehydroabietate (A19, A37) and the unidentified A21, A26, A41 and A45 (Fig. 5.15a). In the dried-up sample (1/11b) main aging marker are A27, A36 and A43. These compounds are all light aging markers, A27 is probably a demethylated 7-oxo-dehydroabietate, A36 a dihydroxy-dehydroabietate and A43 a methoxy-dehydroabietate, please refer to chapter 4.1.1.2. 7-oxo-dehydroabietate (A32) is present only in small amounts similar to 1/11a. Other constituents are the dehydro-derivative of dehydroabietate (A9), 7-hydroxy-dehydroabietates (A16, A22), 7-oxo-15-hydroxy-dehydroabietate (A46), D18 and 7-methoxy- and 15-methoxy-Δ6(7)-dehydro-dehydroabietate (A19, A37) (Fig. 5.15b).

Both samples (1/11a and 1/11b) contain high amounts of 7-oxo-dehydroabietic acid (A42) in the methanol extracts, while in the methylated methanol extracts only traces of the methylester (A32) are found, but high amounts of demethylated derivative of 7-oxo-dehydroabietate (A27). This is the case only for the samples from 1/11 and not for any other Pinaceae resin from the Cabinet, even though some of them contain quite high amounts of 7-oxo-dehydroabietic acid in the methanol extract but always higher amounts of A32 than A27. A27 is proposingly a light aging marker based on the results of the reference analysis, please refer to chapter 4.1.1.2. This however, does not explain the presence of high amounts of 7-oxo-dehydroabietic acid in the methanol extract on the one hand and low of its methylester in the methylated extract on the other. Therefore, A27 might be an artefact of the sample preparation.

Discussion

The composition is typical for several Pinaceae resins, particularly that from *Larix* and *Abies* species. Both contain no pimaric acid. Epimanool, larixol and larixylacetate are marker for *Larix* species, D8, *iso*-abienol, abienol, D10 and L10 as well as epi-manoyloxide for Abies alba Mill. No *cis*-abienol is present, which is reported to be a typical constituent of silver fir resin and is found in the analysed reference samples (chapter 4.1.1.1). It does however polymerise with α-phellandrene (White, Kirby 2001), which may be the reason of its absence in the aged sample of 1/11 "Venic. Turpent.". The mentioned abienols are not present in the resin of Larix species (table 2.2, chapter 4.1.1.1). *Picea* resins contain a differing composition and pimaric acid (chapter 4.1.1.1).

There is some evidence that 1/11 "Venic. Turpent." was made from the resin of the silver fir adulterated with larch resin. This was frequently the case in Europe, where the resin of *Abies alba* Mill. was not traded under the term "strasburg turpentine", please refer to chapter 5.1.1 and 5.1.3. Furthermore, the transport of the resin from the silver fir to Venice and its labelling as "venice turpentine" is mentioned in particular together with the adulteration of fir resin with that from larch from the 16th century on (Mappus, Ehrmann 1742: 1-2; Merrifield 1967: ccl). It is therefore a late example of the use of larch resin as a "common turpentine". Larch resin was used to blend fir resin of higher quality, which was in turn a substitute for the "true turpentine" from the "terebinth".

The material is in an advanced aging state, only pimarane acids are still present in significant amounts. All abietane acids are isomerised and dehydrogenated to dehydroabietic acid, only small amounts of levopimaric acid are present. Levopimaric acid is also present in several other conifer "turpentines" from the Vigani Cabinet, (1/8, 1/9, 1/10, 1/13), for its formation please refer to chapter 4.1.1.1. Other aging marker differ for the two samples of 1/11, the dried-up sample 1/11b contains comparatively low amounts of oxygenagted abietane acids of oxidation state 3 and high amounts of (light) aging markers (A27, A36 and A43) (Fig. 2.4). Comparing the aging state of all coniferous "turpentines", all dried-up samples (1/8, 1/9, 1/11b, 1/13) contain low amounts of 15-hydroxy-dehydroabietic acids (A23, A28, A39) and all bulk samples (1/10, 1/11a) contain high amounts of this acids. While C-15 oxygenated dehydroabietane acids are present in lower amounts in dried-up samples, C-7 oxygenated are still present in significant amounts. As discussed for the other samples before (chapter 5.1.1 – 5.1.3), 15-dehydroabietic acid is transformed to its dihydroxy-derivative (A36), while oxygenation at the C-7 position is the main aging process (Fig. 2.4).

However, the dried-up sample 1/11b contains low amounts of 7-hydroxy-, 15-hydroxy-dehydroabietic acids and also of 7-oxo-15-hydroxy-dehydroabietic acid and A37 compared to the other dried-up samples (1/8, 1/9, 1/13). Instead, the light aging markers A36 and A43 are present in higher amounts. The composition of the aging markers from the bulk sample (1/11a) is similar ambiguous. In contrary to 1/10 "Venice turpentine", which was taken from the bulk as well, it contains significant higher amounts of aging markers such as 7-hydroxy- (A16, A22), 15-hydroxy- (A23, A28) and 7-oxo-dehydroabietic acids (A27, A32) and light aging markers A36 and A43. On the other hand, compounds with a lower oxidation state (A22, A23, A28) are present in relatively higher amounts than in 1/10, and compounds with a higher oxidation state (A27, A32) in relatively lower amounts compared to 1/10. Compared to 1/10 also higher amounts of pimarane acids are present.

In sum, 1/11 "Venic. Turpent." contains higher amounts of aging marker of lower the aging state 3 than other Pinaceae resins from the Vigani Cabinet, but lower of aging markers from the higher aging states 4 and 5. The only reasonable explanation for these findings is the differing initial composition, which influences isomerisation and oxidation reactions. Because A36 and A43 are not identified for certain, yet, the nature of those different aging reactions remains open. The presence of polymerising labdanols in the sample may be a reason, however a similar aging behaviour is present in the larch resins analysed for this work, which does not contain such compounds (see chapter 4.1.1.2).

5.1.5 1/13 Tereb E Chio

Fig. 5.16 1/13 "Tereb E Chio"

Fig. 5.17 Sampling of 1/13

Description

The glass bottle is filled with a dried-up residue of a partly cloudy, partly transparent hard material of a deep orange colour. The more dried-up residues at the inner side of the wall are of a dark orange to red colour. When filled in the glass bottle the material must have been more viscous than the other turpentines in the Cabinet (see chapter 5.1.1 - 5.1.4).

Sampling

A sample of a drop (about 40 mg) from the inner side of the wall was taken on 26 April 2007 (Fig 5.17). It consisted of small brown and transparent platelets like amber. They were brittle and had a dusty smell.

Vigani references

* MS Quns Vig. 4, folio 1, verso, as "Tereb E. Chio", 1 ounce at 12 pence, bottle 1 penny

* Does not appear in LECTURE NOTES UNDATED

* Does not appear in LECTURE NOTES 1707

Contemporary literature

Fine art materials

* SALMON 1701: 859: "Chio and Cyprus Turpentine"

* CARLYLE 2001: ANON. 1795: 192f., 193-5 ("Chios & Cyprus"); ANON. 1808: 72-3 ("Chios & Cyprus")

Science

* POMET 1717: 421-2: "Terpentin aus Chio" ("Terpentinbaum")

* LEMERY 1721: 1116-8: "Terebinthina Chia", "Terebinthine de Chio" ("*Terebinthus vulgaris* C.B., Terebinthe, Terpentinbaum")

* JAMES 1747: 452-3: "Turpentine from Chios and Cyprus" ("*Terebinthus* J.B.,*Terebinthus vulgaris* C. B. P.")

* GEOFFROY, THICKNESSE 1749: 227: "Terebinthina Chia", "Hele/Helt Alimbath" ("*Terebinthus vulgaris* C. B. P. ")

* HILL 1751: 705-6: "Terebinthina Chia", "Chian Turpentine", "Resina Terebinthina", "Hele Alimbat(c)h" ("*Terebinthus*, Turpentine Tree")

* LEWIS 1761: 551: "Terebinthina chia & cypria", "Chio or Cyprus turpentine" ("*Terebinthus Vulgaris* C.B., common terebinth"

Encyclopaedias

* CHAMBERS 1728b: 265: "Turpentine of Chio"

* SAVARY DES BRÛSLON, SAVARY 1748c: 370(2)-372(2): "Terebenthine de Chio" ("Terebinthe")

Terminology

The origin of the term "turpentine" is described in chapter 5.1.3. as well as the transfer of the term to other resins and their connections to the geographical origin instead of the trading route.

The terms "terebinthina de chio", "terebinthina cypria" or "terebinthina chia & cypria" were used for the semi-liquid resin of the "turpentine tree" more or less synonymously (Bauhin 1623: 500; Blanckaert 1690: 616; James 1747: 452-3; Geoffroy, Thicknesse 1749: 227; Hill 1751: 705; Lewis 1761: 551), in the 17th century the labelling "terebinthina cypria" was somewhat more common, even though it seems that is was brought primarily from Chios (Bauhin 1623: 500; Manget 1687: 64, 525; Dale 1693: 456; Zwinger 1724: 499). But the genuine name "terebinthina de chio" for the resin from the "terebinth" could refer to materials from Cyprus as well and the other way around (Hill 1751: 705; Lewis 1761: 551).

Botanical and geographical origin

"Terebinthina de chio" is mentioned in many contemporary sources as the resin of the "turpentine tree" or the "terebinth" ("*Terebinthus Vulgaris* C.B."). The "turpentine tree " grows in different southern parts of Europe, North Africa and the Middle East, but is mainly referred to the islands Chios and Cyprus, from where its resin seemingly have been imported to Europe (Manget 1687: 64, 525; Blanckaert 1690: 616; Chambers 1728b: 265; James 1747: 453; Geoffroy, Thicknesse 1749: 227; Lewis 1761: 551). Apart from Chio and Cyprus (Ray 1693b: 1577; Dale 1693: 456; Zwinger 1724: 499; Linné 1753b: 1026), the "turpentine tree" grew in several regions in Southern Europe (Italy, France and Spain) (Pomet 1717: 421; Lemery 1721: 1116; Chambers 1728b: 265; Seguier 1745: 241; Geoffroy, Thicknesse 1749: 227; Lewis 1761: 551). European trees however seem to be cultivated and did not yield any resin (Seguier 1745: 241; Hahnemann 1799: 310). Linné lists "Europa australis", "Africa borealis" and "India" (Linné 1753b: 1026). The resin obtained on Chios was preferred, but also "Lybrica, tum Pontiea: tandem Cypria, Syriaca, Judaica, Arabica" are mentioned (Bauhin 1623: 500).

Origin and identity of the "turpentine from Chios and from Cyprus" was an object of discussion. While different authors mention the "turpentine from Chios" to be the best (Dale 1693: 456; Pomet 1717: 421; Chambers 1728b: 265; James 1747: 453) and James describes the one from Cyprus as "browner and fuller of Dross" (James 1747: 453), Hill states that the supposed difference of these two balsam does not exist (Hill 1751: 706).

In contrary, mainly French authors from the end of the 17th century made a general difference between the "turpentines from Chios and Cyprus" (Lemery 1721: 1116; Pomet 1717: 421, 424; Chambers 1728b: 265; Savary des Brûslons, Savary 1748c: 370(2), 372(2)). "Terebinthina chia" or "terebinthine de chio" is mentioned as the originally true turpentine, the best of all turpentines, who gave its name to them all (Lemery 1721: 1116; Pomet 1717: 421, 424; Chambers 1728b: 265). It was very rare (Pomet 1717: 419; Lemery 1721: 1116; Chambers 1728b: 265). "Terebinthina cypria", "terebenthine de chypre" or "cyprus turpentine" was listed as well, but without further information (Pomet 1717: 424; Lemery 1721: 1116; James 1747: 453). It was not available in the shops and "chios turpentine" was used instead (Pomet 1717: 424; Lemery 1721: 1117; Savary des Brûslons, Savary 1748c: 371(2)).

Manufacture and trade

The material was imported to Europe from the Orient and the Mediterranean over Venice (Seguier 1745: 241), and named after the trading place (see chapter 5.1.3).

The turpentine flows spontaneously or by wounding the trunk and branches of the "turpentine tree" with picks (Pomet 1717: 421; James 1747: 453; Hill 1751: 706; Lewis 1761: 551; Jacobi 1800: 202; Krünitz 1843: 105-6). From there the resinous balsam flows down on prepared stone plates. It was softened by the sun, cleaned with baskets and bottled. It was harvested from July to October (Pomet 1717: 421; Savary des Brûslons, Savary 1748c: 370(2); Jacobi 1800: 202; Krünitz 1843: 105-6). A clearer sort was made from the exuded drops, and both sorts were stored in earthen pots of about 20 pounds, four in a case (Jacobi 1800: 202). They were brought to Venice, Marseilles and England (Jacobi 1800: 202).

It was sold for 30 to 35 "parat" per "ocque" at the island Chio, one "ocque" 3 ½ "livre" and 1 "ounce", with no more then 300 "ocque" per year (Savary des Brûslons, Savary 1748c: 370(2)). "Livre" was the French mass unit for "pound" used in that time. Without an exact exchange rate, 300 "ocque" are about 520 kg. That corresponds to the quantity of 1000 "Pfund", which is given 50 years later (Hahnemann 1799: 311: Krünitz 1843: 106).

Properties

Historical sources describe the resin from the "turpentine tree" as clear, almost transparent and vitreous. It is thicker and more tenacious than "venice or common turpentine", with the consistency of thick honey (Dale 1693: 456; James 1747: 453; Hill 1751: 706, 710; Lewis 1761: 551). Fresh resin is very sticky and soft and becomes harder with storage (Hill 1751: 706). It is of silvery white colour with a shade of yellow and blue, therefore it looks green against the light (James 1747: 453; Hill 1751: 706; Lewis 1761: 551). It has a warm pungent, bitterish and agreeable taste and a pleasant fragrant smell resembling that of "Balsam of Peru" (ibid.; Dale 1693: 456). The best quality should be solid, clear and transparent, white, very glutinous, of an acrid taste and fragrant when burnt (Hill 1751: 706; Blaenckart 1690: 616). Hill mentioned it was often counterfeit in the “Turpentine House” in London (Hill 1751: 706).

Pomet describes the "terebinthine de chio" as clear and almost transparent. It is thick but only a little tenacious, with a white colour and a green shade and somewhat fragrant (Pomet 1717: 422; Chambers 1728b: 265; Savary des Brûslons, Savary 1748c: 370(2)). The best quality should be solid, without almost any taste and smell (Pomet 1717: 422; Chambers 1728b: 265; Lemery 1721: 1116).

Counterfeit "terebinthine de chio" or false "venice turpentine" sold for "chios turpentine" in the shops is more tenacious and with a stronger taste and smell (Pomet 1717: 422; Chambers 1728b: 265; Savary des Brûslons, Savary 1748c: 370(2)). Pomet also mentioned that the "terebinthine de bois de pilatre" and the one from "Forêz" were sold as "terebinthine de chio" (Pomet 1717: 422). In South-France several kinds of turpentines were harvested from "larch, pine, fir and others" (Lemery 1714: 841), please refer to chapter 5.1.1 and 5.1.3. Hahnemann stated that in Venice "larch turpentine" was mixed under the "chios turpentine", because it was so rare (Hahnemann 1799: 311). Dossie mentions that the "Balsam of Chio is sophisticated with common turpentine" (Dossie 1758b: 376).

Possible chemical composition

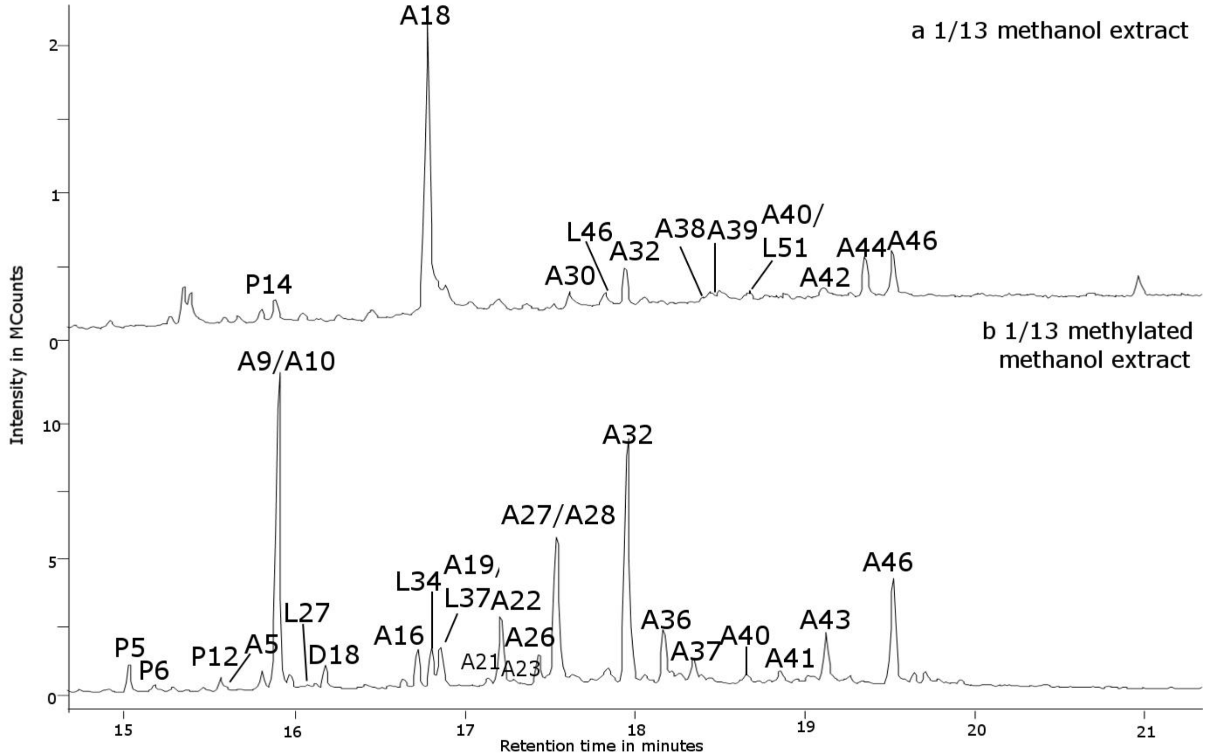
The term "chios turpentine" was used mainly for the resin of *Pistacia* species. "*Terebinthus vulgaris* C.B." was classified by Linné as *Pistacia terebinthus* L. (Linné 1753b: 1026), which is still in use. There is some discussion on the species used for the production of Pistacia turpentines, please refer to chapter 2.1.3 and 5.3.2, 'chemical composition'. Due to its rarity, several Pinaceae resins or mixtures thereof have been used as substitutes.

The composition of Pistacia turpentine is discussed in chapter 5.3.2., that of the Pinaceae genera *Abies*, *Larix*, *Pinus* and *Picea* in chapter 5.1.1 (*Abies, Picea*), 5.1.2 (*Pinus*) and 5.1.3 (*Larix*).

Chemical analysis

In the methanol extract (Fig. 5.18a) pimaric and dehydroabietic acids are present. No palustric, abietic and neoabietic acids are found. Aging markers are 7-methoxy-, 15-hydroxy- and 7-oxo-dehydroabietic acids as well as 7-oxo and 7-oxo-15-hydroxy-dehydroabietate, A38, A40 and A44. Additionally, the two labdanes imbricatoloic acid (L46) and L51 are present, the methylester of which are found in the methylated extract.

In the methylated methanol extract (Fig. 5.18b) pimarate, sandaracopimarate, isopimarate, levopimarate and dehydroabietate are present. The material contains more pimarate than sandaracopimarate. The (di)methylester of L46 and L51 are according to their retention time and mass spectra present as L34, identified as imbricatoloate, and dihydroagathate (L38). L51 is dihydroagathic acid, then. Another unidentified labdane acid (L27) is present in small amounts, too. Main aging markers are dehydroabietate (A10) and 7-oxo-dehydroabietate derivatives (A27, A32). Other aging markers are 7-hydroxy-dehydroabietates (A16, A22), A36, A43 and 7-oxo-15-hydroxy-dehydroabietate (A46) together with small amounts of 12-methoxy-podocarpa-8,9,12-trien-15-oate (D18), 15-hydroxy-dehydroabietates (A23, A28), A26, 7- and 15-methoxy-Δ6(7)-dehydrodehydroabietate (A19, A37), 7-oxo-Δ15(16)-dehydro-



a – methanol extract, b – methylated methanol extract (labels, see table 5.6)

Fig. 5.18 Gas chromatograms of 1/13 "Tereb E Chio" from the Vigani Cabinet, diterpene section (TIC) dehydroabietate (A40) and A41. A36 is probably a dihydroxy-dehydroabietate, A43 a methoxy-dehydroabietate, please refer to chapter 4.1.1.2.

Label	t_R	Name	Main mass fragments
P5	15.03	Pimarate	**121**, 241, 257, 301, 316
P6	15.18	Sandaracopimarate	**121**, 241, 301, 316
P12	15.56	Isopimarate	187, 227, **241**, 256, 287, 316
A5	15.59	Levopimarate	91, **92, 121**, 146, 187, 316
A9	15.87	Tetradehydroabietate (didehydroabietate)	197, **237**, 312
A10	15.89	Dehydroabietate	**239**, 299, 314
P14	15.89	Pimaric acid	91, 107, **121**, 133, 241, 287, 302
L27	16.08	Unidentified labdane acid, ME	79, 93, **121**, 161, 221, 290, 318, 350
D18	16.18	12-methoxy-podocarpa-8,9,12-trien-15-oate	159, 173, **227**, 239, 287, 302
A16	16.72	7-methoxy-dehydroabietate	195, **237**, 253, 312, 344
A18	16.78	Dehydroabietic acid	197, **239**, 285, 300
L34	16.80	Imbricatoloate	**121**, 161, 225, 276, 336
A19	16.85	7-methoxy-Δ6(7)-dehydrodehydroabietate coluates with L38	209, 227, **267**, 283, 327, 342
L37	16.86	Dihydroagathate, diME	79, 93, **121**, 161, 257, 304, 364
A21	17.15	Unidentified oxygenated abietane acid	227, **269**, 329, 344
A22	17.21	7-hydroxy-dehydroabietate	121, 195, **237**, 253, 297, 312, 330
A23	17.29	15-methoxy-dehydroabietate isomer	237, 269, 312, **329**, 344
A26	17.43	Unidentified	162, 195, **237**, 255, 283, 297, 330
A27	17.55	Δ16-demethyl-7-oxo-dehydroabietate (proposed)	155, 197, 211, **253**, 254, 299, 313, 314, 328
A28	17.51	15-hydroxy-dehydroabietate	255, 273, **315**, 330
A30	17.61	7-methoxy-dehydroabietic acid (proposed)	181, 195, **237**, 283, 298
L46	17.83	Imbricatoloic acid	81, **121**, 161, 221, 276, 322
A32	17.96	7-oxo-dehydroabietate	187, 211, **253**, 269, 296, 328
A36	18.16	Unidentified hydroxy-dehydroabietate, probably a dihydroxy-compound	181, 195, 211, **249**, 264, 309, 324
A37	18.34	15-methoxy-Δ6(7)-dehydro-dehydroabietate (proposed)	213, 237, 251, **267**, 311, 327, 342, 360
A38	18.39	Unidentified abietane	**187**, 225, 267, 285, 300
A39	18.45	15-hydroxy-dehydroabietic acid	131, 197, 237, 255, 283, **301**, 316
A40	18.65	7-oxo-Δ15(16)-dehydro-dehydroabietate	211, **251**, 266, 294, 326
L51	18.68	Dihydroagathic acid (proposed)	79, 93, 107, **121**, 161, 175, 290, 300, 318, 336
A41	18.85	Unidentified aging marker, oxygenated abietane	195, 211, **253**, 313, 328, **331**
A42	19.11	7-oxo-dehydroabietic acid	211, **253**, 299, 314
A43	19.12	Unidentified methoxy-dehydroabietate	59, 156, 212, 251, 255, 269, 312, **315**, 329
A44	19.35	Unidentified abietane	209, 239, 251, 253, **266**, 282, 310
A46	19.51	7-oxo-15-hydroxy-dehydroabietate	188, 269, **329**, (344)

Tab. 5.6 Compounds found in 1/13 “Tereb E Chio”, sample analysed with temperature program Diterpenes 1 and column A, mass spectra references see appendix

Discussion

The composition is typical for resins from *Pinus* species, which contain higher amounts of pimaric acid than sandaracopimaric acid. No marker molecules for *Larix*, *Abies* or *Picea* resins are present. The presence of dihydroagathic acid points to *Pinus* species from the section Pinea, for further details please refer to chapter 5.1.1 'Discussion'.

The chemical composition of 1/13 "Tereb. E Chio" is nearly identical to that of 1/8 "Terebin. Strasb." and 1/10 "Venice turpentine" (chapter 5.1.1 and 5.1.3). 1/10 is less aged than 1/8 and 1/13, because the analysed sample was taken from the bulk material and not from the dried-up residuals at the inner wall. 1/13 "Tereb. E Chio" is in an advanced aging state, only pimarane acids are still present in small amounts. The only not oxygenated abietane acid, levopimaric acid, is present in very small amounts. Levopimaric acid is also present in several other conifer "turpentines" from the Vigani Cabinet, (1/8, 1/9, 1/10, 1/11), for its formation please refer to chapter 4.1.1.1. 1/13 "Tereb. E Chio" contains high amounts of Pinaceae aging markers, particularly several derivatives of 7-oxo-dehydroabietic acid. 7-hydroxy- and 7-oxo-15-hydroxy-dehydroabietic acids are present in smaller amounts, together with other aging markers (A36, A43). 15-hydroxy-dehydroabietic acids are present only in small amounts, for a detailed discussion please refer to chapter 5.1.1.

1/13 "Tereb E Chio" shows a composition, which is different from that, which could be expected by its name. In the "Wood of Pilatre" several different coniferous resins were manufactured and particularly "chios turpentine" is mentioned to be adulterated there with the resins from "larch", "pine" and "fir" (Pomet 1717: 421; Lemery 1714: 841; Lemery 1721: 1116-7). A similar process is found for "venice turpentine" (chapter 5.1.3) and very likely for "strasburg turpentine" (chapter 5.1.1).

5.1.6 A/23 Pix Burgundica

Fig. 5.19 A/23 "Pix Burgundica"

Fig. 5.20 Sampling of A/23

Fig. 5.21 Sampling of A/23 (outer layer)

Fig. 5.22 Sampling of A/23 (inner layers)

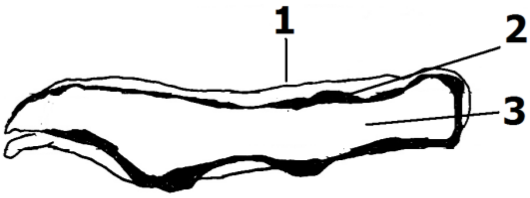


Fig. 5.23 Sketch of the area of fracture of the smaller lump, description of the numbers see text

Description

The box contains two lumps. A sketch was made of the smaller lumps (Fig. 5.23). Both lumps are covered with a brown to black crust (labelled 1 in Fig. 5.23, Fig. 5.21). They are broken and the interior is visible (2 and 3). It is of reddish to orange colour. The more outer layer (2) is transparent and red, the innermost layer (3) is opaque and yellowish to orange. The box additionally contains small lumps of black and red colour.

Sampling

A combined sample of all three layers was taken on 26 April 2007 (about 1 mg) (Fig. 5.20). On 30 March 2009, four samples were taken from the layers separately. From the black crust a brown powder with a sweet and sour smell was scraped (A/23a; Fig. 5.21). A small sample of layer 2 sticking out was split. It was dark orange to red with a sweet and sour smell (A/23b). The sample of layer 3 consisted of one harder part (surface, A/23c) and a still sticky and resinous smelling sample from the interior (A/23d). They were taken separately (Fig. 5.22). A/23c consisted of brown, transparent and brittle platelets with a sweet and sour smell. A/23d consisted of brown to yellow lumps with a resinous smell.

Vigani references

* MS Quns Vig. 2, verso, as "Burg pitch", 2 ounces at 1 penny

* LECTURE NOTES, UNDATED: 301

* LECTURE NOTES 1707: 84

Contemporary literature

Fine art materials

* SALMON 1701: 76, 835: "Burgundy Pitch"

Science

* DALE 1693: 395: "Pix Burgundica", "Burgundy or Burgony Pitch" ("*Picea or Abies rubra,* Common Fir or Pitch-Tree")

* POMET 1717: 428: "Poix blanche de Bourgogne", "Poix grasse" or "schmierichtes weißes Burgunder Pech" ("Fichte")

* LEMERY 1721: 888: "Poix de Bourgogne", "Pix Burgundica" or "Burgunder Pech" ("Fichte")

* JAMES 1747: 201, 403, 405: "Pix Burgundica", "Burgundy Pitch" ("*Abies tenuiori folio, fructu deorsum inflexo,* Common Fir"; "*Pinus Sylvestris* C.B., Mountain pine"; "*Pinus sativa* C.B., Pine Tree")

* GEOFFROY, THICKNESSE 1749: 237: "Pix Burgundiaca", "Burgundy Pitch" (product of "*Pinus sylvestris* C.B.")

* LEWIS 1761: 552: "Burgundy Pitch" ("*Pinus sylvestris* C.B., Wild Pine")

Encyclopaedias

* CHAMBERS 1728b: (818): "white Pitch", "Burgundy Pitch" ("pine, fir")

* SAVARY DES BRÛSLONS, SAVARY 1748b: 1428-9: "Poix grasse", "Poix blanche de Bourgogne" ("pine")

Terminology

In the terminology of the 17th and 18th century "pitch" may referred to pure resin or to heated melted or mixed products of conifers (Dale 1693: 395; James 1747: 402-5; Chambers 1728b: 818; Pomet 1717: 428; Lemery 1721: 888; James 1747: 403; Lewis 1761: 552; see also chapter 5.1.2):

> "Pix. Pitch. This is a Species of Gum obtained from the Pine Tree, by making Incisions in it. It receives different Names according to its different Preparations, Colour-, and Qualities. [..] The pinguious Pitch, which is, also called white Burgundy Pitch, is Galipot melted with Oil of Turpentine. Some however assert, that the Burgundy Pitch flows naturally from Resinous Trees, in the Mountains of Franche Comtè. Resin is, according to some Authors, a Gum discharged from the Turpentine Tree, The Larch Tree, The Mastich Tree, or the Cypress: But the Opinion of others is far more probable, who from Experience, assert, that it is Galipot, boiled to a certain Consistence, and reduced to a Mass of any determinate Weight" (James 1747: 405).

The term "pix burgundica" or "burgundy pitch" was used for a distillation or boiling product of the resinous balsam from "*Pinus Sylvestris* C.B." (Dale 1739: 303; James 1747: 402-3; Lewis 1761: 552; James 1764: 213), a melted mixture of different resinous products from pines, mainly the "pine-tree", "*Pinus Sativa* C.B." (Chambers 1728b: 818; James 1747: 405-6; Pomet 1717: 428; Lemery 1721: 888; Geoffroy, Thicknesse 1749: 237; James 1764: 212) or the solid product of the resin from the "pitch-tree" (Dale 1693: 395; James 1747: 201; Krünitz 1773: 85; Hahnemann 1799: 75).

The reference to Burgundy did not necessarily correspond with its geographical origin or manufacture, as stated by Pomet: according to legend, the best quality is made at St. Nicolaus in Lorraine, but in the 17th century a product of this name was smuggled to France from Holland and Strasbourg (Pomet 1717: 428). A French "burgundy pitch" was probably made initially in Burgundy or Lorraine (Lemery 1721: 888; Pomet 1717: 428; Savary des Brûslons, Savary 1748b: 1429), at the time of Vigani however this was no longer the case. Taking into account that the product was common known in England, even though without detailed information about its origin and manufacture, "pix burgundica" was a generic name for different coniferous resins and products thereof.

Botanical and geographical origin

"Burgundy pitch" is mainly mentioned by English authors, the entries are nevertheless short and partially confusing and tend to refer to each other (Dale 1693: 395; Dale 1739: 303; James 1747: 403; Lewis 1761: 552). It can be assumed that it was not commonly available in England. Other authors mention it as the boiled, melted and mixed product of the resin from different pine species (Pomet 1717: 428; Lemery 1721: 888; James 1747: 405; Geoffroy, Thicknesse 1749: 237), but also other conifers are mentioned (e 1693: 395; James 1747: 402-5; Chambers 1728b: 818; Pomet 1717: 428; Lemery 1721: 888; James 1747: 403; Lewis 1761: 552).

Manufacture and trade

The different preparation methods can be summarized as follows:

1. The "turpentine" from "*Pinus Sylvestris* C. B. " was cooked in water in large vessels or distilled with water until it has reached a specific consistency: solid but somewhat soft and not fully freed from its volatile content (James 1747: 402-3; Lewis 1761: 552; James 1764: 213). It was brought Germany to England (James 1747: 403; Lewis 1761: 552).

Vigani wrote in his *Lecture Notes* about "pix burgundica":

> "[..] but this inconvenience we observe that what remains in the alembic [after the distillation] is sold to the apothecary and passes for pix burgundiae, which they use in emplasters, unguents and the like, but it is to be considered that this resinous body, when deprived of its active spirit by the distillation, is of little or no virtue, and consequently you may suppose the compositions of which this is an ingredient to be less effectual than is to be expected" (Lecture notes 1707: 83f).

This resembles the description of a distillation by Dossie:

> "Distillation of oil of turpentine: Let the oil be distilled from the turpentine in a proper alembic; water being added to it: the caput mortuum, left behind will be white resin. Note: [..] Tar has been substituted, in the place of turpentine, for the obtaining this spirit; which is the same in both; and, in this case, the colophony, or caput mortuum, left after the distillation of the spirit, will be pitch instead of resin: but, to keep this pitch in a vendible state, it is proper not to rob it of too much of the spirit, which would render it of too dry and brittle in nature, for most purposes" (Dossie 1758b: 143-4).

2. A melted mixture of different resinous products from pines, mainly the "pine-tree" ("*Pinus Sativa* C.B."): A clear, white and dry sort of resin from "pines" was called "galipot" or "white rosin" particularly in France. It was melted with "oil of turpentine" and the resulting material was called "white burgundy pitch" (Chambers 1728b: 818; James 1747: 405-6). Other preparation methods used "galipot", "common turpentine" and "oil of turpentine" (Pomet 1717: 428; Lemery 1721: 888; Geoffroy, Thicknesse 1749: 237; James 1764: 212). At the end of the 17th century such products were brought from Strasbourg and Holland to France (ibid.), later they were produced also in France (Bayonne, Bordeaux) (James 1747: 407; Geoffroy, Thicknesse 1749: 236).

3. A solid product of the "pitch-tree", called "rosin of the pitch-tree" (Dale 1693: 395; James 1747: 201). Dale, who describes a number of different products of the "pitch-tree" ("white rosin", "tarr", "common pitch"), cites a traveller named David Kreig, who saw the production of "burgundy pitch" in Saxony (Dale 1739: 303). The manufacture of "burgundy pitch" as a distillation product is described by Dale:

> "[S]olam differentiam inter Resinam & Picem Burgundicam esse in coctione Picis Burgundicae, ex aheno exemptae, cùm primùm bullire incipit, atque idcircò mollior est, & coloris magis brunnei. Hoc [David Kreig] observavit in saxonia solo suo natali" (Dale 1739: 303).
>
> "The only difference between the Burgundy resin and the pitch is that Pix Burgundica is cooked , from [??] removed, as it begins to boil, until it becomes somewhat soft, and has a more brown colour. [David Kreig] observed this in Saxony at his birthday" (own translation)

Salmon mentions a "white rosin", a white and clear sort of "rosin", which is worth about five to six pence a "pound" (Salmon 17101: 858f), which corresponds with the price from the invoices for "Burg pitch" (MS Quns Vig. 2, verso).

According to Geoffroy, incisions are made in the "*Abies*", which is also used for the production of "strasburg turpentine" (see chapter 5.1.1). They are three fingers broad and made every four inches. After some years of exuding they are filled with a thick resin, which is used by Germans to make a kind of pitch by melting it in furnaces (Geoffroy, Thicknesse 1749: 235). This material is not called "burgundy pitch" by Geoffroy but the description resembles that of other authors.

Properties

"Pix burgundica" is described as a resinous solid and somewhat soft material, of a brown to red colour and of an agreeable smell (Dale 1693: 395; James 1764: 212). The melted "galipot" was white and yellowish, dry, clear and solid (Lemery 1717: 888; James 1747: 406). "Burgundy pitch" of lesser quality was thicker, whiter and with a more intense smell (Pomet 1717: 428-9; Savary des Brûslons, Savary 1748b: 1429).

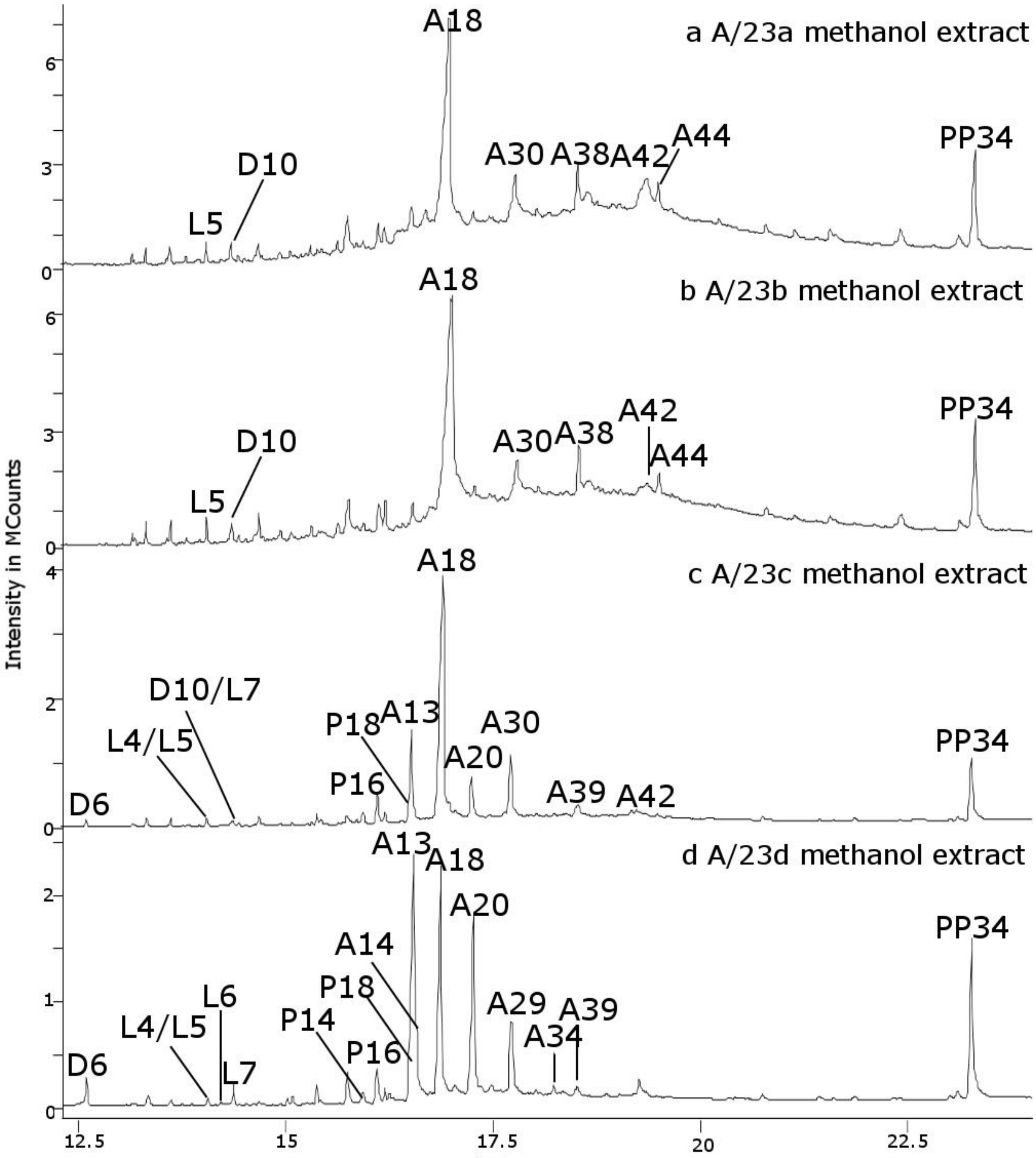
Possible chemical composition

"Pix burgundica" or "burgundy pitch" is used today for melted resins from *Picea abies* Karst., however detailed descriptions of its botanical origin and manufacture are rare. Some descriptions resembles the historical ones of "galipot" or "white incense" (Pitthard et al. 2011; Kremer 2011; Scents of Earth 2012; see also chapter 5.1.2). Other species mentioned in historical sources are *Pinus sylvestris* L. and *P. pinea* L. (Linné 1753b: 1000). The latter is native mainly to coastal region of the Mediterranean area (Euforgen 2008d). A material made from any of these resins should be composed of pimarane and abietane acids, which are typical for resins from the Pinaceae, and their aging products. Literature data are not detailed enough to provide a clearer picture (Pitthard et al. 2011; see also chapter 2.1.1).

For this investigation three modern reference samples of Burgundy pitch or Burgundy resin were analysed, with the results presented in chapter 4.1.1.2. They are composed of pimarane and abietane acids and their aging products. Main compound is dehydroabietic acid, but not isomerised abietane acids, mainly palustric and abietic acids, are still present. All samples are made from pines, because they contain more pimaric than sandaracopimaric acid. Additionally, only small amounts of *iso*-abienol, Δ13-*cis*-neoabienol and D10 are present. Oxygenated abietane acids are present in medium but equal amounts from all oxidation states (see Fig. 2.4). Light aging markes identified in this work in light-aged Pinaceae resins are present only in older samples, which include several compounds reported by Pitthard et al. (Pitthard et al. 2011).

Chemical analysis

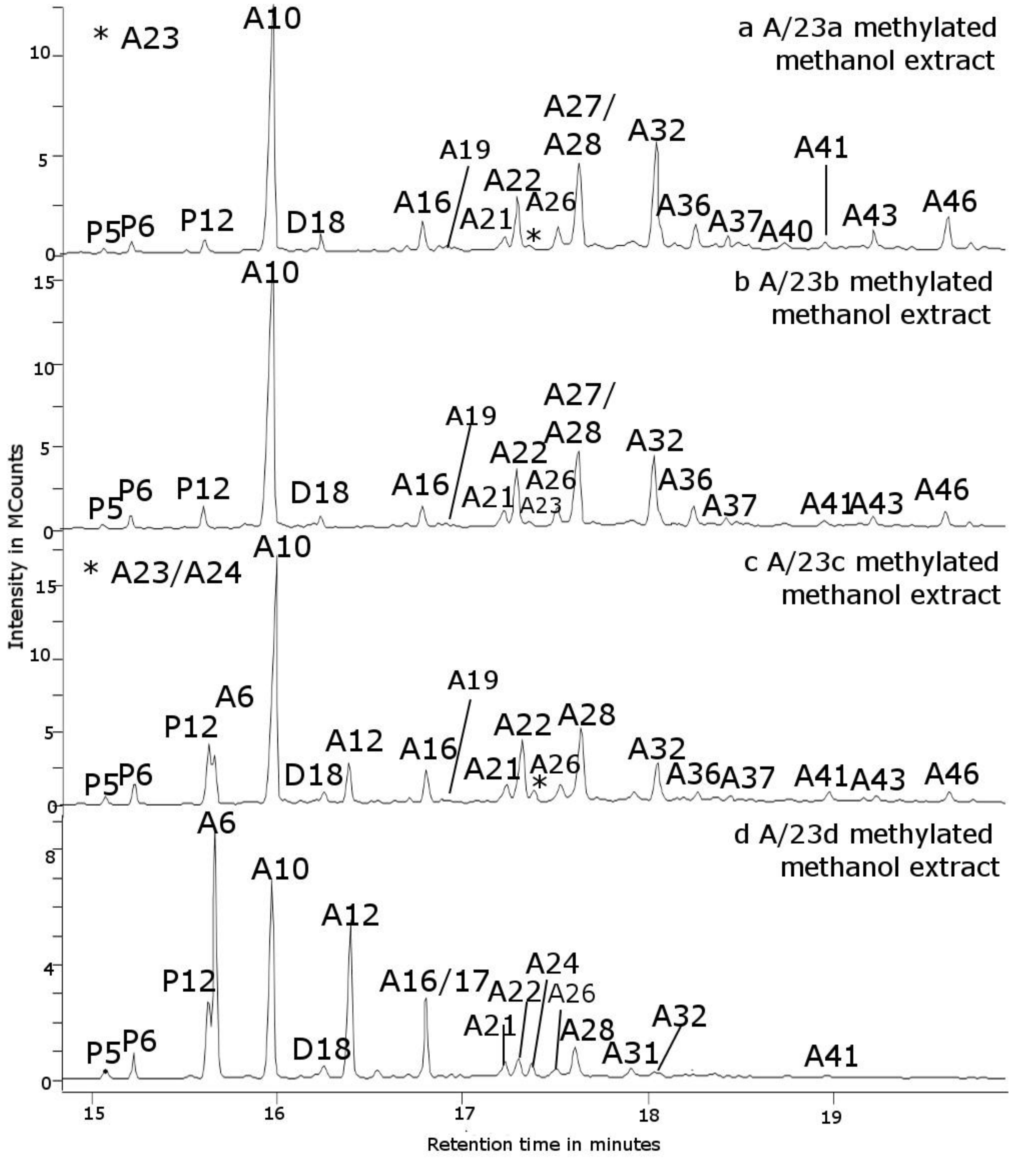
The composition of the different layers varies very much. The methanol extracts of samples A/23a and A/23b from layer '1' and '2' (Fig. 5.24a, b) contain mainly dehydroabietic acid. No other abietane and pimarane acids are present. Aging markers are 7-methoxy- and 7-oxo-dehydroabietic acids as well as unidentified compounds A38 and A44. The methanol extracts of the samples A/23c and A/23d from layer '3' (Fig. 5.24c, d) contain sandaracopimaric, isopimaric, palustric, dehydroabietic, abietic acids, A/23d also pimaric, levopimaric and neoabietic acids. A/23c and A/23d contain small amounts of 15-hydroxy-dehydroabietic acids, A/23c also 7-methoxy- and 7-oxo-dehydroabietic acids. The outer layer (A/23a) contains



Methanol extracts, a – A/23a layer 1, b – A/23b layer 2, c – A/23c layer 3 dried up, d – A/23d layer 3 sticky (labels, see table 5.7)

Fig. 5.24 Gas chromatograms of A/23 "Pix Burgundica" from the Vigani Cabinet, diterpene section (TIC) mainly dehydroabietic acid and oxidised abietane acids. Isomerisation and oxidations decrease inwardly. The composition of A/23d is very similar to an unchanged resin.

A/23a and A/23b contain *iso*-abienol and D10, the inner layers additionally cembrene, Δ13-*trans*-neoabienol, abienol and cis-abienol. All layers contain eudesamin (PP35).



Methylated methanol extracts, a – A/23a layer 1, b – A/23b layer 2, c – A/23c layer 3 dried up, d – A/23d layer 3 sticky (labels, see table 5.7)

Fig. 5.25 Gas chromatograms of A/23 “Pix Burgundica” from the Vigani Cabinet II, diterpene section (TIC)

Label	tR	Name	Main mass fragments
D6	12.61	Cembrene	79, **93**, 105, 119, 145, 229, 257, 272
L4	14.08	Δ13-*cis*-neoabienol	81, 95, 107, 121, **177**, 191, 290
L5	14.04	iso-Abienol	81, 95, 109, **191**, 217, 235, 255, 272, 290
L6	14.23	Abienol	81, 95, 109, **191**, 217, 235, 255, 272, 290
D10	14.34	Unidentified	81, 95, **109**, 121, 161, 177, 217, 234, 245, 278
L7	14.37	*cis*-Abienol	81, 95, **119**, 134, 163, 191, 257, 272, (290)
P5	15.11	Pimarate	**121**, 241, 257, 301, 316
P6	15.24	Sandaracopimarate	**121**, 241, 301, 316
P12	15.62	Isopimarate	187, 227, **241**, 256, 287, 316
A6	15.67	Palustrate	**241**, 301, 316
P14	15.92	Pimaric acid	91, 107, **121**, 133, 241, 287, 302
A10	15.98	Dehydroabietate	**239**, 299, 314
P16	15.98	Sandaracopimaric acid	91, 107, **121**, 133, 241, 287, 302
D18	16.07	12-methoxy-podocarpa-8,9,12-trien-15-oate	159, 173, **227**, 239, 287, 302
A12	16.39	Abietate	185, 213, **241**, 256, 273, 316
P18	16.49	Isopimaric acid	91, 105, 131, 159, 187, 227, **241**, **287**, 302
A13	16.55	Palustric acid	91, 133, 159, 187, 213, 241, **287**, 302
A14	16.58	Levopimaric acid	**92**, 105, 131, 146, 187, 302
A16	16.79	7-methoxy-dehydroabietate	195, **237**, 253, 312, 344
A17	16.78	Neoabietate	121, **135**, 301, 316
A18	16.84	Dehydroabietic acid	197, **239**, 285, 300
A19	16.91	7-methoxy-Δ6(7)-dehydrodehydroabietate	209, 227, **267**, 283, 327, 342
A20	17.15	Abietic acid	105, 131, 185, 213, 241, 259, 287, **302**
A21	17.21	Unidentified oxygenated abietane acid	227, **269**, 329, 344
A22	17.18	7-hydroxy-dehydroabietate	121, 195, **237**, 253, 297, 312, 330
A23	17.30	15-methoxy-dehydroabietate isomer	237, 269, 312, **329**, 344
A24	17.30	Oxygenated 7,13,15-abietatrien18-oate	121, 183, 239, **254**, 299, 314, 315, 329, 330
A26	17.48	Unidentified	163, 195, **237**, 255, 283, 297, 330
A27	17.65	Δ16-demethyl-7-oxo-dehydroabietate (proposed)	155, 197, 211, **253**, 299, 313, 328
A28	17.66	15-hydroxy-dehydroabietate	255, 273, **315**, 330
A29	17.58	Neoabietic acid	91, **135**, 148, 187, 241, 287, 302
A30	17.67	7-methoxy-dehydroabietic acid (proposed)	181, 195, **237**, 283, 298, 330
A31	17.73	Unidentified abietane	107, 147, 229, 239, **289**, 331, 346
A32	18.00	7-oxo-dehydroabietate	187, 211, **253**, 269, 296, 328
A34	18.23	Unidentified	91, 134, 185, 239, 254, 285, **300**
A36	18.38	Unidentified hydroxy-dehydroabietate, probably a dihydroxy-compound	181, 195, 211, **249**, 264, 309, 324
A37	18.41	15-methoxy-Δ6(7)-dehydro-dehydroabietate (proposed)	213, 237, 251, **267**, 311, 327, 342, 360
A38	18.52	Unidentified abietane	**187**, 225, 267, 285, 300
A39	18.54	15-hydroxy-dehydroabietic acid	131, 197, 237, 255, 283, **301**, 316
A41	18.91	Unidentified aging marker, oxygenated abietane	195, 211, **253**, 313, 328, **331**
A42	19.13	7-oxo-dehydroabietic acid	211, **253**, 299, 314
A43	19.38	Unidentified methoxy-dehydroabietate	59, 156, 212, 251, 255, 269, 311, **315**, 329, 343, 358
A44	19.50	Unidentified abietane	209, 239, 251, 253, **266**, 282, 310
A46	19.55	7-oxo-15-hydroxy-dehydroabietate	188, 269, **329**, (344)
PP35	23.36	Eudesamin	151, **165**, 177, 219, 355, 386

Tab. 5.7 Compounds found in A/23 “Pix Burgundica”, samples analysed with temperature program Diterpenes 1 and column A, mass spectra references see appendix

In the methylated methanol extract of the outer layers (A/23a, A/23b) (Fig. 5.25a, b) the main compound is dehydroabietate, together with C-7 oxygenated dehydroabietates (A16, A22, A27, A32) and C-15 oxygenated dehydroabietates (A23, A28). Other constituents are 12-methoxy-podocarpa-8,9,12-trien-15-oate (D18), 7-methoxy- and 15-methoxy--Δ6(7)-dehydrodehydroabietate (A19, A37), A21, A26, A36, A41, A43 and 7-oxo-15-hydroxy-dehydroabietate. A/23a also contains A40. A36 is probably a dihydroxy-dehydroabietate, A43 a methoxy-dehydroabietate, please refer to chapter 4.1.1.2. Small amounts of pimarate, sandaracopimarate and isopimarante are present.

The methylated methanol extracts of the inner layer (A/23c, A/23d) (Fig. 5.25c, d) are composed different. A/23c is composed similar to A/23b. The relative amounts of A32, A36, A37, A43 and A46 are decreased, while A27 is not present. Additonally palustrate and abietate are still present. A/23d contains mainly palustrate, dehydroabietate, abietate and also medium amounts of neoabietate. Smaller amounts of several aging markers are present as well, particularly 7-hydroxy-dehydroabietates and their derivatives (A16, A22) and 15-hydroxy-dehydroabietate (A28). Smaller amounts of 7-oxo-dehydroabietate and D18, A21, A24, A26, A31 and A41 are present as well.

All layers contain more sandaracopimarate than pimarate. In summary, the changes in the compostions from inside to outside are similar in the methanol and the methylated extracts. The isomerisation and from A/23c on also oxidation increases. The inner layer ‘3’ contain higher amounts of C-15-oxygenated dehydroabietates, the outer layers ‘1’ and ‘2’ of 7-oxo-dehydroabietates and the light aging marker A27, A36, A37 and A43, which are not present in the sticky sample from the inner layer (A/23d).

Discussion

The composition is typical for a *Picea* resin, which contains higher amounts of sandaracopimaric than pimaric acid. The aging state is strongly dependent on the sampled layer, but the ratio of pimaric and sandaracopimaric acid is constant in all layers and points to a *Picea* species. The presence of cembrene, Δ13-*cis*-neoabienol, abienol and *cis*-abienol indicate the resin of *Picea abies* Karst., which shows the same composition of neutral diterpenes and alcoholic labdanes. D10 is present only in the outer layers and the dried-up sample from the inner layer, for which reason it is probably no original constituent.

The inner parts are composed very similar to modern Burgundy pitch, which is produced by heating and melting at lower temperatures (see chapter 4.1.1.2). From its appearance, A/23 "Pix Burgundica" was obviously heated, whether by Vigani or by the supplier of the material is unclear. The treatment resulted in solidification and change in colour. The production process, however, did not heat up all parts of the resin in the same manner, which resulted in the formation of different coloured layers. Taken into account the appearance of the outer layer, the resin was probably heated very short at high temperatures. During this process the inner parts were not heated up strongly and the composition was modified only moderately.

The sticky part of the orange inner layer (A/23d) can therefore be considered to be as near as possible at the composition of the original resin. Only small amounts of oxygenated abietane acids are present, but, more important, the high amounts of palustric, abietic and neoabietic acids indicates a low isomerisation state, which is nearly identical to that of some month old untreated botanical resins analysed in the reference section (chapter 4.1.1.1). None of the light aging markers (A27, A36, A37, A43) are present. The dried-up part of the orange inner layer (A/23c) shows a much more advanced isomerisation state and slightly increased amounts of oxygenated abietane acids. It contains small amounts of light aging markers. Its composition resembles that of other less aged Pinaceae resins from the Cabinet (1/10 "Venice Turpentine", 1/11a "Venic. Turpent.", chapter 5.1.3, 5.1.4). The thin red layer (A/23b) and the black crust (A/23a) are nearly identical in composition, with mainly dehydroabietic acid, medium to high amounts of oxygenated abietane acids and significant amounts of light aging markers A27, A36 and A43. 15-dehydroabietic acid, which is present in the inner layer in significant amounts, is nearly absent. This supports the observation made for the other Pinaceae resins in the Cabinet: C-15 oxygenated dehydroabietic acids are intermediates, formed at the beginning of the aging process. They are further oxygenated to dihydroxy-dehydroabietic acids (A36). When the aging process proceeds, the C-7 position is preferred to the C-15 position and mainly 7-hydroxy- and 7-oxo-dehydroabietic acids are formed. Small amounts of C-7 and C-15 oxygenated tetradehydroabietates (A19, A37) are present in all samples exposed to light (A23a-c).

It is noticeable that the composition of the sticky sample from the inner layer (A/23d) differs slightly more in the isomerisation and oxidation state from the dried-up part of the same layer (A/23c) than the composition of the red layer (A/23b) from that of the black surface crust (A/23a). Also, the outer layer A/23a, which consisted of a black and brittle powder, is composed nearly identical to that of dried-up samples (1/8, 1/9, 1/13). It seems reasonable to assume that aging after the original treatment contributed more to the actual compostion of the layers exposed to air and light (A/23a-c) than the original treatment. This is supported by the composition of the sticky part from the inner layer (A/23d), which is less aged compared to the sticky samples taken from 1/10 and 1/11b. It is known from literature that (polar) solvents enhance the oxidation of the abietane acids (Enoki 1976). It is possible that the brief heating of the material was sufficient to remove enough of the monoterpenes in the fresh resin to decrease the isomerisation and oxidation rate.

5.1.7 A/26 Sandaracha

Fig. 5.26 A/26 "Sandaracha"

Fig. 5.27 Sampling of A/26

Description

The box is filled with different shaped longish lumps in a deep orange colour. They have a powdered surface. They are hard, slightly brittle, and nearly odourless.

Sampling

A sample of one lump of about 130 mg was taken on 26 April 2007 (Fig. 5.27). It was yellow tear with a powdered surface and a clear and transparent interior.

Vigani references

* Probably in MS Quns Vig. 4, folio 3, verso: as "Gum Juniper", 2 ounces at 4 pence

* Does not appear in LECTURE NOTES UNDATED

* Does not appear in LECTURE NOTES 1707

Contemporary literature

Fine art materials

* DALE 1693: 401: "Gummi Sandaracha Arabum"

* POMET 1717: 143, 433: "arabische Sandaraca und Vernix"

* SALMON 1701: 68: "Gum of Juniper"; ibid. 867f, 872-4: "Gum-Sandarack"

* JAMES 1764: 227: "Sandarach"

* DOSSIE 1758a: 160, 211-4: "Sandarac"

* CARLYLE 2001: WILLIAMS 1787: 51, 52 (adulterant for mastic); TINGRY 1804: 20 (adulterant for mastic); ANON. 1808: 77

Science

* DALE 1693: 401: "Gummi Sandaracha Arabum" ("*Juniperus vulgaris fruticola* C.B., Juniper Tree")

* POMET 1717: 143: "arabische Sandaraca und Vernix", "truckne Vernix" ("Great Juniper"); "wahrhafte Sandaraca" ("small cedar or oxycedrus")

* LEMERY 1721: 265-6, 1174: "Vernix" ("*Cedrus Lycia* J.B., *Oxycedrus Lycia* Dod. Ger".); 587, 1174: "Sandaracha Arabum" ("*Juniperus Vulgaris Arbor* C. B., Great Juniper")

* GEOFFROY 1743: 75-82: "Sandaraque", "Vernix", "Gome ou Résine de Genévrier", "Sandaracha", "Gummi Juniperum", "Κομμs Αρχευϑιδος" ("*Juniperus vulgaris arbor* C.B.P., *Oxycedrus Lycia* Dod.")

* JAMES 1747: 347, 429: "Gum-Sandarac of the Arabians" ("*Juniperus vulgaris fruticola* C.B."); "Sandaracha", "Vernix Arabum" ("*Cedrus Lycia major* Dodon.")

* HILL 1751: 737f: "Resina Sandaracha", "Sandarach Resin" ("*Juniperus Arbor* & *Oxycedrus Lycia* Dodon.")

* LEWIS 1761: 324: "Sandaracha", "Gummi juniperum" ("*Juniperus vulgaris fruticola* C.B.")

Encyclopedias

* CHAMBERS 1728b: 19: "Sandarach" ("great Juniper-Tree"); "Sandarach of Oxycedron"

* SAVARY DES BRÛSLONS, SAVARY 1748c: 29(2)-30(2), 661: "Sandaraque" ("grand Genévre"); "Sandarac" ("Oxicedre")

Terminology

The term "sandarac" or "sandaracha" is connected to two different groups of materials (Wagner 2007c: I/31). First there is a connection to red pigments as realgar or minium, the Greek term σανδαραχη (= sandarach) means realgar or red arsenic (Coles 1685; Harris 1704: sandaracha; James 1747: 429). Secondly, the term is used by authors contemporary to Vigani for the resin of different trees. To distinguish "sandarac(h)a" for the pigment from the resin the two materials were called "sandaracha arabum" (resin) and "sandaracha graecorum" (pigment) (Dale 1693: 401; Pomet 1717: 143; Lemery 1721: 1174; James 1747: 429; Dale 1735: 26; Lemery 1721: 948; James 1747: 429). The different meanings originate from the Persian root *sand or *sant(a), which is attributed to different plant materials, resins and dye stuffs (Flattery, Schwartz 1989: 142). Tschirch mentions the origin of the word from Sanskrit "sandhyaruc" meaning the sunset (Tschirch 1935b: 536). It was assumed that the term was connected to resins by the Arabs (Wagner 2007c: I/31; Tschirch 1935b: 557), while the reference to the pigment is notably older (Dioscorides, Ruel 1552: 758). The resin was called "sindarus" or "sandarûs" by the Arabs. That term did not necessarily refer only to the resin of the North African Sandarac cypress but also to different "copals" from Africa or Zanzibar traded over Arabian ports (Langenheim 2003: 397; Al-Sulami 2004: 63[6]; Regert et al. 2008). The Arabian name was possibly transferred during their reign in North Africa to a similar resin obtained there. By the time of Vigani most of the western ports of the North-African territory were held by the Portuguese, who used to call that resin "glassa" or "vernix" (Merrifield 1967: 114-115). Merrifield additionally mentions the Spanish "el grassa" or "grasilla" for the resin (Merrifield 1967: ccliii). "Glassa" was a collective term, which was used for amber as well.

Botanical and geographical origin

In the 17th century, mainly juniper species are mentioned as the botanical source of a resin called "sandarach(a) (arabum)". The "small juniper" or "*Juniperus vulgaris fruticola* C.B." was connected with "sandaracha arabum" (Dale 1693: 401; James 1747: 347; Lewis 1761: 324) (Fig. 5.28a). It was thought, though native to all of Europe, to yield the resin only in hot areas (James 1764: 175). It was imported to England, mainly under its trading name "juniper gum". The "small juniper" is also listed by Lemery and Pomet with its French common name "genevrier" or "Wacholder" in the German translation (Pomet 1717: 144; Lemery 1721: 586). The botanical name of this tree "*Juniperus vulgaris fruticola*" was derived from Bauhin (Bauhin 1623: 488), and it was classified as *Juniperus communis* by Linné (Linné 1753b: 1040).

Another juniper species as the source of "sandaracha arabum”, the "Juniperus arbor", "great juniper" or "*Juniperus vulgaris Arbor* C.B.", is mentioned primarily by the French authors, and, from the 30’s of the 18th century on, also in England (Pomet 1717: 143f; Lemery 1721: 588, 1174; Hill 1751: 737). It is described as very similar to the "small juniper", only differing from it in height. It grew in Spain, Italy and Africa (Pomet 1717: 143; Lemery 1721: 588, 1174; Hill 1751: 738). Listed also by Bauhin as one of the various juniper species, it was classified by Linné as *Juniperus communis*, too (Bauhin 1623: 500; Linné 1753b: 1040). Because the common juniper can grow to different height, the "small juniper" and the "great juniper" are probably the same tree.

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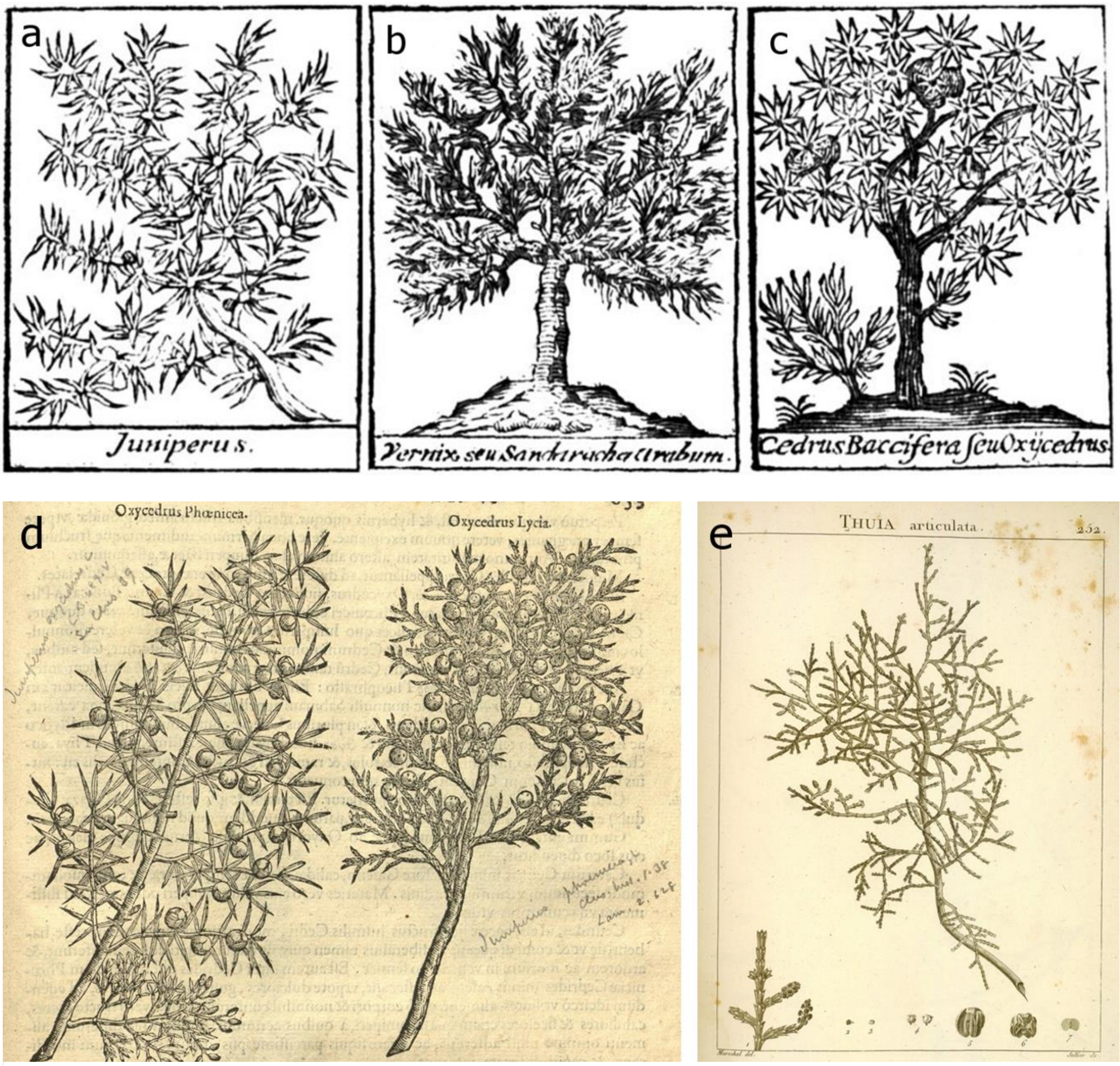
[6] Al-Sulami mentions "sandarac" as a resin, which is dug from the earth. This probably refers to Zanzibar copal (see chapter 5.3.3).



a - "small juniper" (Lemery 1721: 587), b- the botanical source of "vernix" (Lemery 1721: 1174), c - "Cedrus Baccifera" or "Oxycedrus" (Lemery 1721: 266), d - "Oxycedrus Phoenicia" (left) and "Oxycedrus Lycia" (right) (Dodoens 1616: 853) and e - "Thuia Articulata", the source of "sandaraque" (Desfontaines 1799: Tab. 252)

Fig. 5.28 Historical trees mentioned in connection with "sandaracha"

The "small juniper" is described as widespread, and its branches, leaves and berries were used for different pharmaceutical and food purposes (Dale 1693: 401; James 1747: 347; Lewis 1761: 324). It grew "in erectis agri Cantiani, Effexiensis, & alibi in Anglia copiosé" (Ray 1690: 214). The "great juniper" grew particularly in hot areas, in Spain, Italy and Africa (Pomet 1717: 143; Lemery 1721: 588; Hill 1751: 738).

In Fig. 5.28b, the botanical source of "vernix or sandaracha arabum" is shown (Lemery 1721: 1174). From the text it is not clear whether it is the mentioned "great juniper" or another tree called "small cedar" or "oxycedrus". That "small cedar" (Fig. 5.28c) is mentioned from the beginning of the 18th century on. It is the source of the "vrai sandaracha" or "gomme qu’on appelle Vernix" and "sandarach of oxycedron", to differentiate it from the resin obtained from "junipers" (Pomet 1717: 143; Lemery 1721: 265f; Chambers 1728b: 19; James 1747: 429; Hill 1751: 738). The "vernix" is described to be superior to the resin from "junipers" but also to very rare (Pomet 1717: 141, 143; Lemery 1721: 1174; Geoffroy 1743: 76). The "*oxycedrus*" grew in Italy, Spain, Provence and Languedoc (Lemery 1721: 266).

It is noticeable that the two trees in Fig. 5.28b and Fig. 5.28c look different, the "oxycedrus" of Lemery additionally have different leaves in the big and the small bush. Dodoens describes two different species of "oxycedrus" (Fig. 5.28d), "*Oxycedrus Lycia*" and "*Oxycedrus Phoenicea*", which similarly have different shaped leaves (Dodoens 1616: 852f). Dodoens describes it as very similar to junipers, Bauhin and Lemery mention that its leaves are similar to cypress' (Dodoens 1616: 852; Bauhin 1623: 487; Lemery 1721: 265). The reason for these different descriptions may be the different appearance of young (needle-like) and adult (scale-like) leaves of *Juniperus* trees, even though the tree in Fig. 5.28c has needle-like leaves in the bigger hence older part of the tree. Nevertheless, the Sandarac cypress has scale-like leaves as well. Because the Sandarac cypress was not known (see below), the differing shaped trees may be a Sandarac cypress described under the wrong name or another species, particularly from junipers or cypress.

Neither Dodoens nor Bauhin mention the "*Oxicedrus Lycia* Dodoens" in connection with a resin or "sandarac". In contrary, Dodoens lists "sandaracha, arabian", "sandarax" or "vernix" as synonyms of "lacryma juniperi" in the chapter about junipers (Dodoens 1616: 852). It is not known by whom and at which time "the small cedar" was connected to "sandaracha". "*Oxycedrus Lycia* Dodo." grew in France near Marseilles, Greece and "Asia Minor" (Dodoens 1616: 853). Lemery mentions Italy, Spain, Provence and Languedoc (Lemery 1721: 266)[7].

In the middle of the 18th century, Thomas Shaw described after travelling North Africa a tree he called "*Cupressus fructu quadrivalvi*". This tree was later classified as "*Thuia Articulata*" by Vahl, a student of Linné (Vahl 1791: 96). It is also mentioned by Linné as "*Thuia cupressoides*" (Linné 1767: 125). The "sandaraque" resin was connected to that tree 1799 by Desfontaines, who cited Broussonet, another Africa traveller (Desfontaines 1799: 353, Fig. 5.28e). The tree grew in the Atlas mountains and in uncultivated hills. The resin flows from the tree and is traded in the Kingdom of Morocco (Desfontaines 1799: 353).

By the middle of the 19th century mainly "*Thuia Articulata*" or synonymously "*Callistris Quadrivalis* Vent." are mentioned as the source of sandarac, however occasionally attributions to *Juniperus Communis* L. occurred (Krünitz 1824: 74; Pereira 1842: 1070). By the end of the 19th century it became clear that the Sandarac cypress was a monotypic genus. It was classified as *Tetraclinis articulata* by Masters (Masters 1893).

Manufacture and trade

The trunk and the branches of the "great juniper" are wounded by the inhabitants, and during great heat the resin poured out. The resin is traded over Sweden, England and Hamburg

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[7] The two "*oxycedrus*" species of Dodenens are called "*Oxicedrus Lycia*" and "*Oxycedrus Phoenicea*" (Fig. 5.28d), the latter is not mentioned in connection with "sandarac" (Dodoens 1616: 852). However, Dodoens describes it to yield a mastic-like resin. Both species are mentioned by Bauhin, the Lycian named "*Cedrus folio cupressi major fructu flavescente*" and the Phoenician "*Juniperus major baccâ rusescente*" (Bauhin 1623: 487, 489). The Lycian species was classified by Linné as *Juniperus Phoenicia* L., the Phoenician as *Juniperus Oxycedrus* L., called prickly cedar (despite being a juniper), which is mentioned by Culpeper as the source of (juniper) tar (Culpeper 1814: 271; Linné 1753: 1038). Another "small cedar", the "*Cedrus folio cupressi media majoribus baccis* C.B.", was classified by Linné as "*Juniperus Lycia*" (Linné 1753bn: 1039-40). This confusion of geographic origins and botanical genera is probably the reason Hahnemann lists "*Juniperus Lycia* L." as the source of "sandaracha" (Hahnemann 1799: 120), even though this species is never mentioned in connection with "sandarac". There is reason to believe that Hahnemann confounded "*Juniperus Lycia* L." with "*Oxycedrus Lycia* Dodo."

(Pomet 1717: 143; Savary des Brûslons, Savary 1748c: 30(2)). Resin from that tree was used as a substitute of "sandarach(a)" from the "oxycedrus" (Pomet 1717: 141, 143; Lemery 1721: 1174).

The resin of the "*Thuia Articulata*" flows from the tree and is traded in the Kingdom of Morocco (Desfontaines 1799: 353).

According to Geoffroy, the "great juniper" as well as the "*Oxycedus Lycia*" are sources of "sandaraque", which was brought from the coast of Africa to Marseilles (Geoffroy 1743: 75-82). Salmon mentions the "Barbary" as the origin of the (botanical unspecified) "gum-sandarack", which costs 12 pence a pound (Salmon 1701: 858), which is only half the prize Vigani paid for the "Gum Juniper" (MS Quns Vig. 4, folio 3, verso).

Properties

"Sandarac" is described as drop-shaped or in the form of longish tears, transparent, semi pellucid, pale and of white or yellow colour. It is dry, solid and brittle, arid and of acrid, aromatic taste and resinous smell (Dale 1693: 401; Pomet 1717: 144; Hill 1751: 737). Hill mentions that the resin obtained from the "oxycedrus" is more fragrant, especially when burnt (Hill 1751: 737). It is not soluble in water but in oil or spirit of wine (Geoffroy 1743: 76).

Possible chemical composition

Today, sandarac is obtained from the Sandarac cypress, *Tetraclinis articulata* Mast. This species and its basionyms were seemingly unknown in Europe at the time of Vigani, and the tree described by Shaw was connected not until the end of the 18th century to a material called "sandarac(ha)" (Vahl 1791: 96; Desfontaines 1799: 353).

According to the historical sources, the "great juniper" grew in Spain, Italy and Africa (Pomet 1717: 143; Lemery 1721: 588; Hill 1751: 738), which makes it the probable candidate for the contemporary name of the Sandarac cypress. The "small juniper", which is probably *Juniperus communis* L., yields only small quantities of resin, which would indicate that it was used only occasionally. Due to its connection to the contemporary "vrai sandaracha" "*Oxycedrus (Lycia* Dodo.)" cannot be excluded, although its geographical origin (South France, Itlay, Greece and "Asia Minor" (Dodoens 1616: 853; Lemery 1721: 266)) does not match with that of the Sandarac cypress. The description of contemporary junipers and cypress' are so confusing that it is not possible to assign them to modern species for sure. Whether "juniper gum" was just a trading name or whether juniper resin was really used as a substitute for the real "sandarac" cannot be said based on the information in the historical sources. From a chemical point of view, resins from the subfamilies of *Cupressoideae* (see Fig. 2.5) are very difficult to distinguish, also because more detailed chemotaxonomical data on resin composition are unavailable. They contain mainly sandaracopimaric, communic and several C-19 and C-15 oxygenated labdanes (Mills, White 1977; Hegnauer 2001: 493; van den Berg et al. 2002; Cox et al. 2007; see also chapter 2.1.2).

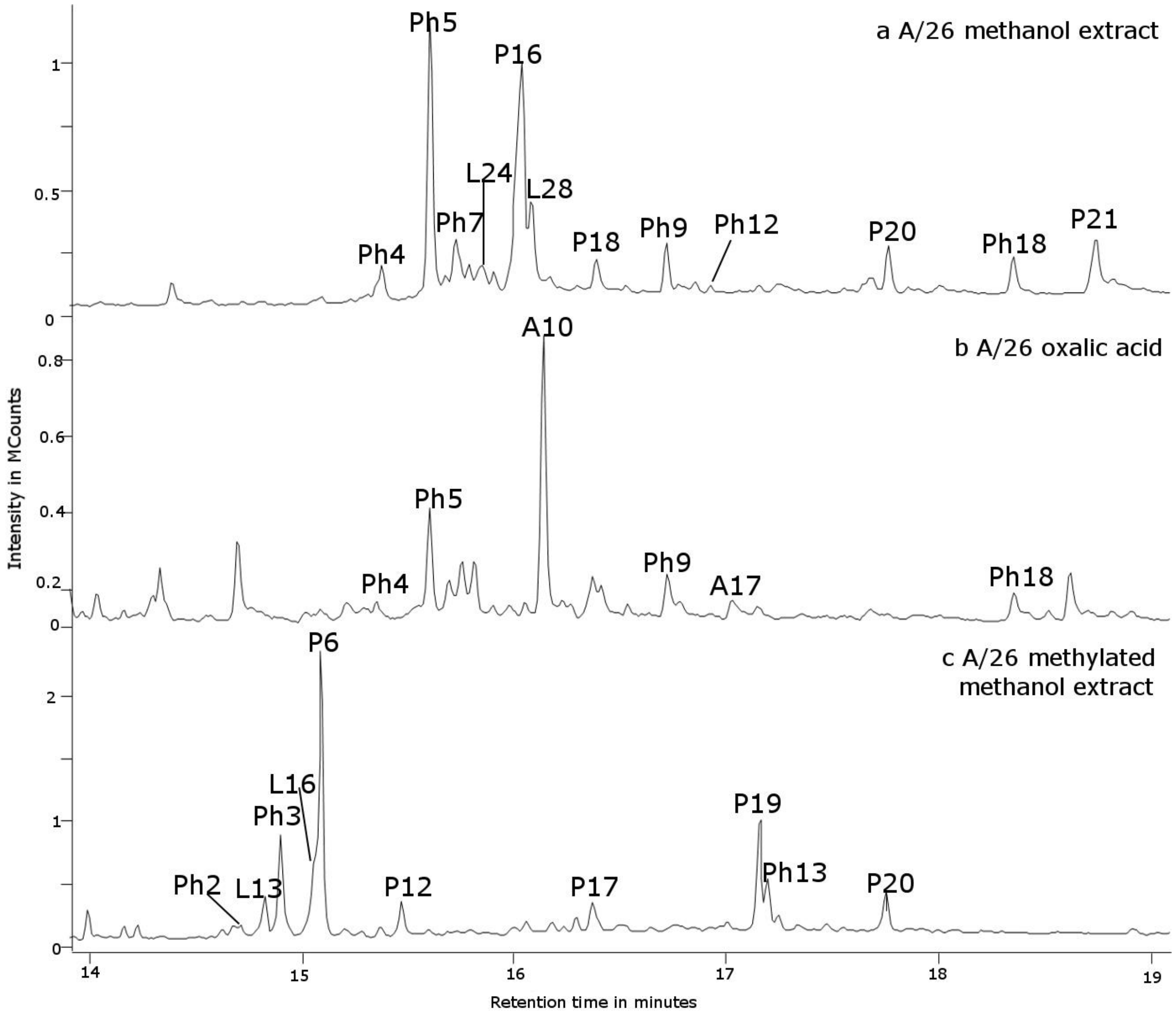
Different commercial reference samples called sandarac, two botanical samples from *Tetraclinis articulata* Mast. and one from *Juniperus communis* L. were analysed for this investigation, with the results presented in chapter 4.1.2. Resins from *Tetraclinis articulata* Mast. and *Juniperus communis* L. can be distinguished by the presence of oxygenated sandaracopimaric acids (hydroxy- and 12-acetoxy-sandaracopimaric acids) and small amounts of (dehydro)abietic acids, which are present in the resin of *Tetraclinis articulata*. The presence of the phenolic abietatrienes is not sufficient for an unambiguous identification of true sandarac, although the resin from *Tetraclinis articulata* Mast. shows a typical distribution of the phenolic makers. High amounts of sandaracopimaric, communic and the presence of phenolic abietatrienes such as totarol, ferruginol, sugiol but also hinokinol and several others are present in both resins.

Chemical analysis

In the methanol extract (Fig. 5.29a), compound Ph4, totarol, ferruginol, totarolone, compound Ph9 and sugiol are present. The sample contains *cis*- and *trans*-communic, isopimaric, sandaracopimaric, 12-acetoxy-sandaracopimaric acids and 12-acetoxy-sandaracopimarate. Main compounds are totarol and sandaracopimaric acid. The prominent presence of sandaracopimaric acid in relation to communic acids is a consequence of the polymerisation process, where communic acids are incorporated into the polymer.

In the methanol extract acidified with oxalic acid (Fig. 5.29b), Ph4, totarol, Ph9, sugiol, dehydroabietate and dehydroabietic acids are present.

In the methylated methanol extract (Fig. 5.29c), methoxy-ferruginol, –totarol and -sugiol, *cis*- and *trans*-communate, sandaracopimarate, isopimarate, methoxy- and hydroxyl-sandaracopimarate and 12-acetoxy-sandaracopimarate are present.



a – methanol extract, b- methanol extract treated with oxalic acid and c- methylated methanol extract (labels, see table 5.8)

Fig. 5.29 Gas chromatograms of A/26 “Sandaracha” from the Vigani Cabinet, diterpene section (TIC)

Discussion

The composition is typical for Cupressaceae resins, particularly for that of *Tetraclinis articulata* Mast. Typical are higher amounts of totarol (Ph5) than ferruginol (Ph7) with low amounts of sugiol (Ph18), together with dehydroabietic acids in the acidified extract. Hydroxy- and acetoxy-sandaracopimaric acids are highly characteristic for that species as well, together with the absence of C-15 and C-19 oxygenated labdane acids such as agathic and cupressic acids.

A/26 "Sandaracha" is the resin of the Sandrac cypress and true sandarac. Because a material of that name is not mentioned within the conserved invoices, the "juniper gum" mentioned in the invoices (MS Quns Vig. 4, folio 3v) may be a trading name, which would indicate that botanical different resins were traded under this name.

Label	t_R	Name	Main mass fragments
Ph2	14.71	Methoxy-ferruginol	**189**, 203, 215, **285**, 300
L13	14.83	*cis*-communate	79, 121, 175, **241**, 301, 316
Ph3	14.90	Methoxy-totarol	189, 203, 215, 243, **285**, 300
L16	15.06	*trans*-communate	79, 119, 175, **241**, 316
P6	15.03	Sandaracopimarate	**121**, 241, 301, 316
Ph4	15.34	Unidentified phenolic abietatriene	175, 189, 201, **271**, 286
P12	15.48	Isopimarate	187, **241**, 256, 301, 316
Ph5	15.60	Totarol	175, 189, 201, 253, **271**, 286
Ph7	15.73	Ferruginol	175, **189**, 201, 253, **271**, 286
L24	15.85	*cis*-communic acid	**79**, 105, 119, 175, 241, 287, 302
P16	16.04	Sandaracopimaric acid	91, **121**, 241, 287, 302
A10	16.14	Dehydroabietate	**239**, 299, 314
L28	16.08	*trans*-communic acid	**79**, 119, 175, 241, 287, 302
P17	16.37	Methoxyether of sandaracopimarate	91, 105, **121**, 199, 213, 239, 289, 299, **346**
P18	16.39	Isopimaric acid	95, 119, 145, 187, **241**, 273, 287, 302
Ph9	16.72	Abieta-8,11,13-triene-one	197, 203, 215, 243, **267**, 285, 300
Ph12	16.93	Totarolone	215, 243, 257, **285**, 300
A18	17.02	Dehydroabietic acid	**239,** 285, 300
P19	17.16	Hydroxy form of sandaracopimarate	91, 105, **121**, 199, 239, 255, 299, 314, 332
Ph13	17.20	Methoxy-sugiol	177, 219, 257, **299**, 314
P20	17.76	12-acetoxy-sandaracopimarate	**121**, 239, 255, 299, 314
Ph18	18.35	Sugiol	163, 203, 215, 243, **285**, 300
P21	18.99	12-acetoxy-sandaracopimaric acid (proposed)	119, **134**, 185, 239, 285, 300

Tab. 5.8 Compounds found in A/26 “Sandaracha”, sample analysed with temperature program Diterpenes 1, mass spectra references see appendix

5.2 Angiosperm resins I - Fabales

Resins from the order Fabales analysed in this work originate from the family Fabaceae. Their chemical composition is summarised in chapter 2.2. A variety of reference samples was analysed (chapter 4.2), with the analysis results discussed in chapter 4.2.4. Based on these data profiles, this chapter presents all materials from the Vigani Cabinet containing mainly ent-labdane acids and phenylpropanoids.

5.2.1 1/4 Balsam Cipivi

Fig. 5. 30 1/4"Balsam Cipivi"

Fig. 5. 31 Sampling of 1/4

Fig. 5.32 Sampling of 1/4, details, left – leather cap and oil paper, right – opening of the knot

Description

The glass bottle is filled with a dried-up transparent material of dark red colour. The surface is hard and brittle. The leather cap is partly soaked with a brownish material. It was still close-fitting and the knot firmly tied.

Sampling

The knot and the leather cap were removed on 30 March 2009. The surface cracked when touched with a scalpel. A sample of the material below the brittle surface was taken. It consisted of light yellow, and somewhat opaque lumps, which were still sticky to some extent. They had a slight resinous smell (Fig. 5.31).

Vigani references

* MS Quns Vig. 2, recto, as "Bals Capivi", 2 ounces at 1 shilling

* Does not appear in LECTURE NOTES UNDATED

* Does not appear in LECTURE NOTES 1707

Contemporary literature

Fine art materials

* CARLYLE 2001: ANON. 1795: 215; ANON. 1808: 11-2

Science

* BLANCKAERT 1690: "Copayvae Balsamum"

* DALE 1693: 503: "Capivus" ("*Copaiba Pis. & Marg.*, *Arbor balsamifera Brasiliensis*, *fructu monospermo* R.H., "*Balsamum Americanum* C.B., The White American Balsam-Tree")

* POMET 1717: 417-8: "Copayva-Balsam", "Copaiba", "Gamelo", "Copau", "Copaif", "Campaif"

* LEMERY 1721: 145: "Balsamum Copahu", "Copaii", "Copalyova", "Copaif", "Campaif", "Gamelo"

* JAMES 1747: 248: "Balsamum Capivi", "Balsamum Copaiba" ("*Capivus*, *Copaiba*, The white American Balsam Tree")

* GEOFFROY, THICKNESSE 1749: 223: "Balsam of Capivi", "Balsamum Brasiliense", "Balsamum Oleumve Copaiba", "Copaiva", "Copaii" ("*Copaiba* Piso et Marcgrav., *Arbor balsamifera Brasiliensis*, *fructu monospermo* Raii Hist. ")

* HILL 1751: 704: "Balsamum Capivi", "Balsam Braziliensibus", "Balsamum Copaiba", "Copaiva", "Copaic", "Oleum

Capivi" ("*Copaiba* Pis., *Arbor balsamifera Brasiliensis fructu monospermo* Ray")

* LEWIS 1761: 119: "Balsamum Copaiba", "Balsamum Copaiva", "Balsamum copaibae", "Balsamum brasiliense", "Balsam of Copaiba or Capivi" ("Copaiba braziliensibus Marcg., Arbor balsamifera braziliensis fructu monospermo Raii Hist.")

Encyclopaedias

* CHAMBERS 1728a: 79: "Balsam of Copaif", "Balsam of Copayba", "Balsam of Copa, Copaif, Campaif"

* SAVARY DES BRÛSLONS, SAVARY 1748b: 1433: "Gamelo", "Copau"; 1748a: 912: "Baume de Copaü", "Copaif", "Campaif"

Terminology

Not "cipivi" but "capivi" is mentioned mainly by English authors as a liquid resin (James 1747: 248; Geoffroy, Thicknesse 1749: 223; Hill 1751: 704; Lewis 1761: 119). Continental authors call the material "copayva" and "copaiba" ("Brazilian") "copa(h)u", "copaü", "copaif" and "campaif" (French) or "gamelo" (Portuguese) (Blanckaert 1690: 159; Pomet 1717: 417; Lemery 1721: 145; Chambers 1728a: 79; Savary des Brûslons, Savary 1748a: 912). "Capivi" is derived from "copaiba", the name of the botanical source (Piso 1648: 56).

Apart from 1/4 "Balsam Cipivi", the Cabinet contains another material labelled "Balsam Capivi" (compartment 2/2)[8]. The invoices list two different materials: "Bals Capivi" (2 ounces) and "Balsam Capivae" (1 ounce) (MS Quns Vig. 2, recto; MS Quns Vig. 4, folio 4, recto). They were bought on different occasions from different traders. Because the Cabinet was to some extent designed according to the materials which were stored inside (Wagner 2007a: 62), it is assumed by Wagner that the size of the container – in this case the bottles – corresponds to the purchased amounts. As 1/4 is stored in a much larger bottle, it is assigned to "Bals Capivi" (2 ounces). "Cipivi" is very likely a misspelling, then.

Botanical and geographical origin

English authors name the "*Copaiba Brasiliensibus* Pis. et Marcgrav. " or the "White American Balsam tree" as the botanical source of "capivi" (James 1747: 248; Geoffroy, Thicknesse 1749: 223; Hill 1751: 704; Lewis 1761: 119), while continental authors only refer to a Brazilian or American tree, from which the liquid balsam is obtained.

a - "Copaiba Brasiliensibus" (Marcgrave 1648: 131), b - "Coapoiba Brasiliensibus" (Marcgrave 1648: 131), c - "Copiiba Brasiliensibus Marcgrav." (Marcgrave 1648: 121) and d - Copaiba" (Piso 1658: 118)

Fig. 5.33 Historical trees mentioned in connection with "capivi"

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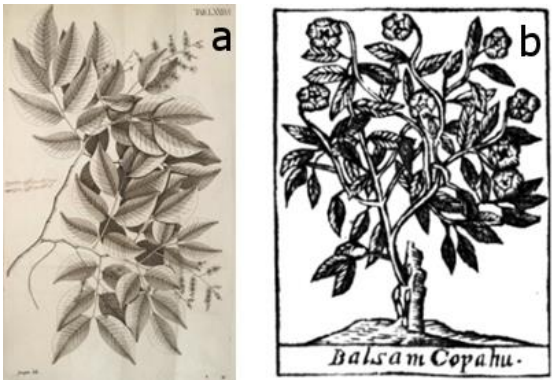
[8] It is not investigated in this work, because it turned out to be no *Copaifera* resin. Its botanical origin is still unclear.



a - "Copaifera officinalis Jacq." (Jacquin 1763: t.86) and
b - "Balsam Copahu" (Lemery 1721: 145)

Fig. 5.34 Historical trees mentioned in connection with "capivi" II

"*Copaiba Braziliensibus* Pis. et Marcgrav." is described by Piso and Marcgrave in the *Historia naturalis Brasiliae* (1648) and in the later edition entitled *De Indiae utriusque re naturali et medica* (1658). The book can be regarded as an early form of a multiple author work, both Piso and Marcgrave published their findings in separate parts within the book. They are therefore referenced separately. In the edition from 1648, the tree is called "*Copaiba* Piso" (without picture) and "*Copiiba Brasiliensibus* Marcgrave" (Piso 1648: 56; Marcgrave 1648: 121; Fig. 4.33c). The description is identical. Marcgrave however mentions other trees called "*Copaiba Brasiliensibus*" (Fig. 4.33a) and "*Coapoiba Brasiliensibus*" (Fig. 5.33b) (Marcgrave 1648: 130-1). The latter is called also "Pao Gamelo Lusitanis", and the chapter describes several species, which can be assumed to cover all possible botanical sources for the contemporary "copaiba" (Marcgrave 1648: 131).

In the edition from 1658, descriptions have changed: The description previously used to describe "*Copaiba* Piso" is now is applied to "*Copaiba Brasiliensibus* Marcgrave", and the picture is a mixture of the different plants described by Marcgrave in 1648 (Fig. 5.33d) (Piso1658: 118; Pickel, de Almeida 2008: 106). The fruits are from the homonymic species, the flowers from "*Coapoiba Brasiliensibus*" (Fig. 5.33b) and the leaves from "*Copiiba Brasiliensibus* Marcgrav." (Fig. 5.33c) (Pickel, de Almeida 2008: 106).

This tree grows in "Brazil", the island "Marabou" "in densis nemoribus mediterraneis reperitur" and the neighbouring Antilles (Dale 1693: 503; Ray 1693b: 1759; Chambers 1728a: 79; Geoffroy, Thicknesse 1749: 223; Hill 12751: 704). Other mentioned areas are Pernambucco, the Rio de Janeiro, the "Land of the Holy Spirit" and "Saint Vincent" (Pomet 1717: 859; James 1747: 248).

The tree was classified by Linné as *Copaifera officinalis* (Linné 1762: 557). This classification is still valid today. Linné gives several references, which include the additional trees described by Marcgrave (Marcgrave 1648: 131), the "*Copaiba*" from 1658 (Piso 1658: 118) and, via a reference to his own *Materia medica*, the original "*Copaiba* Piso" (Linné 1749: 181). He additionally includes "*Copaifera officinalis* Jacq." (Fig. 5.34a), a new species described shortly before by Jacquin (Jacquin 1760: 21; Linné 1762: 557). Obviously, Linné considered all trees mentioned to refer to the same species.

Towards the end of the 18th century and after, increasingly different species of the genus *Copaifera* were described, with new names proposed and older species renamed (Hayne 1826; Dwyer 1951). In modern literature, *Copaifera officinalis* L. is considered the actual name of the plant described by Marcgrave and Piso (Pickel, de Almeida 2008: 106). Nevertheless, it is more likely that Piso and Marcgrave described different trees, which all produced contemporary "copaiba" balsam, and the tree known as its source (Fig. 5.34b) was a mixture of different species, in the same way as the one originally described by Piso and Marcgrave.

Manufacture and trade

"Capivi" is imported to Europe by the Portuguese in earthen bottles (Pomet 1717: 417; Lemery 1721: 145; Chambers 1728a: 79; Savary de Brûslons, Savary 1748a: 912). It was traded in two sorts. The first sort is clear, white and oily with a resinous smell. To obtain this sort, the tree was incised and the resulting exudation collected (Pomet 1717: 417-8; Lemery 1721: 145). The tree was incised in the summer and yielded "twelve Pounds [..] from one Wood properly made in the Space of three or four Hours" (Hill 1751:705). The second sort was thick and yellowish and of lesser quality. It was obtained from incised trees some time after the incision (Pomet 1717: 417-8; Lemery 1721: 145). It is described as hygroscopic and less transparent than the first sort (Pomet 1717: 418; Hill 1751: 704), obtained in different seasons (James 1747: 248) or by boiling the bark of the tree (Geoffroy, Thicknesse 1749: 223; Hill 1751: 704). Pomet mentions a third sort called "Copaigba" obtained from an ash-coloured tree of the same name in the "Land of the Holy Spirit". A hole is drilled into the trunk to the heartwood, and the resinous balsam flows out of the hole until it is blocked (Pomet 1717: 860). This possibly refers to "*Copiiba Brasiliensibus* Marcgrav.", which is described having an ash-coloured bark (Marcgrave 1648: 121).

Properties

"Capivi" or "Copaiba" is described as a resinous liquid of white and yellowish colour. It has an acrid, pungent and bitter taste and a pleasant aromatic smell (Dale 1693: 503; Hill 1751: 704). The first sort has the consistency of oil and is of white or pale yellow colour (Pomet 1717: 418; Lemery 1721: 145; Hill 1751: 704). The smell is described as "turpentine"-like with some "lignum aloes" in it or resembling that of "Wood called Calambourg" (Geoffroy, Thicknesse 1749: 223; Hill 1751: 704). It becomes thick as honey with aging (Geoffroy, Thicknesse 1749: 223; Hill 1751: 704). The second sort is white, cloudy and less pellucid than the first sort and has the consistency of honey. Its taste is similar to "turpentine", and the smell is less agreeable than that of the first sort (Pomet 1717: 418; Hill 1751: 704). It is described as hygroscopic, with the water collecting in a layer at the bottom of the vessel (Pomet 1717: 418; Geoffroy, Thicknesse 1749: 223; Hill 12751: 704), which, according to Pomet, is the reason for its cloudiness.

Dossie mentions that "Copaiba" is adulterated with "common turpentine" (see chapter 5.1.2) (Dossie 1758b: 374).

Possible chemical composition

"Capivi" or "copaiba" is clearly connected to the genus of which at least one species was described first by Piso and Margrave ("*Copaiba Brasiliensibus Marcgrave*") (Plowden 2003). Several trees described by Piso and Marcgrave beared similar names such as "*Copaiba*", "*Coapoiba*" and "*Copiiba*". The majority of these trees were classified as *Copaifera officinalis* L. (Linné 1762: 557). However, more than 20 *Copaifera* species are known today (GRIN 2012). *C. officinalis* L. is mentioned by Tschirch in the 1930ies as a source of modern Copaiba balsam (Tschirch 1936: 1359f). A variety of other species are mentioned as botanical sources of Copaiba balsam today (see notes in table 2.3).

Different reference samples called Copaiba, Kopaivabalsam or Balsamum Copaive were analysed for this investigation, with the results presented in chapter 4.2.1. They are found to be largely consistent with published data that describe two different types of Copaiba balsam and attributes them to different botanical species (table 2.3). In this work, marker compounds for type A (attributed to *Copaifera multijuga* Hayne and *C. cearensis* Ducke from

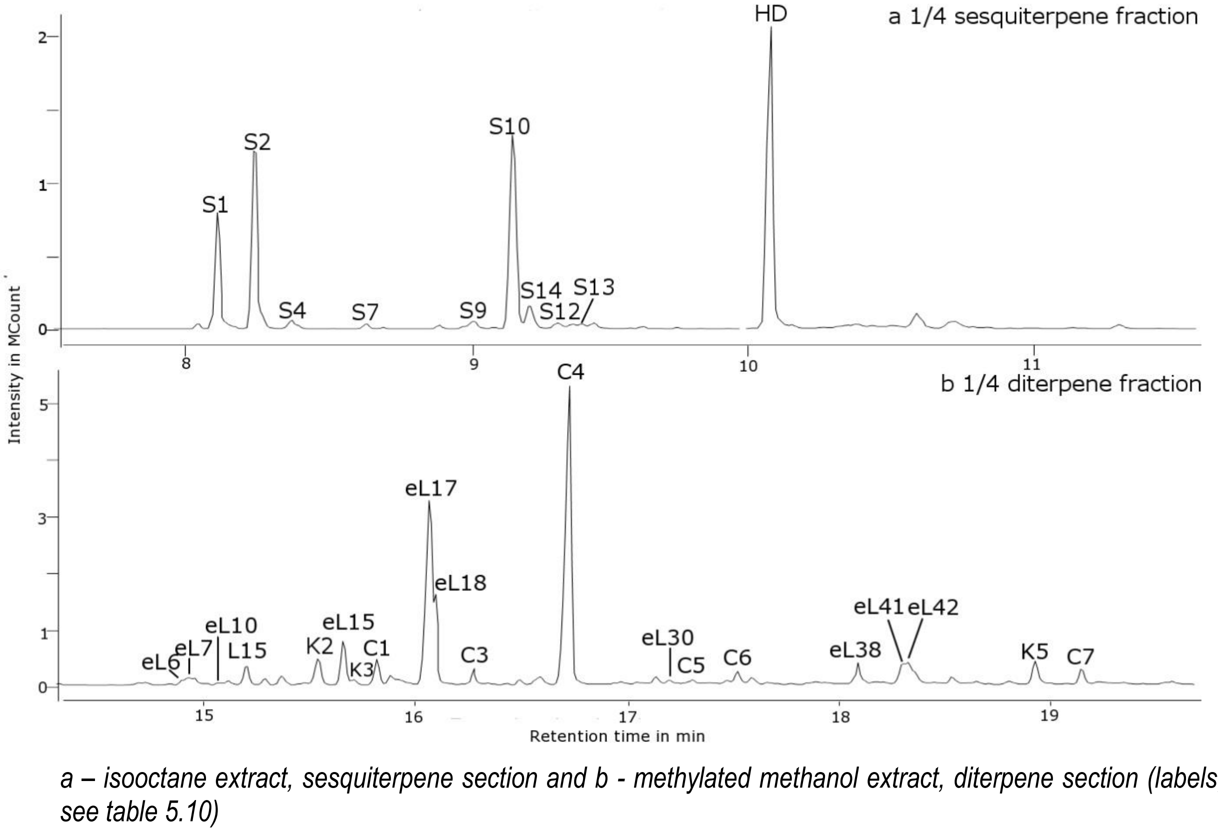
Western, middle and Eastern Brazil) are γ-muurolene, δ-cadinene and kovalenic acid. Marker compounds for type B (attributed to *C. duckei* Dwyer, *C. guianensis* Desf. and *C. langsdorfii* Desf. from Eastern, Northern and Southern Brazil, Bolivia, Argentina, Paraguay, Guyana and Suriname) are β-selinene, β-bisabolene, kauran-19-oic and polyalthic acid. These compounds may be only minor constituents. The main differences between the two types are rather characteristic compositions than single compounds.

In summary, the analysed samples show a surprisingly consistent chemical composition, also when compared to literature data. It is assumed that the export to Europe is a restricting factor, which possibly influences the availability of different species and therefore compositions in Europe.

Chemical analysis

In the isooctane and the methanol extracts, the sesquiterpene fraction (8 – 12 minutes) is identical. Here, the isooctane extract is shown, because it was of better chromatographic resolution. Main constituents are α-copaene, β-elemene and β-selinene together with small amounts of cyperene, trans-α-bergamotene, γ-muurolene, α-selinene, β-bisabolene and compound S13 (Fig. 5.35a). No β-caryophyllene and caryophyllene oxide are present. Although there are some differences, this composition resembles the type B more than the type A composition.

The methylated methanol extract (Fig. 5.35b) mainly contains the unidentified compound eL17 and hardwickiate together with smaller amounts of cativate, kaur-16-en-19-oate, copalate, compounds C1 and C3, ent-pinifolate, C6, eL38, eL41, eL42, K5 and 12-acetoxy-hardwickiate. Very small amounts of eperuate, labda-8-en-15-oate, labdanate, kauran-19-oate and C5 are also present.



a – isooctane extract, sesquiterpene section and b - methylated methanol extract, diterpene section (labels, see table 5.10)

Fig. 5.35 Gas chromatograms of 1/4 "Balsam Cipivi" from the Vigani Cabinet, sesqui- and diterpene section (TIC)

No kovalenic acid is present, but two other compounds with a mass spectrum very similar to that acid (C1, C3). C1 is found in Congo copal, which also contains kovalenic acid (see chapter 4.2.2). Because the molecular ion is present at m/z 318 in both cases, these compounds are probably isomers of kovalenic acid eluting right before and after it. Two further clerodanes (C5, C6), both dicarboxylic derivatives of kovalenic acid, are identified according to mass spectral data from literature (Pinto et al. 2000). According to these data, C6 is the dihydro- and C5 is the didihydro-derivative of kovalenic acid. They are found in the resin of *Copaifera cearensis* Ducke, which belongs to the type A composition (ibid.).

Label	t_R	Name	Main mass fragments
S1	8.13	α-Copaene	91, **105**, 119, 161, 204
S2	8.27	β-Elemene	79, **93**, 105, 119, 147, 161, 189, 204
S4	8.40	Cyperene	79, 91, 105, 119, 133, 161, 189, **204**
S7	8.66	trans-α-Bergamotene	79, 93, **119**, 204
S9	9.06	γ-Muurolene	91, 105, 119, **161**, 204
S10	9.18	β-Selinene	**79**, 93, 105, 119, 133, 161, 189, 204
S14	9.24	α-Selinene	79, 93, **105**, 119, 161, 189, 204
S12	9.34	β-Bisabolene	67, 79, **93**, 119, 161, 204
S13	9.39	Unidentified	79, 91, 105, 119, **161**, 189, 204
eL6	14.90	Eperuate	**81**, **95**, 121, 137, 177, 191, 305, 320
eL7	14.96	Ent-labda-8-en-15-oate	**95**, 107, 121, 191, 277, 305, 320
eL10	15.07	Labdanate	67, 81, 95, 109, **123**, 257, 275, 307, (322)
L15	15.20	Cativate	79, 93, **107**, 122, 149, 191, 305, 320
K2	15.54	Kaur-16-en-19-oate	91, 119, 131, 187, 213, **241**, 257, 273, 301, 316
eL15	15.66	Copalate	**81**, 95, 114, 121, 137, 243, 271, **303**, 318
K3	15.71	Kauran-19-oate	79, **91**, 105, 121, 149, 243, **259**, 286, 303, 318
C1	15.82	Unidentified	79, 91, 93, 95, **107**, 121, 135, 189, 243, 303, 318
eL17	16.06	Probably ent-labda-13-en-8-ol-15-oate	81, **109**, 135, 161, 189, **204**, 243, 271, 303, 318
eL18	16.09	Polyalthate	81, **121**, 189, 255, 330
C3	16.27	Unidentifed clerodane	95, 107, 120, **189**, 243, 253, 303, 318
C4	16.72	Hardwickiate	96, **139**, 175, 203, 219, 235, 283, 299, 330
eL30	17.20	ent-Pinifolate	93, **121**, 161, 235, 304, 332, 364
C5	17.30	Probably clerodan-15,18-oate, diME	79, 95, 121, 177, 187, 205, **237**, 251, 307, 335, (366)
C6	17.52	Clerod-3-en-15,18-oate, diME	79, 105, 139, 175, 203, 235, 281, 313, **332**, (364)
eL38	18.08	Unidentified labdane	81, **95**, 121, 147, 180, 191, 217, 297, 329, 344
eL41	18.30	Unidentified labdane	79, 91, 107, 121, **135**, 205, 304, 332
eL42	18.32	Unidentified labdane	**81**, 95, 119, 131, 163, **173**, 201, 233, 281, 313, 328
K5	18.92	Probably oxo-kaurenoate	79, 95, 121, 135, 205, 243, 259, **285**, 301, 317, 332
C7	19.15	12-Acetoxy-hardwickiate	81, 139, 173, 187, 201, **219**, 233, 281, 296, 328, 357, (388)

Tab. 5.9 Compounds found in 1/4 “Balsam Cipivi”, sample analysed with temperature program Diterpenes 1 at column A, mass spectra reference see appendix

Discussion

The composition is typical for resins from *Copaifera* species, with a high similarity to the type B composition both for sesquiterpene and diterpene constituents. Typical marker compounds are β-selinene, β-bisabolene, kauran-19-oic and polyalthic acid. The presence of α-copaene, trans-α-bergamotene, kaur-16-en-19-oic, copalic, eL17 and high amounts of hardwickiic acid are characteristic as well. Further marker compounds found only in own reference analysis are cativic and ent-pinifolic acid.

The sesquiterpene composition slightly differs from that found in reference samples. It therefore probably indicates that a different species not available today in Europe was used for its production. This is supported by the absence of β-caryophyllene and caryophyllene oxide, which are found in all investigated reference samples and reported widely in modern literature for different species (see table 2.3). Kovalenic acid, which is typical for type A, is not present, but two isomers and dicarboxylic derivatives of it are, with the latter two as well present in a type A *Copaifera* resin. Because the remaining composition resembles that of type B much more closely, those minor compounds probably originate from a different species used or are of environmental origin.

In contrary to the reference samples analysed in this work, no pimarane and abietane acids are present. Because these compounds originate from adulterations with colophony and pine resin, 1/4 "Balsam Cipivi" can be considered a pure *Copaifera* resin. It is, however, very likely not that of *Copaifera officinalis* L., which has probably a type A composition. Furthermore, the historical descriptions indicate the use of different species.

5.2.2 A/5 Gum Animi

Fig. 5.36 A/5 "Gum Animi"

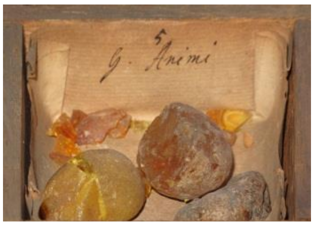


Fig. 5.37 Sampling of A/5

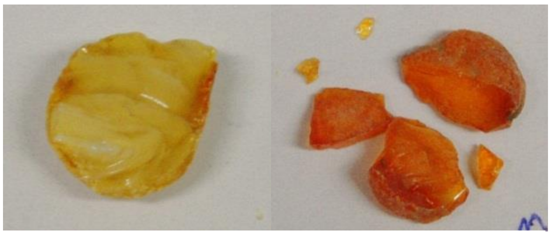


Fig. 5.38 Sampling of A/5, details, left - yellow, right - brown-cherry

Description

The box contains four big lumps of a yellow to greyish colour ad several smaller lumps of a yellow to orange colour. They are hard, transparent with an opaque crust and odourless.

Sampling

Samples of a yellow and clear lump and a of a dark orange to red lump were taken in February 2011 (Fig. 5.38).

Vigani references

* MS Quns Vig. 4, folio 3, verso, as "Gum Annimi", 2 ounces at 1 shilling

* Does not appear in LECTURE NOTES UNDATED

* Does not appear in LECTURE NOTES 1707

Contemporary literature

Fine art materials

* SALMON 1701: 867, 872-4: "Gum Animi"

* DOSSIE 1758a: 179, 213: "Gum Animi"

Science

* BAUHIN 1623: 498: "Anime"

* RAY 1693b: 1846: "Gummi Anime"

* DALE 1693: 506: "Gummi Animi", "Resina Animae" (botanical names see text)

* POMET 1717: 403: "Gummi Animae"

* LEMERY 1721: 64: "Anime", "Anime gummi", "Gomme anime"

* BRADLEY 1730: 92: "Gum Animae"

* JAMES 1747: 333: "Gummi Anime"

* GEOFFROY, THICKNESSE 1749: 213: "Anime"

* HILL 1751: 730: "Anime" ("*Arbor siliquosa ex Virginia lobo fusco scabro* C.B., *Courbaril bifolia flore pyramidato* Plumier")

* LEWIS 1761: 53: "Anime", "Resina courbaril"

Encyclopaedias

* CHAMBERS 1728a: 191: "Gum Anima", "Animi" ("Courbari")

* SAVARY DES BRÛSLONS, SAVARY 1748a: 671: "Gomme Anime"; ibid. 1748b: 1490: "Gomme Anime", "Gomez Amie", ("Courbaril")

Terminology

The term "anime" originates from the ancient "(myrrha) aminea" or "minea" used by ancient Greek physicians (Bauhin 1623: 498; Lemery 1721: 64; James 1747: 333). According to Ray the name is a corruption of "serapio aminaeam", a material mentioned by Bauhin as the "cancamum of Dioscorides" (Bauhin 1623: 498; Ray 1693b: 1846). The connection to "cancamum" can be found in several others authors, while it remains open whether the two materials were once the same or not (Fragoso, Spachii 1601: 96, 97; Bauhin 1623: 498; Salmon 1701: 858; Pomet 1717: 403; Lemery 1721: 216).

According to Tschirch, "anime" is a transformation of the older "elemi" (Tschirch 1935a: 205-6).

The material is mentioned as having been known for a long time, but it was also rare, particularly the "oriental" sort (Hill 1751: 731; Lewis 1761: 53).

Botanical and geographical origin

"Anime" was used in Vigani's time for two sorts of materials, an "oriental" and an "occidental anime". The "oriental anime" originated from Africa and is mentioned only occasionally. From the 16th century on, the name was seemingly in use for the American resin, "occidental anime" (Fragoso, Spachii 1601: 97; Bauhin 1623: 499; Ray 1693b: 1846).

1. "Oriental anime" or "Ethiopian Anime", "Animum", "Anijmum", "Gum Anime": A material of this name is described in 1563 by Fragoso in his translation of the *Colóquios dos Simples e Drogas e Cousas Medicinais da Índia* of Garcia de la Orta, a work about medicines and drugs from India. He mentions three sorts, which were still known in the 17th century: a transparent yellow sort resembling "succinum", a blackish sort, "taurino glutini", which resembles "Pica graeca" and is the "vera Myrrham aminneam", and a pallid and "resinaceum retorridumque" sort (Fragoso, Spachii 1601: 96, 97; Bauhin 1623: 498-9). Ray list four sorts: "animes species ad succinum luteum accendes", "anime similis resina ex albo flavescens", "anime alba perlucida, sapore Vernicis, odore Mastiches" and "anime colore Colophoniae" (Ray 1693b: 1846). According to Fragoso, the "oriental" sort originated from West Africa. Its botanical source was a tree of medium high with leaves similar to "aloë" (Fragoso, Spachii 1601: 96)[9].

Authors contemporary to Vigani mention "oriental anime" to originate from the "East Indies" or "Ethiopia on the Confines of Arabia" (Salmon 1701: 858; Hill 151: 730). There are several geographic references to Arabia and the west coast of the Red Sea (Monardes, Clusius 1579: 3-4; Bauhin 1623: 498). This is probably the origin of the connection to "cancanum". A material of this name is mentioned by Pliny to be traded from a colony of the "Nabateans" on the west coast of the Red Sea (Pliny 1855: 12,22). This connection to Eastern Africa was still known at the beginning of the 20th century, when Tschirch derived the name from East African "elemi" (Tschirch 1935a: 205-6, see above). An "Elemi Aethiopicum" located in "Aethiopia" or "Arabia Felix" was also known at Vigani's time (see chapter 5.3.4). In the old inventory found in the Cabinet and assumingly made at the beginning of the 20th century A/5 "Gum

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[9] The similarity of a West African resin buried from the sandy grounds in the province "Benin" at the coast of "Guinea" to "succinum", or "Bernstein", is also mentioned in the "Naturgeschichte des Kopals" from 1776. According to Bloch, this "Kopal" was called "Pseudo-succinum" by Nathanael Sendel. It was traded by the Englisch African company from the fort "Sierra Leona" to London (Bloch 1776).

Anime" is described as "Exudation of Boswellia" (Wagner 2007b: Drawer A), a species which is mentioned until today as the source of African elemi (see chapter 2.3.2).

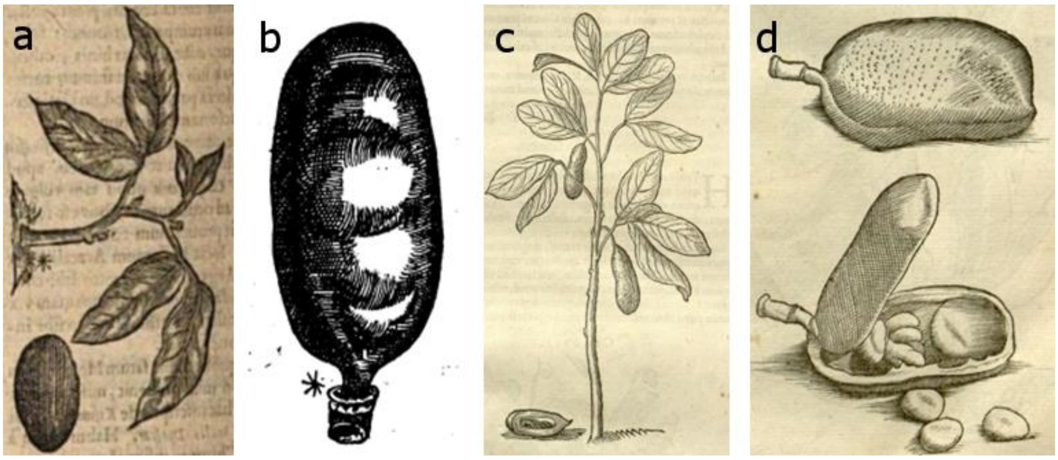
2. "Occidental anime", "resin of the courbaril": This American sort exudes from a tree with leaves similar to myrtle and a big fruit named "lobus" (Lemery 1721: 64; James 1747: 333). It grows in different parts of the New World ("Brazil", "New Spain") (Lemery 1721: 64; Chambers 1728a: 191; James 1747: 333; Lewis 1761: 53), but islands of the West Indies, such as Hispaniola, Cuba and Jamaica, are also mentioned (Salmon 1701: 858).

There is a particular confusion about the source tree. Dale lists ten different botanical names for what he calls the "Locust-Tree". The name probably refers to the characteristic fruit (Fig. 5.39b, d). A North American species was called "*Lobus ex Wingandecaouw* Clusii" and "*Arbor siliquosa ex Virgina lobo fusco scrabo* C.B" (Bauhin, Cherler 1650: 436; Bauhin 1623: 404; Plumier 1703: 49) (Fig. 5.39a, b).

A "Brazilian" species is named by different authors "*Jetaiba Braziliensibus* Piso & Marcgrave", "*Arbor siliquosa ex qua Gummi Anime elicitur* C.B.", "*Animifera Arbor Brasiliana* P.B.P." and *Ceratia diphyllos* Pluk." (Piso 1658: 123; Bauhin 1623: 404; Dale 1693: 506; Plukenet 1691b: t.82, Fig. 5.39c, d). They were classified by Linné as *Hymenaea courbaril* (Linné 1653b: 1192). A Portuguese tree named "courbari(l)" is mentioned by several of the contemporary authors as the botanical source of American "anime" (Chambers 1728a: 191; Savary des Brûslons, Savary 1748b: 1490; Lewis 1761: 53). "*Arbor Anime gummi sundens* Breyn" and "*Courbaril bifolia flore pyramidato* Plumier" are probably of "Brazilian" origin as well (Dale 1693: 506; Plumier 1703: 49).

Ray considers "*Jetaiba Braziliensibus* Piso & Marcgrave" and "*Lobus ex Wingandecaouw* Clusii" to be the same tree, which he calls "*Arbor Brasiliensis siliquosa, gummifera gummi Anime similis*" (Ray 1693b: 1760). According to J. Bauhin, Clusius described the "Brazilian" and a Virginian species of that tree, but ascribed the resin to a third species from "Guyana" or "Hayti" (Monardes, Clusius 1579: 4; Bauhin, Cherler 1650: 437). Ray mentions "Parayba" (Ray 1693: 1760). The resin of the "Brazilian" "*Jetaiba Braziliensibus* Piso & Marcgrave" or "*Arbor Brasiliensis siliquosa, gummifera gummi Anime similis* Ray" was called "jetica-eica", "joticacica" and "jetaicica" (Ray 1693b: 1760; Hill 1751: 731).

According to Ray, this resin is called "anime" by the Portuguese because of its similarity to another sort from Mexico (Ray 1693b: 1760). The Mexican sort originated from "*Mizaquix-*



Left - "Lobus ex Wingandecaow" leaves (a) and fruit (b) (Bauhin, Cherler 1650: 436) and right - "Ietaiba Arbor" tree (c) and fruits (d) (Piso 1658: 123)

Fig. 5.39 Historical trees mentioned in connection with "occidental anime" *ochicopalli* Hernandez", a tree of medium height (Piso 1658: 123; Ray 1693b: 1760; Monardes, Clusius 1579: 4). The description by Hernandez however, does not permit any conclusions about the identity of the tree (Hernandez 1651: 50). The tree is one of the "*Copallifera*" (several other species are shown in chapter 5.3.3), a "copal"-producing tree, and its resin is called "anime" or "vero Copallis" (Hernandez 1651: 50).

The botanical source of American "anime" (Fig. 5.39) is somewhat similar to that of "oriental copal" described in the 18th century. Despite its name, this material originated from Mesoamerica, from a tree of medium height with long, broad and attenuated leaves and brown fruits similar to cucumbers, which contain an edible flour (Pomet 1717: 401-402; Lemery 1721: 336, chapter 5.3.3). Similar descriptions, particularly referring to the edible flour, are found for "anime" as well (Lemery 1721: 64; James 1747: 333; Savary des Brûslons, Savary 1748b: 1490).

Manufacture and trade

According to Fragoso, the "oriental" sort was traded by the Portuguese ("Lusitanians") and originated from "Guinea, & alijs regionibus Africae, & insulis circumuicinis". The Portuguese trade from their colony at the Indian Malabar coast, which is the "India occidentalis" of Fragoso and Monardes, seems to have been included materials originating from the West African coast (Fragoso, Spachii 1601: 96; Monardes, Clusius 1579: 4; Bauhin 1623: 498). In the 18th century, the Portuguese "anime" trade from West Africa was still known (Bradley 1730: 92), while in the 19th century India was assumed as a possible origin of this material (Hope 1837). From the 16th century on, the Eastern African coast is also mentioned (Monardes, Clusius 1579: 3-4; Bauhin 1623: 498; Salmon 1701: 858; Hill 151: 730, see above).

"Occidental anime" was traded in two forms, in small pure tears and larger lumps polluted with earth (Ray 1693b: 1760; Hill 1751: 731; James 1764: 333; Lewis 1761: 53). The tears exude from the trunk without incision (Hill 1751: 731; James 1764: 333). The Mexican sort was obtained by incision in the same way as "thus" and "mastic" (Monardes, Clusius 1579: 4, see chapter 5.3.1). Other authors describe larger lumps, which exude from the trunk and run down to the earth and under the roots, from where they are dug up (Ray 1693b: 1760; Lewis 1761: 53). The best time for this is February (Ray 1693b 1760).

Although several authors believed that the term "anime" originated from the "Spaniards", similar to the term "copal" (see chapter 5.3.3), and to have been transferred to the "Brazilian" sort through the Portuguese trade with "oriental anime" (Ray 1693b: 1760; Hill 1751: 730-1), the term "anime" obviously is of old world origin (see ‘terminology’). There is some evidence that suggests that the name was transferred by Portuguese traders from the African material to the "Brazilian" resin. Then the Mesoamerican "anime" was probably a "copal", also because "copal" originated from Nahuatl (chapter 2.3.2).

Properties

"Oriental anime" is dry, solid, and packed in cakes or irregular lumps. It is of an uncertain colour, green, red or brown and the colour of "myrrh". It is somewhat pellucid and "of a tolerably compact Texture, light and easily powdered". It is easily inflammable. Its taste is resinous and bitter, and it has a fragrant smell (Hill 1751: 730-31). Fragoso distinguishes it from the less white and bright "occidental anime", which is traded in smaller and less transparent pieces (Fragoso, Spachii 1601: 97). It dissolves only in oil (Bradley 1730: 92).

"Occidental anime" is dry, solid and whitish. It is of a fine yellowish white between that of "incense" and that of "mastic", the purest pieces being clean and transparent. It is friable, oleaginous to the touch, very fragrant and with a resinous, acrid and somewhat bitter taste. The finest pieces are small tears of white or pale yellow colour much resembling amber, friable, fragrant and easily inflammable (Pomet 1717: 404; Lemery 1721: 64; James 1747: 333; Hill 1751:731-2; Lewis 1761: 53). Material of lesser quality came into trade in larger lumps mixed with earth, which was a result of its harvest (Lewis 1761: 53). It does not dissolve in water or oil but in "rectified spirit" (Chambers 1728a: 191; Lewis 1761: 53).

The exact hardness of the material is not certain, because it is described both as friable, solid and very hard and transparent (Chambers 1728a: 191; Hill 1751:731-2). On the other hand, "copal", which does not soften in the mouth like "anime", is distinguished further by its less intense fragrance, softness and oiliness (Monardes, Clusius 1579: 3; Salmon 1701: 858; Hill 1751: 732; Lewis 1761: 53, 225). Nevertheless, the resins seem to have been very similar. Hernandez mentions the Mexican "anime" to be also called "vero Copallis" and the softer "anime" is frequently compared to amber (Hernandez 1651: 50; Salmon 1701: 858).

The (Mexican) sort, described by Monardes, is found in white tears of the colour of frankincense, sometimes also somewhat greenish and inside of a deep yellow. It is "verum Copali magis oleaginosa" and with a most agreeable and sweet smell and easy to burn (Monardes, Clusius 1579: 3).

Four sorts of "cancamum" are described, all obtained from the same source, a myrtle-leaved tree growing in Africa, "Brazil" and on the island "S. Christophel" (Pomet 1717: 403; Lemery 1721: 216). They differ in hardness, colour and smell when burned. Only one of them, a dry and white material with no particular smell, is also called "gummi anima" (ibid.). According to Pomet, "cancamum", contrary to "anime", is soluble in oil (Chambers 1728a: 191; Pomet 1717: 404). Because "oriental anime" from Africa is mentioned to be soluble in oil as well (Bradley 1730: 92), this probably refers to "occidental anime".

According to 18th century literature, "anime" and "copal" have frequently been confused (Hill 1751: 732; Lewis 1761: 225), with "anime" apparently having been used as an inferior substitute for "copal (Salmon 1701: 857; Chambers 1728a: 191; Savary des Brûslons, Savary 1748b: 1490).

Possible chemical composition

"Anime" can be considered a generic name for different resins from Africa and America. Together with elemi and copal, the term is used today only for South American resin-producing trees (Hugh 1910: 54; Langenheim 2003: 357-359, 398; Case et al. 2003; Rüdiger et al. 2007), mainly from *Hymenaea*. *Hymenaea* resins are sometimes called jutaisica or jutahyica (Doménech-Carbó et al. 2009), which resembles the "jetica-eica" and other names for the resin of the historical Brazilian "anime" tree ("*Arbor Brasiliensis siliquosa, gummifera gummi Anime similis* Ray"). They originate from the word yataiwa, which in the Tupi language refers to a tree of hard fruit (ibid.). The Jatobá tree, *Hymenaea courbaril* L., which is also called Locust-Tree, is known to be a possible source of "anime" (Boisson 1988). South-American *Hymenaea* resins are sometimes soft and sometimes hard like amber, with a significant polymeric fraction (Anderson et al. 1992; Anderson, Botto 1993; Anderson 1994; Doménech-Carbó et al. 2009). This diverging polymeric fraction is a possible explanation for the confusing historical descriptions of hard "anime" and soft "copals". The Mexican "*Mizaquixochicopalli* Hernd." as one of the "Copalliferae" may be a *Bursera* species or *Amyris elemifera* L.

(see chapter 5.3.3), additionally *Protium* resins are mentioned as modern anime (see table 2.6). These resins can be distinguished by their chemical composition. *Hymenaea* resins consist of ent-labdanes (chapter 2.2), *Protium* and *Bursera* resins of triterpenes (chapter 2.3.2).

According to the literature, main constituents of *Hymenaea* resins are eperuic, labda-8-en-15-oic, copalic, pinifolic, guamáic and several labdanolic acids (with the hydroxy group at positions C-8 and C-18). For the trunk resin of *Hymenaea courbaril* L., high amounts of labda-13-en-8-ol-15-oic acid are reported. Minor compounds are (iso-)ozic, kovalenic and cativic acids. In the East African *H. verrucosa* Gaertn., the source of Zansibar copal, additional caryophyllene-oxide, 13-epimanool, 18-hydroxy-epimanool and labda-8(20)-en-15,18-diol are found (Hugel et al. 1966; Cunningham et al. 1973; Cunningham et al. 1974; Doménech-Carbó et al. 2009).

Two reference samples analysed in this work are attributed to *Hymenaea* resins, both containing a high polymeric and low soluble fraction. They mainly contain epimanool, iso-ozic, 18-hydroxy-labda-7(8)-en-15-oic acid and two rearranged labdanes (L17, L41). Lower amounts are present of eperuic, copalic, labda-13-en-8-ol-15-oic and a 18-hydroxy-8(20)-en-15-oic acid. Ent-labda-8(20)-en-15,18-diol mentioned in literature is probably identified as well. Because this is more closely to the reported composition of *Hymenaea* resins than to that of other legume copals, and both reference samples have a terminological connection to *Hymenaea*, they are identified as a South American and an African *Hymenaea* copal. However, because several constituents could not identified, and *Hymenaea* resins are reported in literature to have a variable composition (Cunningham et al. 1973), these findings does not permit general conclusions.

An anime resin was analysed for this work together with other differently labelled resins from Burseraceae, with the results presented in chapter 4.3.3. Modern anime contains several alcoholic pentacyclic triterpenes with the lupane, ursane and oleanane skeleton in high amounts, mainly α- and β-amyrin derivatives, epi-lupeol, acetoxy- and 11-oxo-derivatives of the mentioned alcoholic triterpenes. It is therefore more likely a *Bursera* resin and not obtained from a *Protium* species. The chemical composition of *Protium* and *Bursera* resins is discussed in detail in chapter 5.3.3.

The botanical origin of African anime is unknown, and a wide range of botanical origins are possible. Because of the terminological connection to "elemi", several soft resins from African species of *Canarium* and *Commiphora* (triterpene, chapter 2.3.2) or *Copaifera* and *Daniellia* (diterpene, chapter 2.2) are possible. *Boswellia frereana* Birdw., the source of African elemi (triterpene, chapter 2.3.2) is also probable, as are several African species containing iso-ozic acid, considering the mentioned dissolubility of "oriental" and "occidental anime". From the historical sources, it is apparent that "oriental anime" is soluble in oil, while the American sort is soluble in ethanol ("rectified spirit"). Several recent copals from America are soluble in alcohols but no in oil (Schramm 1989: 102). African copals on the other hand, with a higher polymeric fraction (composed of iso-ozic acid), possess a small alcohol-soluble fraction. Possible botanical sources are the West or Central African genera *Guibourtia*, *Tessmania* and *Daniellia* (diterpene, chapter 2.2) or *Hymenaea verrucosa* Gaertn. (see above). None of these trees has leaves similar to "aloë". The leaves of some *Daniellia* species are similar to myrtle, this tree is, however, mentioned only in connection with "cancamum", the identity of which is unknown (Pomet 1717: 403; Lemery 1721: 216). Zansibar copal is mentioned to be traded from East Africa to Arabia (Regert et al. 2008) and may be a source for "Ethiopian anime" or the East African materials mentioned in connection with "oriental copal".

The African species can be divided into two groups: ent-labdane containing diterpene (*Guibourtia*, *Tessmania* and *Daniellia* and the softer materials from *Copaifera* species and *Daniellia oliveri*) and triterpene (*Canarium*, *Commiphora* and *Boswellia*) resins.

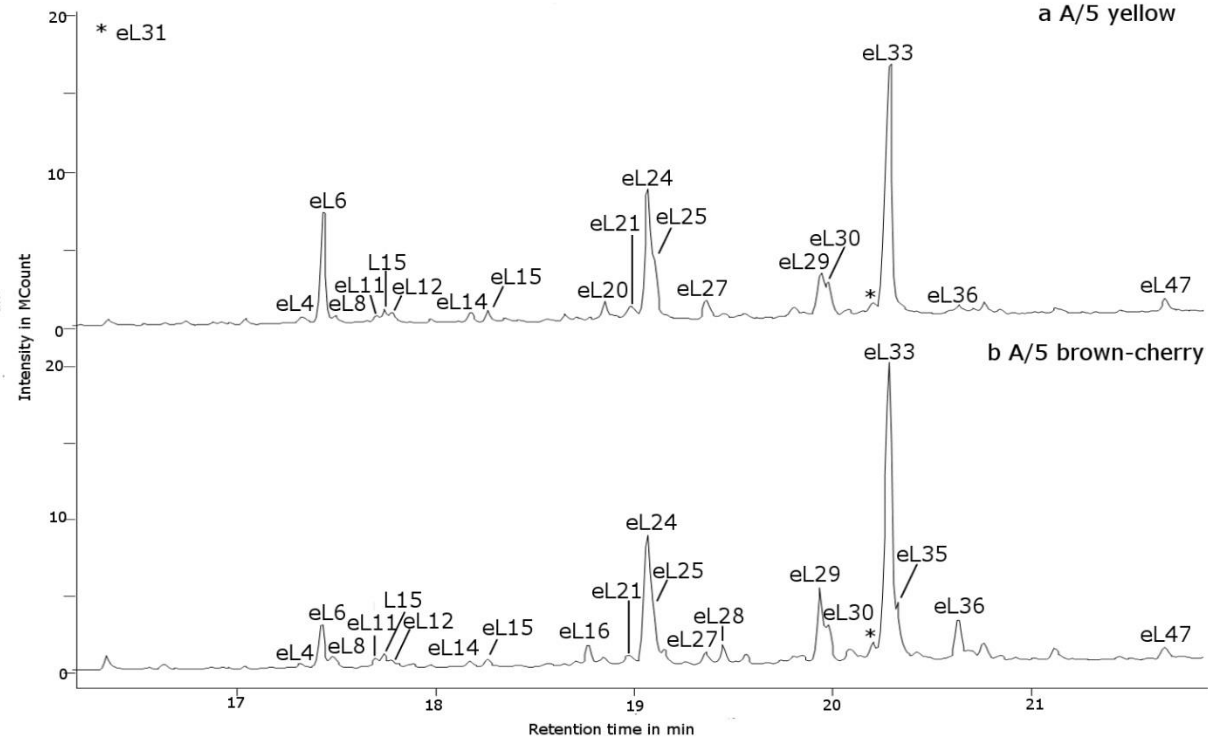
Several diterpene copals (*Guibourtia*, *Tessmania* and *Daniellia*) from Africa were analysed, with the results presented in chapter 4.2.2. All Congo copals are composed very similarly. They contain high amounts of ent-labda-8(20)-en-15-oic and isomers, labdanolic (labda-8-ol-15-oic) and kovalenic acids. Smaller amounts of oxygenated derivatives of eperuic and labdanolic acid are present, too. All Sierra Leone copals contain high amounts of 18-hydroxy-8(20)-en-15-oic acid and other oxygenated ent-labdanes, including hydroxy-labda-8(20)-en-18-oic acid, nor-labdanes and 18-hydroxy-15-methoxy-ent-labdane. Not-oxygenated ent-labdane acids such as eperuic and copalic acid are present in small amounts or even in traces.

The composition of triterpene copals from Africa is summarised in chapter 5.3.3, that of African elemis in 5.3.4.

Chemical analysis

Both samples were dissolved in methanol, whereupon they turned white and rubbery.

In the methylated methanol extracts of the two samples (Fig. 5.40), high amounts of eperuate, 18-methoxy-ent-labda-8(20)-en-15-oate and 18-hydroxy-ent-labda-8(20)-en-15-oate (eL24, eL33) are present. Other constituents are eL4, ent-labda-8-en-15-oate, eL11, cativate, ent-labd-8(20)-en-18-oate, 18-methoxy-nor-ent-labda-13(14)-en-15-oate and its methoxy form (eL14, eL27), copalate, ent-labdanolate, 15,18-dimethoxy-ent-labdane and its hydroxy form (eL21, eL31), a methoxy-ent-labda-8(20)-en-18-oate and a hydroxy form of it (eL25, eL29), ent-pinifolate and compound eL47. The identification of the mentioned compounds is described in chapter 4.2.2.



Methylated methanol extracts of A/5, a - yellow piece and b - brown-cherry piece (labels, see table 5.10)

Fig. 5.40 Gas chromatograms of A/5 “Gum Animi” from the Vigani Cabinet, diterpene section (TIC)

Label	t_R	Name	Main mass fragments
eL4	17.32	Unidentified ent-labdane acid, ME	**95**, 109, 135, 191, 277, 305, (320)
eL6	17.44	Eperuate	**81**, 95, 107, 121, 137, 177, 191, 305, 320
eL8	17.49	Ent-labda-8-en-15-oate	**95**, 107, 121, **191**, 277, 289, 305, 320
eL11	17.57	Unidentified ent-labdane acid, ME	67, 81, 93, **107**, 121, 135, 191, 207, 277, 305, 320
L15	17.75	Cativate	95, **107**, 122, 191, 289, 305, 320
eL12	17.77	Ent-labd-8(20)-en-18-oate	79, **121**, 161, 215, 231, 247, 263, 275, 290, 322
eL14	18.18	18-Methoxy-nor-ent-labda-13(14)-en-15-oate (proposed)	**81**, 93, 107, 121, 149, 175, 291, 309, (324)
eL15	18.27	Copalate	**81**, 95, 114, 121, 137, 243, 271, 303, 318
eL16	18.76	Daniellate	81, **121**, 189, 255, 315, 330
eL20	18.85	Labdanolate	81, **101**, 109, 121, 123, 177, 235, 291, 305, 320
eL21	18.99	15-Methoxy-ent-labane	81, 95, 121, 149, 195, **277**, 290, 307, 322
eL24	19.07	18-Methoxy-15-hydroxy-ent-labda-8(20)-en-15-oate	81, 107, 121,175, 223, 291, **305**, 318, 334, 350
eL25	19.10	15-Methoxy-ent-labda-8(20)-en-18-oate	**121**, 161, 235, 290, 303, 318, 335, 350
eL27	19.37	18-Hydroxy-nor-ent-labda-13(14)-en-15-oate (proposed)	**81**, 95, 107, 121, 135, 163, 277, 291, 304, 322
eL28	19.45	Unidentified hydroxy- or methoxy-ent-labdanoate	95, **109**, 122, 135, 189, 221, 271, 305, 318
eL29	19.94	Hydroxy-ent-labda-8(20)en-18-oate	**121**, 161, 253, 276, 304, 318, 336
eL30	19.98	ent-Pinifolate, diME	**121**, 161, 235, 304, 364
eL31	20.21	15,18-Dihydroxy-ent-labane	81, 95, 121, 149, 263, **277**, 290, 308
eL33	20.28	18-Hydroxy-ent-labda-8(20)-en-15-oate	81, 107, 121, 135, 175, 223, 291, **305**, 318, 336
eL35	20.33	Unidentified ent-labdane	**95**, 107, 121, 135, 149, 189, 207, 291, 305, 318, 354
eL36	20.63	18-Hydroxy-ent-labda-7(8)-en-15-oate	**107**, 109, 122, 149, 189, 207, 291, 305, 318, (336)
eL47	21.67	Unidentified ent-labdane acid, ME	79, 93, **107**, 121, 135, 175, 189, 271, 318, 334, 352

Tab. 5.10 Compounds found in A/5 “Gum Animi”, samples analysed with temperature program Diterpene on column B, mass spectra references see appendix

The methoxy derivatives are artefacts of the sample preparation, because TMSH does methylated hydroxyl groups only to a minor extent (see chapter 3.1.2). Compound eL24, however, is present in very high amounts, and it is identified by several other investigators, which used differing derivatisation agents, in Fabaceae resins (van den Berg et al. 2002; Doménech-Carbó et al. 2009). In the methanol extract a compound with a similar mass spectrum is present at 20.51 minutes (not shown). Main mass fragments are at m/z 81, 93, 107, 123, 135, 149, 175, 207, 223, 305 and 318, with the base peak at m/z 81. The molecular ion ought be present at m/z 336. Compound eL24 is therefore an original constituent. On the other hand, it is not present in any of the other samples analysed in this work containing its hydroxyl form eL33 in smaller amounts, such as Congo copals, several *Hymenaea* resins and the unknown materials La2/7 (see chapter 4.2.2, 5.2.3). These materials also do not contain the unmethylated compound eluting in the methanol extract.

The two samples show only little differences. The brown-cherry coloured sample additionally contains daniellate, 18-methoxy-ent-labda-7(8)-en-15-oate and its hydroxy form (eL28, eL36) and compound eL35 are present. Very small amounts of compound eL36 are present in the yellow coloured sample as well. Compound eL35 has a mass spectrum very similar to that of compound eL40, which is identified in chapter 4.2.2 as ent-labda-8,18-diol-15-oate, a 18-hydroxy form of ent-labdanolate. Compound eL36 is probably a double bond isomer.

Discussion

The composition is typical for legume copals, particularly Sierra Leone copal. It is characterised by high amounts of 18-hydroxy- and 18-methoxy-labda-8(20)-en-15-oic acids and only small amounts of eperuic, cativic and copalic acids. Other typical constituents of Sierra Leone copal are hydroxy-labden-18-oic acid and 18-hydroxy-15-methoxy-labdane. Labdanolic and daniellic acids are present in a Sierra Leone copal analysed in this work as well. The compounds eL8 and eL11 as well as eL36 are not present in Sierra Leone copals investigated in this work, but in Congo copals and *Hymenaea* resins, respectively. The compounds eL35 and eL47 are not present in any of the reference samples. The white rubbery appearance indicates a polymeric fraction.

The material resembles a sort of "occidental copal", which is described to be found in tears the colour of amber in historical sources, but also the yellow and transparent African "anime" described by Fragoso. Because it does not contain triterpenes, it is no *Protium* resin. If it originates from America, it belongs to the genus *Hymenaea*. The double harvesting in tears and big lumps running down the trunks of the trees, described in the historical sources, corresponds to modern findings about the resin production in *Hymenaea* trees. They accumulate resin in lysigenously formed cavities in the trunk (Cunningham et al. 1973; Langenheim 2003: 394f.). The chemical composition of A/5 "Gum Animi" however does not resembles any *Hymenaea* resins analysed in this work or reported in the literature.

Although *Hymenaea* resins are reported to have a very variable composition (Cunningham et al. 1973), the material more likely derives from an African Leguminosae species, because its composition is nearly identical to that of several Sierra Leone copals analysed in this work. Species mentioned in literature for Sierra Leone copals are *Guibourtia copallifera* Benn. and *Daniellia thurifera* Benn. As mentioned above, *Daniellia* species have leaves somewhat similar to myrtle but not to aloe. In Vigani's time the Portuguese trade with West African resins was apparently still existent, although an African "anime" it is mentioned mainly for East Africa. The only mention of a West African "anime" resin from the 18th century found was made by the botanist Thomas Bradley. He lectured about "materia medica" upon the Vigani Cabinet and another material collection from Cambridge some years after Vigani's death (Bradley 1730: 92). It must be assumed that West-African copal resins such as Congo, Sierra Leone or Accra copal were called "anime" in the 17th and 18th century.

It has been mentioned above and for A/21 "Gum copal" (chapter 5.3.3) that both "occidental anime" and "oriental copal" probably derived from the same botanical source, a *Hymenaea* species, probably *Hymenaea courbaril* L. Because neither the material labelled "anime" nor the material labelled "copal" turned out to originate from this genus, this question remains open. Additionally, the modern anime analysed in this work, is related to another genus as well, the triterpene *Bursera* resins. Today, Mexican *Bursera* species are known as the main copal producers, while the copal-producing "*Mizaquixochicopalli* Hernd." is probably also a *Bursera* species. This indicates that this tree is not identical to the Brazilian source of "anime".

The geographical origin of A/21 "Gum Copal" is not clear either, because it was not possible to distinguish between the triterpene *Protium* (America) and *Canarium* (Africa) resins. However, in historical sources, only American locations are mentioned for this material (see chapter 5.3.3). The old-world term "anime" can be related to a particular African resin and was used in Vigani’s time for American resins as well. The new-world term "copal" was used only for American resins. While the transfer of these terms to materials other than the original ones, had just begun for "copal", the transfer of "anime" from the old world to America was nearly completed.

5.2.3 La2/7 Unknown resin

Fig. 5.42 Unknown resin La2/7

Fig. 5.41Unknown resin La2/7 in its compartment

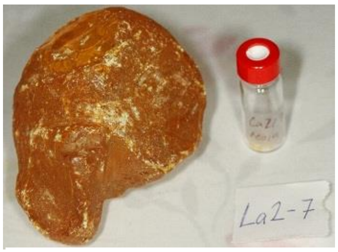


Fig. 5.43 Sampling of La2/7

Description

The box contains one big lump of a yellow transparent resin and two halves of a broken stone. The resin is hard and odourless and has an opaque whitish crust.

Sampling

A sample of a yellow and clear fragment was taken on 27 April 2007 (Fig. 5.43).

Vigani references

The material is located in storage drawer. It is not labelled. No information about its origin or identity has been preserved. Therefore, no information from the invoices and lecture notes can be given.

As a result, no information from historical sources concerning terminology, origin, trade and properties are given.

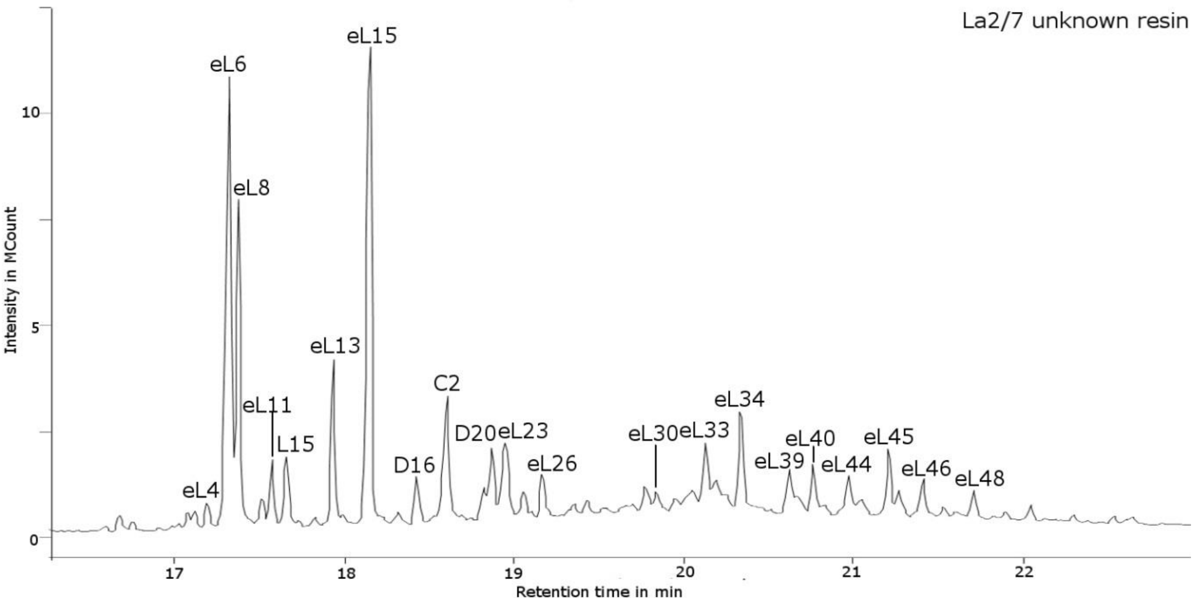
Chemical analysis

In the methylated methanol extracts (Fig. 5.44), high amounts of eperuate, ent-labda-8-en-15-oate and copalate are present together with lower amounts of compound eL11, cativate, compound eL13 and D16, kovalenate, compounds D20, eL23 and eL26, 18-hydroxy-ent-labda-8(20)-en-15-oate (eL33), a hydroxy-ent-labda-8(20),13(14)-dien-15-oate (eL34), a ent-labda-8,18-diol-15-oate (eL40) and compound eL45. Other constituents are ent-pinifolate and the compounds eL39, eL44, eL46 and eL48. The identification of the mentioned compounds is described in chapter 4.2.2.

Discussion

The composition is typical for legume copals, particularly for Congo copal. It is characterised by high amounts of eperuic and labda-8-en-15-oic acids together with copalic, D16, kovalenic, labdanolic, D20, eL32, eL34 and eL40. D20 is found in Congo copals in this work and in literature (van den Berg et al. 2002). eL11 is present in A/5 "Gum Animi" (chapter 5.2.2). The compounds eL13, eL23, eL26, eL39, eL44, eL45, eL46 and eL47 are not present in any of the investigated samples.

In chapter 5.2.2, the exudation of *Hymenaea* resins is described (‘discussion’), which resembles the harvesting of "occidental anime" described in historical sources. Accumulated resin in cavities formed in the trunk runs out and accumulate on the ground in big and irregular masses. A similar exudation is described for African copaliers, hence copal-producing trees (Leonard 1950). Because the chemical composition resembles the modern Congo copals more closely, the resin very likely originates from Africa.



Methylated methanol extract (labels, see table 5.11)

Fig. 5.44 Gas chromatogram of La2/7 unknown resin from the Vigani Cabinet, diterpene section (TIC)

Label	t_R	Name	Main mass fragments
eL4	17.19	Endocyclic ent-labden-15-oate	**95**, 109, 135, 191, 277, 305, (320)
eL6	17.31	Eperuate	**81**, 95, 107, 121, 137, 177, 191, 305, 320
eL8	17.38	Ent-labda-8-en-15-oate	**95**, 107, 121, **191**, 277, 289, 305, 320
eL11	17.57	Unidentified ent-labdane acid, ME	67, 81, 93, **107**, 121, 135, 191, 207, 277, 305, 320
L15	17.66	Cativate	95, **107**, 122, 191, 289, 305, 320
eL13	17.94	Unidentified ent-labdane acid, ME	67, 79, **95**, 107, 121, 136, 191, 277, 289, 305, 320
eL15	18.14	Copalate	**81**, 95, 114, 121, 137, 243, 271, 303, 318
D16	18.43	Unidentified diterpene	67, 79, 95, 107, 119, 135, **189**, 207, 277, 305, 321, 336
C2	18.61	Kovalenate	95, 107, 120, **189**, 243, 253, 303, 318
D20	18.88	Unidentified	95, 109, 135, **191**, 207, 289, 305, (320)
eL23	18.95	Unidentified hydroxy-ent-labdanoate	67, 81, **95**, 109, 123, 189, 207, 271, 303, 321, 336
eL26	19.16	Unidentified ent-labdane	67, 79, **95**, 107, 120, 135, 189, 243, 253, 271, 305
eL30	19.84	Ent-pinifolate, diME	**121**, 161, 235, 304, 364
eL33	20.13	18-hydroxy-ent-labda-8(20)-en-15-oate	67, **81**, 95, 107, 121, 175, 203, 223, 291, **305**, 336
eL34	20.33	Hydroxy-ent-labda-8(20),13(14)-diene-15-oate	121, 135, **205**, 287, 303, 319, 334
eL39	20.63	Unidentfied ent-labdane	109, **121**, 123, 135, 205, 235, 287, 303, 334
eL40	20.76	Ent-labda-8,18-diol-15-oate (proposed)	95, 137, 163, **189**, 207, 304, 322, 354
eL44	20.96	Unidentified ent-labdane	**79**, 81, 91, 93, 107, 121, 135, 147, 189, 203, 251, 289, 301, 319, 348
eL45	21.20	Unidentified ent-labdane	95, **121**, 135, 163, 187, 205, 287, 302, 319, 334
eL46	21.41	Unidentified ent-labdane	95, 109, 123, 137, 163, **189**, 207, 243, 286, 304, 322,354
eL48	21.71	Unidentified ent-labdane	95, 107, 121, 135, 161, 189, 205, 243, 259, **285**, 300

Tab. 5. 11 Compounds found in La2/7 unknown resin, sample analysed with temperature program Diterpenes 1 on column B, mass spectra references see appendix

5.2.4 1/31 Bals Peruv

Fig. 5.45 1/31 "Bals Peruv"

Fig. 5.46 Sampling of 1/31

Description

The compartment contains a glass bottle made of thick glass and approx. ten centimetres high. It differs from the other glass bottles found in drawers 1 and 2, which are smaller and made from thinner glass, and possess a smaller opening.

The bottle is filled with a semifluid and transparent material of a dark blue to black colour. It smells of vanilla. Both the soaked leather cap and the frayed string are loose. The knot of the string differs from that of the other glass bottles investigated.

Sampling

A sample of about 100 mg was taken with a scalpel on 26 April 2007 (Fig. 5.46). It was a dark brown liquid that smelled of vanilla. On the bottom of the bottle, glass splinters were found. Further investigation revealed broken uncoloured glass tubes with a diameter of about 3 to 5 millimetres.

Vigani references

* MS Quns Vig. 2, recto, as "Bals Peru", 2 ounces at 3 shilling & 4 pence; ibid., verso as "Balsam Peru", 2 ounces at 3 shilling & 4 pence.

* Does not appear in LECTURE NOTES UNDATED

* Does not appear in LECTURE NOTES 1707

Contemporary literature

Fine art materials

* SALMON 1701: 387, 390, 423, 425: "Balsam of Peru", "Gum of Peru"

Science

* DALE 1693: 503: "Balsamum Peruanum", "Balsamum Peruvianum nigrum" ("*Hoitziloxitl*, *Arbor Balsami Indici*, sive *Balsamifera prima* Hern., *Cabu(r)eiba sive Balsamum Peruvianum* Pis. & Marg., The Natural Balsam-Tree")

* POMET 1717: 411: "Peruvianischer Balsam"

* LEMERY 1721: 146: "Balsamum Peruvianum seu Indicum", "Baume de Perou", "Peruvianischer Balsam"

* JAMES 1747: 248: "Balsamum peruvianum", "Peruvian Balsam" ("*Balsamum ex Peru* J.B.")

GEOFFROY, THICKNESSE 1749: 220: "Balsam of Peru" ("*Hoitziloxitl*, *Arbor Balsami Indici, Balsamifera prima* Hern., *Balsamum ex Peru* J.B., *Cabureiba, seu Balsamum Peruvianum* Piso, *Cabui Iba* Marg.")

HILL 1751: 701: "Balsamum Peruvianum", "Balsam of Peru" ("*Hoitziloxitl*, *Arbor Balsami Indici* Hern., *Cabureiba, seu Balsamum Peruvianum* Piso")

LEWIS 1761: 120: "Balsamum Peruvianum, indicum, mexicanum, americanum", "Balsam of Peru" ("*Cabureiba* Piso, *Hoitziloxitl seu Arbor balsami indici* Hern.")

Encyclopaedias

CHAMBERS 1728a: 78-9: "Balsam of Peru"

SAVARY DES BRÛSLONS, SAVARY 1723a: 310: "Baume de Perou"

Terminology

"Balsam" or "balm" was used for liquid "resins" such as "turpentines", "balsam of gilead" or "balsam of capivi" (see chapter 5.2.1) (Hill 1751: 699) or more general for a "kind of gum, in very great Reputation in Medicine and Chirurgery; used to be liquified by means of Spirit of Wine or Oil" (Chambers 1728a: (78); also in Savary des Brûslons, Savary 1723a: 309).

It was called from "Peru", because it was originally traded over this place (Harms 1908). Contemporary to Vigani, Hill refers to Peru as the origin of the material and Geoffroy to the origin of the botanical source (Geoffroy, Thicknesse 1749: 221; Hill 1751: 702). By other authors, the material despite called "of Peru" is related to the origin of its botanical source, Meso- and South America.

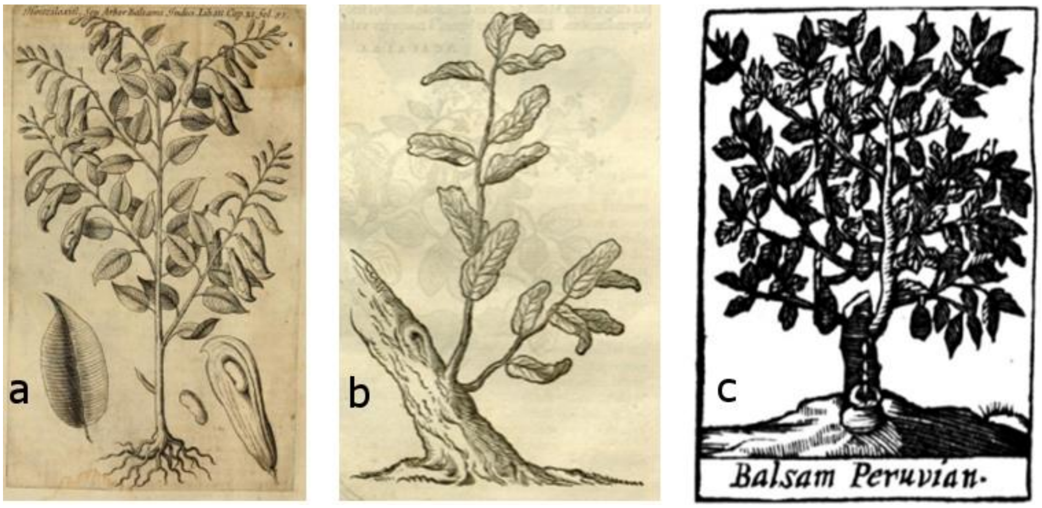
Botanical and geographical origin

"Balsam of Peru" was brought from America, mainly from "New Spain" (Dale 1693: 503; James 1747), but "Peru" and other parts of South America are also mentioned (Geoffroy, Thicknesse 1749: 221; Hill 1751: 702).

The material is already mentioned by Monardes as "Balsamum nouae Indiae, Xilo" (Monardes, Clusius 1579: 13), by J. Bauhin as "balsamum ex Peru" (Bauhin, Cherler 1650: 295) and by Hernandez as "balsamum indicum" (Hernandez 1651: 51). According to Monardes, the tree has leaves similar to "urtica" (stinging nettle), which are serrated and tenuous (Monardes, Clusius 1579: 13, 14). This is not the case with the tree depicted in Hernandez (Fig. 5.47a). It is called "*Hoitziloxitl, seu Arbor Balsami Indici* Hern." (Hernandez 1651: 51). Hernandez describes another "*Hoitziloxitl*" tree with serrated leaves, which is, however, never mentioned in connection with "balsam of Peru" (Hernandez 1651: 37).

Another botanical source mentioned is "*Cabureiba, seu Balsamum Peruvianum* Piso" (Fig. 5.47b) (Piso 1658: 119). This tree was endemic to central South America ("beyond the Brazilian mountains") and its resin was called "cabureiçica". It is obtained in "Ieneiro & in districtibus Divi Vincentii & Spiritus Sancti, quam in Parnambucensi" (Piso 1658: 119). This more closely resembles the consistence and geographical origin of Balsam of Tolu (see chapter 2.2, 5.2.6).

The confusion of the source tree of "balsam of Peru" with that of "balsam of Tolu" can be observed for some time. Linné f. classified both "*Hoitziloxitl*" and "*Cabureiba*" as *Myroxylon peruiferum* L. f. (Linné f. 1781: 233). Harms showed that this tree is not the source of balsam of Peru, nor of Tolu, which is another species of the same genus, *Myroxylon balsamum* (L.) Harms, a reclassification of "*Toluifera balsamum* L." (Linné 1753a: 384; Harms 1908). The latter was also the name Linné gave to the source tree of "balsam of Peru" (see also chapter 5.2.6). In other words, the source tree of balsam of Peru is identical to that of balsam of Tolu. In fact, the two materials are produced by two different varieties of this species (chapter 2.2). The "*Hoitziloxitl*" (yielding "balsamum indicum") shows the typical elongated fruits of *Myroxylon* species (Fig. 5.47a). According to Harms, *Myroxylon balsamum* Harms and *M. peruiferum* L. f. differ mainly by their seeds. *M. peruiferum* possesses furrowed and *M. balsamum*



a - "Hoitziloxitl, seu Arbor Balsami Indici" (Hernandez 1651: fol. 51), b - "Cabureiba" (Piso 1658: 119) and c - "Balsamum Peruvanum" (Lemery 1721: 147)

Fig. 5 47 Historical trees mentioned in connection with "Balsam of Peru"

smooth seeds (Harms 1908). Because "*Hoitziloxitl*" has smooth seeds, it is very likely not *M. peruiferum* L. f., which furthermore is not endemic to Mesoamerica but to Northern South America (Venezuela, Columbia, Brazil, Ecuador).

Manufacture and trade

"Balsam of Peru" was traded in three different sorts as follows.

1. "White balsam of Peru" or "balsam of incision" is obtained by making incisions into the strong branches and the trunk. This sort was considered to be the best and approaches the quality of "balsam of Gilead". It is of a pale white colour (Pomet 1717: 411; Lemery 1721: 146; Chambers 1728a: 79; James 1747: 249; Geoffroy, Thicknesse 1749: 220; Hill 1751: 702).

2. "Common or black balsam of Peru" is prepared by boiling the branches, bark, leaves and roots of the tree in water for several hours. When the water has cooled down, the balsam swims on the surface and is skimmed off (Pomet 1717: 411f; Lemery 1721: 146; James 1747: 249; Hill 1751: 702). Lewis points out that "black balsam of Peru" partly swims and partly sinks when placed in water, which points towards a different preparation method (Lewis 1761: 120). This sort is used most frequently. It is of a black colour (Pomet 1717: 411; Lemery 1721: 146; Chambers 1728a: 79; James 1747: 249; Geoffroy, Thicknesse 1749: 221; Hill 1751: 702).

3. "Dry Balsam" or "balsamum siccum" runs from small branches or from cut branches and is collected in small vessels or coconuts fastened to the tree. It hardens in the sun for several days or is slightly heated to remove the moisture until it turns hard (Pomet 1717: 411f; Lemery 1721: 146; Chambers 1728a: 79). It is initially milky white and turns reddish to black through exposure to the sun (ibid.).

The "*Hoitziloxitl, seu Arbor Balsami Indici* Hern." of Hernandez ("balsamum indicum") yields a yellow to black balsam by incision and by cooking the branches (Hernandez 1651: 51-2), the resin of "*Cabureiba, seu Balsamum Peruvianum* Piso" ("cabureiçica") was extracted from wounded bark ("ex laeso cortice") and seed capsules (Piso 1658: 119).

"Balsam of Peru" is traded via Amsterdam in pots or bottles (Savary des Brûslons, Savary 1748a: 912). "White balsam of Peru" is traded in gourd shells (Lewis 1761: 121). Pomet mentions that the Portuguese sell it to the Dutch (Pomet 1717: 413).

Properties

"Balsam of Peru" is a thick and viscous liquid similar to thin "turpentine". It is resinous and inflammable (Dale 1693: 503; Hill 1751: 701). It is of a reddish to black colour, with a bitter and acrid but aromatic taste and a fragrant smell similar to "benjamin" (Dale 1693: 503; Hill 1751: 701). It is poorly soluble in water and does not turn the water milky, but it is soluble in "rectified spirit of wine" and in heated "alkaline lixivia" (Lewis 1761: 121).

"Balsam of Peru" is adulterated with "turpentine" (Dossie 1758a: 376) or almond oil (Pomet 1717: 413). The sort traded by the Portuguese to the Dutch was mixed with aromatic oils and spices (Pomet 1717: 413). Sometimes "bijon turpentine", which has similar properties, is sold as a substitute (Savary des Brûslons, Savary 1748c: 371(2)) (see chapter 5.1.3).

A recipe for the imitation of "balsam of Peru" is given by Pomet: a pound of "therebenthine fine", a pound of "galipot", six ounces of "gomme elemy" and six ounces of "huile de ben" are mixed and melted. A powder is made from a pound of "oliban", a pound of "labdanum", four ounces of "fleur de lavande", four ounces of "muscade", two ounces of "spic nard", two ounces of "bois d'aloes", three lots of "myrrhe", three lots of "sang dragon", two lots respectively of "pett valerienne", "iris", "sourchet long", "acorus verus", "azarum", "macis", "benjoin" and "storax". One and a half lots respectively of "petit galanga", "zedoare", "girosle", "canelle", "castor" and "mastic" are added. The mixture is distilled and the third part is a black balsam, which is taken fo "balsam of Peru" by some (Pomet 1694: 278).

"White balsam of Peru" is fluid and of the consistence of "turpentine". It has a white colour and a fragrant smell similar to "balsam of Gilead" or "opobalsamum". It is clear and pellucid, very viscous and of an agreeable, aromatic and pungent taste (Hill 1751: 702). It turns solid and brittle with aging (James 1747: 249; Lewis 1761: 121). It is soluble in "rectified spirit" and in oil. It is often adulterated with "venice turpentine" (James 1747: 249). Its smell resembles that of "benzoe" or "storax", while that of "balsam of Gilead" is similar to lemons (Pomet 1717: 412; Lemery 1721: 146; Chambers 1728a: 79; Hill 1751: 702). Both behave similarly when dropped in water, forming a "pellicle cohesive" (Lewis 1761: 122). The "cabureiçica" from the South American "*Cabureiba*" is described as "compacta & tenaci, sed calfactum sequci & ductili" (Piso 1658: 119).

"Black balsam of Peru" is blackish to brown, fragrant and sticky like "turpentine", with the consistence of thin honey (Lemery 1721: 146; Lewis 1761: 120). Its smell is described as sweet, similar to that of "storax" (Lemery 1721: 146) or "benzoe" (Geoffroy, Thicknesse 1749: 221). It has a pungent taste (Lemery 1721: 146). It is often adulterated, probably with "liquid storax" (ibid.). When adulterated, it is thick and coagulated, does not have the penetrating smell and taste of the original and is poorly soluble in "spirit of wine" (James 1747: 249).

"Balsamum siccum" is hard, reddish and fragrant (Lemery 1721: 146).

Possible chemical composition

"Balsam of Peru" was a frequently used material in Vigani's time, except for the white sort, which is mentioned to be very rare (James 1747: 249). As discussed under 'Botanical origin' the botanical source of "balsam of Peru" described by Hernandez is probably identical to *Myroxylon balsamum* Harms var. *pereirae*. It grows mainly at the Balsam coast in Central

America, from where it was shipped to Europe via Peru (Harms 1908; Mammerler 2007: 5, 6). While the black and fluid sort is still traded today, "white balsam of Peru" and "balsamum siccum" are not available anymore (chapter 2.2).

Different reference samples of commercially available Balsam of Peru were analysed for this investigation, with the results presented in chapter 4.2.3. The analysis is largely consistent with published data (see chapter 2.2). Characteristic compounds are benzyl, cinnamyl and coniferyl alcohols together with benzoic, cinnamic and ferulic acids as well as their esters. p-Coumaryl alcohol and p-coumaric acid are not found, but small amounts of a compound proposed to be benzyl-p-coumarate are. Additionally, several phenylpropanoid esters not described in literature are found. The main differences to Balsam of Tolu are the presence of cinnamylbenzoate and the lack of triterpene compounds, as well as a generally more complex composition (see also ‘chemical composition’ in chapter 5.2.6). This corresponds to results from early chemical analysis that indicate that both resins differ quantitatively rather than qualitatively (Harms 1908).

An adulteration with "(bijon) turpentine" is recognisable by the presence of diterpene acids with an abietane and pimarane skeleton (see chapter 5.1.3). An adulteration with "venice turpentine" is recognisable by the presence of the same compounds and possible marker compounds of larch turpentine such as epimanool, larixol and larixylacetate (see chapter 5.1.4). "Liquid storax" is the resinous balsam of several *Liquidambar* species (Howes 1950; Hsu, Andrews 2006; Lardos et al. 2011). An adulteration with a *Liquidambar* resin would be recognisable by the presence of 3-phenylpropanyl alcohol and the corresponding cinnamate as well as triterpene compounds such as oleanolic, oleanonic and 3-epi-oleanoic acids (Hafizoğlu et al. 1996; Pastorova et al. 1998; Modugno et al. 2006a; Hovaneissian et al. 2008).

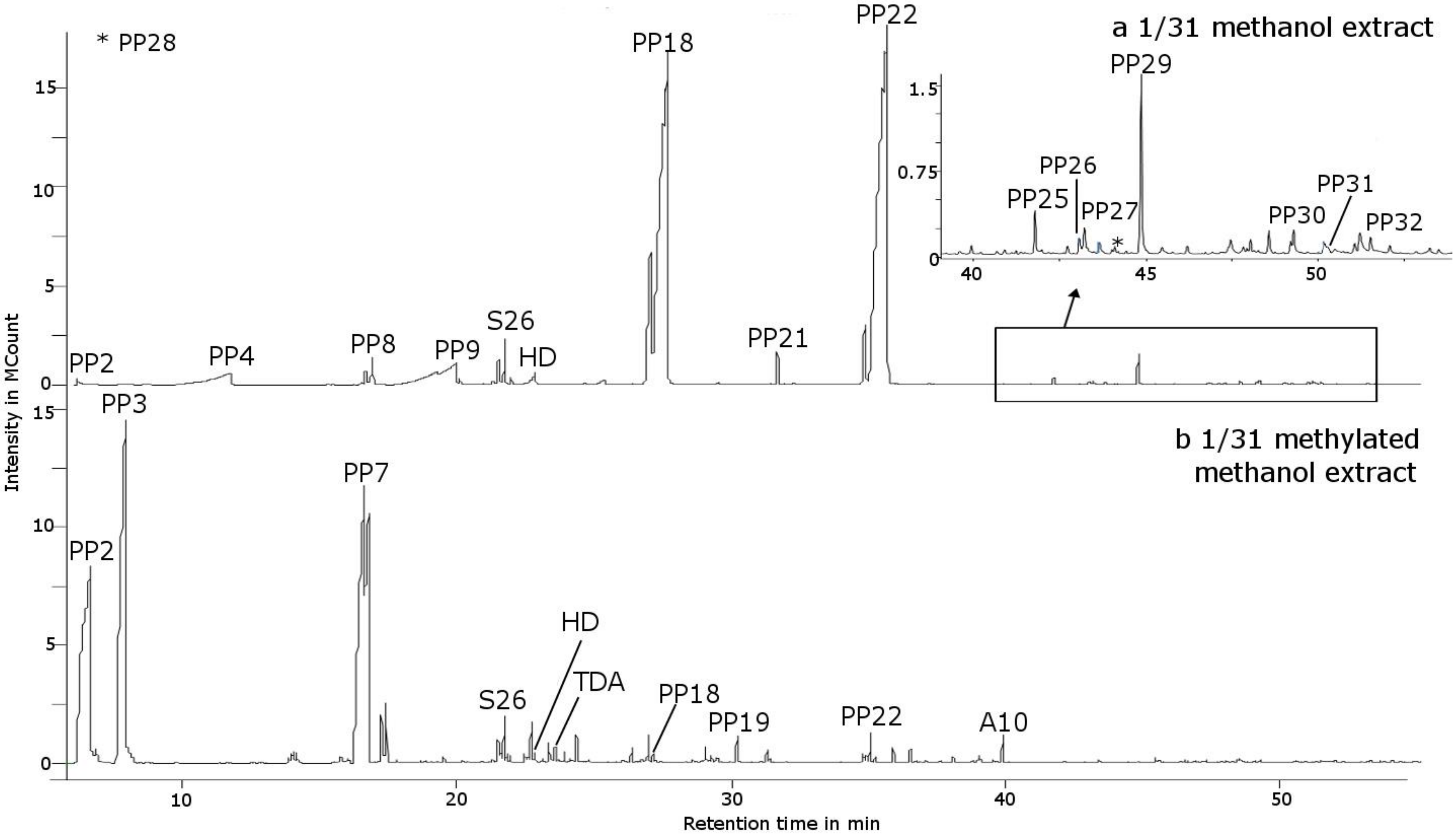
Chemical analysis

The methanol extract (Fig. 5.48a) contains high amounts of benzylbenzoate and benzylcinnamate together with smaller amounts of benzyl alcohol, benzoic and cinnamic acids, vanillin, trans-nerolidol, cinnamylbenzoate, cinnamylcinnamate and (iso)benzylferulate. Other compounds are benzyl-p-coumarate, methyl-dihydroconiferylbenzoate and -cinnamate, PP_{28}, PP_{31} and PP_{32}. The identification of the phenylpropanoid esters is discussed in chapter 4.2.3, see also table 4.19. In the methylated methanol extract (Fig. 5.48b), benzoate and cinnamate, 3,4-dimethoxybenzoate and dehydroabietate are additionally present.

Discussion

The composition is typical of Balsam of Peru (Myroxylon balsamum var. pereirae). The main constituents are high amounts of benzylbenzoate and benzylcinnamate with small amounts of cinnamylbenzoate and cinnamylcinnamate. Free benzoic and cinnamic acids are present as well, but none of the compounds described in the historical sources above as possible markers for adulterations. Because dehydroabietate is not accompanied by other pimarane and abietane acids, its presence is more likely the result of a contamination than of an adulteration. On the other hand, small amounts of dehydroabietic may be present naturally. An adulteration with colophony as found in one of the modern reference samples should be accompanied by much higher amounts of pimaranes and abietanes, such as pimaric, isopi maric, dehydroabietic acids and their aging products.

"Balsam of Peru" is mentioned twice in the invoices from Fran Porter dated March 1703 (MS Quns Vig.2). According to Wagner, the material was transported in two separate containers



a - methanol extract and b - methylated methanol extract (labels, see table 5.12)

Fig. 5.48 Gas chromatograms of 1/31 “Bals Peruv” from the Vigani Cabinet, diterpene section (TIC)

Label	t_R	Name	Main mass fragments
PP2	6.16	Benzyl alcohol	77, **79**, 91, 108
PP3	7.79	Benzoate	51, 77, **105**, 135, 136
PP4	11.54	Benzoic acid	51, 77, **105**, 122
PP7	16.47	Cinnamate	51, 77, 103, **131**, 161, 162
PP8	16.88	Vanillin	81, 109, 123, **151**, 152
PP9	19.78	Cinnamic acid	77, 91, 103, 131, **147**, 148
S26	21.73	trans-Nerolidol	67, 79, 81, **93**, 107, 121, 161, (222)
PP18	27.39	Benzylbenzoate	77, 91, **105**, 167, 194, 212
PP19	30.21	3,4-Dimethoxy-cinnamate	91, 147, 191, 207, **222**
PP21	31.65	Cinnamylbenzoate	77, **91**, 103, 115, 131, 147, 178, 195, 220, 238
PP22	35.49	Benzylcinnamate	77, **91**, 103, 115, 131, 192, 220, 238
A10	39.91	Dehydroabietate	**239**, 299, 314
PP25	41.77	Cinnamylcinnamate	77, 91, 103, 115, 117, **131**, 219, 235, 264
PP26	43.06	Benzyl-p-coumarate	**91**, 120, 147, 208, 209, 236, 254
PP27	43.22	Dihydroconiferylbenzoate, methoxy	77, **105**, 137, 150, 163, 300
PP28	44.09	Unidentified	77, **105**, 131, 179, 284
PP29	44.86	Isobenzylferulate	91, 145, 150, 161, 177, 207, 239, 266, **284**
PP30	49.28	Dihydroconiferylcinnamate, methoxy	103, **131**, 137, 150, 189, 326
PP31	50.28	Unidentifed	103, **131**, 265, 298, 310
PP32	51.53	Unidentified	139, 175, 189, **312**

Tab. 5.12 Compounds found in 1/31 "Bals Peruv", samples analysed with temperature program Phenylpropanoids 2 at column A, mass spectra references see appendix

and is therefore listed twice (Wagner 2007a: 85). A third "Bals peru" is mentioned in another invoice from Henry Colchester dated April 1704 (MS Quns Vig. 4). It was delivered in a smaller quantity and for a somewhat lower price. According to the existent quantities, the material invoiced in 1703 was related to 1/31 "Bals Peruv" and the one invoiced in 1704 to 2/1 "Bals Peru" (chapter 5.2.5). Both were obtained from a *Myroxylon* species, very likely *Myroxylon balsamum* var. *pereirae* Harms, and both are certainly of the black and liquid sort ("Black balsam of Peru"). The material in compartment Z/17 labelled "Balsamum Tolutanum" proved to be a Balsam of Peru as well (see chapter 5.2.6). The identity and chemical composition of the first sort, "white balsam of Peru" cannot be determined within this work.

The bottle was opened for analysis at the beginning of the 20th century (Evers 1933). As described by Wagner, the bottles of drawer 1 were moved, probably after 1933 (Wagner 2007a: 65; Wagner 2007c: Drawer 1). Most probably, the original bottle was destroyed and the material rebottled. The colourless broken glass tubes found inside the bottle are probably remains of the previous sampling.

A final conclusion is given in chapter 5.2.6.

5.2.5 2/1 Bals Peru

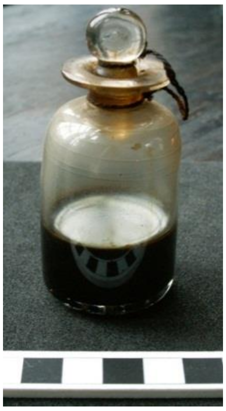


Fig. 5.49 2/1" Bals Peru"

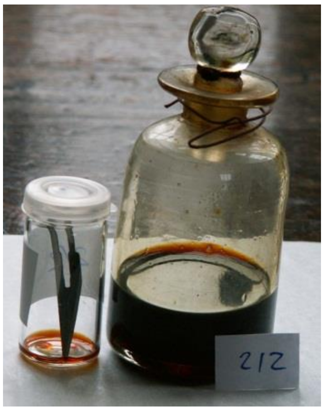


Fig. 5.50 Sampling of 2/1

Description

The glass bottle is filled with a semifluid material of a dark blue to black colour. The plug was tight, probably because of sticky residues of the content.

Sampling

The bottle was opened through carefully heating. A sample was taken with a scalpel on 30 March 2009 (Fig. 5.50). It was a dark brown liquid with a sweetish smell.

Vigani references

* MS Quns Vig. 4, folio 4, recto as "Bals peru", 1 ounce at 1 shilling & 6 pence, bottle 1 penny

Contemporary literature

See chapter 5.2.4

Terminology

See chapter 5.2.4

Botanical and geographical origin

See chapter 5.2.4

Manufacture and trade

See chapter 5.2.4

Properties

See chapter 5.2.4

Possible chemical composition

See chapter 5.2.4

Chemical analysis

The methanol extract (Fig. 5.51a) contains high amounts of benzylbenzoate and benzylcinnamate together with smaller amounts of benzoate, cinnamate, benzoic and cinnamic acids, vanillin, trans-nerolidol and cinnamylbenzoate. Other compounds are very small amounts of cinnamylcinnamate and isobenzylferulate. In the methylated methanol extract (Fig. 5.51b), 3,4-dimethoxy-cinnamate and dehydroabietate are additionally present. Benzyl alcohol is not found, because the solvent delay was too long.

Discussion

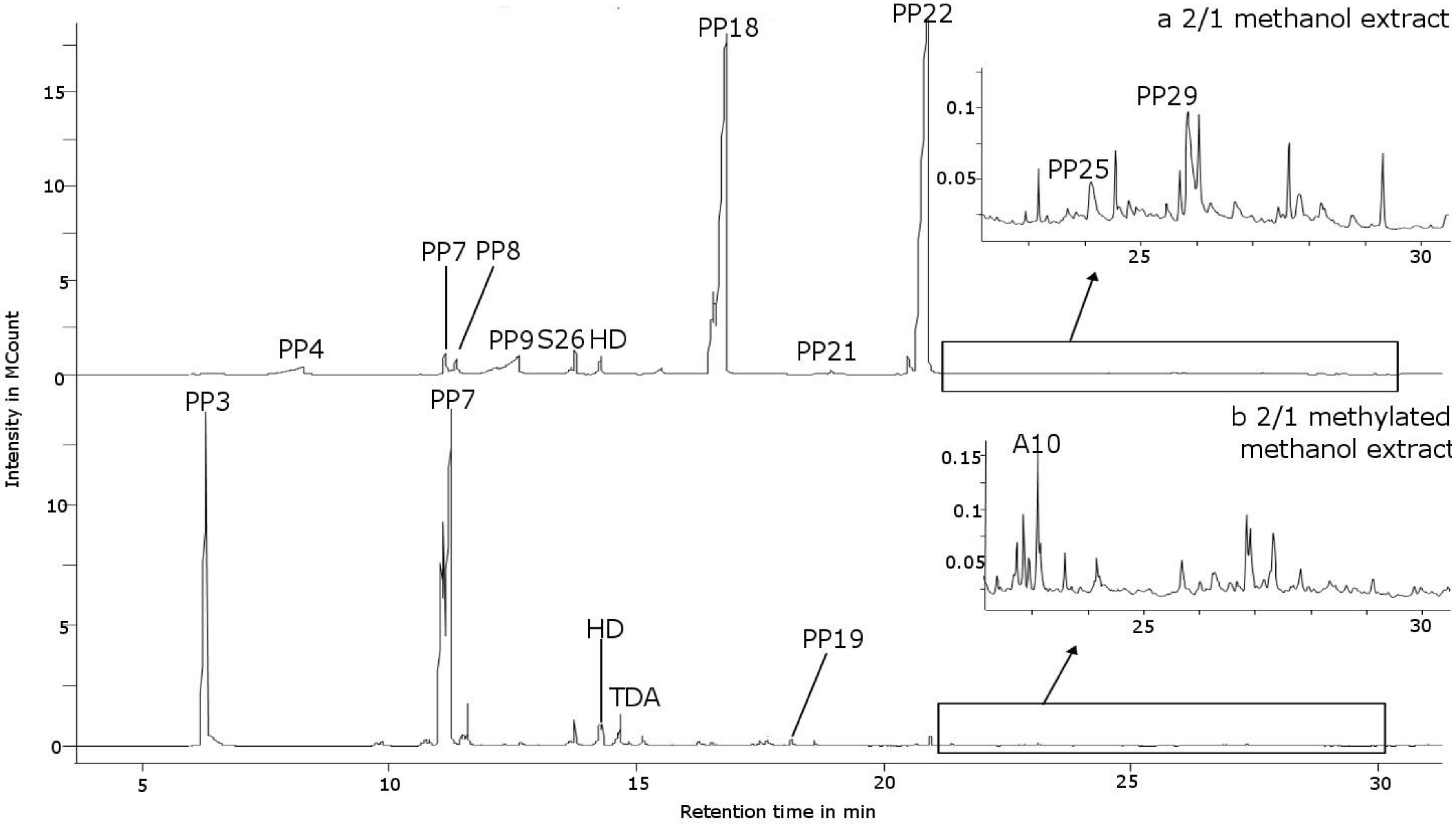
The composition is typical for Balsam of Peru (*Myroxylon balsamum* var. *pereirae)*. The main constituents are high amounts of benzylbenzoate and benzylcinnamate. Cinnamyl esters are present only in very small amounts. Contrary to 1/31 "Bals Peruv", 2/1 "Bals Peru" contains the natural methylesters of benzoic and cinnamic acids. The presence of the natural methylester corresponds to similar findings in modern Balsam of Peru. It is probably the result of heating the wood, which releases methanol. They are present in Z/17 "Balsam Tolutanum" as well (chapter 5.2.6). The presence of dehydroabietic acid is discussed in chapter 5.2.4.

The composition slightly differs from that of 1/31 "Bals Peruv" (chapter 5.2.4), mainly by the absence of some compounds. However, both materials were obtained from a *Myroxylon* species, very likely *Myroxylon balsamum* var. *pereirae* Harms, and both are certainly of the black and liquid sort ("Black balsam of Peru"). For a further discussion of the three sorts described in historical sources see chapter 5.2.4, 'discussion'.

A final conclusion is given in chapter 5.2.6.

Label	t_R	Name	Main mass fragments
PP3	6.24	Benzoate	51, 77, **105**, 135, 136
PP4	8.12	Benzoic acid	51, 77, **105**, 122
PP7	11.10	Cinnamate	51, 77, 103, **131**, 161, 162
PP8	11.35	Vanillin	81, 109, 123, **151**, 152
PP9	12.50	Cinnamic acid	77, 91, 103, 131, **147**, 148
S26	13.75	trans-Nerolidol	67, 79, 81, **93**, 107, 121, 161, (222)
PP18	16.56	Benzylbenzoate	77,91, **105**, 167, 194, 212
PP19	18.12	3,4-Dimethoxy-cinnamate	91, 147, 191, 207, **222**
PP21	18.91	Cinnamylbenzoate	77, **91**, 103, 115, 131, 147, 178, 195, 220, 238
PP22	20.82	Benzylcinnamate	77, **91**, 103, 115, 131, 192, 220, 238
A10	23.10	Dehydroabietate	**239**, 299, 314
PP25	24.14	Cinnamylcinnamate	77, 91, 103, 115, 117, **131**, 219, 235, 264
PP29	25.84	Isobenzylferulate	91, 145, 150, 161, 177, 207, 239, 266, **284**

Tab. 5. 13 Compounds found in 2/1 "Bals Peru", sample analysed with temperature program Phenylpropanoids 1 on column A, mass spectra references see appendix



a - methanol extract andb - methylated methanol extract (labels, see table 5.13)

Fig. 5. 51 Gas chromatograms of 2/1 "Bals Peru" from the Vigani Cabinet, diterpene section (TIC)

5.2.6 Z/17 Balsam Tolutanum

Fig. 5.52 Z/17 "Balsam Tolutanum"

Fig. 5.53 Sampling of Z/17

Description

The box contains a brown nut shell filled with a dark brown to black material. It is dried-up and very brittle and has a slight smell of vanilla. It is of a glassy and glossy appearance. The material has partly been removed from the shell.

Sampling

A sample (about 230 mg) was taken on 26 April 2007 (Fig 5.53). It consisted of brown glassy splinters with a glossy fracture.

Vigani references

* MS Quns Vig. 4, folio 4, recto as "Bals Tolu", 5 ¼ ounces at 7 shilling & 10 ½ pence

A different Balm of Tolu is mentioned in MS Quns Vig. 2, recto, as "Bals Tolu", 2 ounces at 3 shilling. This material could not be found in the Cabinet.

* Does not appear in LECTURE NOTES UNDATED

* Does not appear in LECTURE NOTES 1707

Contemporary literature

Fine art materials

* SALMON 1701: 425: "Gum of Tolu"

Science

* DALE 1693: 397: "Balsamum de Tolu" ("*Balsamum Tolutanum, foliis Ceratiae similibus* C.B., *Balsamifera quarta seu Provinciae Tolu* Hern., The Balsam-Tree of Tolu")

* POMET 1717: 417: "Tolutanischer Balsam"

* LEMERY 1721: 146: "Balsamum de Tolu"

* JAMES 1747: 249: "Balsamum Tolutanum", "Balsam of Tolu" ("*Balsamum Tolutanum, foliis Ceratiae Similibus, quod candidum* C.B., The Balsam tree of Tolu")

* GEOFFROY, THICKNESSE 1749: 222: "Balsam of Tolu", "Balsamum Tolutanum", "Balsamum solidum" ("*Balsamum tolutanum, foliis Ceratio similibus* C.B., *Balsamum de Tolu* J.B., *Balsamum Provinciae Tolu* Hern.")

* HILL 1751: 703: "Balsamum Tolutanum", "Balsam of Tolu" ("*Balsamifera Quarta* Hern. ")

* LEWIS 1761: 122: "Balsamum Tolutanum", "Balsam of Tolu"

Encyclopaedias

* CHAMBERS 1728a: 79: "Balsam of Tolu"

* SAVARY DES BRÛSLONS, SAVARY 1748a:
912: "Baume de Tolu"

Terminology

The origin of the name "Tolu" was related to a region in South America or "New Spain" (Dale 1693: 397; Hill 1751: 703; Lewis 1761: 122).

It is derived from the native tribe of Tolúes. The region mentioned is probably located in Columbia or Panama, where several modern names of towns and regions are reminiscent of "Tolu" and "Carthagena".

Botanical and geographical origin

The term "balsam of Tolu" was used for a resinous balsam obtained from a tree growing in different parts of America (Lemery 1721: 146; Hill 1751: 703). It was called the "Balsam-tree of Tolu" or just "Tolu" (Dale 1693: 397; Lemery 1721: 146; James 1747: 249). Its botanical name is "*Balsamum Tolutanum foliis Certatiae similibus, quod candidum est*" from Bauhin, who refers to Monardes: "Balsamum de Tolu, Monardi, ex insulis Tolu, Ind. Occid.” (Bauhin 1623: 401[10]). It is described as similar to "spruces" and small "pines" (Bauhin 1623: 401; Dale 1693: 397; Lemery 1721: 146). Another name mentioned is "*Balsamifera quarta seu Provinciae Tolu* Hern." (Hernandez 1651: 53; Dale 1693: 397; Geoffroy, Thicknesse 1749: 222; Hill 1751: 703).

Manufacture and trade

"Balsam of Tolu" runs from incisions made into the tree at hot weather. It is removed with spoons made from black wax and collected in gourd shells (Dale 1693: 397; Pomet 1717: 418; Lemery 1721: 146; Chambers 1728a: 79; Hill 1751: 703; Lewis 1761: 122).

"Balsam of Tolu" was traded from "Carthagena" (Hernandez 1651: 52; Pomet 1717: 417; Lemery 1721: 146). Another place mentioned is "Nombre de Dios", (Hernandez 1651: 52; Pomet 1717: 417; Lemery 1721: 146). Hill mentions "Honduras", which, according to Geoffroy, is the Spanish name of the native "Tolu" (Geoffroy 1748: 222; Hill 1751: 703).

"Balsam of Tolu" was rare in France but common in England (Pomet 1717: 418; Geoffroy, Thicknesse 1749: 223; Savary des Brûslons, Savary 1748a: 911).

Properties

"Balsam of Tolu" is a sticky and viscous liquid of reddish, brown or yellowish colour. It has a fragrant smell resembling a mixture of "benjamin", "storax" and "balm of Gilead" with a note of lemons and "benzoine" (Dale 1693: 397; Lemery 1721: 146; Geoffroy, Thicknesse 1749: 222; Hill 1751: 703; Lewis 1761: 122). It is initially very thin and thickens over time (Hill 1751: 703; Lewis 1761: 122). The material found in the shops is of the consistence of honey (Dale 1751: 703). It turns hard and brittle with aging (James 1747: 249; Geoffroy, Thicknesse 1749:

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[10] The cited passage was not found. Monardes mentions a "resina carthaginensis" in the Latin edition of the *Historia medicinal* (Monardes, Clusius 1579: 17).

222; Lewis 1761: 122). It has an agreeable, sweetish and slightly pungent taste (Dale 1693: 397; Lewis 1761: 122). It dissolves completely in "rectified spirit of wine" (Lewis 1761: 122).

Possible chemical composition

The botanical classification of *Myroxylon* resins is discussed in chapter 5.2.4 ('Botanical and geographical origin'). *M. balsamum* var. *balsamum* is endemic to Northern South-America, mainly Venezuela and Columbia (chapter 2.2).

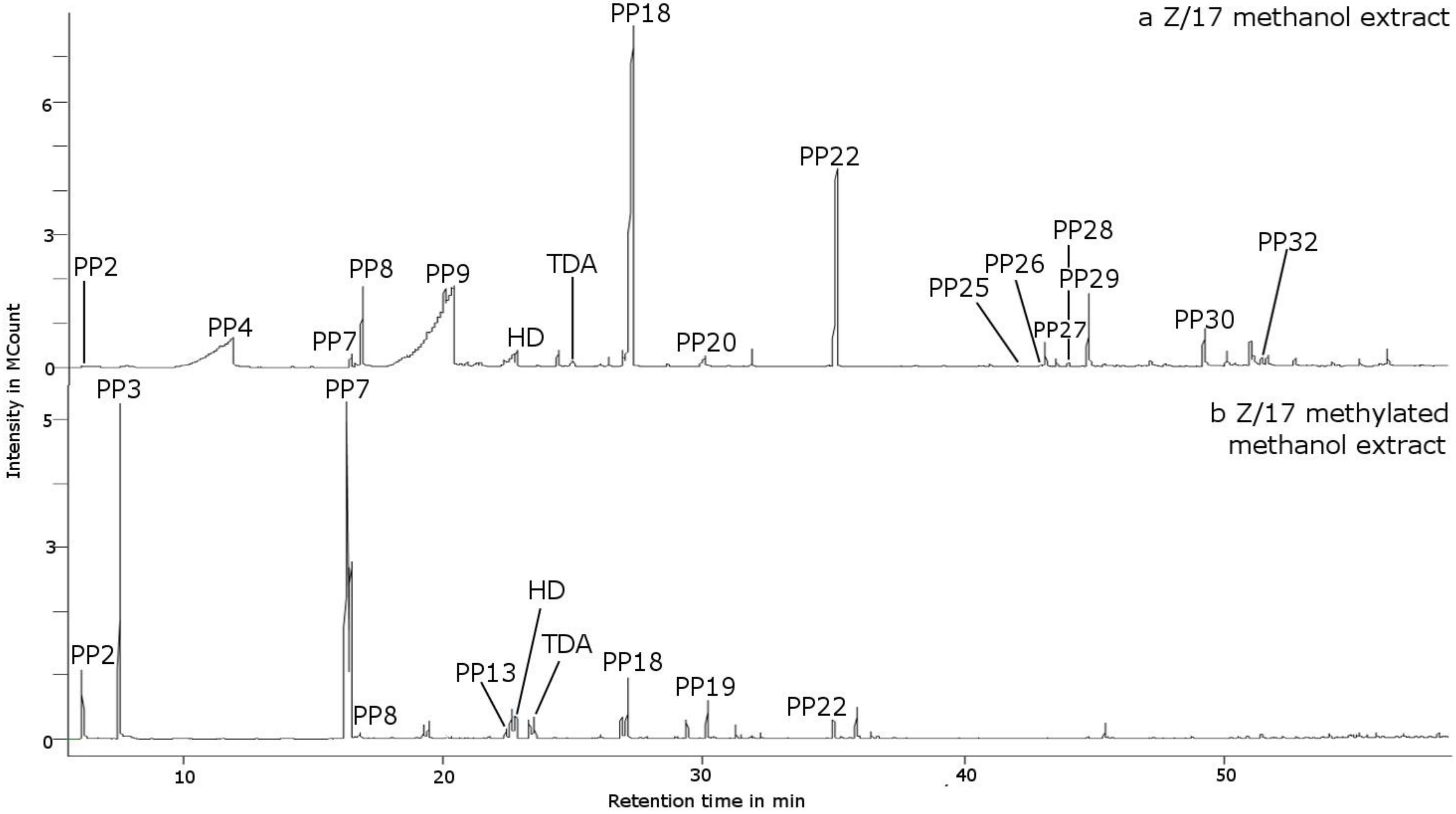
Different reference samples of commercial available Balsam of Tolu were analysed for that investigation, with the results presented in chapter 4.2.3. The phenylpropanoid composition is very similar to that of Balsam of Peru. Characteristic compounds are high amounts of benzyl- and cinnamyl alcohols with benzoic and cinnamic acids as well as their esters. Balsam of Peru differs from Balsam of Peru by the absence of cinnamylbenzoate. (Iso)benzylferulates reported in literature are present only in small amounts. In one of the samples small amounts of dihydroconiferylcinnamate are present as well. The characteristic triterpene fraction (hydroxydammarenone, oleanonic, oleanolic, acetoxy-oleanolic and acetoxy-ursolic acids) described in literature is found, too.

Chemical analysis

The methanol extract (Fig. 5.54a) contains high amounts of benzylbenzoate and benzylcinnamate with smaller amounts of benzoic, cinnamic, vanillic and ferulic acids, isobenzylferulate and dihydroconiferylbenzoate and -cinnamate. Other compounds are benzyl alcohol, benzoate, cinnamate, cinnamylcinnamate, benzyl-p-coumarate, PP$_{28}$ and PP$_{32}$. In the methylated methanol extract (Fig. 5.54b), 3,4-dimethoxycinnamate is additionally present.

Label	t$_R$	Name	Main mass fragments
PP2	6.10	Benzyl alcohol	77, **79**, 91, 108
PP3	7.79	Benzoate	51, 77, **105**, 135, 136
PP4	11.54	Benzoic acid	51, 77, **105**, 122
PP7	16.24	Cinnamate	51, 77, 103, **131**, 161, 162
PP8	16.85	Vanillin	81, 109, 123, **151**, 152
PP9	20.23	Cinnamic acid	77, 91, 103, 131, **147**, 148
PP13	21.98	Vanillic acid	57, 71, 97, 125, 153, **168**
PP18	27.22	Benzylbenzoate	77, 91, **105**, 167, 194, 212
PP20	30.03	Ferulic acid	77, 133, 179, **194**
PP19	30.15	3,4-Dimethoxy-cinnamate	91, 147, 191, 207, **222**
PP22	35.09	Benzylcinnamate	77, **91**, 103, 115, 131, 192, 220, 238
PP25	42.08	Cinnamylcinnamate	77, 91, 103, 115, 117, **131**, 219, 235, 264
PP26	43.06	Benzyl-p-coumarate	**91**, 120, 147, 208, 209, 236, 254
PP27	43.16	Dihydroconiferylbenzoate, methoxy	77, 105, **137**, 150, 163, 300
PP28	44.05	Unidentified	77, **105**, 131, 179, 284
PP29	44.81	Isobenzylferulate	91, 145, 150, 161, 177, 207, 239, 266, **284**
PP30	49.26	Dihydroconiferylcinnamate, methoxy	103, **131**, 137, 150, 189, 326
PP32	51.48	Unidentified	139, 175, 189, **312**

Tab. 5.14 Compounds found in Z/17 "Balsam Tolutanum", sample analysed with temperature program Phenylpropanoids 2 on column A, mass spectra references see appendix



a - methanol extract and b - methylated methanol extract (labels, see table 5.14)

Fig. 5.54 Gas chromatograms of Z/71 "Balsam Tolutanum" from the Vigani Cabinet, diterpene section (TIC)

Discussion

The composition is typical for Balsam of Peru (*Myroxylon balsamum* var. *pereirae*). The main constituents are high amounts of benzylbenzoate and benzylcinnamate. Cinnamyl esters are present only in very small amounts. Additionally, Z/17 "Balsam Tolutanum" is composed very similarly to 1/31 "Bals Peruv" and 2/1 "Bals Peru", which both were identified as Balsam of Peru (chapter 5.2.4, 5.2.5). The presence of vanillic acid and the lower relative amounts of benzylcinnamate points to Balsam of Peru as well. Balsam of Tolu (*M. balsamum* var. *balsamum*) should contain several triterpenes.

On the other hand, trans-nerolidol and cinnamylbenzoate, which were found as a marker for Balsam of Peru in the reference analysis (chapter 4.2.3), are not present in Z/17, but in 1/31 and 2/1. Z/17 "Balsam Tolutanum" resembles the third sort of "balsam of Peru" "balsamum siccum", which is described to be a red and hard material traded in coconuts or gourd shells. Because historical "balsam of Tolu" was traded in gourd shells as well, Z/17 was probably mistaken for "balsam of Tolu".

In contrary, the presence of natural methylester of cinnamic and benzoic acids points to another manufacture. It should include the heating of wood, such as described for "black balsam of peru" (see chapter 5.2.5). This, however, disagrees with the assumed identity of Z/17 "Balsam Tolutanum" as "balsam siccum", which was obtained by incision. However, such natural methylesters are not present in 1/31 "Bals Peruv", too. 1/31 was certainly obtained from *Myroxylon balsamum* var. *pereirae* and is true Balsam of Peru, for which reason they are probably not the result of manufacture.

In summary, based on the chemical compositions, the three materials from the Cabinet with a phenylpropanoid composition (1/31, 2/1, Z/17) are Balsam of Peru obtained from the same variety of *Myroxylon balsamum*. They resemble two of the three sorts of "balsam of Peru" described in historical sources. The variations in the chemical composition very likely result from natural variations or differing harvesting methods and manufacture, because all three materials have a (slightly) different appearance.

Despite the geographical connotation, both "balsam of Peru" and "balsam of Tolu" were related to different regions in America, such as "New Spain" and South America. This was obviously based on the attribution to the different botanical sources mentioned. Particularly for "balsam of Peru", this was in contrast to its name. Because it is known today that *Myroxylon balsamum* var. *pereirae* is found only in Mesoamerica but not in South America, "*Cabureiba, seu Balsamum Peruvianum* Piso" can only be the source of "white balsam of Peru" or, if not, it is a false information. This, however, would imply that the two species mentioned as the source of "balsam of Tolu" are historical names of *M. balsamum* var. *balsamum*, which cannot be clarified within this work, because no true Balsam of Tolu is found in the Cabinet.

5.3 Angiosperm resins II – Sapindales

Resins from the order Sapindales originate from the families Anacardiaceae, Burseraceae and Rutaceae. The chemistry of Sapindales is summarised in chapter 2.3. A variety of reference samples was analysed (chapter 4.3), with the results discussed in chapter 4.3.2. Based on these data profiles, this chapter presents all materials from the Vigani Cabinet containing mainly triterpenes.

5.3.1 A/11 Mastiche

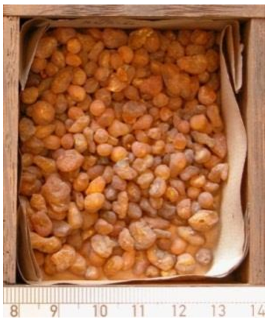


Fig.5.55 A/11"Mastiche"


Fig. 5.56 Sampling of A/11

Description

The box is filled with almost round lumps of orange to red colour. The surface is darker than the transparent and dark orange interior. They are hard, slightly brittle and odourless.

Sampling

A sample of about 100 mg was taken on 26 April 2007 (Fig. 5.56). It was a dark orange to brown longish and brittle drop. It had a transparent and orange interior and an opaque layer at the surface

Vigani references

* MS Quns Vig. 4, Folio 3, verso, as "Gum Mastich", 2 ounces at 1 shilling

* Does not appear in LECTURE NOTES UNDATED

* Does not appear in LECTURE NOTES 1707

Contemporary literature

Fine art materials

* SALMON 1701: 68, 76f, 835, 840, 867f, 872-4: "Gum Mastick", "Mastich(e)"

* CHAMBERS 1728b: 508: "Mastic"

* DOSSIE 1758a: 160, 179, 212-4: "Gum mastic"

* CARLYLE 2001: WILLIAMS 1787: 51f., 56; ANON. 1795: 46, 195; ANON. 1801: 69; IBBETSON 1803: 15; TINGRY 1804: 87, 133; ANON. 1808: 74f., 77, 221

Science

* BAUHIN 1623: 399, 501: "Resina lentiscina sive Mastiche, hodie Mastix" ("*Lentiscus vulgaris* Dod.")

* MANGET 1687: 518: "Mastiche"

* DALE 1693: 457: "Gummi Resina Mastiche" ("*Lentiscus Vulgaris* C.B., Mastick-Tree")

* POMET 1717: 135: "Mastic" ("*Lentiscus*")

* LEMERY 1721: 705, 626: "Mastiche, Mastic, Mastix" ("*Lentiscus* Dodon. Raji, *Lentiscus vulgaris* C.B. Tournef.")

* JAMES 1747: 355: "Resina Mastiche" ("*Lentiscus ex chio, ex qua fluat Mastiche* Tourn., Mastich-Tree")

* GEOFFROY, THICKNESSE 1749: 254: "Mastiche", "Mastix et Resina lentiscina", "Mastech" ("*Lentiscus Vulgaris* C.B.")

* HILL 1751: 718: "Mastiche", "Resina Lentiscina" ("*Lentiscus Vulgaris* C.B., Lentisk tree")

* LEWIS 1761: 365, 340: "Mastiche" ("*Lentiscus Vulgaris* C.B., Lentisk tree")

Encyclopaedias

* CHAMBERS 1728b: (508): "Mastic" ("Mastic or Lentisk Tree")

* SAVARY DES BRÛSLONS, SAVARY 1723b: 691: "Mastic" ("Lentisque")

Terminology

"Mastiche" comes from "masticando" or chewing (Lemery 1721: 705). The word is derived from Greek μαστιχειυ, to gnash the teeths. The term "mastiche" is used by Pliny for the resin of the "lentisco" from Chios (Bauhin 1623: 501; Pliny 1855: 12, 36). It was used by Ottoman women as a chewing gum for fresh breath and healthy teeth (Savary des Brûslons, Savary 1723b: 692; Chambers 1728b: (508); Hill 1751: 718; Lewis 1761: 365f).

Botanical and geographical origin

"Mastiche" is the resin of the "mastick tree" or the "*Lentiscus*" (Bauhin 1623: 501; Dale 1693: 457; Salmon 1701: 586; Pomet 1717: 135; Lemery 1721: 627). The material was traced to the "resina lentiscina" of Plinius (Bauhin 1623: 501), which differs from a sort, called "black mastic", originating from Egypt or "Asia minor" also mentioned by Pliny (Bauhin 1623: 501; Pliny 1855: 12, 36). Another resin from "Brazil" was called "mastiche" at the time of Vigani, too (Bauhin 1623: 501).

The originating tree was known since the antique and used for the production of resin. The "mastic tree" is an evergreen tree or bush native to the southern parts of Europe and the Mediterranean area (Bauhin 1623: 501; Hill 1751: 719; Lewis 1761: 365), "India" (Pomet 1717: 135; Lemery 1721: 627) and Crete (Bauhin 1623: 501; Krünitz 1802: 410f). The tree was cultivated at the island of Chios (Dale 1693: 457; James 1747: 355; Lewis 1761: 340). It is very similar to the "turpentine tree", from which it differs only by absent "odd leaf at the end of the Pianae" (Hill 1751: 719) (see chapter 5.3.2). At the time of Vigani it was classified as "*Lentiscus vulgaris* Dod., C.B." (Bauhin 1623: 399; Dale 1693: 457; Lemery 1721: 626; Geoffroy, Thicknesse 1749: 254; Hill 1751: 718; Lewis 1761: 340).

Manufacture and trade

The main trading place for "mastic" from the "*Lentiscus*" was Chios (Dale 1693: 457; Salmon 1701: 586; James 1747: 355; Hill 1751: 719; Lewis 1761: 365). The resin flew from the bark of the "mastic tree" with or without incisions (James 1747: 355; Hill 1751: 719; Lewis 1761: 365). The incisions were made transverse to the branches at the beginning of August and the resin was harvested until September (Savary des Brûslons, Savary 1748c: 329; Hill 1751: 719; Lewis 1761: 365). It exuded as small drops, which grew bit by bit to tears. They ran down in pits covered with stones on the swept ground, from where they were swept up (Savary des Brûslons, Savary 1748c: 330; Pomet 1717: 135; Lewis 1761: 365). The main part of the harvest was done until the middle of August, if the weather was dry. Otherwise the resin became wet and was worthless. Later in the year only small quantities were harvested (Savary des Brûslons, Savary 1748c: 330).

The trees were highly valued on Chios and cutting of them was punished (Chambers 1728b: 508; Hill 1751: 719; Pomet 1717: 135). The harvest was owned by the "grand seignior" and was leased to the tax collector of Constantinople in Smyrna (Chambers 1728b: 508; Hill 1751: 719; Pomet 1717: 135; Savary des Brûslons, Savary 1723b: 692; Krünitz 1802: 411-2). From there and from Aleppo it was brought to Europe (Salmon 1701: 586). "Mastic" was sold for 25 to 27 "sou" a "pound" in Amsterdam and in La Mastre and Masulipatan (Savary des Brûslons, Savary 1748c: 331).

French authors mention a sort of lesser quality from the Levant (Pomet 1717: 135; Lemery 1721: 705; Chambers 1728b: 508). It was seemingly only available only in France and is not mentioned by any of the English authors. It was of a coarse and less balsamic quality than the one from Chios, mixed with dirt and traded in different layers in the same container. It came to France from Smyrna over Marseilles in 300 cases per annum, each of a one-third centner (Pomet 1717: 136; Savary des Brûslons, Savary 1723b: 601). It was called "mastiche in fortis" or "en sorte" (Pomet 1717: 135; Lemery 1721: 705)[11].

Properties

"Mastic" consists of solid, dry, transparent, pale yellow small drops or tears. They has the size of a pea or rice grain (Geoffroy, Thicknesse 1749: 254). It has a resinous and astringent taste and a fragrant, light and agreeable smell (Dale 1693: 457; Lemery 1721: 705; James 1747: 365; Hill 1751: 718; Lewis 1761: 365). The best quality should be odorant, clear and bright, brittle and free of dirt and additions (Dale 1693:457; James 1747: 365). It should have the form of big tears of a golden yellow colour (Pomet 1717: 135; Savary des Brûslons, Savary 1723b: 692). "Black mastic" resembles bitumen. Chambers mentions it as an adulterant for "camphor" (Bauhin 1623: 501; Chambers 1728b: 508; Hill 1751: 718). The resin was chewed and in doing so it crumbled, then stuck together forming a soft and whitish wax-like mass without a strong taste (Hill 1751: 718; Lewis 1761: 365f). It dissolves totally in "rectified spirit of wine" with a pale yellow colour (Hill 1751: 719; Lewis 1761: 365).

"Mastic" was adulterated with conifer resins such as "thus", the dry resin of the "silver firr" used as incense, and "pine" resin (Bauhin 1623: 501; Manget 1687: 518). Pomet mentions a material made from "mastic" mixed with powdered bricks, which was called "mastic ou ciment" or "mastic en larme" (Pomet 1717: 125). In France, the true mastic therefore was called "Lentisque" (or "Lintisque") to distinguish it from the mixed one (Pomet 1694: 112; ibid. 1717: 135; Savary des Brûslons, Savary 1723b: 691). Hill mentions a material made from mastic and several other components, which was used by lapidaries as a binder or glue to fill up cracks in the stones (Hill 1751: 718). Other materials for adulteration were "sandarac", "juniper resin" and "rosin" (Carlyle 2001: 74).

Possible chemical composition

"Mastic" is obtained from *Pistacia lentiscus* L., the modern name of "*Lentiscus vulgaris* C.B." (Linné 1753b: 1026). The main source is a variety growing only on Chios, but resins similar to mastic are reported from the Mediterranean region and the Middle East (Ierapetritis 2010). The resin consists of a complex mixture of triterpenes with the oleanane, lupanes, tirucallane and dammarane skeleton with a very characteristic acidic and a complex neutral fraction. It has been shown that shortly after exudation mastic resin starts to alter mainly through sunlight (van der Doelen et al. 1998; Colombini et al. 2000; Dietemann 2003, 44; see also chapter 2.3).

For this investigation, different mastic reference samples were analysed, with the results presented in chapter 4.3.1. Mastic resin consists of a characteristic mixture of neutral and

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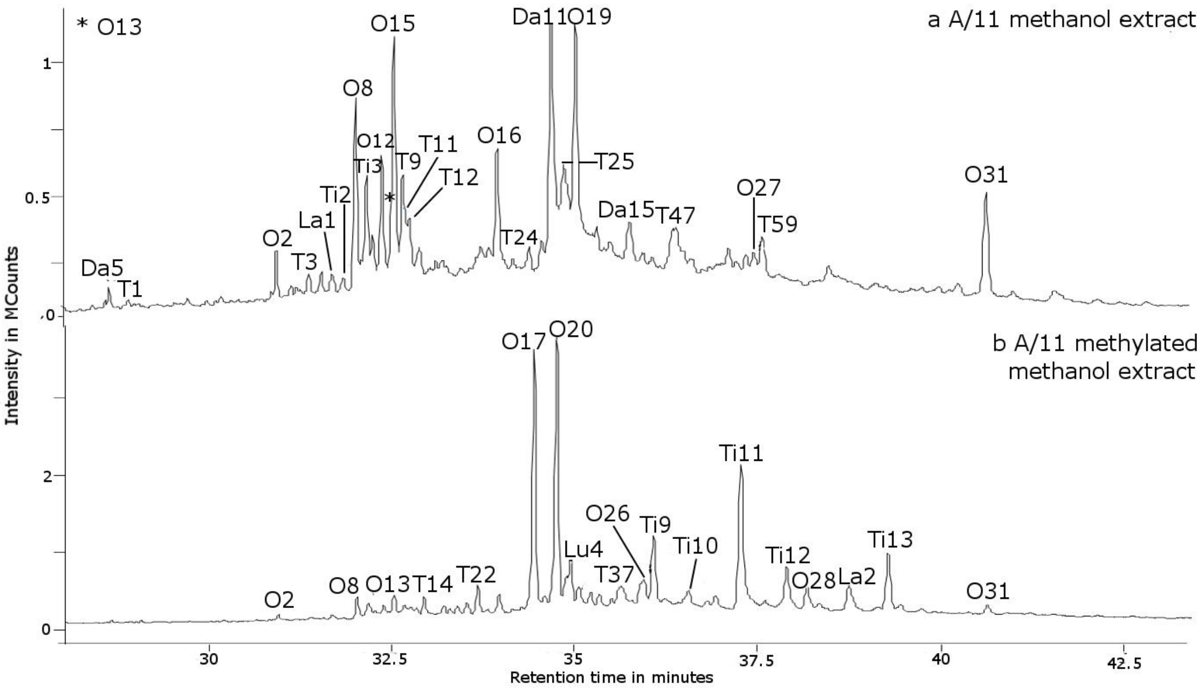
[11] The Ottoman Empire had a special mastic tax, which owned to the Valide Sultan and was on lease to the Aga of the mastic, a superordinate tax officer. Remaining quantities of the resin were traded in the 17th and 18th century by independent merchants. Trading ports in Europe were Venice and Southern Italy, later also Marseilles, London and Amsterdam. The best quality therefore was sent to Constantinople. After supplying the Imperial Court the remaining material of less quality was sold (Ierapetritis 2010). They were very likely composed of resin of poor quality and mixed with dirt from the ground but obtained from the same tree (White, Kirby 2001). This is the source of the less quality mastic from the Levant mentioned by several authors (above and Carlyle 2001: 73).

acidic compounds, with the neutral part eluting in the methanol extract and the acidic part in the methylated methanol extract. Main compounds of the neutral part are tirucallol, olean-17-ene, β-amyrin, 3,8-dihydroxy-polypoda-13,17,21-triene and oleanonic aldehyde. Main compounds in the acidic part are moronic, oleanonic, 18α-oleanonic and (iso-)masticadienonic acids. No hydroxy-dammarenone is present, which is probably the result of a differing (modern) harvesting method (Assimopoulou, Papageorgiou 2005a). Certain aging marker are present such as (nor-)β-amyrone, 28-norolean-17-en-3-one, 17β-hydroxy-28-norolean-12-en-3-one, 20,24-epoxy-25-hydroxy-dammaran-3-one, O31, 11-oxo-oleanonic and 3-oxo-lup-20(29)-en-28-onic acids. The analysis is mainly consistent with literature data. In summary, the acidic fraction is highly characteristic for *Pistacia* resins, while the neutral fraction shows a higher varability notably for the minor constituents.

Chemical analysis

In the methanol extract (Fig. 5.57a), main compounds are nor-β-amyrone, tirucallol, compound O12, 28-norolean-17-en-3-one, 17β-hydroxy-28-norolean-12-en-3-one, 20,24-epoxy-25-hydroxy-dammaran-3-one, oleanonic aldehyde, and an oxo-oleanane (O31). Other constituents are hexakisnor-dammaran-3,20-dione, compound T1, 28-norolean-12,17-dien-3-one, compound T3, lanosterol, tirucallone, β-amyrin, 3,8-dihydroxy-polypoda-13,17,21-triene, compounds T11, T12, T24 and T25, 3-oxo-25,26,27-trisnor-dammarano-24,20-lactone (Da15), compound T47, 17-hydroxy-11-oxo-nor-β-amyrone and compound T59. In the methylated methanol extract (Fig. 5.57b), main constituents are moronate, oleanonate, (iso-) masticadienonates and acetoxy-(iso-)masticadienonates. Other constituents are compounds T14 and T22, 3-oxo-lup-20(29)-en-28-oate, compound T37, 18α-oleanonate, epi-isomasticadienoate, 11-oxo-oleanonate and compound La2.



a - methanol extract and b - methylated methanol extract (labels, see table 5.15)

Fig. 5.57 Gas chromatograms of A/11 "Mastiche" from the Vigani Cabinet, triterpene section (TIC)

Label	t_R	Name	Main mass fragments
Da5	28.63	Hexakisnor-dammaran-3,20-dione	95, 135, 205, 273, 297, **315**, 325, 340, 358
T1	28.89	Unidentified	93, 107, 135, 189, 207, **299**, 317, 327, 342, 360
O2	30.92	28-Norolean-12,17-dien-3-one	189, 241, 269, 393, **408**
T3	31.35	Unidentified	107, 159, 257, 365, 383, **409**, 424
La1	31.69	Lanosterol	95, 187, 241, 259, **393, 411**, 426
Ti2	31.83	Tirucallone	109, 245, 257, 391, **409**, 424
O8	32.00	Nor-β-amyrone	79, 105, 175, 189, **204**, 395, 410, 424
Ti3	32.16	Tirucallol	119, 203, **393**, 411, 426
O12	32.36	Olean-17-ene-one	105, 163, 175, **189**, 204, 393, 395, 408
O13	32.49	β-Amyrin	189, **203**, 218, 393, 411, 426
O15	32.52	28-Norolean-17-en-3-one	95, **163**, 175, 191, 377, 395, 410
T9	32.64	3,8-Dihydroxy-polypoda-13,17,21-triene	**81**, 107, 147, 175, 190, 203, 393, 408, 426, 444
T11	32.67	Unidentified	239, 295, 391, **406**, 424
T12	32.79	Unidentified	95, 121, 189, 203, **205**, 218, 313, 381, 409, 424
T14	32.93	Unidentified	81, 119, 133, 189, **203**, 262, 440, 468, 500
T22	33.66	Unidentified	133, 187, 239, 299, 392, 406, **466**
O16	33.94	17β-Hydroxy-28-norolean-12-en-3-one	91, 105, 132, 146, 173, 187, **202**, 393, 408, (426)
T24	34.36	Unidentified	132, 146, 187, **202**, 379, 393, 408, 426
O17	34.47	Moronate	119, 173, **189**, 203, 248, 262, 409, 468
Da11	34.68	20,24-Epoxy-25-hydroxy-dammaran-3-one	107, 125, **143**, 161, 175, 205, 381, 399, 411, 443, (458)
O20	34.71	Oleanolate	133, **203**, 262, 395, 411, 470
T25	34.86	Unidentified	119, 173, 189, **203**, 306, 391, **408**, 436
Lu4	34.98	3-Oxo-lup-20(29)-en-28-oate	119, 133, 173, **189**, 203, 249, 262, 393, 409, 437, 453, 468
O19	35.01	Oleanonic aldehyde	105, 133, 175, **203**, 232, 311, 355, 409, 424, 438
T37	35.64	Unidentified	119, **189**, 203, 219, 248, 262, 424, 438, 467, 482
Da15	35.75	3-Oxo-25,26,27-trisnor-dammarano-24,20-lactone	99, 135, **205**, 287, 315, 328, 396, 414
O26	35.94	18α-Oleanonate	119, 133, 189, **203**, 262, 393, 453, (468)
Ti9	36.10	Isomasticadienonate	95, 121, 159, 189, 257, 393, 403, 421, 435, **453**, 468
T47	36.37	Unidentified	105, 133, **203**, 391, 409, 422, 440
Ti10	36.58	Epi-isomasticadienolate	241, 378, 396, 406, 424, **437**, 455, 470
Ti11	37.31	Masticadienonate	95, 121, 159, 187, 257, 393, 403, 421, 435, **453**, 468
O27	37.44	17-Hydroxy-11-oxo-nor-β-amyrone	145, 161, 189, **216**, 257, 407, 422, 440
T59	37.57	Unidentified	95, 107, 119, 133, 189, **203**, 245, 409, 422, 440
Ti12	37.87	Acetoxy-isomasticadienolate	95, 187, 377, 405, 422, **437**, 453, 497, 512
O28	38.20	11-oxo-oleanonate	119, 189, **217**, **257**, 276, 317, 407, 423, 435, 454, 467, 482
La2	38.78	Lanost-8-en-ol-oate	95, 173, 301, 341, 427, 449, **467**, 482
Ti13	39.29	Acetoxy-masticadienolate	95, 187, 377, 406, **437**, 497, (512)
O31	40.60	Oxo-oleanane	119, 147, 175, 189, 204, **217**, 233, 365, 407, 422, 435, 453, 468

Tab. 5.15 Compounds found in A/11 "Mastiche", analysed with temperature program Triterpened 1 and column A, mass spectra references see appendix

Discussion

The composition is typical for *Pistacia* resins, particularly for mastic. High amounts of tirucallol, β-amyrin and oleanonic aldehyde together with several aging markers such as nor-β-amyrone, 28-norolean-17-en-3-one, 17β-hydroxy-28-norolean-12-en-3-one, 20,24-epoxy-25-hydroxy-dammaran-3-one and O31 are typical for methanol extractable fraction of aged mastic. Other aging markers (Da5, O2, T11, T12, Da15, O27) are present, too. The composition of the acidic fraction dominated by moronic, oleanonic and (iso-)masticadienonic acids together with smaller amounts of acetoxy-(iso-)masticadienonic acids is typical for *Pistacia* resin as well. Isomasticadienonic acid is present in slightly decreased amounts compared to fresh samples.

Some aging marker with a dammarane skeleton (Da5, Da11, Da15) are present in high amounts, which indicates significant initial amounts of hydroxy-dammarenone. As discussed in chapter 4.3.1, this is probably the result of traditional harvesting compared to the use of chemicals. The high amounts of oleanonic aldehyde and the presence of other aging markers with an oleanane skeleton (O2, O8, O12, O15) are typical for mastic resins, particularly the reference samples analysed for this investigation.

In summary, A/11 "Mastiche" is in a low aging state, only dammaranes underwent some degradation.

5.3.2 1/14 Tereb i E Cypri

Fig. 5.59 1/14 "Tereb I E Cypri"

Fig. 5.58 Sampling of1/14

Description

The glass bottle is stuck in the wooden compartment and cannot be removed. The leather cap is loose, the string lost. The glass bottle is filled with a dried-up brownish material. It is very brittle and has a slight resinous smell.

Sampling

A sample of dried residuals of the inner wall (about 130 mg) was taken on 26 April 2007 (Fig. 5.59). The material was brown and brittle, with an aromatic sweetish smell.

Vigani references

* MS Quns Vig. 4, folio 1, verso, as "Tereb Cypria", 1 ounce at 6 pence, bottle at 1 penny

* Does not appear in LECTURE NOTES UNDATED

* Does not appear in LECTURE NOTES 1707

Contemporary literature

Fine art materials

* SALMON 1701: 859 "Chio and Cyprus Turpentine"

* CARLYLE 2001: ANON. 1795: 192f, 193-5 (Chios & Cyprus); ANON. 1808: 72-3 (Chios & Cyprus)

Science

* MANGET 1687: 64, 525: "Terebinthina Cypria seu Veneta"

* POMET 1717: 424: "Cyprischer Terpentin"

* LEMERY 1721: 1116-7: "Terebinthina Cypria", "Terebinthine de Cypre" ("*Terebinthus vulgaris* C.B., Terebinthe, Terpentinbaum")

* ZWINGER 1724: 499: "Terebinthi Resina s. Terebinthina Cypria"

* JAMES 1747: 452: "Turpentine from Chios and Cyprus" ("*Terebinthus vulgaris* C.B.")

* GEOFFROY, THICKNESSE 1749: 227: "Terebinthina Cypria", "Hele/Helt Alimbath" ("*Terebinthus* J. B.,*Terebinthus vulgaris* C.B. ")

* LEWIS 1761: 551: "Terebinthina Chia", "Terebinthina chia & cypria", "Chio or Cyprus turpentine"

Encyclopedias

* CHAMBERS 1728b: 265: "Cyprus Turpentine"

* SAVARY DES BRÛSLONS, SAVARY 1748c: 371(2)-372(3): "Terebenthine de Chypre" ("Terebinthe")

Terminology

The terms "terebinthina de chio", "terebinthina cypria", or "terebinthina chia & cypria" for the resinous balsam of the "turpentine tree" were used more or less synonymously (Bauhin 1623: 500; Blanckaert 1690: 616; James 1747: 452; Blanckaert 1748: 660; Geoffroy, Thicknesse 1749: 227; Lewis 1761: 551). Both were genuine names for the turpentine from the "turpentine tree" and did not necessarily point to a certain geographical origin (Bauhin 1623: 500; Manget 1687: 525; Dale 1693: 456; Zwinger 1724: 499).

In the 17th century and again at the end of the 18th century, "terebinthina cypria" was more common (Bauhin 1623: 500; Manget 1687: 525; Zwinger 1724: 499; Hahnemann 1799: 311; Jacobi 1800: 202; Krünitz 1844: 105-6). In the 18th century the resin of the "turpentine tree" was labelled rather after Chios or both Islands (James 1747: 452; Hill 1751: 705; Lewis 1761: 551).

Notably in the 17th century, the material bore several additional different names: "terebinthina vera" (Bauhin 1623: 400, 500) and "terebinthina veneta" (Manget 1687: 64; Blanckaert 1690: 616). "Venice turpentine" was the original name of that material, but due to shortages first mentioned at the end of the 16th century (Merrifield 1967: ccII) that term was given to several other "fine turpentines" of good quality, which were used as a substitute (ibid.; Pomet 1717: 419, 423; Lemery 1721: 1117; Savary des Brûslons, Savary 1748c: 470(2); Geoffroy, Thicknesse 1749: 230). In the 17th century, the material was no longer connected to the trading route or place but to its geographical origin (mainly Chios and Cyprus). This is discussed in detail in chapter 5.1.3. In the 18th century, the term "venice turpentine" in connection with the resin of the "turpentine tree" was no longer in use.

French authors mention "terebinthina cypria", "terebenthine de chypre" or "cyprus turpentine" but without any further information, probably because it was not available (Lemery 1721: 1117; Pomet 1717: 424; Chambers 1728b: 265; Savary des Brûslons, Savary 1748c: 372(2)). "Chios turpentine" was used instead (Lemery 1721: 1117; Pomet 1717: 424; Savary des Brûslons, Savary 1748c: 371(2); see chapter 5.1.5).

Botanical and geographical origin

"Terebinthina cypria" is mentioned in many contemporary sources as the resin of the "turpentine tree" or the "terebinth", "*Terebinthus Vulgaris* C.B.". It was mainly referred to the island Chios and Cyprus, from where its resin was seemingly imported to Europe (Bauhin 1623: 500; Pomet 1717: 424; Lemery 1721: 1116; Chambers 1728b: 265; James 1747: 452; Geoffroy, Thicknesse 1749: 227; Lewis 1761: 551).

The "turpentine tree" grew on the islands Chio and Cyprus (Ray 1693b: 1577; Dale 1693: 456; Zwinger 1724: 499 and in several regions in Southern Europe, too (Italy, France and Spain) (Pomet 1717: 421; Lemery 1721: 1116; Chambers 1728b: 265; Seguier 1745: 241; Geoffroy, Thicknesse 1749: 227; Lewis 1761: 551). European trees however were cultivated and did not yield any resin (Seguier 1745: 241; Hahnemann 1799: 310). Linné lists "Europa australis", "Africa borealis" and "India" for *Pistacia terebinthus* L. (Linné 1753b: 1026). The resin obtained on Chios was preferred, but also "Lybrica, tum Pontiea: tandem Cypria, Syriaca, Judaica, Arabica" are mentioned in historical sources (Bauhin 1623: 500).

European writers obviously lacked exact information about the tree, the resin and its harvesting. It became rare at the latest from the end of the 17th century on (Lemery 1721: 1116;

Chambers 1728b: 265), but the shortening of "turpentine" and its substitutions started already in the 16th century (see above and chapter 5.1.3). I

Manufacture and trade

The turpentine flows spontaneously or by wounding the trunk and branches of the "turpentine tree" with picks (Pomet 1717: 421; James 1747: 453; Hill 1751: 706; Lewis 1761: 551; Jacobi 1800: 202; Krünitz 1844: 105-6). From there the resinous balsam flows down on prepared stone plates. It was softened by the sun, cleaned with baskets and bottled. It was harvested from July to October (Pomet 1717: 421; Savary des Brûslons, Savary 1748c: 370(2); Jacobi 1800: 202; Krünitz 1844: 105-6). A clearer sort was made from the exuded drops, and both sorts were stored in earthen pots of about 20 pounds, four in a case (Jacobi 1800: 202). They were brought to Venice, Marseilles and England (Jacobi 1800: 202).

It was sold for 30 to 35 "parat" per "ocque" at the island Chio, one "ocque" 3 ½ "livre" and 1 "ounce", with no more than 300 "ocque" per year (Savary des Brûslons, Savary 1748c: 370(2)). "Livre" was the French mass unit for "pound" used in that time. Without an exact exchange rate 300 "ocque" are about 520 kg. That corresponds to the quantity of 1000 "Pfund", which is given 50 years later (Hahnemann 1799: 311: Krünitz 1844: 106).

Properties

"Terebinthina cypria" or the resin of the "turpentine tree" is described as viscous, pellucid and more vitreous than the resin from "larch". It is white with blue and yellow shades and becomes green against the light. It tastes acrid and has an only little pleasant smell. It is tenacious and sticky (Bauhin 1623: 500; Manget 1687: 525; Dale 1693: 456; Chambers 1728b: 265). The best quality should be clear, pellucid and white, vitreous with a shade of blue to green, acrid and fragrant (Manget 1687: 525). While different authors mention the "turpentine from Chios" to be the best (Dale 1693: 456; Pomet 1717: 421; Chambers 1728b: 265; James 1747: 453) and James describes the one from Cyprus as "browner and fuller of Dross" (James 1747: 453), Hill states that the supposed difference of these two balsam does not exist (Hill 1751: 706).

Pomet mentions the addition of "verdigris" to other "turpentines" in order to adulterate the green shade (Pomet 1717: 424). For further information about adulteration please refer to chapter 5.1.5 (‘Properties’).

Possible chemical composition

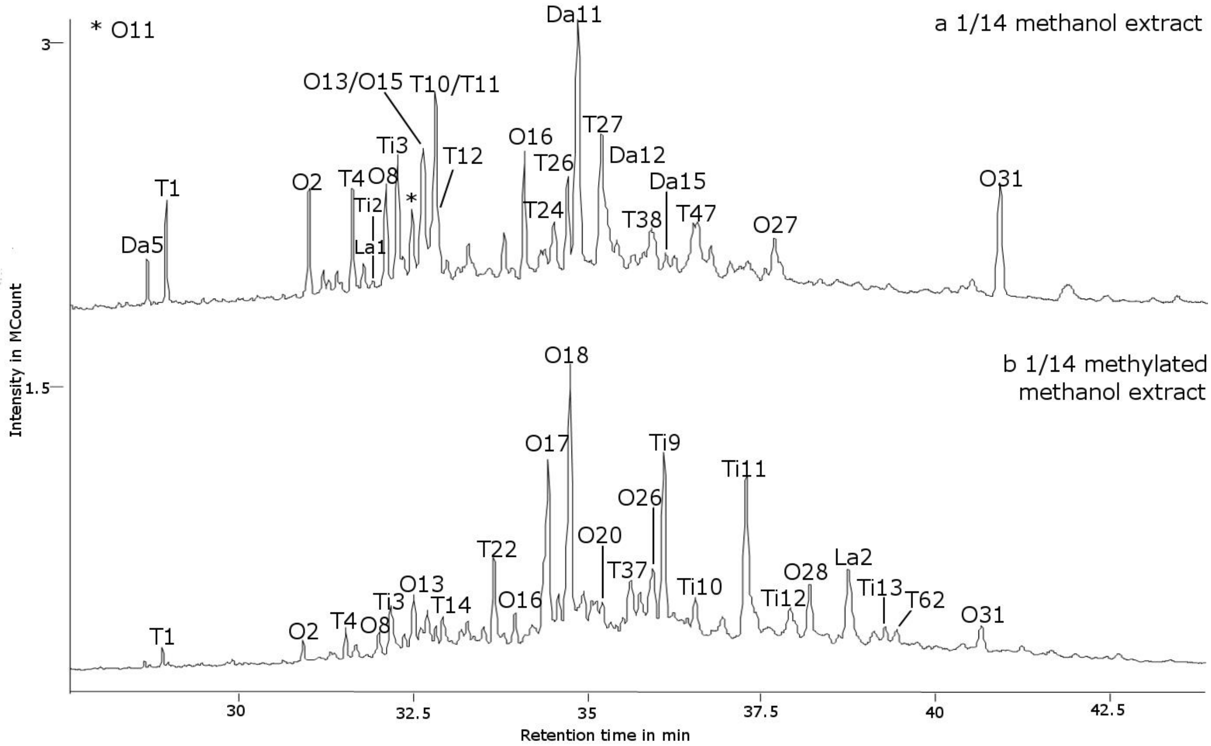
The term "cyprus turpentine" was used for the resin of a *Pistacia* species. "*Terebinthus vulgaris* C.B." was classified by Linné as *Pistacia terebinthus* L., which is still in use. There is some discussion on the species used to produce the resin, either *Pistacia terebinthus* L. or *P. atlantica* Desf. (see chapter 2.3.1). *P. atlantica* Desf. was described by Desfontaines in 1799. The tree was endemic upon the mountains near "Mayane" and and "Tlemsen", the latter a town in Algeria and yielded a resin similar to "mastiche" (Desfontaines 1799: 365). Because this species was not known in Europe at the time of Vigani, "*Terebinthus vulgaris* C.B." probably referred to both species. This is supported by Linné, who lists southern Europe ("Europa australis") and northern Africa ("Africa borealis") as geographical origins of *P. terebinthus* (Linné 1753b: 1026).

Pistacia turpentine is no longer available. In literature, Pistacia turpentine is composed very similar to mastic with a characteristic mixture of oleananes, lupanes, tirucallanes and dammaranes. It possesses however a ten times higher monoterpene fraction. It is not possible until today to distinguish different *Pistacia* species by GC-MS (Mills, White 1989; Koller et al. 1997b; Serpico, White 2000; Stern et al. 2008; see also chapter 2.3.1).

For this investigation, a sample of *P. terebinthus* L. was analysed, with the results presented in chapter 3.3.1. The sample consists of a characteristic mixture of neutral and acidic triterpenes, main compounds are tirucallol, β-amyrin, 28-norolean-17-en-3-one, T10, T16, hydroxydammarenone (methanol extract, neutral part) and moronic, oleanonic and (iso-)masticadienonic acids (methylated methanol extract, acidic part). No oleanonic aldehyde is present. Additionally, several aging compounds are present: (nor-)β-amyrone, 28-norolean-17-en-3-one, 17β-hydroxy-28-norolean-12-en-3-one, 20,24-epoxy-25-hydroxy-dammaran-3-one and 11-oxo-oleanonic acid. Compared to commercial mastic, the resin of *P. terebinthus* showed a lower content of neutral oleanane compounds and their aging markers and several additional constituents (T4, T10, T26, T33 and T53). From the present data, it is not possible to determine whether that is of environmental or botanical origin. The analysis is consistent with literature data, also regarding the indistinguishability of mastic and Pistacia turpentine. An analysis of the low molecular content did not yield results.

Chemical analysis

In the methanol extract (Fig. 5.60a), main constituents are compound T1, 28-norolean-12,17-dien-3-one, compound T4, nor-β-amyrone, tirucallol, β-amyrin, compound T11, 17β-hydroxy-28-norolean-12-en-3-one, compound T26 20,24-epoxy-25-hydroxy-dammaran-3-one and compounds T27 and O31. Minor constituents are hexakisnor-dammaran-3,20-dione, compound La1, tirucallone, compound O11, 28-norolean-17-en-3-one, compounds T10, T12 and T24, 20,24-epoxy-25-hydroxy-dammaran-3-ol, compound T38, 3-oxo-25,26,27-trisnor-dammarano-24,20-lactone (Da15), compound T47 and 17-hydroxy-11-oxo-nor-β-amyrone.



a - methanol extract and b - methylated methanol extract (labels, see table 5.16)

Fig. 5.60 Gas chromatograms of 1/14 "Tereb I E Cypri" from the Vigani Cabinet, triterpene section (TIC)

Label	t_R	Name	Main mass fragments
Da5	28.63	Hexakisnor-dammaran-3,20-dione	81, 95, 107, 135, 205, 273, 297, **315**, 358
T1	28.89	Unidentified	81, 95, 107, 135, 189, 207, **299**, 317, 342, 360
O2	30.92	28-Norolean-12,17-dien-3-one	119, 133, 145, 190, 241, 269, 351, 375, 393, **408**
T4	31.54	Unidentified	133, 159, 255, 391, 410, **424**
La1	31.69	Lanosterol	95, 119, 159, 187, 241, 259, 311, **393**, **411**, 426
Ti2	31.82	Tirucallone	109, 245, 257, 391, **409**, 424
O8	31.99	Nor-β-amyrone	105, 175, 189, **204**, 395, 410
Ti3	32.17	Tirucallol	95, 119, 145, 187, 241, 259, 311, **393**, 411, 426
O11	32.36	Unidentified oleanen-ol	93, 105, 119, 161, 175, **189**, **204**, 393, 408, 426
O13	32.50	β-Amyrin	95, 189, **203**, **218**, 238, 313, 393, 411, 426
O15	32.54	28-Norolean-17-en-3-one	95, 107, **163**, 175, **191**, 395, 410
T10	32.66	Unidentified	81, 105, 119, 173, 189, 241, 259, **393**, 411, 426
T11	32.69	Unidentified	239, 295, 391, **406**, 424
T12	32.76	Unidentified	95, 121, 189, 203, **205**, 218, 313, 381, 409, 424
T14	32.92	Unidentified	81, 119, 133, 189, **203**, 262, 440, 468, 500
T22	33.66	Unidentified	133, 187, 239, 299, 392, 406, **466**
O16	33.95	17β-Hydroxy-28-norolean-12-en-3-	91, 105, 132, 146, 173, 187, **202**, 393, 408
T24	34.38	Unidentified	132, 146, 187, **202**, 379, 393, 408, 426
O17	34.42	Moronate	119, 173, **189**, 203, 248, 262, 409, 468
T26	34.59	Unidentified	107, 135, 177, 255, 273, 353, 407, 423, **438**
Da11	34.73	20,24-Epoxy-25-hydroxy-dammaran-	107, 125, **143**, 161, 175, 205, 381, 399, (458)
O18	34.73	Oleanonate	133, 189, **203**, 262, 393, 409, 468
T27	35.05	Unidentified	**135**, 203, 218, 259, 285, 396, 409, 424, 466, 484
Da12	35.13	20,24-Epoxy-25-hydroxy-dammaran-3-ol	107, 125, **143**, 175, 191, 365, 383, 401, 445, 460
O20	35.20	Oleanolate	133, 189, **203**, 262, 395, 411, (470)
T37	35.62	Unidentified	119, **189**, 203, 219, 248, 262, 424, 438, 467, 482
T38	35.75	Unidentified	135, 161, 217, 232, **257**, 273, 315, 407, 422, 440
O26	35.93	18α-oleanonate	119, 133, 189, **203**, 262, 393, 453, (468)
Da15	35.97	3-Oxo-25,26,27-trisnordammarano-24,20-lactone	81, 95, 99, 107, 121, 135, **205**, 287, 315, 396, 414
Ti9	36.09	Isomasticadienonate	95, 121, 159, 189, 257, 393, 403, 421, 435, **453**, 468
T47	36.41	Unidentified	107, 133, 189, **203**, 216, 409, 422, (440)
Ti10	36.55	Epi-isomasticadienolate	241, 378, 396, 406, 424, **437**, 455, 470
Ti11	37.28	Masticadienonate	95, 121, 159, 187, 257, 393, 403, 421, 435, **453**, 468
O27	37.50	17-Hydroxy-11-oxo-nor-β-amyrone	145, 161, 189, **216**, 257, 407, 422, 440
Ti12	37.89	Acetoxy-isomasticadienolate	95, 187, 377, 405, 422, **437**, 453, 497, 512
O28	38.18	11-Oxo-oleanonate	119, 189, **217**, **257**, 276, 317, 407, 423, 435, 454, 467, 482
La2	38.75	Lanost-8-en-ol-oate	95, 173, 301, 341, 427, 449, **467**, 482
Ti13	39.29	Acetoxy-masticadienolate	95, 187, 377, 406, **437**, 497, (512)
T62	39.76	Unidentified	95, 159, 203, 301, 407, 435, 449, **467**, 482
O31	40.63	Oxo-oleanone	119, 175, 189, 204, 217, 233, 407, 422, 453, 468

Tab. 5.16 Compounds found in 1/14 "Tereb I E Cypri",analysed with temperature program Triterpenes 1 and column A, mass spectra references see appendix

In the methylated methanol extract (Fig. 5.60b), main constituents are moronate, oleanonate and (iso-)masticadienonates. Other constituents are compounds T14 and T22, oleanolate, compound T37, 18α-oleanonate, epi-isomasticadienolate, acetoxy-(iso-)masticadienolates, 11-oxo-oleanonate and compound La2.

Discussion

The composition is typical for *Pistacia* resins. High amounts of tirucallol and β-amyrin together with several aging markers such as hexakisnor-dammaran-3,20-dione, 28-norolean-12,17-dien-3-one, nor-β-amyrone, T11, 17β-hydroxy-28-norolean-12-en-3-one, 20,24-epoxy-25-hydroxy-dammaran-3-one and O31 are typical for the methanol extractable fraction of aged *Pistacia* resins. Other aging markers (O15, T12, Da12, Da15, O27) are present as well. The composition of the acidic fraction dominated by moronic, oleanonic and (iso-) masticadienonic acids together with smaller amounts of acetoxy-(iso-)masticadienonic acids is typical for a *Pistacia* resin as well. While in the neutral fraction significant amounts of aging markers are present, this is not the case in the acidic fraction. The sample is nearly identical with that of fresh mastic and the resin of *P. terebinthus* L., respectively.

Some aging marker with a dammarane skeleton (Da5, Da11, Da12, Da15) are present in high amounts, which indicates significant initial amounts of hydroxy-dammarenone. Medium amounts of aging markers with an oleanane skeleton (O2, O8, O15) are present, oleanonic aldehyde and O12 are absent. Slightly decreased amounts of neutral oleananes are found in the sample of *P. terebinthus* analysed in this work as well. This is also the case with several additional constituents, which are not present in commercial mastic, in 1/14 "Tereb I E Cypri" namely Da12, T4, T10 and T26. As discussed in chapter 4.3.1, it remained open whether these compounds are (phytochemical) markers for Pistacia turpentine or *Pistacia* species other than *P. lentiscus*. All in all, the presence of Da12, T4, T10 and T26, the lower amounts of neutral oleananes are indications that 1/14 "Tereb I E Cypri" was obtained from *P. terebinthus*. It is in any case a *Pistacia* resin.

In contrary, the resin of 1/13 "Tereb E Chio" is a pine resin, probably adulterated in South France (chapter 5.1.5). This corresponds with mentions that "cyprus turpentine" was not available in France and "chios turpentine" was used instead (which in turn was adulterated). The true "turpentine" was obviously still available at the time of Vigani compiled the Cabinet. In the invoices, 1/13 "Tereb E Chio" is accounted for twice the price of 1/14 "Tereb I E Cypri" (MS Quns Vig. 4, folio 1, verso). This probably indicates that the two "turpentines" were traded as different materials, and "cyprus turpentine" was of lower quality, such as mentioned by some historical sources (James 1747: 453).

5.3.3 A/21 Gum Copal

Fig. 5.61 A/21 "Gum Copal"

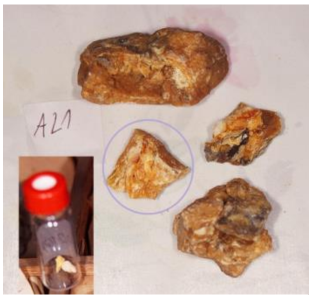


Fig. 5.62 Sampling of A/21, the sampled piece marked with a circle

Descripition

The box contains four big lumps of changing yellow colour with inclusions of dirt. The lumps have layers of different transparency. The material is hard and odourless. Inside the paper box, other small particles are visible.

Sampling

A sample from one of the big lumps (about 130 mg) was taken on 26 April 2007 (Fig. 5.62). The sample consisted of yellowish to brownish small pieces. Several different coloured and transparent layers are visible.

Vigani references

* MS Quns Vig. 4, folio 3, verso, as "Gum Copall", 2 ounces at 1 shilling

* Does not appear in LECTURE NOTES UNDATED

* Does not appear in LECTURE NOTES 1707

Contemporary literature

Fine art materials

* SALMON 1701: 858, 867, 873: "Gum-Copal"

* LEMERY 1721: 336: "Gummi Copal" ("Antillen")

* DOSSIE 1758a: 211, 213: "Gum Copal"

* CARLYLE 2001: WILLIAMS 1787: 53f.; ANON. 1795: 181-4, 193-5, 196-7; 290-2, 292-4; ANON. 1808: 72-3, 77

Science

* BAUHIN 1623: 503: "Copal Monardi", "Copal aut Pancopal"

* RAY 1693b: 1846: "Resina Copal Monard." ("*Copallifera arbor* Hern.")

* DALE 1693: 461: "Resina Copal", "Copal", "Gummi Copal" ("*Copalli quahvith patlahoca* Hern., *Rhus Obsoniorum similis Americana* P.P.")

* POMET 1717: 401, 403: "Gummi Copal aus dem Orient oder von den Amerikanischen Inseln"

* LEMERY 1721: 336: "Copal Monardi sive Pancopal" ("Orientalisches & Antillen")

*GEOFFROY 1743: 8: "Résine Copal" ("*Copalli Quahuitl* Hern.")

* JAMES 1747: 334: "Gummi Copal", "Resina Copal" ("*Rhus Virginanum Lentisci foliis* R. H., Virginian Sumach")

* BLANCKAERT 1748: 222: "Copal gummi"

* HILL 1751: 732: "Copal" ("*Copalli Quahuitl* Hern., true Copal Tree")

* LEWIS 1761: 225: "Copal"

Encyclopedias

* CHAMBERS 1728a: 322: "Gum Copal"

* SAVARY DES BRÛSLONS, SAVARY 1723a: 1498: "Copal"

Terminology

An American resin called "copal" is mentioned by Nicolás Monardes, who in turn refers to Francisco López de Gómara, an accompanist of Hernán Cortés (Monardes, Clusius 1579: 4). The appearance of the term in the English translation of Monardes work about the medical plants in West Indies by John Frampton, *Joyfully Newes of the newe founde Worlde*, is taken as the first in English language (Watson 1938). In the Latin translation, Monardes distinguishes two sorts, "xolochcopalli", a soft and wrinkled sort resembling "thus", and "copalcahuitl", which is of better quality and resembles "myrrh" (Monardes, Clusius 1579: 4; Bauhin 1623: 503; Blanckaert 1748: 222). The bilingual dictionary of Spanish and Nahuatl by Alonso de Molina from 1571 mentions the terms "copalli" ("incienso") and "copallo" ("arbol gomoso, o cosa semjante") (Molina 1571: 24v) for the resin used for fumigation and the related trees thus.

In the 17th century the resin was called "copal aut pancopal Monardi" after Nicolas Monardes and Johannes Fragoso (Monardes, Clusius 1579: 3; Fragoso, Spachii 1601: 97; Bauhin 1623: 503; Lemery 1721: 336). Contemporary to Vigani, the "gummi copal" or "resina copal" was stil referred to the indigenous people of Mesoamerica, where the resin was used for fumigation in religious ceremonies (Hill 1751: 730; James 1747: 334). There it was a "generic name for all white or whitish sweet scented resins" and the term "copal" referred to all white or transparent resins (Hill 1751: 730).

Botanical and geographical origin

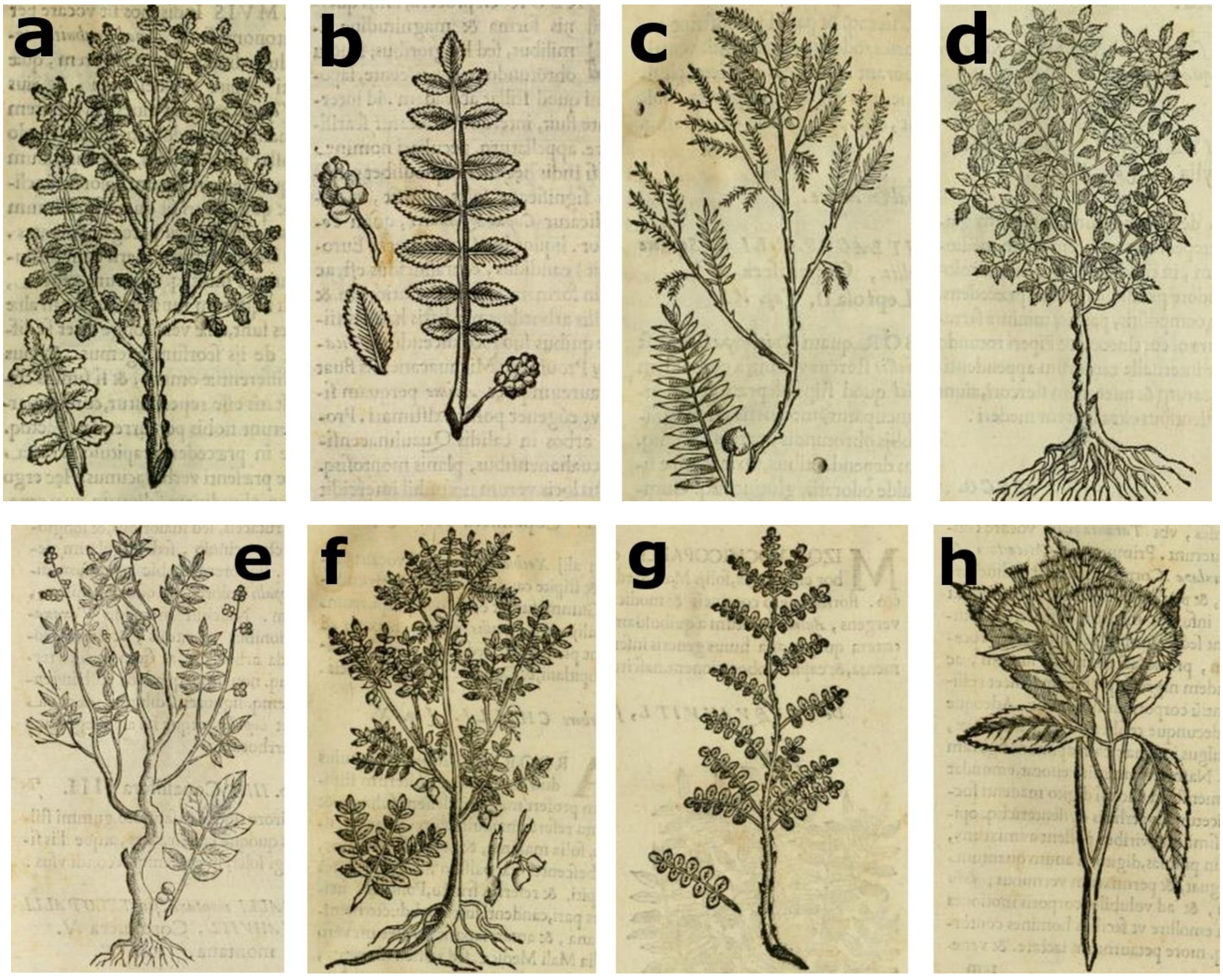
In Europe, the term "copal" was used mainly for the "copal monardi", which was thought to originate from the "copalliferae arbores" or from the "sumac". That resin originated from "New Spain" and from "Hispaniola", "Cuba" and other place of the "Spanish West Indies" (Salmon 1701: 858 Chambers 1728a: 322; Lemery 1714: 253; Pomet 1717: 401-402; James 1747: 334).

The "copalliferae arbores" (Fig. 5.63), hence copal-bearing trees, were described by Francisco Hernández de Toledo, his work on medicines from the New world was published from the beginning of the 17th century on in different editions (Hernandez 1651: 45-49). Afterwards, mainly the first one, "*Copalli Quahuitl* Hern.", is mentioned as the botanical source of "american copal" (Geoffroy 1743: 8; Hill 1751: 732), sometimes also the second one "*Copalli quahvith patlahoca* Hern." (Dale 1693: 461). "*Copalli Quahuitl* Hern." is a large tree, with leaves similar to that of the European oak, but somewhat longer and with a round purple coloured fruit (Hill 1751: 732).

Another botanical source mentioned by authors contemporary to Vigani is the "*Rhus Virginianum Lentisci foliis* R.H." or "virginiam sumac" as the source of "copal" from "Spanish West Indies" (Dale 1693: 461; James 1747: 334). Plukenet describes it as "*Rhus Obsoniorum similis Americana*" (Fig. 5.64a) and refers to "Yztac *Quauxihotl alia Galiopifera* Hernd." (Fig. 5.64b) or "*Aroeira Lusitanis* Piso" (Fig. 5.64c). Plukenet mentions that the tree has several varieties with serrated leaves such as "*Lentisco Peruviana* Hernd.", "*Copalli-quahuitl Tepoztlani* Terent." and "*Copalli-quahutl Patlahoac*, seu *Arbore Copalli latifoliâ* Hernd." (Plukenet 1696: 318-9, Fig. 5.63b, g). It is not clear from the text whether Plukenet thought the "copalliferae arbores" to be real varieties of the "*Rhus Obsoniorum*" or if he mentioned them only as examples for serrated varieties from another group of trees such as the "copalliferae arbores". According to Dale, Plukenet obtained a white "gum" from the "sumac" (Dale 1693: 462). The "*Rhus Obsoniorum similis Americana* P.P." was classified by Linné as "*Rhus copallinum* L."

(Linné 1753a: 266), while the "*Aroeira Lusitanis* Piso" was mentioned by Ray as very similar to "Gummi elemi Offic." (Ray 1693b: 1582) (for "elemi" see chapter 5.3.4).

French authors, who list only the "Antilles" as a geographical origin" of an American "copal", additionally mention an "oriental copal" (Lemery 1714: 253; Pomet 1717: 401-402; Lemery 1721: 336, Savary des Brûslons, Savary 1723a: 1498). The "oriental copal was sometimes called incorrectly "carabe" or "karabe" (Pomet 1717: 403-404; Lemery 1721: 336-7; Savary des Brûslons, Savary 1723a: 1499). It is a soft and friable sort. It was obtained from a medium-rise tree similar to sweet chestnut with long, broad and attenuate leaves and brown fruits like cucumbers, which contains a delicious flour (Pomet 1717: 401-402; Lemery 1721: 336; Savary des Brûslons and Savary 1723a: 1498; Fig. 5.64d). It melts easily when chewed and over fire, which distinguishes it from the other American sorts. Pomet and Lemery both mention "Grandes Indes" and "New Spain", Savary des Brûslons and Savary and Chambers only "New Spain" (Lemery 1714: 253; Pomet 1717: 401-402; Lemery 1721: 336, Savary des Brûslons, Savary 1723a: 1498; Chambers 1728a: 322). The latter do not call the material "oriental", Chambers not even gives a description of the tree, but uses a phrase, which is retrieved at Savary des Brûslons and Savary: the resin "oozes out from Incisions made in the Bark of a large Tree; much after the manner in which the Vine yields it's Water, when cut in



a - "Copalli Quahvitl" (I),b - "Copalli Quahvitl Patlahoc" (II), c - "Copalli Quahxiotl" (III), d - "Copalli montana, seu Tecopalli Quavitl" (V), e - "Cuitlacopali seu Sterc ore copallis" (VI),), f - "Quavhtecopalli Pitzahvac" (VII), g - "Tecopal Quahvitl Tepotz Lani" a variation of VII (VII) and h - "Xochicopalli" (VIII); "Copalli Totpocense" (IV) is described without a picture (Hernandez 1651: 45-49)

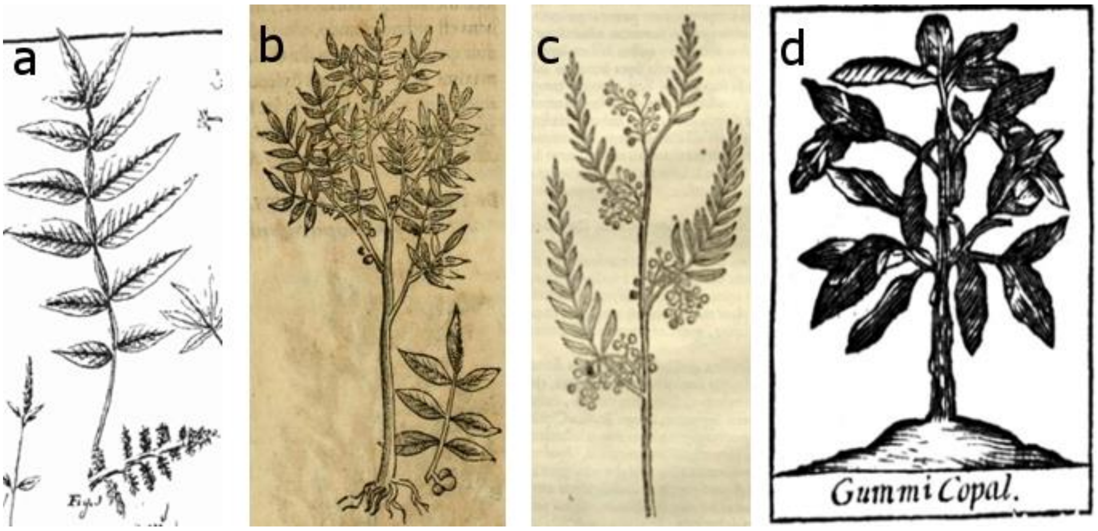
Fig. 5.63 The "copal-bearing trees" ("copalliferae arbores") of Hernandez, in parenthesis the respective number the Spring" (Chambers 1728a: 322) or "il jette le Copal à peu près de meme que la vigne rend son eau, quand on l'a taillée au printemps" (Savary des Brûslons, Savary 1723a: 1498)[12]. In contrary, Savaray des Brûslons and Savary list "copalxocotl", a sort of "copal" from "New Spain", which is, however, of lower quality than the true "copal". It is obtained from a tree with leaves similar to European cherry and fruits like apples. It is called "pompoqua" by the indigenous people and "cerise gommneüse" (Savary des Brûslons and Savary 1723a: 1499).

In summary, three sorts of "copal" were traded in Europe at the time of Vigani. An American "copal" from New Spain, one from the "Antilles" and an "oriental" sort, of which no clear geographical origin is known. However, the tree shown by Lemery and Pomet (Fig. 5.64d) resembles the botanical source of "occidental anime" (Fig. 5.39), particularly for the characteristic cucumber-like fruits containing an edible flour. Both materials are soft and friable sorts. "Copal" and "anime" have frequently been confused (Hill 1751: 732; Lewis 1761: 225), additionally the resin of the fifth "copallifera arbor" is called "anime" by Hernandez (Hernandez 1651: 47) while a Mexican "anime" is called to be truly a "copal" (ibid. 50). While "anime" is of old world origin and was transferred to new-world resins after the colonisation (see chapter 5.2.2), it is the other way round with "copal". It is, however, not clear from the descriptions from which time on an "oriental copal" from "Grandes Indes" was in trade or whether it originated from Eastern ports anyway.

Manufacture and trade

American "copal" exuded after incisions were made into the bark of the tree (Dale 1693: 462; Chambers 1728a: 322; Hill 1751: 732).

"Copal" from the "Antilles" exuded from the trees and was washed into the rivers by rain (Pomet 1717: 403-404; Lemery 1721: 336-7). It was imported to Europe over Nantes or Rochelle (Pomet 1717: 403-404; Lemery 1721: 336-7; Savary des Brûslons, Savary 1723a: 1499).



a - "Rhus Obsoniorum similis Americana, Gummi candidum fundens, non serrate, foliorum rachi media alata, Rhus virginianum Lentisci foliis Ray" (Plukenet 1691a: Tab. 56, Fig.1), b - "Yztac Quavhxiotl ali Galiopifera" (Hernandez 1651: 57), c - "Aroeira Lusitanis" (Piso 1658: 132) and d - "Gummi Copal" tree (Lemery 1721: 336)

Fig. 5.64 Other historical tree mentioned in connection with "copal"

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[12] French and English information often differs, compare chapter 5.1.1, 5.1.5, 5.1.7, 5.2.1, 5.1.2, 5.3.1, 5.4.1. Chambers often is closer to the French authors than to contemporary English publications.

"Oriental copal" is obtained by making incisions into the bark or by barking the tree (Savary des Brûslons, Savary 1723a: 1498). The resin flows "much after the manner in which the Vine yields its water" especially when the tree is wounded in the spring (Chambers 1728a: 322; Savary des Brûslons, Savary 1723a: 1498).

Properties

There was some discussion on its true nature whether being a resin or a gum. It was often listed as "gummi copal Offic." but also as "resina copal". Hill mentions it to be a true resin being inflammable and soluble in oil (Hill 1751: 732). On the other hand Lewis describes that it was very poor soluble in "rectified spirit of wine", which could be improved by adding "vitriolic acid", "volatile alkaline salts" or "camphor" (Lewis 1761: 225-6).

"American copal" or "(gum) copal" is solid with a firm texture, yellowish white or of watery colour, very clear and transparent. Other pieces are more brown and semitransparent. It has a subastringent and aromatic taste. In contrary to "anime", it is less fragrant, less soft and oily and does not soften in the mouth (Monardes, Clusius 1579: 3; Fragoso, Spachii 1601: 97; Salmon 1701: 858; Hill 1751: 732; Lewis 1761: 225). Salmon suggests it for mechanical uses (Salmon 1701: 858). It came into trade in bigger lumps and drops resembling "amber" (Hill 1751: 732; Lewis 1761: 225). It is less sweet and fragrant, fat and oily than "anime" but more clean and white (Salmon 1701: 858).

"Oriental copal" is clear, transparent, of yellow to golden colour, soft and friable. It softens in the mouth and is easy to melt over fire. It has a very fragrant smell like that of frankincense (Pomet 1717: 401-403; Lemery 1721: 336; Chambers 1728a: 322; Savary des Brûslons and Savary 1723a: 1498).

Possible chemical composition

"Copal" in the modern sense is a generic name for different resins from Africa, Asia and America. Contemporary to Vigani it was used only for resins from America, even though "oriental copal" may originate from other parts of the world ("Grandes Indes"). Additionally, there is some confusion with another material called "anime", the term of which is, in contrary to "copal", of old-world origin. In the following, a possible chemical composition of historical "copal" resins based on the information from the historical sources is given. All species and their geographical origins are summarized in Fig. 5.65.

1. "American copal" may originate from different "copalliferae arbores". Several of these trees were mentioned in connection with a "sumac" tree now classified as *Rhus copallifera* L. (John Carter Brown University 2012), whether due to external or taxonomical similarities is not known. No definite description of a copal resin from this species or another one from the genus *Rhus* is found in modern literature. Modernly, American copals are mainly thought to originate from *Protium* and *Bursera* species. From the historical description it is not clear whether the poplar-like tree from the "Antilles" is a *Protium* or *Bursera* species (see also chapter 2.3.2), but several of the "copalliferae arbores", particular those shown in Fig. 5.63a, b, f, g and probably 5.63d, are probable *Bursera* species because of the characteristic pinnate leaves. The "copalliferae arbores" in Fig. 5.63e has bigger leaves, which is more typical for *Protium* trees.

In the literature, *Protium copal* is mentioned as the main source for Mesoamerican copals resins (Case et al. 2003), but no investigation about its chemical composition has been published and no investigations were made in this work. Other (more soft) *Protium* resins, which

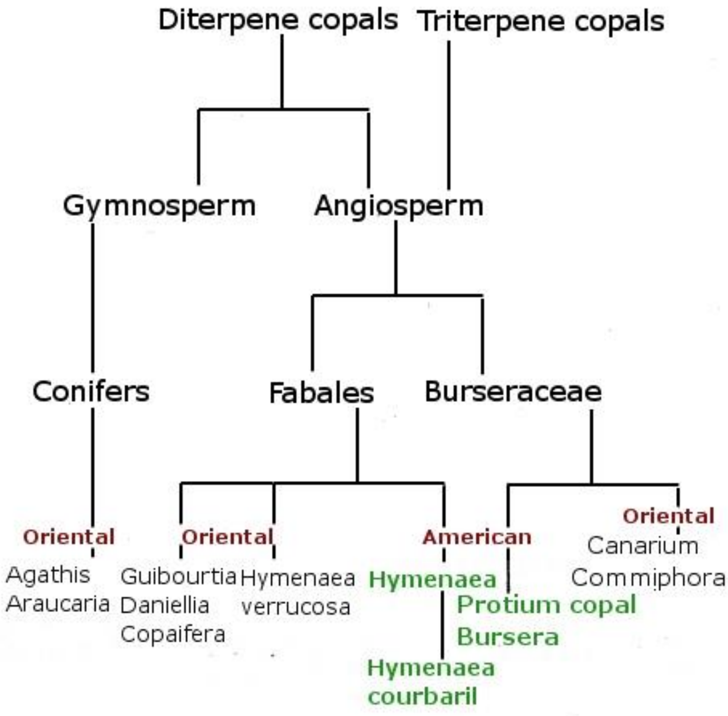


Fig. 5.65 Possible botanical (black and green) and geographical origin (red) of "copal" labelled materials; green – botanical origin of historical "copal" labelled materials

are not called copal but elemi, consist mainly of α- and β-amyrin (1:2), maniladiol, brein, tirucallane acids and taraxasterol (Rüdiger et al. 2007; Stacey et al. 2006; see also chapter 2.3.2). No chemotaxonomical data are available, which makes it impossible to deduce a possible chemical composition of American *Protium* copal resins. *Bursera* resins are composed similar and contain additionally high amounts of (epi-)lupeol, lupenone and the 3-epimers of α- and β-amyrin (Peraza-Sánchez et al. 1995; de la Cruz-Caňizares et al. 2005; Stacey et al. 2006; see also chapter 2.3.2).

In this work, a variety of Burseraceae resins were investigated, with the results presented in chapter 4.3.2. No botanical samples were available. Two Mexican copals labelled Prontium copals belong to *Bursera*, because they contain high amounts of epi-lupeol and higher amounts of 3-epi-β-amyrin than β-amyrin. A Gum Anime analysed was assigned to *Bursera*, too, because of its high amounts of epi-lupeol and 3-epi-β-amyrin. In addition it contains several other pentacyclic triterpenes with additional functional groups (T17, T19, T20, T67). The analysed materials all show highly characteristic compositions. Due to the high chemical variability of the family and lacking ethnobotanical and chemotaxonomical data it is not possible to generalize the characterised composition.

2. "Copal" from the "Antilles" is described as to be washed into the river and dug out afterwards, a method also described in modern literature for American *Hymenaea* resins (Cunningham et al. 1973; Langenheim 2003: 394f.). It is typical for some sorts of amber, too (Langenheim 2003: 147-9), which in turn may explain the wrong labelling as "amber" or "carabe" of related materials mentioned in historical sources (see above). *Hymenaea* resins are of diterpene composition, and triterpene copals do not show a maturation process as common for diterpene copals and amber dug from the ground (Anderson et al. 1992; Anderson, Botto 1993; Anderson 1994; Langenheim 2003: 154f).

Another possible *Hymenaea* resin is "oriental copal", the botanical source of which resembles that of "occidental anime". This tree is probably identical with *Hymenaea courbaril* L. (see chapter 5.2.2), which is known today as a source of American anime (Case et al. 2003). Several other *Hymenaea* species yield resins with a changing polymeric fraction (Anderson et al. 1992; Anderson, Botto 1993; Anderson 1994; Doménech-Carbó et al. 2009), which may be a possible explanation for the confusing historical descriptions of hard "anime" and soft "copals". In the case, both "copal" from the "Antilles" and "oriental copal" from New Spain were obtained from *Hymenaea* species, then very likely of different ones.

In the literature, *Hymenaea* resins contain high amounts of ent-labdanes (Cunningham et al. 1973; Cunningham et al. 1974; Doménech-Carbó et al. 2009; see also chapter 2.2). The composition of these copals is summarised in chapter 5.2.2 (A/5 "Gum animi") together with that of other legume copals (*Guibourtia*, *Tessmania* and *Daniellia*).

3. A "copal" from "Grandes Indes" may have been originated from Asia or Africa. In that case, a wide range of botanical sources are possible (Fig. 5.65, black genera). Although many of these materials are called copals today, there is no indication in contemporary sources on their use or trade in Europe. East African hard resins, particularly Zansibar copals (*Hymenaea verrucosa* Gaertn., chapter 2.2), are known to be traded from the middle ages on over the Arabian pensinsula (Merrifield 1967: cclviii; Regert et al. 2008), but it is not mentioned from which time on they were called copal. Asian materials are rarely mentioned in the consulted literature 17th and 18th century), even though there was a regular trade between Asia and Europe from the 17th century on (East Indian trading companies). As discussed for "elemi" (chapter 5.3.4 ‘chemical composition’), a Pacific sort was very likely in trade from the 15th century on under a differing name (Tschirch 1935: 265-6), and there is no reason why this should be not the case with Manila copal as well. Kauri copal came on the market not earlier than the mid-nineteenth century, but Manila copal was brought much earlier to Europe (Mills, White 1977). Possible sources are: conifer copals from Asia (diterpene, chapter 2.1.3), African legume copals from the genera *Guibourtia*, *Tessmania* and *Daniellia* (diterpene, chapter 2.2) and *Canarium* and *Commiphora* (triterpene, chapter 2.3.2).

Zansibar copal and other legume copals are discussed in chapter 5.2.2. Conifer copals originate from *Agathis* (Manila and Kauri copals) and *Araucaria* and are composed of pimaranes, labdanes and abietanes (Caputo et al. 1974; Caputo, Mangoni 1974; van den Berg et al. 2002; Scalarone et al. 2003; Cox et al. 2007; see also chapter 2.1.3).

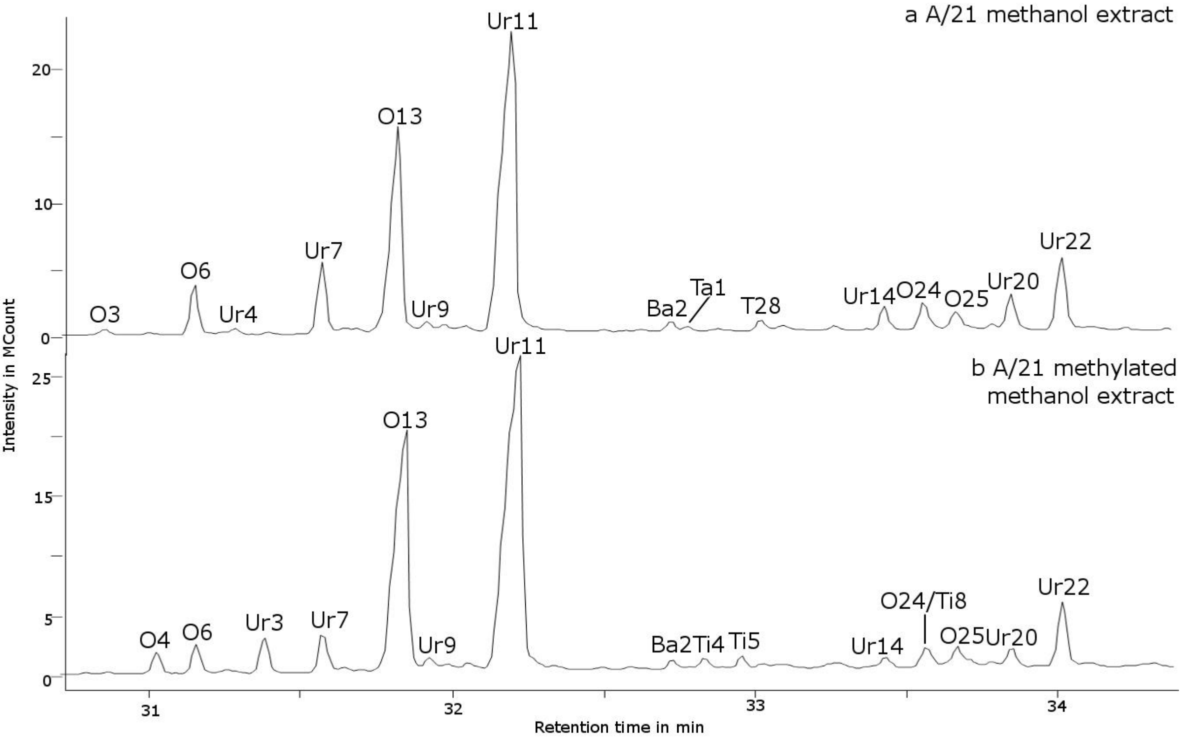
For this investigation, a number of Manila and Kauri copals, called conifer copals, were analysed, with the result presented in chapter 4.1.3. These copals contain high amounts of sandaracopimaric and C-15 oxygenated labdane acids, Kauri copals also abietane acids. They are therefore well distinguishable from legume copals, which contain mainly ent-labdanes and abietanes.

African *Canarium* and *Commiphora* copals are not described in the literature. Similar to *Protium*, only the resins from other species, which are not called copal, are investigated in literature. They are of triterpene composition (Provan, Waterman 1986; Dekebo et al. 2002; Langenheim 2003: 371; Hanuš et al. 2005; chapter 2.3.2). In this investigation two triterpene copals labelled as Angola and Kongo copal were analysed and the results are presented in chapter 4.3.2. They contain high amounts of oleanane and ursane aldehydes and smaller of α- and β-amyrin, lupanes and oleanane and ursane acids. The Angola copal contains high amounts of dammarane alcohols, aldehydes and acids, which indicates a *Commiphora* origin.

Chemical analysis

The methanol extract (Fig. 5.66a) mainly contains β- and α-amyrin, together with smaller amounts of olean-9(11),12-dien-3β-ol, urs-9(11),12-dien-3β-ol, 11-oxo-olean-12-en-3β-ol, brein, 11-oxo-urs-12-en-3β-ol and maniladiol. Small amounts of olean-9(11),12-dien-3-one, urs-9(11),12-dien-3-one, α-amyrone, baurenol, taraxasterol, ursolic aldehyde and compound T28 are present as well.

The methylated methanol extract (Fig. 5.66b) additionally contains small amounts of the methyl ether of β- and α-amyrin, elemonate and α-elemolate.



a – methanol extract and b – methylated methanol extract (labels, see table 5.17)

Fig. 5.66 Gas chromatograms of A/21 "Gum Copal" from the Vigani Cabinet, triterpene section (TIC)

Discussion

The composition is typical for non-acidic Burseraceae resins, particularly from the genera *Canarium* and *Protium*. α- and β-amyrin, brein, maniladiol and tirucallane acids such as elemonic and elemolic acids are characteristic for these resins. In *Bursera* resins lupanes and the 3α-epimers of α- and β-amyrin are much more prominent.

Due to the composition found in the analysis, legume copals and resins from the African genera *Commiphora*, *Boswellia* and American genus *Bursera* can be excluded. Triterpene copals from *Protium* species are of American origin, particularly from *Protium copal*. The chemical composition of resins from this species is unknown (see above). Therefore, it remains open whether A/21 "Gum Copal" is a *Protium* copal.

Canarium resins originate from Asia and Africa. African *Canarium* copals are sometimes mentioned in the literature without precise information about the species produce it and its geographical origin (see table 2.6). Similar to *Protium copal* no phytochemical data are available. Chemotaxonomical considerations would indicate tirucallane acids, maniladiol and

Label	t_R	Name	Main mass fragments
O3	30.86	Olean-9(11),12-dien-3-one	255, 269, 293, 352, 389, 407, **422**
O4	31.02	3β-Methoxy-olean-12-ene	81, 95, 107, 189, **203**, 218, 393, 408, 425, 440
O6	31.14	Olean-9(11),12-dien-3β-ol	119, 159, 255, 271, 391, 409, **424**
Ur4	31.28	Urs-9(11),12-dien-3-one	133, 159, 255, 269, 311, 389, 408, **422**
Ur3	31.39	3β-Methoxy-urs-12-ene	119, 147, 161, 189, 203, **218**, 393, 408, 425, 440
Ur7	31.57	Urs-9(11),12-dien-3β-ol	133, 159, 255, 295, 391, 409, **424**
O13	31.81	Olean-12-en-3β-ol (β-amyrin)	95, 119, 175, 189, **203**, 218, 393, 411, 426
Ur9	31.92	α-amyrone	107, 147, 189, 203, **218**, 409, 424
Ur11	32.18	Urs-12-en-3β-ol (α-amyrin)	107, 147, 161, 175, 189, 203, **218**, 393, 408, 411, 426
Ba2	32.72	Baurenol	95, **229**, 241, 247, 393, 411, 426
Ta1	32.78	Taraxasterol	93, 107, 121, 175, **189**, 207, 229, 393, 408, 426
Ti4	32.82	Elemonate (proposed)	189, 257, 297, 311, 393, 421, **453**, 468
Ti5	32.96	3α-hydroxytirucall-8,24-dien-21-oate (α-elemolate)(proposed)	187, 281, 299, 377, 405, **437**, 455, 470
T28	33.02	Unidentified	143, 205, 235, 407, 425, **440**
Ur14	33.42	Ursolic aldehyde (3-hydroxy-urs-12-en-28-al)	253, 271, 289, 407, 422, **440**
O24	33.55	11-oxo-olean-12-en-3β-ol	**135**, 175, 217, 232, 273, 287, 407, 425, 440
Ti8	33.58	3α-hydroxy-7,24-dien-21-oate (β-elemolate) (proposed)	187, 282, 378, 406, **437**, 455, 470
O25	33.67	Maniladiol	160, 187, 190, 201, **216**, 219, 234, 391, 409, 424, 442
Ur20	33.84	11-oxo-urs-12-en-3β-ol	105, **135**, 149, 175, 232, 273, 407, 425, 440
Ur22	34.02	Brein	110, 150, 191, 207, 219, **234**, 409, 424, 442

Tab. 5.17 Compounds found in A/21 "Gum copal", analysed with temperature program Triterpenes 3 and column A, mass spectra references see appendix

brein as constituents of such a potential African *Canarium* resin. However, all these compounds have been found in different *Protium* species as well (see chapter 2.3.2).

According to historical sources, the origin of A/21 "Gum copal" is America, most probably one of the "copalliferae arbores". The mentioned confusion of "copal" with "anime" is reflected insofar as the clear and hard A/5 "Gum animi" proved to originate from Africa legume genera (and would be labelled copal today), and the more soft and whitish A/21 "Gum copal" is most likely from America.

A/21 "Gum copal" is composed very similar to A/24 "Elemi" (chapter 5.3.4). Differences are minor amounts of 3-epimers of β- and α-amyrin (O9, Ur10), friedelan-3-one and dammaranes (Da9, Da12) in A/24. The term "elemi" was used as a generic one as well, mainly for soft whitish resins. While the soft American resins later became elemis, the hard became copal, and anime was probably used as an intermediate for both. The similarity of A/21 "Gum copal" and A/24 "Elemi" indicate a common botanical origin, the most probable one, based on the chemical analysis and the information from the historical sources, are American *Protium* resins. Due to slight chemical differences, A/21 "Gum copal" was probably obtained from a different species. With the present data it is not possible to definitly exclude an African *Canarium* resin.

An "oriental copal" originating from "New Spain" and "Grandes Indes" is reported to flow from the tapped tree like water", which resembles the harvesting of Manila elemi. "Oriental copal" is described as a soft form. This connection is reasonable, because Pacific materials – or even any materials ariving in Europe over Eastern trading routes - are rarely mentioned in the consulted European literature, but are referenced occasionally in modern literature (Tschirch 1935a: 266; Mills, White 1977; de la Cruz-Canizares et al. 2005). On the other hand, both "occidental anime" and "oriental copal" are mentioned in connection *Hymenaea* species, which points to an African origin of "oriental copal", too. As mentioned in chapter 5.2.2 (footnote 7), legume resins from Eastern Africa were called "copals" towards the end of the 18th century, at leat in Germany but probably also in England (Bloch 1776), while in the 1730ies still "anime" was in use. Because neither the material labelled "anime" nor the material labelled "copal" turned out to originate from *Hymenaea*, this question remains open.

The resin "pomquoa" of the "apple tree" mentioned by Savaray corresponds with pom as the Maya term for incense (Langenheim 2003: 359f; see also chapter 2.3.2).

5.3.4 A/24 [.] Elemi

Fig. 5.67 A/24 [.] Elemi (upper side)

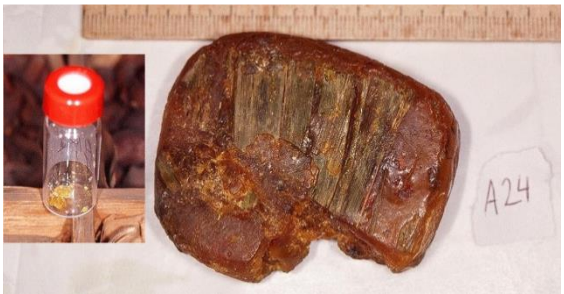


Fig. 5 68 Sampling of A/24 (lower side)

Description

The box contains one big flat lump of a brownish grey colour. The surface is brittle and opaque; the upper side, which was exposed much more to air and light, is darker than the lower side. On both sides, imprints of the former wrapping, probably palm leaves, are visible. The interior is more yellow but opaque. The material has a slightly spicy smell. The paper in the box is strongly decomposed and discoloured.

Sampling

A sample from the small side of the big lump, where the interior was visible, was taken on 26 April 2007 (about 10 mg) (Fig. 5.68). It consisted of yellow pieces with a slightly spicy smell.

Vigani references

* MS Quns Vig. 4, folio 3, verso, as "Gum Elemi", 2 ounces at 1 shilling

* Does not appear in LECTURE NOTES UNDATED

* Does not appear in LECTURE NOTES 1707

Contemporary literature

Fine art materials

* SALMON 1701: 859: "Gum-Elemi"

* DOSSIE 1758a: 211: "Gum Elemi"

* CARLYLE 2001: ANON. 1808: 77

Science

* BAUIN 1623: 504: "Gummi Elemi officinarum", "Oleae Aethiopicae lacryma"

* RAY 1693b: 1847: "Gummi Elemi", "Gum Elemi Offic", "Elemi resina." ("*Olea Aethiopica*"); ibid. 1546: "Gummi Elemi" ("*Icicariba Brasiliensibus* Marcgr., *Arbor Brasiliensis gummi Elemi simile fundens*")

* DALE 1693: "Gum Elemi Offic", "Elemi resina" ("*Arbor Brasiliensis gummi Elemi similie fundens* R.H., *Icicariba Brasiliensibus* Marcgr., *Icicariba Gummi Icica sive Elemni* Pis., *Prunifera Fago similis arbor Gummi Elemi fundens* P.P., The Gum Elemi-Tree")

* POMET 1717: 391: "Gummi Elemy im Rohr", "Gummy Elemy aus America"

* LEMERY 1721: 420: "Gummi Elemi im Rohr", "Gomme Elemi en roseaux" (kind of "Olive tree in Aethiopia")

* JAMES 1747: 313: "Elemi" ("*Arbor brasiliensibus Gummi Elemi simile fundens, foliis pinnatis, flesculis verticillatis, fructu Olivae figura & Magnitudine* R.H., The Gum Elemi Tree")

* GEOFFROY, THICKNESSE 1749: 248-9: "Elemi verum seu Aethiopicum" (an "Olive tree in Aethiopia"); "Elemi Americanum"

("*Icicariba Brasiliensibus* Marcgr., *Icicariba, et illius gummi Icica, sive Elemni* Pison., *Arbor Brasiliensis gummi Elemi simili fundens, foliis pinnatis, flosculis verticillatis, fructu Olive figura et magnitudne* R.H.")

* HILL 1751: "Aethiopian Elemi", "American Elemi" ("*Icicariba* Marcgr., *Arbor Brasiliana Gummi Elemi fundens foliis pinnatis flosculis verticillatis fructu Olivae figura et magnitudine* R.H.")

* LEWIS 1761: 252: "Gum Elemi" (kind of "Olive tree")

Encyclopedias

* CHAMBERS 1728a: [289]: "Elemi", "Elemy"

* SAVARY DES BRÛSLONS, SAVARY 1723a: 1799: "Elemy" ("Olivier sauvage")

Terminology

"Elemi" is commonly related to the Greek "enhaimon" ("εναιμον") of Pliny (Tschirch 1935a: 265). The material is related to several other ancient resins used as a styptic medicine labelled "elaia", such as "ελαια, επανω χοπτου" (Theophrast) and "δαχρυ ελαιασ αιδιοπιχησ" (Dioskurides) (Tschirch 1935a: 265). They all originate from an African or Ethiopian "olive tree" (Tschirch 1935a: 265). Contemporary to Vigani, the term was related to "elea" or "pro olea" derived from the "olive tree as well (Ray 1693b: 1847; Lemery 1721: 421).

For American resins, the term is mentioned by Piso as "gummi Icica, sive Elemni". The related tree is called "*Icicariba*" (Piso 1658: 122). "Icica(riba)" originate from the Tupi language, a Lingua Franca in Mesoamerica, South America and the Caribbean, meaning a timber tree or various Brazilian resin producing trees (Boisson 1988).

Botanical and geographical origin

Historical sources mention "gum elemi" in two sorts as follows:

1. "Elemi aethiopicum" or "elemi verum" is a yellowish or whitish resin with a shade of green (Ray 1693b: 1847; Savary des Brûslons, Savary 1723a: 1799; Geoffroy, Thicknesse 1749: 248-9; Hill 1751: 721-2). The tree, from which it was obtained, was unknown, but was thought to be a sort of "olive tree" growing in "Aethiopia" or "Arabia Felix" (Pomet 1694: 262[13]; Lemery 1721: 420; Savary des Brûslons, Savary 1723a: 1799; Chambers 1728a: [289]; Geoffroy, Thicknesse 1749: 248-9; Hill 1751: 722; Lewis 1761: 252) (Fig. 5.69a). It has long and narrow leaves of a whitish green and silvered colour. The flowers are red, the calyx is red or of the colour of the leaves. The fruit is similar to an olive (Pomet 1717: 391; Lemery 1721: 420; Savary des Brûslons, Savary 1723a: 1799).

A variety wrapped in the leaves of "seuilles de cannes d’inde", "indianische Rohrblätter" in the German translation, or "canna indica" is mentioned by several authors (Ray 1693b: 1847; Pomet 1694: 262; Lemery 1714: 317; Pomet 1717: 391-2; Lemery 1721: 420). It was called "gomme elemi en roseaux" and attributed to the "olive tree" as well by the French authors (Pomet 1717: 391-2; Lemery 1721: 420). Towards the end of the 18th century several different species are mentioned: "*Amyris zeylanicum* L." ("Aethiopia" and "East India") and "*Amyris elemifera* L." ("Mexico", "Aethiopia", "Brazil") (Krünitz 1777: 705; Hahnemann 1798: 102; Jacobi 1798: 294).

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[13] In the French editions from 1694 and 1735 Pomet mentions "Aethiopia" or "Arabia Felix", in the German translation from 1717 the "Spanish Indies" are mentioned (Pomet 1694: 262; Pomet 1635b: 33; Pomet 1717: 391).

a - "Gummi Elemi" tree (Lemery 1721: 421), b - "Icicariba Pis., Marcgr." (Piso 1648: 59 and Marcgrave 1648: 98), c - "Prunifera Fago similis arbor Gummi Elemi Pluken." (Plukenet 1692: Tab. 217 Fig.4) and d - "Icica Heptaphylla Aublet" (Aublet 1775b: Tab. 130)

Fig. 5.69 Historical trees mentioned in connection with "elemi"

2. "Elemi americanum", a false sort, is a whitish, yellowish or greenish resin, somewhat transparent with a strong resinous smell. It is mentioned from the end of the 17th century on (Ray 1693b: 1847, 1546; Dale 1693: 448), while older sources only refer to the "ethiopian" sort (Bauhin 1623: 504; Manget 1684: 515; Blanckaert 1690: 222). The tree, from which it was obtained, is "*Icicariba* Piso" or "*Icicariba Brasiliensibus* Marcgr." (Fig. 5.69b). Its resin is called "icica(riba)" by the natives and "almaciga" by the Portuguese (Marcgrave 1648: 98; Piso 1648: 59). In the first edition of the *Historia naturalis Brasiliae* from 1648, the resin of the tree is described to be similar to "gummi elemni" (Piso 1648: 59). In the edition from 1658, Piso calls it "gummi Icica, sive Elemni" and adds that according to "Fr. Ximenes" the same tree and "gum" is found in "New Spain" (Piso 1658: 122). According to Ray, the resin of the "*Arbor Brasiliensis gummi Elemi simile fundens*" originates from "Brazil", "New Spain" and the "Islands of America", respectively (Ray 1693b: 1546), in the 17th century mainly "New Spain" and other places of the "West Indies" are mentioned (Dale 1693: 448[14]; Salmon 1701: 859; James 1764: 313; Geoffroy, Thicknesse 1749: 248-9; Hill 1751: 722-3).

The "*Icicariba*" of Piso and Margrave is described by several authors under differing names: "*Prunifera Fago similis arbor Gummi Elemi fundens*" from "Barbados" at Plukenet (Plukenet 1692: Tab. 217 Fig. 4; Fig. 5.69c), "*Arbor ex Surinama, sive Americana, Myrti Laureae foliis, Elemi resinam fundens*" from "Suriname" by Breyne (Dale 1693: 448) and "*Arbor Brasiliensis gummi Elemi similie fundens*" at Ray (Ray 1693b: 1546). That tree is tall with a greyish and smooth bark, pinnate leaves with two or three pairs with an odd leave at the end. A single leaf looks like that of a pear tree. It has small, clustered greenish white edged flowers. The fruits contain a soft resinous material (Hill 1751: 722). In 1775, Aublet described "*Icica Heptaphylla*" endemic to the forests and beaches of "Guianae", which according to him was identical with "*Icica Brasiliensibus* Georg. Marcg." (Aublet 1775a: 337-8; Fig. 5.69d).

Manufacture and trade

"Elemi verum" was traded in masses rolled to cylindrical pieces about two palms long wrapped in leaves of reed or palm (Ray 1693b: 1847; Pomet 1717: 391; Lemery 1721: 420; Geoffroy, Thicknesse 1749: 248-9; Hill 1751: 721-2). Lewis mentions oblong roundish cakes generally wrapped in "flag leaves" (Lewis 1761: 252). Pomet lists additionally a sort similar to

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[14] Dale equates the ("ethiopian") "gummi elemi officinarum" of Bauhin with the resin from the "*Arbor Brasiliensis gummi Elemi simile fundens R.H.*" or "Icicariba Brasiliensibus Margg." (Dale 1693: 448).

"poix-résine" wrapped in the leaves similar to that of "bois de gerofle"[15] and an ash-grey and brown sort in brittle big lumps (Pomet 1717: 394). "Gomme elemi en roseaux" was traded in irregular flat masses of about two to three "pounds" wrapped in the leaves of "canne d'inde" (Pomet 1694: 262; Lemery 1714: 317; Pomet 1717: 391-2; Lemery 1721: 420; Chambers 1728a: [289]; Savary des Brûslons, Savary 1723a: 1799). Hill additionally mentions irregularly shaped flattish masses, which were not packed (Hill 1751: 722). It was imported "in Cakes of two or three Pounds a-piece" to Europe over Holland or Marseilles (Pomet 1717: 393; Chambers 1728a: [289]).

The "*Icicariba Brasiliensibus* Marcgr." was wounded overnight by the "Brasilians" and in the morning the resin was collected (Hill 1751: 722). It was traded in irregular masses (Dale 1693: 448). The "american galipot" mentioned by Pomet in connection with "elemi" is wrapped in big leaves and traded in barrels (Pomet 1717: 394; Savary des Brûslons, Savary 1723a: 1799). The material was also sold labelled "elemy, anime or tacamahaca" (Pomet 1717: 393). Lemery describes something similar under "gummi chibou", which is traded in small barrels, which are wrapped in the leaves of the "chachibou". This material is sometimes sold as "elemi" (Lemery 1721: 299). Lewis mentions "gummi chibou" as well, as a false sort of "elemi" (Lewis 1761: 252). "Elemi" is often mentioned to be adulterated with a mixture of "galipot" (see chapter 5.1.3), or made of "rosin" washed in "spic oil" of bad quality. It can be distinguished by its smell of "turpentine" and bright white colour (Pomet 1717: 392; Chambers 1728a: [289]).

Geoffroy and Hill mention that several different resins of yellowish, whitish or greyish colour were sent from America to Europe and sold for "elemi", which have a similar smell but different colour (Geoffroy mentions an inferior smell) and are inferior in virtues. They are distinguishable from true "elemi" by the lacking green shade (Geoffroy, Thicknesse 1749: 249; Hill 1751: 723).

Properties

"Elemi verum" is a hard dry resin with a soft, tough and sticky inside (Geoffroy, Thicknesse 1749: 248-9, Lemery 1721: 420; Hill 1751: 721). It is of yellowish and whitish colour with a small cast of green. Geoffroy mentions a pleasant smell like that of fennel, Hill calls it acrid and resinous but pleasant. Also Ray mentions the smell of fennel, his "elemi" is a uniform white substance like wax, which softens when chewed with an acrid and bitterish taste (Ray 1693b: 1847; Chambers 1728a: [289]; Geoffroy, Thicknesse 1749: 249; Hill 1751: 721). It is inflammable and readily dissolves in oil or any other fat substance over fire (Hill 1751: 721). Best quality should be outside dry and inside soft, of a pure and white colour with a shade of green and a sweet and pleasant smell (Lemery 1721: 420; Pomet 1717: 392).

"American elemi" is pellucid, partly transparent, yellowish white and somewhat green inside. Sometimes it is dry and friable, but usually it is soft, sticky, tough and fat to the touch. It has a strong resinous pleasant smell and an acrid and slightly bitterish taste (Dale 1693: 448; Salmon 1701: 859; Geoffroy, Thicknesse 1749: 248-9; Hill 1751: 722; Lewis 1761: 252). Best quality should be stiff, white and greenish, clear and transparent and free from dirt with a fragrant smell (Salmon 1701: 859; Geoffroy, Thicknesse 1749: 249; Hill 1751: 722). It should

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[15] "Bois de gerofle" is translated to "Nägleinholtz" in the German edition (Pomet 1694: 262; Lemery 1714: 317; Pomet 1717: 391-2; Lemery 1721: 420), which is the historical term for clove. Because the leaves used are only vaguely similar to that of clove, the term probably means another member of the genus.

be soft and fat, tough and sticky (Geoffroy, Thicknesse 1749: 249). It almost totally dissolves in "rectified spirit, tinging the fluid a pale gold colour" (Lewis 1761: 252).

Possible chemical composition

"Elemi" in a modern sense is a generic term for soft, friable and fragrant resins from America and Asia. Contemporary to Vigani primarily an African sort was in use. The botanical and geographical origin of this medieval "elemi" was, according to Tschirch, always unknown or at least unsure (Tschirch 1935a: 265f). Additionally, he mentions an Asian or Manila elemi, probably traded from the 15th century on under a differing name ("incense in pasta"), but not during the 18th century (ibid.). The American sort seems to have been labelled after the original one due to similar properties.

1. "Ethiopian elemi" or African elemi in general is seldomly covered in modern literature. At the beginning of the 20th century, Tschirch lists five sorts of African elemi from "Belgisch-Kongo" (several *Canarium* species), two West-African sorts from "Kamerun" and "French Congo" ("Ocumé-Elemi", traded over Gabon, probably from *Canarium schweinfurthii* Engl.), "Mauritius-Elemi" (*Canarium* species) and "Luban-Matti" (Somalia, probably *Boswellia frereana* Birdw.) (Tschirch 1935a: 329-335). The latter is described as stalactitic masses of yellow or whitish-grey colour, sometimes with a smell of citron and wrapped in palm leaves (Tschirch 1935a: 333). This resembles the description of "ethiopian elemi" (see above). "*Amyris zeylanicum* L.", which is mentioned in the 19th century for "gomme elemi en roseaux" (Hahnemann 1798: 102), was reclassified as *Canarium zeylanicum* L. This species is mentioned in modern literature as the source of African elemi together with *Dacryodes edulis* Lam. (Gurib-Fakim, Brendler 2004: 158; University of Melbourne 2006; Regert et al. 2008; see also chapter 2.3.2).

In the literature, African elemi from *Canarium schweinfurthii* Engl. contains high amounts of tirucallanes acids, for other African *Canarium* species α-amyrin and canaric acid are reported, the latter also for the resin of *Dacryodes edulis* Lam (Hinge et al. 1965; Baas 1985; Gurib-Fakim, Brendler 2004: 158). The resin of *Boswellia frereana* Birdw. contains high amounts of epi-lupeol and lupeol with smaller amounts of lupenone, α-, β-boswellic and elemonic acids. Additionally, several dammaranes are found (Fattorusso et al. 1985; Basar 2005: 148; Mathe et al. 2009; see also chapter 2.3.2). No reference samples belonging to this group were examined in this work.

2. In modern literature, Asian sorts from the Malayan Archipelago are mentioned to be traded not later than in the 17th century (Tschirch 1935a: 265-6; de la Cruz-Cañizares et al. 2005), but no materials from that region are listed in the consulted historical sources. Furthermore, materials from the Pacific region and Asia are nearly absent. "Oriental" sorts of several resins investigated in this work originate from Africa or even America, if the origin is not unknown at all (see for example "oriental anime", chapter 5.2.2, and "oriental copal", chapter 5.3.3). A *regular* trade with "East India" started in the 16th century, much later than trade with America. According to Tschirch, a soft "incense" ("incenso in pasta") probably originating from the Pacific region traded from the 15th century on over the Red Sea very likely was Manila elemi. It was however not available in the 18th but again – even though rare – from the beginning 19th century on (Tschirch 1935a: 265-6).

Although Manila and other Asian *Canarium* elemis most likely were not in trade at the time of Vigani, it cannot be excluded that such resins have been found their way to Europe. Manila and other Asian elemis are investigated in detail, particularly the resin of *C. luzonicum*

Gray possesses a characteristic sesquiterpene fraction and contain high amounts of neutral pentacyclic triterpenes and tirucallane acids (Khalid 1983; Mills, White 1999: 108; Chiavari et al. 2008; Regert et al. 2008; see also chapter 2.3.2).

For this investigation, six samples of Asian elemis were analysed, with the results presented in chapter 3.3.2. In the volatile fraction of Manila elemi high amounts of elemol, elemicin and lower amounts of γ- and β-eudesmol are present. Main compounds of the triterpene fraction are high amounts of β- and α-amyrin, smaller amounts of their 3α-epimers, maniladiol and brein and their isomers as well as α-elemonic, β-elemonic, 3β-hydroxytirucall-8,24-dien-21-oic and elemonic acids are found. An Indonesian elemi is composed nearly identically, apart from the characteristic volatile fraction. Instead, it contains high amounts of isomeric dimers of α-phellandrene.

3. Today, American elemi is obtained from different *Protium* species, which possess a high volatile fraction (Siani et al. 1999; Rüdiger et al. 2007; see also chapter 2.3.2 and table 2.10). "*Icica heptaphylla* Aubl." is the basionym of *Protium heptaphyllum* March, which is mentioned as one of the main sources of modern American elemi. It originates from Colombia and Venezuela, and is also called tacamahaca (Langenheim 2003: 358) (table 2.10). The genus "icica", derived from the resin of the "*Icicariba*" of Piso, was later replaced by *Protium*. Due to the assumingly wide distribution of the term "icica(riba)" in the Caribbean several different species may be possible. *Amyris elemifera* L., one of the botanical sources of "gomme elemi en roseaux" at the end of the 18th century (Krünitz 1777: 705; Jacobi 1798: 294), is mentioned as the source of Mexican elemi (Mills, White 1999: 108). The genus *Amyris* belongs to the Rutaceae.

In the literature, *Protium* resins consist mainly of α- and β-amyrin (1:2), maniladiol, brein, tirucallane acids and taraxasterol (Stacey et al. 2006; Rüdiger et al. 2007). The resin of *Protium heptaphyllum* contains α-amyrin and β-amyrin, α- and β-amyrone, the corresponding 9(11)-dienes, minor amounts of maniladiol, brein, friedelan-3-one, lupenone, taraxastan-3-one-20-ol, taraxastandiol, epi-Ψ-taraxastan-one-diol, α- and β-elemolic acids (Susunaga et al. 2001; Mora et al. 2001; Rüdiger et al. 2007). Additionally a more prominent sesquiterpene fraction with α-copaene, β-elemene, methyleugenol, β-selinene, myristicin, elemicin and high amounts of dillapiole is reported (Siani et al. 1999; Rüdiger et al. 2007). Based on the present literature data, resins from *Canarium* and *Protium* speices are difficult to distinguish (see also chapter 2.3.1). No reference samples belonging to this group were examined in this work.

The resin *of A. elemifera* L. contains high amounts of lupeol and α-amyrin together with smaller amounts of lupenone and epimers of α- and β-amyrin (Stacey et al. 2006). It resembles *Bursera* resins apart from the absence of β-amyrin, which is however probably due to aging. No reference samples belonging to this group were examined in this work.

Chemical analysis

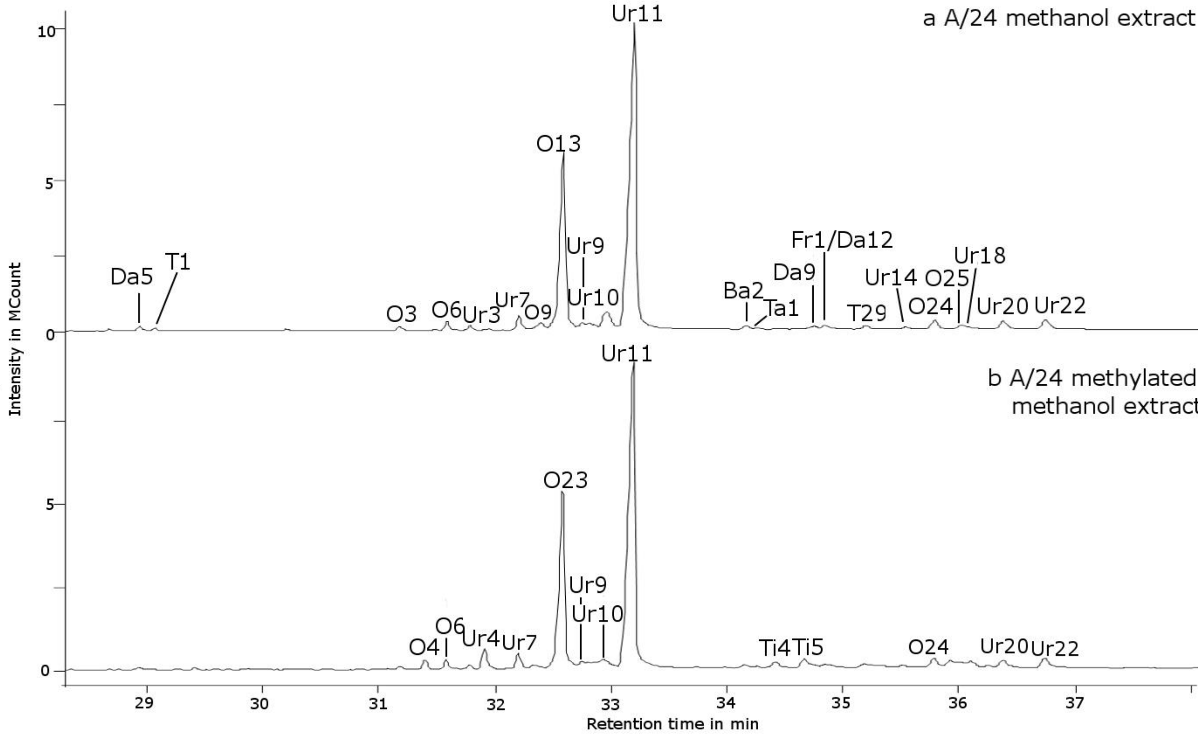
The methanol extract (Fig. 5.70a) mainly contains β- and α-amyrin, together with smaller amounts of olean-9(11),12-dien-3β-ol, urs-9(11),12-dien-3β-ol, 3epi-β- and 3epi-α-amyrin, 11-oxo-olean-12-en-3β-ol, brein, 11-oxo-urs-12-en-3β-ol and maniladiol. Small amounts of hexakisnor-dammaran-3,20-dione, compound T1, olean-9(11),12-dien-3-one, urs-9(11),12-dien-3-one, α-amyrone, baurenol, taraxasterol, friedelan-3-one, 20,24-epoxy-dammaran-3-one, the compounds Da12 and T29, ursolic aldehyde, and 11-oxo-urs-12-en-3a-ol are present as well. Even though small amounts of dammarane aging products (Da6, Da9, Da12) are present, no unaltered dammarane compound is found. The methylated methanol extract (Fig. 5.70b) additionally contains small amounts of the methyl ether of β- and α-amyrin, elemonate and α-elemolate.

Discussion

The composition is typical for non-acidic Burseraceae resins, particularly from the genera *Canarium* (Africa) and *Protium* (America). α- and β-amyrin, brein, manildadiol and tirucallane acids such as elemonic and elemolic acids are characteristic for these resins. As discussed under 'chemical composition', *Protium* and *Canarium* resins are distinguishable mainly by their volatile fraction. If no significant volatile fraction is present, which is the case for A/24 "Elemi", no clear differentiation based on the triterpene composition is possible. The presence of the 3α-epimers of β- and α-amyrin and the absence of phenylpropanoids and elemol are uncharacteristic for Manila elemi. Another Asian or African *Canarium* species is, however, possible.

Even though A/24 "Elemi" resembles the description of "ethiopian elemi" (oblong flat cakes, wrapped in palm leaves), it does not originate from *Boswellia frereana* Birdw., the resin of which contains high amounts of (epi-)lupeol, lupenone and boswellic acids but no amyrins (Basar 2005: 148). A/24 "Elemi" also does not originate from an *Amyris* species, which show a composition more similar to *Bursera* resins (Stacey et al. 2006). *Dacryodes edulis* Lam. contains canaric acid (Baas 1985), which is no found in the sample.

A/24 "Elemi" contains small amounts of dammarane aging products, which is a limited indication that it was obtained from a *Boswellia* or *Commiphora* species. Dammaranes are reported to be markers for species from *Commiphora* and *Boswellia* with a composition dominated by alcoholic triterpenes, hence old-world resins. However, there is no indication in modern literature for an African *Commiphora* resin called elemi. Additionally, those traces of



a – methanol extract and b – methylated methanol extract (labels, see table 5.18)

Fig. 5.70 Gas chromatograms of A/24 "Elemi" from the Vigani Cabinet, triterpene section (TIC) dammaranes compounds do not correspond with the high amounts of dammarane aldehydes, alcohols and acids found in an African copal attributed to *Commiphora* in this work (chapter 4.3.2).

In summary, it must remain open whether A/24 "Elemi" is an old-world *Canarium* resins originating from Asia or Africa or a new world resin from *Protium heptaphyllum* March. The term "elemi" is of old-world origin and was seemingly used in Vigani's time only occasionally for a material from America. On the other hand, Asian elemis were very likely not traded at this time (see above). Because the appearance and the former wrapping resemble that described for "ethiopian elemi" A/24 "Elemi" very likely originates from Africa. An Africa *Canarium* species, such as mentioned by Tschirch (Tschirch 1935a: 329-335), is therefore the most likely candidate. Whether the mentioned "olive tree" was a *Canarium* species or *Boswellia frereana* cannot be figured out.

Label	t_R	Name	Main mass fragments
Da5	28.69	Hexakisnor-dammaran-3,20-dione	95, 107, 135, 205, 273, 297, **315**, 325, 340, 358
T1	28.93	Unidentified	95, 135, 189, 207, **299**, 317, 327, 342, 360
O3	31.18	Olean-9(11),12-dien-3-one	255, 269, 293, 352, 389, 407, **422**
O4	31.39	3β-Methoxy-olean-12-ene	81, 95, 107, 189, **203**, 218, 393, 408, 425, 440
O6	31.58	Olean-9(11),12-dien-3β-ol	119, 159, 255, 271, 391, 409, **424**
Ur3	31.77	3β-Methoxy-urs-12-ene	81, 95, 107, 189, **203**, 218, 393, 408, 425, 440
Ur4	31.90	Urs-9(11),12-dien-3-one	133, 159, 255, 269, 389, 407, **422**
Ur7	32.20	Urs-9(11),12-dien-3β-ol	133, 159, 255, 295, 391, 409, **424**
O9	32.38	Olean-12-en-3α-ol (epi-β-amyrin)	95, 107, 119, 175 189, **203**, 218, 393, 411, 426
O13	32.58	Olean-12-en-3β-ol (β-amyrin)	95, 119, 175, 189, **203**, 218, 393, 411, 426
Ur9	32.75	α-amyrone	107, 147, 189, 203, **218**, 409, 424
Ur10	32.97	Urs-12-en-3α-ol (epi-α-amyrin)	107, 147, 189, 203, **218**, 393, 411, 426
Ur11	33.17	Urs-12-en-3β-ol (α-amyrin)	107, 147, 161, 175, 189, 203, **218**, 393, 408, 411, 426
Ba2	34.16	Baurenol	95, **229**, 241, 247, 393, 411, 426
Ta1	34.26	Taraxasterol	93, 107, 121, 175, **189**, 207, 229, 393, 408, 426
Ti4	34.41	Elemonate (proposed)	189, 257, 297, 311, 393, 421, **453**, 468
Ti5	34.66	3α-hydroxytirucall-8,24-dien-21-oate (α-elemolate)(proposed)	187, 281, 299, 377, 405, **437**, 455, 470
Da9	34.74	20,24-Epoxy-dammaran-3-one (proposed)	107, **143**, 205, 381, 399, 407, 425, **440**
Fr1	34.83	Friedelan-3-one	**107**, 125, 163, 191, 205, 218, 231, 273, 341, 411, 426
Da12	34.98	Unidentified oxygenated dammarane	107, 125, **143**, 191, 383, 408, 426
T29	35.20	Unidentified oxygenated oleanane or ursane	**135**, 217, **232**, 273, 285, 299, 410, 423, 438
Ur14	35.55	Ursolic aldehyde (3-hydroxy-urs-12-en-28-al)	253, 271, 289, 407, 422, **440**
O24	35.78	11-oxo-olean-12-en-3β-ol	**135**, 175, 217, **232**, 273, 407, 425, 440
O25	36.02	Maniladiol	160, 187, 190, 201, **216**, 219, 234, 391, 409, 424, 442
Ur18	36.13	11-oxo-urs-12-en-3α-ol	105, **135**, 149, 175, 232, 273, 407, 425, 440
Ur20	36.39	11-oxo-urs-12-en-3β-ol	**135**, 175, 232, 273, 407, 425, 440
Ur22	36.73	Brein	110, 151, 191, 207, 219, **234**, 409, 424, 442

Tab. 5.18 Compounds found in A/24 "Elemi", analysed with temperature program Triterpenes 1 and column A, mass spectra references see appendix

5.3.5 A/22 Tacamahaca

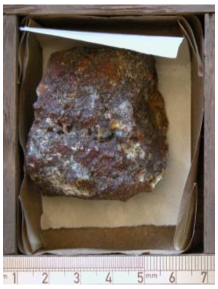


Fig. 5.72 A/22 "Tacamahaca"

Fig. 5.71 Sampling of A/22 (yellow interior is visible at the top left edge)

Description

The box contains one big lump in a brownish, grey colour. The surface is brittle and opaque. An aged crust and a more yellow and transparent interior are visible (Fig. 5.72). The material is placed on a white piece of paper, which is not the original one. Also the label was made by another person. It is not known whether the material was originally placed in another compartment or added later by another person.

Sampling

Two samples, from the aged surface crust (about 20 mg) and from the transparent interior (about 30 mg) were taken on 26 April 2007 (Fig. 5.72). The interior was yellow and transparent with small brown inclusions. The crust was opaque and brown.

Vigani references

* MS Quns Vig. 4, folio 3, verso, as "Gum Taccemhac", 2 ounces at 8 pence

* Does not appear in LECTURE NOTES UNDATED

* Does not appear in LECTURE NOTES 1707

Contemporary literature

Fine art materials

There is no mention of "gum tacamahaca" as a fine arts material in the consulted sources, because this resin was used mainly for medical purposes.

Science

* RAY 1693b: 1846: "Tacamahaca" ("*Tacamahaca Populo simile fructu colore Paeniae* J. B., *Arb. Populo simile resinosa alstera* C.B.")

* DALE 1693: 436: "Tacamahaca" ("*Arbor Populo similis, fructu colore Paeniae simili* J.B., *Tecomahaca* Hern., Tacamahac-Tree")

* POMET 1717: 393: "Tacamhaca" ("Harame")

* LEMERY 1721: 1098: "Tacamahaca", "Tacamaca", ("*Tacamahacca* Park., *Tacamahaca Populo similis fructu colore Paeonae* C. B., *Tecomahaca* Hern., *Arbor Populo similis resinosa alstera* C.B., *Harame* Pomet")

* GEOFFROY 1743: 103: "Tacamahaca", ("*Arbor Populo similis resinosa altera* C. B., *Tecomahaca* Hern. ")

* JAMES 1747: 334: "Gummi Tacamahaca" ("*Tacamahaca Populo similis, fructu colore Paeniae simili* J.B., *Tecomahoica* Hern. ")

* HILL 1751: 734: "Tacamahacca", "Tacamahac" ("*Arbor populo similis resinosa altera* C.B., *Tecomahaca* Hern.")

* LEWIS 1761: 545: "Tacamahaca"

Encyclopedias

* CHAMBERS 1728b: [169]: "Tacamacha", "Tacamahaca"

* SAVARY DES BRÛSLONS, SAVARY 1748c: 285(2): "Tacamacha", "Tacamahaca", "Tamacha"

Terminology

A resin called "tacamahac(a)" seems to be known in Europe from the 16th century on (Monardes, de L'Ecluse 1579: 5; Fragoso, Spachii 1601: 97-8; Tschirch 1935a: 266). Its first reference in an English dictionary is given by Traister in 1577 (Traister 2001: 44). It was introduced into Spanish language from the Nahuatl "tecoma hiyac" meaning stinking-pot tree (Watson 1938).

Botanical and geographical origin

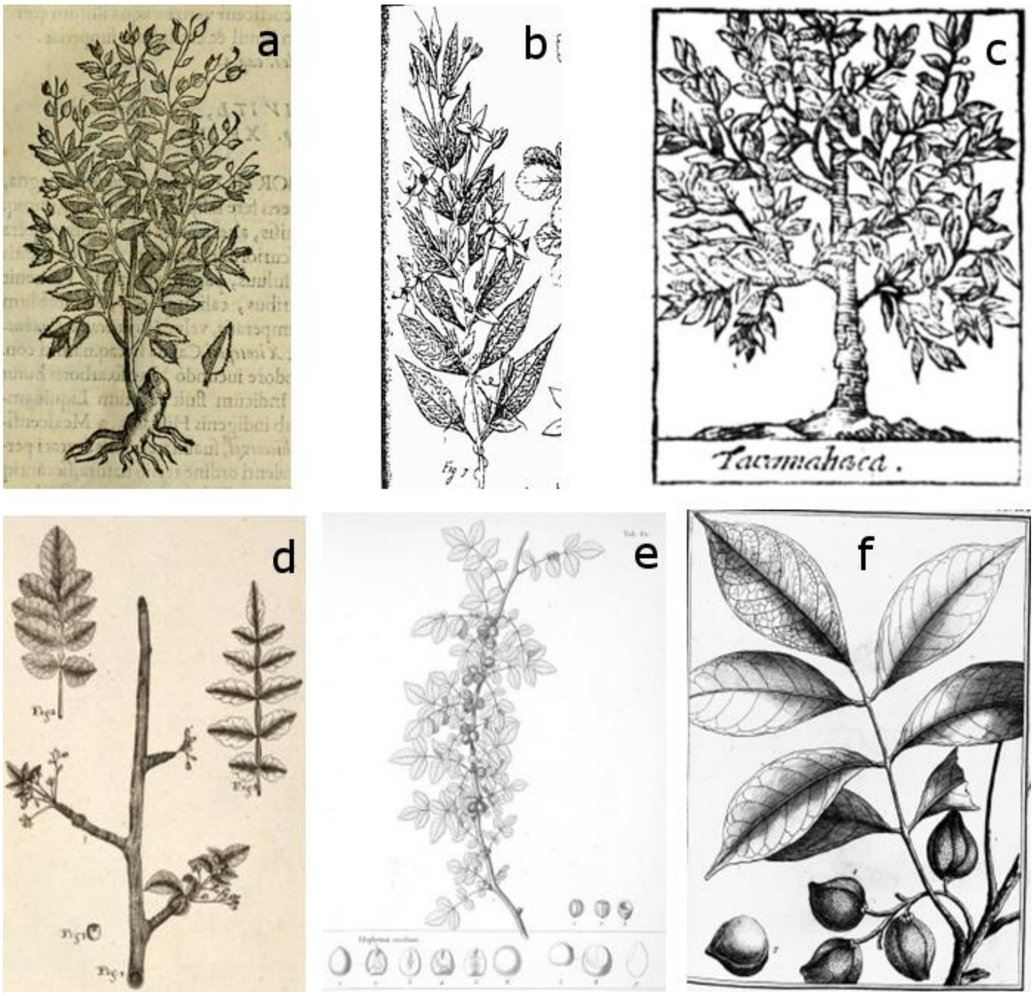
"Tacamahaca" originated until the end of the 17th century only to American trees, later the tree is mentioned to grow in Madagascar as well. Historical sources mention two sorts, which are distinguished by the method of harvesting not by their geographical and botanical origin. Nevertheless, for "tacamahaca in massis" South America and the Caribbean (Pomet 1717: 394; Chambers 1728b: [169]; Lemery 1721: 1098; Lewis 1761: 546), for the rare "tacamahaca en coque" "S. Laurentius" ("l'Isle Saint-Laurent") are mentioned additionally (Pomet 1694: 263; Pomet 1717: 394; Lemery 1721: 1098; Lewis 1761: 546).

The botanical source of the resin was the "*Tecomahaca* Hern." or the "Tacamahac-Tree" (Dale 1693: 436; Lemery 1721: 1098; Geoffroy 1743: 103; James 1747: 334; Hill 1751: 734; Fig. 5.73a, c). Several other authors mention the tree under differing names (Bauhin 1623: 430; Bauhin, Cherler 1650: 346; Plukenet 1692: 228, see Fig. 5.73b; see also 'Contemporary literature'). It is a big tree similar to poplar and has small green leaves similar to "Buchsbaum". Its fruit is as big as green nuts or walnuts with a stone inside similar to peaches stone. The colour of the fruit is red, similar to "*Paeonia*", and it contains an aromatic resin (Monardes, Clusius 1579: 5; Fragoso, Spachii 1601: 97; Ray 1693b: 1846; Pomet 1717: 393; Lemery 1721: 1099; see Fig. 5.73c).

From the end of the 17th century on, Madagascar is mentioned as a place of origin, the tree called "harame" there, later also "hazamc" (Pomet 1694: 263; Lemery 1721: 1098; Savary des Brûslons 1748b: 1577; Barham 1794: 185). The latter is probably of Arabian origin (Huenecke 2008). Throughout the 18th century both places are mentioned together (Pomet 1717: 393; Chambers 1728b: [169]; Geoffroy 1743: 104; James 1747: 334; Savary des Brûslons, Savary 1748c: 285(2); Hill 1751: 734; Barham 1794: 185).The description of the tree stays the same (Chambers 1728b: [169]; Lemery 1721: 1098; Lewis 1761: 545).

At the end of the 18th century both sorts were located in America, but obtained from different trees: "tacamahaca in massis" from "*Fagara octandra* L." growing in "Curaßao", and "tacamahaca en coque" from another tree with pinnate rose leaves growing in "Brazil" and "Guyan" (Hahnemann 1799: 303).

Firstly in the 19th century, the two sorts are mentioned as geographically and botanically different. The term "west indian tacamahaca" is attributed to a wide range of eventually reclassified species such as "*Elaphrium tomentosum* Jacq." (= "*Fagara octandra* L.", then *Bursera tomentosa* Triana & Planch) (Fig. 5.73d), "*Elaphrium excelsum* Kunth" (= *Bursera excelsa* Engl.; Fig. 5.73e), "*Bursera gummifera* L." (= *Bursera simaruba* Sarg.) and "*Icica altissima* Aubl" (= *Bursera altissima* Baill.; Fig. 5.73f) (Hahnemann 1799: 303; Krünitz 1842: 316; Liebig et al. 1861: 466; Wiesner 1873: 79; Thenius 1895: 101-2; Balfour 1976: 799; Remington et al. 1918: Tacamahac; Tschirch 1935a: 343, 336).



a - "Tecomahaca" Hernd. (Hernandez 1651: 55),b - "Tacamahaca foliis crenatis Sadelhouts Lignum ad ephippia consiciendum aptum Pluk." (Plukenet 1692: Tab. 228, Fig. 1), c - "Tacamahaca" tree (Lemery 1721: 1099), d - "Elaphrium tomentosum Jacq." (Jacquin 1763: t. 71) (the leave top left is from another species), e - "Elaphrium excelsum Kunth" (Kunth 1825: t. 611) and f - "Icica altissima Aubl." (Aublet 1775b: t.132)

Fig. 5.73 Historical trees mentioned in connection with "tacamahaca"

The sort traded in gourds, "tacamahaca en coque", became "east indian tacamahaca", for details please refer to chapter 5.3.6.

Only occasionally *Populus balsamifera* L., the Balsam poplar, is mentioned as a botanical source of "tacamahaca" (Lewis 1791: Tacamahaca; Krünitz 1842: 316; Fowler 1867; Balfour 1976: 799). According to Traister, "tacamahac" was traded in the 16th century from North America, particularly from Virginia (Traister 2001: 44), where the Balsam poplar is common.

Manufacture and trade

In the 17th century the resin was imported from "New Spain" (Hernandez 1651: 55; Schröder 1644: 4.210; Manget 1687: 531). "Tacamahaca in tears, in masses" or "tacamahaca ordinaire" exuded after wounding from the tree in tears or drops or in irregular masses (Pomet 1717: 394; Chambers 1728b: [169]; Lemery 1721: 1098; Lewis 1761: 546). "Tacamahaca sublimis" was traded in gourds, for further details please refer to chapter 5.3.6.

Properties

"Tacamahaca in tears, in masses" is dried-up and has the form of tears, drops or lumps (Pomet 1717: 394; Chambers 1728b: [169]; Lemery 1721: 1098; Lewis 1761: 546). It is of red, yellow, brown and whitish colour, but also brown and spotted. It has an aromatic, bitter and somewhat spicy taste and a fragrant smell, the best quality resembling that of lavender (Dale 1693: 436; Lemery 1721: 1098; Lewis 1761: 546). It is dry and transparent (Pomet 1717: 394; Lemery 1721: 1098; Chambers 1728b: [169]; James 1747: 334; Lewis 1761: 545). It should be clean, dry and with a smell similar to the "tacamahaca sublimis" (Pomet 1717: 395-6). "Tacamahaca sublimis" is described in chapter 5.3.6.

Possible chemical composition

1. Tacamahaca is mentioned in modern literature only for the resin of *Protium heptaphyllum* March., which is also called elemi from Colombia and Venezuela (Langenheim 2003: 358). Its basionym is "*Icica Heptaphylla* Aubl.", which was, according to Aublet, identical with "*Icica Brasiliensibus* Georg. Marcgr.". The resin or the tree was called "icica(riba)" (Tupi), "almecega" (Portuguese) or "elemni" (Marcgrave 1648: 98; Piso 1658: 122; Tschirch 1935a: 266). A resin of this name and the corresponding tree are discussed in chapter 5.3.4. French authors mention an "american galipot", which is sold as "elemy", "anime" or "tacamahaca" according to knowledge of the merchant (Pomet 1717: 393; Savary des Brûslons, Savary 1723a: 1799-1800), which makes it impossible to determine whether the resin of *Protium heptaphyllum* March. was originally or wrongly labelled "tacamahaca" or was even sold under this name.

In the literature, *Protium* resins consist mainly of α- and β-amyrin (1:2), maniladiol, brein, tirucallane acids and taraxasterol (Stacey et al. 2006; Rüdiger et al. 2007). The resin of *Protium heptaphyllum* contains α-amyrin and β-amyrin, α- and β-amyrone, the corresponding 9(11)-dienes, minor amounts of maniladiol, brein, friedelan-3-one, lupenone, taraxastan-3-one-20-ol, taraxastandiol, epi-Ψ-taraxastan-one-diol, α- and β-elemolic acids (Susunaga et al. 2001; Mora et al. 2001; Rüdiger et al. 2007; see also chapter 2.3.2). No reference samples belonging to this group were examined in this work.

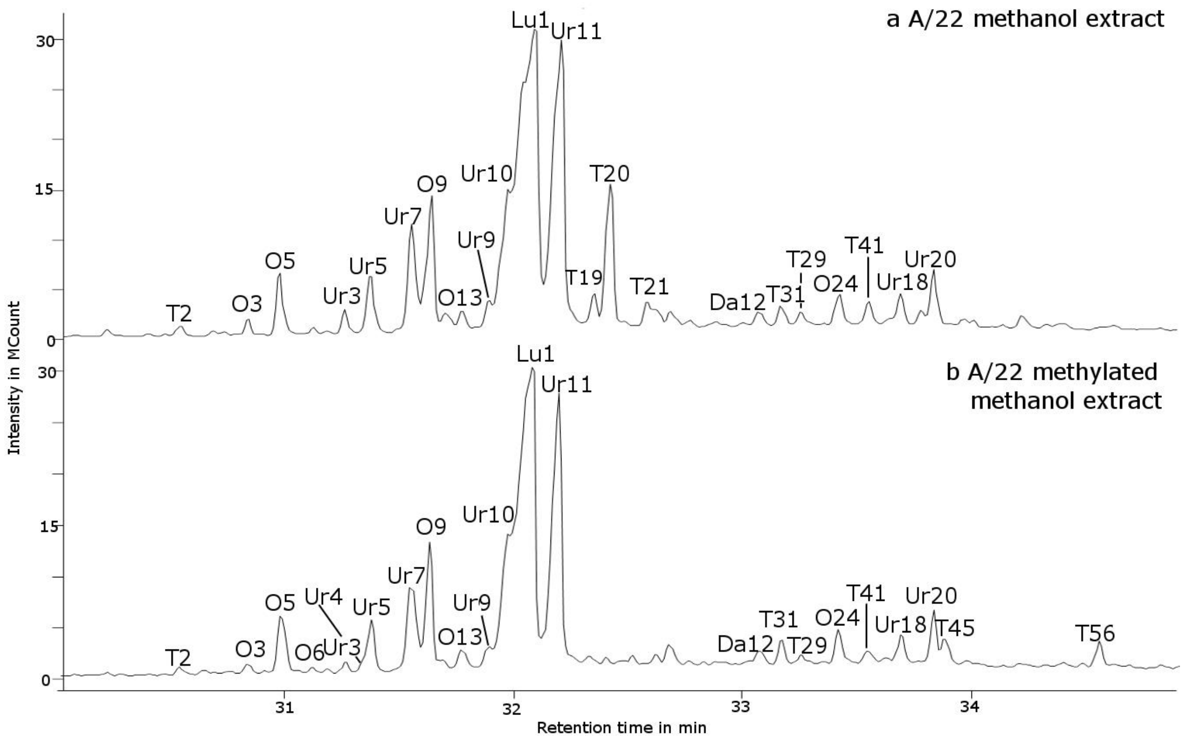
2. From historical sources contemporary to Vigani, it remains unclear whether the "*Tecomahaca* Hernd." is a *Bursera*, *Protium* or any other American resin producing species. In the 19th century, "west indian tacamahaca" is related to several *Bursera* species, and the described leaves and fruits of the "*Tecomahaca* Hernd." actually have similarities to that of *Bursera* trees. "*Elaphrium tomentosum* Jacq." was called "copal" by the native people (Kunth 1825: 30). However, no connection between these species and the botanical sources given in the 17th and beginning 18th century is found.

In the literature, *Bursera* resins contain high amounts of α- and β-amyrin, (epi-)lupeol, lupenone and the 3α-epimers of α- and β-amyrin (Peraza-Sánchez et al. 1995; de la Cruz-Caňizares et al. 2005; Stacey et al. 2006; see also chapter 2.3.2). A variety of Burseraceae resins were investigated in this work, with the results presented in chapter 4.3.2. No botanical samples were available, but several reference samples can be assigned to *Bursera* resins based on literature data. Mexican *Bursera* copals are well distinguishable from *Protium* resins by high amounts of epi-lupeol and higher amounts of 3-epi-β-amyrin than β-amyrin. A Gum Anime analysed was assigned to *Bursera* as well, because of its high amounts of epi-lupeol and 3-epi-β-amyrin. In addition, it contains several other pentacyclic triterpenes with additional functional group (T17, T19, T20, T67, T43, T48). The analysed materials all show highly characteristic compositions. The results are mostly consistent with literature data, but due to the wide range of Burseraceae resins used and terminological confusion, there are still knowledge gaps. A Tacamahak resin analysed was of a completely different composition, probably not even belonging to Burseraceae. It contains several unidentified constituents, which are not described in literature for *Bursera* or *Amyris* resins, and shows a completely different aging profile resembling more that of *Pistacia* than other Burseraceae resins investigated here.

3. "Tacamahaca" resin from Madagascar was traded at the time of Vigani as well, but is attributed to the same botanical source as the American "tacamahaca". In the 19th century several Asian (mainly *Calophyllum*) species are mentioned for the "east indian tacamahaca" from Asia and Madagascar, which was traded in gourds (Krünitz 1842: 317; Liebig et al. 1861: 466; Wiesner 1873: 79; Thenius 1895: 101-2; Balfour 1976: 799). Whether the "tacamahaca" from Madagascar at the time of Vigani originated from the same tree as the American one or from other species, first mentioned in the 19th century, cannot be clarified here. A detailed discussion of the Asian (mainly *Calophyllum*) species is given in chapter 5.3.6.

4. "Tacamahaca" resin from the Balsam poplar is a possible botanical source as well. The bud resin of this tree is reported to contain mono- and sesquiterpenes, mainly 1,8-cineol, *trans*-nerolidol and α-bisabol (Mattes et al. 1987). No report on significant amounts of di- or triterpenes is found.

There are indications that this material is probably identical with the oil expressed from the seeds of *Calophyllum inophyllum* (Tamanu oil) (Dweck, Meadows 2002). It contains mainly several fatty acids such as palmitic, stearic, oleic, linoleic and linolenic acids. Other (pharmacological effective) constituents are callophyllic acid, 4-phenyl coumarin-calophyllolide, inophyllolide as well as several neoflavonoids (Gurib-Fakim, Brendler 2004: 15; Dweck, Mea-



a – methanol extrac and b – methylated methanol extract (labels, see table 5.19)

Fig. 5.74 Gas chromatograms of A/22 "Tacamahaca" interior from the Vigani Cabinet, triterpene section (TIC)

Label	t_R	Name	Main mass fragmentes
T2	30.54	Unidentified	95, 135, **189**, 353, 368, 386, 420
O3	30.83	Olean-9(11),12-dien-3-one	255, 269, 293, 352, 389, 407, **422**
O5	30.98	Olean-9(11),12-dien-3α-ol	159, 189, 255, 391, 409, **424**
O6	31.13	Olean-9(11),12-dien-3β-ol	119, 159, 255, 271, 391, 409, **424**
Ur3	31.26	Ursa-9(11),12-dien-3-one	133, 159, 255, 269, 389, 407, **422**
Ur4	31.35	3β-Methoxy-urs-12-ene	119, 147, 161, 189, 203, **218**, 393, 408, 425, 440
Ur5	31.37	Urs-9(11),12-dien-3α-ol	159, 255, (395), 391, 409, **424**
Ur7	31.56	Urs-9(11),12-dien-3β-ol	133, 159, 255, 295, 391, 409, **424**
O9	31.64	Olean-12-en-3α-ol	95, 107, 119, 175 189, **203**, 218, 393, 411, 426
O13	31.77	Olean-12-en-3β-ol (β-amyrin)	95, 119, 175, 189, **203**, 218, 393, 411, 426
Ur9	31.89	α-amyrone	107, 147, 189, 203, **218**, 409, 424
Ur10	31.98	Urs-12-en-3α-ol (epi-α-amyrin)	107, 147, 189, 203, **218**, 393, 411, 426
Lu1	32.09	Epi-lupeol	107, 135, **189**, 203, 207, 218, 229, 257, 393, 411,
Ur11	32.19	Urs-12-en-3β-ol (α-amyrin)	107, 147, 161, 175, 189, 203, **218**, 393, 408, 411,
T19	32.35	Unidentified	107, 147, 189, 203, **218**, 393, 408, 426, 439, 454
T20	32.42	Unidentified	107, 147, **189**, 203, 216, 229, 297, 341, 393, 408, 439, 454
T21	32.59	Unidentified	147, 189, 203, **218**, 393, 439, 454
Da12	33.08	Unidentified oxygenated dammarane	107, 125, **143**, 175, 191, 365, 383, 408, 426
T31	33.17	Unidentified	107, 121, **189**, 203, 377, 395, 410, 428
T29	33.25	Unidentified oxygenated oleanane or ursane	**135**, 217, **232**, 273, 285, 299, 410, 423, 438
O24	33.42	11-oxo-olean-12-en-3β-ol	**135**, 175, 217, **232**, 273, 407, 425, 440
T41	33.55	Unidentified oxygenated oleanane or ursane	**135**, 175, 217, **232**, 273, 407, 425, 438
Ur18	33.69	11-oxo-urs-12-en-3α-ol	**135**, 175, 221, 232, 273, 407, 425, 440
Ur20	33.84	11-oxo-urs-12-en-3β-ol	**135**, 175, 232, 273, 407, 425, 440
T45	33.88	Unidentified	107, 121, 135, **189**, 203, 367, 385, 439, 454, 472
T56	34.55	Unidentified	107, 121, 175, **189**, 367, 385, 439, 454, 472

Tab. 5.19 Compounds found in A/22 "Tacamahaca", analysed with temperature program Triterpenes 3, and column A mass spectra references see appendix

dows 2002; Su, He 2007). The seed oil of a Brazilian species contains several chromanone carboxylic acids such as (iso-)apetalic and blancoic acids (Plattner et al. 1974).

Chemical analysis

The methanol extract (Fig. 4.74a) mainly contains of epi-lupeol and α-amyrin, together with smaller amounts of olean-9(11),12-dien-3α-ol, urs-9(11),12-dien-3α-ol, urs-9(11),12-dien-3β-ol, 3α-β-amyrin, 3α-α-amyrin and T20. Small amounts of olean- and urs-9(11),12-dien-3-one, olean-9(11),12-dien-3β-ol, β-amyrin, α-amyrone, compounds T19, T21, Da12, T31, T29 and T41, 11-oxo-olean-12-en-3β-ol, 11-oxo-urs-12-en-3α- and 3β-ol are present as well. Between epi-upeol and α-amyrin elutes an epimer of baurenol (Ba2), which is visible only in EIC (see 5.3.6). In the methylated methanol extract (Fig. 4.74b), also compounds T45 and T56 are present.

The interior and the crust are composed identically.

Discussion

This composition is typical for non-acidic Burseraceae resins, particularly from the genus *Bursera*. High amounts of (epi-)lupeol and the prevalence of 3α-epimers of α- and β-amyrin are characteristic for these resins. Additionally, the unidentified compounds T19 and T20 are present in reference materials related to *Bursera* resins in this work. The composition resembles that reported for the resin of *Amyris elemifera* (Stacey et al. 2006), which cannot be verified here due to imcomplete chemotaxonomical data.

A/22 "Tacamahaca" is not obtained from *Protium heptaphyllum* March., which contains maniladiol, brein and tirucallane acids but no epi-lupeol. Taking literature data and result of own analysis together, the presence of (epi-)lupeol and the compounds T19, T20 and T21 is uncharacteristic for *Protium* resins. Additionally, *Protium heptaphyllum* March. is possibly identical with "*Icica Brasiliensibus* Georg. Margr.", the source of Brazilian "elemi". The "elemi" present in the Cabinet (A/24 "Elemi", chapter 5.3.4) indeed shows the typical composition of a *Protium* resin. Although a *Canarium* resin cannot be excluded for A/24 "Elemi", the chemical composition of both genera is clearly different from that of A/22 "Tacamahaca". Also a modern Gummi tacamahacae analysed in this work (chapter 4.3.2) shows a composition clearly different from that reported for *Protium* resins.

Although "*Tecomahaca* Hernd." cannot be assigned for sure to a *Bursera* species, the composition of A/22 "Tacamahaca" makes it likely that the sample from the Cabinet was obtained from a *Bursera* species.

The two materials in the Cabinet labelled as "tacamahaca" A/22 and Z/1 are of nearly identical composition (see chapter 5.3.6). Z/1 contains higher amounts of 3α-β-amyrin and 3α-α-amyrin and lower amounts of epi-lupeol. The varying amounts of other constituents, particularly the aging compounds (O3, O5, O6, Ur3, Ur5, Ur7, T29, O24, T41, Ur18, Ur20), result from the varying amounts of the related initial constituents. Historical information indicates that "tacamahaca in tears" and "tacamahaca sublimis" were obtained from the same tree by different harvesting methods. The composition of A/22 and Z/1 support this assumption. None of the characteristic compounds described in literature for *Calophyllum* materials and the resin of Balsam poplar are present. It may be assumed that the tree used for the production of "tacamahaca" in America was brought to Madagascar similar to vanilla and cultivated there for some time, before the resin from an endemic tree (*Calophyllum* species) was used instead. This assumption, however, requires further investigation.

5.3.6 Z/1 Tacamahaca

Fig. 5.75 Z/1 Tacamahaca, left - interior and right - outside

Fig. 5.76 Sampling of Z/1

Description

The box contains a brown coconut shell filled with a brown dried-up material. Under the brown crust a yellow brittle material is visible.

Sampling

Samples from the aged surface crust (about 15 mg) and from the yellow interior (about 12 mg) were taken on 26 April 2007 (Fig. 5.76). The interior was dark yellow and somewhat opaque. The crust was opaque and of grey to brown colour.

Vigani references

* MS Quns Vig. 2, recto, as "Tacamahacca opt", 5 ¾ ounces at 8 shilling & 7 ½ pence

* Does not appear in LECTURE NOTES UNDATED

* Does not appear in LECTURE NOTES 1707

Contemporary literature

See chapter 5.3.5

Terminology

See chapter 5.3.5

Botanical and geographical origin

"Tacamahaca" originated during the 17th and 18th century from the "Tacamahac-Tree", which grew in America and in Madagascar (Dale 1693: 436; Pomet 1717: 393; Lemery 1721: 1098; Geoffroy 1743: 103; James 1747: 334; Savary des Brûslons 1748b: 1577; Hill 1751: 734; Barham 1794: 185). Historical sources distinguish tow sorts, which are distinguished by the method of harvesting not by their geographical and botanical origin: "tacamahaca in massis" and "tacamahaca en coque" (Pomet 1717: 394; Chambers 1728b: [169]; Lemery 1721: 1098; Lewis 1761: 546). The situation is described in detail in chapter 5.3.5. First in the 19th century, the two sorts are mentioned as geographically and botanically different.

The sort traded in gourds, "tacamahaca en coque", became "east indian tacamahaca" originating from *Calophyllum inophyllum* L. or *C. calaba* L., a sort from Madagascar, also called "bourbon tacamahaca" from *C. tacamahaca* Willd. (Krünitz 1842: 317; Liebig et al. 1861: 466; Wiesner 1873: 79; Thenius 1895: 101-2; Balfour 1976: 799). "Bourbon tacamamaca" smells like "faenum graecum", "east indian tacamahaca" smells like lavender (Tschirch 1935a: 253). Balfour also mentions *Canarium commune* (Balfour 1976: 799).

Manufacture and trade

"Tacamahaca sublimis" or "tacamahaca en coque" exuded without wounding the tree. It was collected in shells or gourds of cucurbits and covered with a palm leaf (Pomet 1717: 394; Lemery 1721: 1098; Chambers 1728b: [169]; Lewis 1761: 545).

Properties

"Tacamahaca sublimis" is a liquid resin filled in gourds. It is of red, yellow and whitish colour. It has an aromatic, bitter and somewhat spicy taste and a fragrant smell resembling that of lavender. It is dry, reddish and transparent (Pomet 1717: 394; Lemery 1721: 1098; Chambers 1728b: [169]; James 1747: 334; Lewis 1761: 545). It has an aromatic smell like lavender or "angelica" and a bitter spicy taste (Pomet 1717: 394; Chambers 1728b: [169]; James 1747: 334). Lewis describes it as soft and unctuous, pale yellow or greenish, with an aromatic bitter taste and a smell of lavender and ambergris (Lewis 1761: 545-6). "East indian tacamahaca" smells like lavender, too (Tschirch 1935a: 253).

Possible chemical composition

The botanical and geographical differentiation of the sort traded in gourds from the coarse sort into "east indian tacamahaca" and "west indian tacamahaca" appearing in the 19th century, supports the assumption that at the time of Vigani "tacamahaca" from Madagascar was also botanical different from the American sort. The information from the historical sources, however, does not allow a definite conclusion. If a "tacamahaca" resin from Madagascar was harvested from the same tree or at all does not originate from that island, American *Protium* and *Bursera* species have to be considered for Z/1 "Tacamahaca". Their chemical composition is discussed in chapter 5.3.5.

In the 19th century "tacamahaca" filled in nuts or gourds and smelling of lavender originates from *Calophyllum tacamahaca* Willd. (Madagascar) or *Calophyllum inophyllum* L. or *C. calaba* L. (South-East Asia). The genus *Calophyllum* belongs to the family Clusiaceae (Malpighales) and is rich in xanthones, steroids, triterpenes, coumarins and benzopyrans (Gurib-Fakim, Brendler 2004: 154-6). In the bark resins of *Calophyllum* species high amounts of dihydrocoumarinic acids are found (blancoic acid, (iso-)papuanic acids; Stout, Sears 1968; Stout et al. 1968). Similar findings are reported for other constituents of the plant (Plattner et al. 1974; Govindachari et al. 1967).

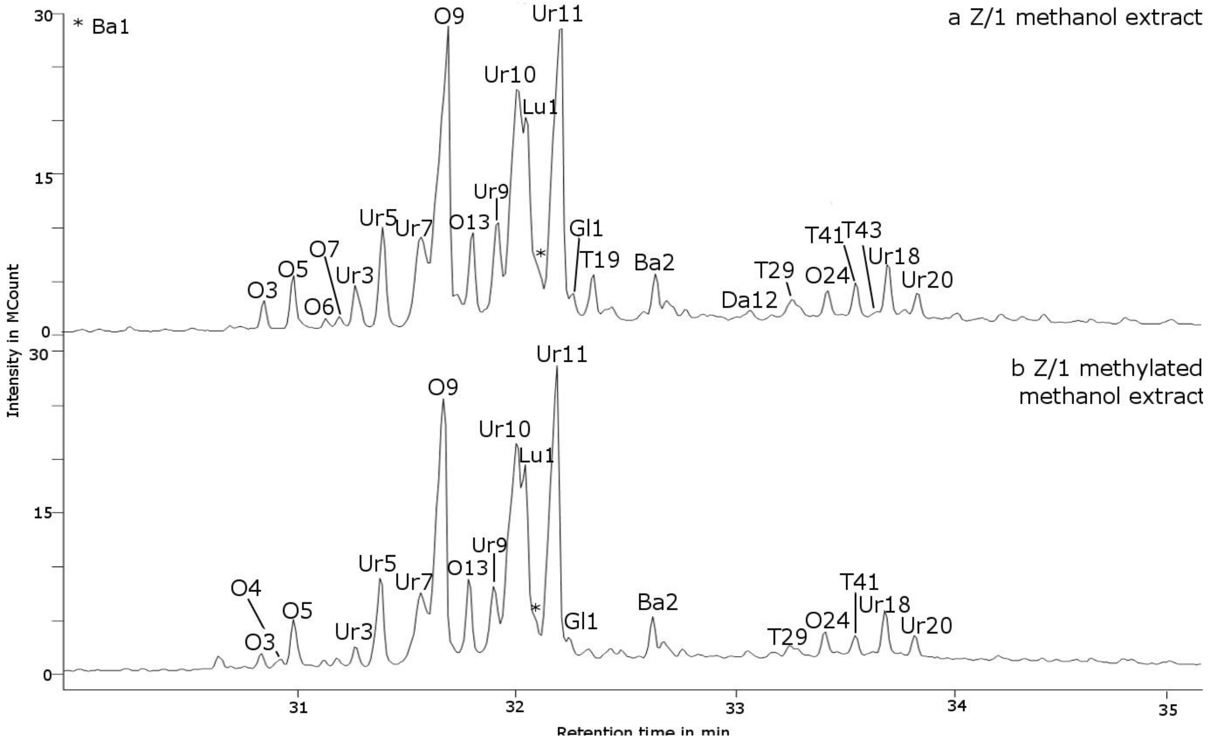
Chemical analysis

The methanol extract (Fig. 5.77a) mainly contains 3α-β-amyrin, 3α-α-amyrin, epi-lupeol and α-amyrin, together with smaller amounts of olean-9(11),12-dien-3α-ol, urs-9(11),12-dien-3α-ol, urs-9(11),12-dien-3β-ol, β-amyrin, α-amyrone, epi-baurenol (Ba1), compound T19, baurenol (Ba1) and 11-oxo-urs-12-en-3α-ol. Small amounts of olean- and urs-9(11),12-dien-3-one, olean-9(11),12-dien-3β-ol, compounds O7, Da12, T29 and T41, 11-oxo-olean-12-en-3β-ol and 11-oxo-urs-12-en-3β-ol are present as well. The compound Ba1 is also present in A/22, but is visible there only with EIC at m/z 229 (chapter 5.3.5). In the methylated methanol extract (Fig. 4.77b), no additional compounds are present. The interior and the crust are composed identically.

Discussion

This composition is typical for non-acidic Burseraceae resins, particularly from the genus *Bursera*. High amounts of (epi-)lupeol and the prevalence of 3α-epimers of α- and β-amyrin are characteristic for these resins. Additionally, the unidentified compounds T19 and T20 are present in reference materials related to *Bursera* resins in this work. The composition resembles that reported for the resin of *Amyris elemifera* (Stacey et al. 2006), which cannot be verified here due to imcomplete chemotaxonomical data.

Z/1 "Tacamahaca" is not obtained from the resin or other plant parts of an Asian *Calophyllum* species. None of the characteristic compounds mentioned in the literature are found. Additionally, *Protium heptaphyllum* March., which is mentioned in modern sources for tacamahaca, is unlikely as well. The two materials in the Cabinet labelled as "Tacamahaca", Z/1 and A/22, are composed nearly identical (see chapter 5.3.5). Z/1 "Tacamahaca" was obtained, similar to A/22 "Tacamahaca", most likely from an American *Bursera* species, for details please refer to chapter 5.3.5. Based on the descriptions from historical sources Z/1 may be a "tacamahaca en coque", which was traded in gourd or nut shells. The matching composition of A/22 and Z/1 support the assumption that the two sorts of historical "tacamahaca" were obtained from the same tree and, in case a resin of this name was traded really from Madagascar at this time, this tree grew in different parts of the world.



a – methanol extract and b – methylated methanol extract (labels, see table 5.20)

Fig. 5.77 Gas chromatograms of Z/1 "Tacamahaca" interior from the Vigani Cabinet, triterpene section (TIC)

Label	t_R	Name	Main mass fragments
O3	30.84	Olean-9(11),12-dien-3-one	255, 269, 293, 352, 389, 407, **422**
O4	30.92	3β-Methoxy-olean-12-ene	81, 95, 107, 189, **203**, 218, 393, 408, 425, 440
O5	30.97	Olean-9(11),12-dien-3α-ol	159, 189, 255, 391, 409, **424**
O6	31.12	Olean-9(11),12-dien-3β-ol	119, 159, 255, 271, 391, 409, **424**
O7	31.19	Olean-10(11),12-dien-3-acetoxy	255, 295, 391, 424, 451, **466**
Ur3	31.26	Urs-10(11),12-dien-3-acetoxy	133, 159, 255, 269, 389, 407, **422**
Ur5	31.38	Urs-9(11),12-dien-3α-ol	159, 255, (395), 391, 409, **424**
Ur7	31.56	Urs-9(11),12-dien-3β-ol	133, 159, 255, 295, 391, 409, **424**
O9	31.65	Olean-12-en-3α-ol	95, 107, 119, 175 189, **203**, 218, 393, 411, 426
O13	31.78	Olean-12-en-3β-ol (β-amyrin)	95, 119, 175, 189, **203**, 218, 393, 411, 426
Ur9	31.90	α-amyrone	107, 147, 189, 203, **218**, 409, 424
Ur10	32.01	Urs-12-en-3α-ol (epi-α-amyrin)	107, 147, 189, 203, **218**, 393, 411, 426
Lu1	32.04	Epi-lupeol	107, 135, **189**, 203, 207, 218, 229, 257, 393, 411,
Ba1	32.09	Epi-baurenol	95, 119, **229**, 241, 247, 393, 411, 426
Ur11	32.19	Urs-12-en-3β-ol (α-amyrin)	107, 147, 161, 175, 189, 203, **218**, 393, 408, 411,
Gl1	32.25	Epi-glutinol or glutinol	95, 119, 229, 247, **259**, 274, 393, 408, 426
T19	32.34	Unidentified	107, 147, 189, 203, **218**, 393, 408, 426, 439, 454
Ba2	32.63	Baurenol	95, **229**, 241, 247, 393, 411, 426
Da12	33.07	Unidentified oxygenated dammarane	107, 125, **143**, 175, 191, 365, 383, 408, 426
T29	33.25	Unidentified oxygenated oleanane or ursane	**135**, 217, **232**, 273, 285, 299, 410, 423, 438
O24	33.42	11-oxo-olean-12-en-3β-ol	**135**, 175, 217, **232**, 273, 407, 425, 440
T41	33.56	Unidentified oxygenated oleanane or ursane	**135**, 175, 217, **232**, 273, 407, 425, 438
T43	33.64	Unidentified	**135**, 175, 232, 273, 383, 407, 422, 482
Ur18	33.69	11-oxo-urs-12-en-3α-ol	**135**, 175, 221, 232, 273, 407, 425, 440
Ur20	33.82	11-oxo-urs-12-en-3β-ol	**135**, 175, 232, 273, 407, 425, 440

Tab. 5.20 Compounds found in Z/1 "Tacamahaca", analysed with temperature program Triterpene 3, mass spectra references see appendix

5.4 Fossil Resins

The origin and chemistry of fossil resins particularly amber or succinite is summarized in chapter 2.4. A sample of Baltic amber from the Polish Baltic sea coast was analysed, with the results presented in chapter 4.4. Several solvents are given in literature for the analysis of the soluble part of amber. No significant differences are found in this work for methanol, methanol-chloroform and dichloromethane. Heating the methanol extract improves in a limited way, but concentration of the solvents extracts yield chromatograms of satisfying intensites (table 4.29). A summary is given in chapter 4.4.2. Based on that investigation all materials from the Vigani Cabinet with a chemical or terminological connection to Baltic amber are discussed in this chapter. A chemical connection is given by the presence of constituents in the solvent-extractable part characteristic for Baltic amber, such as found in chapter 4.4.1. Additionally, the material from the compartment F/13 "L. Gagatis" is investigated due to a terminological connection to "black amber" and external similarity to "Succinum nigrum" from compartment E/16. In order to analyse the whole material they were analysed additionally with infrared spectroscopy.

5.4.1 E/13 Succinum Citrinum

Fig. 5.78 E/13 "Succinum Citrinum"

Fig. 5.79 Sampling of E/13

Description

The box is filled with small lumps of dark orange to brown and black colour. They are opaque. Single red lumps are more transparent. All are hard and have a cloudy crust.

Sampling

A sample of a brown lump (about 130 mg) was taken on 26 April 2007 (Fig. 5.79). It was powdered to small, transparent and light brown fragments prior to analysis.

Vigani references

* MS Quns Vig. 4, folio 4, recto, as "Succ: Citr", 2 ounces at 6 pence

* LECTURE NOTES UNDATED: 6

* LECTURE NOTES 1707: 12-14, 90

Contemporary literature

Fine art materials

* SALMON 1701: 76f, 218, 402, 423f, 872f: "Amber"

* HILL 1751: 159: "Amber"

* CARLYLE 2001: WILLIAMS 1787: 53-4; ANON. 1795: 181-4, 188, 192-3, 193-5; ANON 1808: 71, 72-3

Science

* DALE 1693: 55: "Succinum", "Carabe", "Amber"

* POMET 1717: 785: "Agtstein", "Ambre jaune", "gelber Amber", "Succinum", "Carabe", "Birnstein"

* LEMERY 1721: 590: "Karabe", "Carabe", "Glessum", "Succinum", "Ambra citrina", "Electrum", "Sacal"

* JAMES 1747: 590: "Succinum", "Carabe", "Amber"

* HILL 1751: 155: "Amber", "Succinum"

* LEWIS 1761: 538: "Succinum", "Carabe", "Ambarum citrinum", "Electrum", "Ambe"

Encyclopaedias

* CHAMBERS 1728a: 74: "Amber", "Succinum", "Carabe", "Karabe", "Glessum", "Electrum", "Chrysolectrum"

* SAVARY DES BRÛSLONS, SAVARY 1748a: 646: "Ambre jaune", "Karabe", "Succinum"

Terminology

The Latin name "succinum" from succus refers to an assumingly resinous origin already known in the ancient world, which was, however, considered to be wrong at the time of Vigani (Lemery 1717: 591; Hill 1751: 157; James 1747: 591). Occasionally, the formation of "amber" was located within the plant kingdom: the resinous part of Swedish poplars and firs are washed into the sea, hardened at the sea bottom and washed ashore by storm at the Baltic coast (Pomet 1717: 864-5). The author lists "amber" within "minerals" such as others do, which does not prevent him from discussing whether "amber" belongs to gums or resins (Pomet 1717: 868)[16].

Other names referred to the properties of the material: "karabe" from Farsi "kahraba" (كهرب اي ي, transcription khrbâyy) and "electrum" from Greek and Latin, both referring to its contact electrification (triboelectric effect) as well as "chryso(-e)lectrum" from Greek chrysos meaning gold. "Birnstein" or "Bernstein" derives from low German "boernen" meaning burning referring to its flammability. "Glessum" is the latinized Germanic name (Tacitus, Bachmeister 1868: 72), probably referring to its glassy appearance. Finally, the German "Agtstein" or "Augenstein" is connected to its medical use in ophthalmology or to Greek "aiqein" (αιθειν) meaning burning[17].

The Englisch term "amber" probably derives from from Arabic "anbar", originally for ambergris. Another etymological connection was drawn to Egypt "sacal", which is probably ambergris as well (Pliny 1855: 37; 36; Lemery 1717: 591; Chambers 1728a: 75). The connection to ambergris originates from the common find site.

Botanical and geographical origin

"Succinum" or "amber" was classified mainly under "minerals" or "fossils" (Dale 1693: 54; Pomet 1717: 785[18]; Lemery 1721: 591; James 1747: 560; Hill 1751: 155) and mentioned only occasionally as a "resin" (Pomet 1717: 868; Chambers 1728a: 74; Savary des Brûslons, Savary 1748a: 646). There were apparently difficulties to assign the material to a plant, mineral or even animal origin (Dale 1693: 55; Lemery 1717: 591; Chambers 1728a: 74). Contemporary assumptions favoured an origin from the "mineral" kingdom. The class, "amber" was included, contained other materials such as "petroleum", "bitumen judaicum", "naphtha" and "ambergrease", which shared their origin from the sea or water bearing places with "amber" (Dale 1693: 53-5; Hill 1751: 148).

Contemporary to Vigani, the "succinum", also called "succus bituminous seu Resina terrae" was thought to trickle from subterranean places such as "bitumen" or "petroleum" or distill from fossil wood, "optimè digesta, exinde in mare traducta, atque ibidem praecipuè concreta" (Dale 1694: 55; Chambers 1728a: 74; James 1747: 591). Onshore found "amber" is described as "a kind of laminated Substance resembling fossil Wood, which has lain in the way of the Pyrites" (Hill 1751: 157). An excavation made in Prussia found it to be buried under a layer of sand, a "stratum of white clay", a "ligneous stratum" and a layer of "Ore of Vitriol" (James 1747: 590-1). The liquid "earth resin" trickled through the vitriol layer and coagulated (Pomet 1717: 786; Chambers 1728a: 74; Hill 1751: 157; James 1747: 590-1).

"Succinum" originated mainly from the Baltic region, including Brandenburg-Prussia, Poland and some place in Norther Germany, Bohemia and Silesia (Pomet 1717: 787; Chambers 1728a: 75; James 1747: 590; Hill 1751: 157; Savary des Brûslons, Savary 1748a: 646; Lewis 1761: 538). Other European places mentioned are Marseilles, the river Po, the Mountains of Sicily and England (Chambers 1728a: 74-5; James 1747: 590; Hill 1751: 156-7).

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[16] "Ambre" should be rather a resin than a gum because of its insolubility in water and flammability. This information are given in an appendix of the earlier editions, which is partly included into the chapter about "ambre jaune" in later editions. The notes about the resinous nature of "ambre" were taken out, yet (Pomet 1694: appendix; Pomet 1717: 863-9; Pomet 1735: 352-4).

[17] Augenstein is used today also for zinc sulfate or "white vitriol", which is mentioned in connection with "amber" formation (James 1747: 590-1; Hill 1751: 157).

[18] Pomet lists "ambre" under "bitumes", which became "Hartze" in the German translation (Pomet 1694: 83; Pomet 1717: 785).

Manufacture and trade

"Amber" was traded mainly from several regions at the Baltic sea coast such as "Pomerania" (Brandenburg-Prussia) and "Polish Prussia" (belonging to the Kingdom of Poland) (Pomet 1717: 787; James 1747: 590; Hill 1751: 157; Savary des Brûslons, Savary 1748a: 646; Lewis 1761: 538). Mentioned places are "Fisch-hausen", "Gross-ductein", "Wernichen", "Palmoniet", "Kustrin" and the "Territories of Stolpen and Dantzic" (ibid.). Chambers mentions "Sambia" as the main region in Brandenburg-Prussia from "Neve Tiff" to "Urantz Urug" and additionally the coast of "Samegitia", "Courland" and "Livonia" (Chambers 1728a: 75). Other regions in Northern Europe were "Silesia", "Bohemia", "Jutland", "Holstein" and "Denmark" (Chambers 1728a: 75). Apart from its emergence from the water it was known to be dug in several places (James 1747: 590; Hill 1751: 156-7; Lewis 1761: 538). It was then found in in the neighbourhood of vitriolic and metallic particles or layers (Chambers 1751: 74; James 1747: 591; Hill 1751: 155).

Pomet mentions the high profit made by the prince-elector of Brandenburg-Prussia with the amber trade (Pomet 1717: 788). Main trade areas were Germany, Italy (Venice) and Poland, but also Hungary, the latter two known for their highly priced and elaborated amber goods (Pomet 1717: 788; Savary des Brûslons, Savary 1748a: 647). It was also brought to China (James 1747: 592).

Artificial "amber" was made from boiled "turpentine" hardened by the sun (Salmon 1701: 771; Pomet 1717: 869). Salmon gives another three recipes for artificial "amber", one from mixed and melted egg yolk, "gum arabick" and "cherry-tree gum" and two from egg white (Salmon 1701: 771). "Amber" was confused with "american copal" (see chapter 5.3.3) (Pomet 1717: 403-404; Lemery 1721: 336-7; Savary des Brûslons, Savary 1728: 1499).

Properties

"Amber" is found in three colours, "album sc. & flavum seu citrinum" or "yellow, white and brown" (Dale 1693: 56; Pomet 1717: 785; Lemery 1721: 590; Chambers 1728a: 75; Hill 1751: 155; Lewis 1761: 538). Additionally green and reddish colours are mentioned (Hill 1751: 155). There is some indication that these three colours were handled as different sorts, which are of differing quality: the best quality is pellucid and free from spots, the next in white, then yellow and finally brown (Dale 1694: 55; Chambers 1728a: 75; James 1747: 592). The white sort is the most valuable, because it is best "digested" with most the most odoriferous smell and highest quantity of volatile salts (Dale 1694: 55; Chambers 1728a: 75). But several authors mention "amber" as a genuine material of commonly golden or yellow colour, which has differing colours according to its "digestion" state (Dale 1693: 55; Hill 1751: 590). Due to the changing opinions about that issue all "succinum" labelled materials are discussed together and not separate for each colour. The only exception is "black amber", which is sometimes mentioned separately as a black sort in connection with "jet" (Dale 1693: 54; Pomet 1717: 789; Chambers 1728a: 75; James 1747: 560; James 1747: 592; Hill 1751: 155). Similarily, brown "amber" is mentioned in connection with "ambergrease" (Chambers 1728a: 75), both referring to the classification of "amber" into the "mineral" kingdom, to which also "jet" or "gagat" belonged. The issue is discussed in detail in chapter 5.4.4.

"Amber" is a solid, brittle and bituminous substance changing opaque or transparent and pellucid (Chambers 1728a: 74; James 1747: 590, 592; Lewis 1761: 538). It has a rough and opaque surface or crust and a glossy and fine yellow inside when broken (Hill 1751: 155). Opacity is caused by included particles (ibid.). The authors, who preferred its classification as a "mineral", describe it as nearly tasteless and without any smell unless heated or rubbed (Dale 1693: 55; James 1747: 590; Hill 1751: 155; Lewis 1761: 538). Chambers in contrary mentions a resinous taste and smell like "oil of turpentine" (Chambers 1728a: 74). It was found in pieces of very different size and shape (Hill 1751: 155).

It is not soluble in water and partly dissolved in "rectified spirit of Wine" yielding a yellowish or brownish dissolution with a fragrant smell and bitterish aromatic taste (Pomet 1717: 864; Hill 1751: 155; Lewis 1761: 538). It is also partly soluble in "essential oils of plants" or "linseed oil" (Hill 1751: 155). When burned it melts to a black mass, takes flame and emits a black smoke smelling somewhat like pit-coal (Pomet 1717: 864; Lewis 1761: 538-9). Chambers describes it as inflammable but meltable by fire (Chambers 1728a: 74).

It attracts other materials when rubbed and yields light in the dark (Pomet 1717: 788; Lemery 1721: 592; Chambers 1728a: 74; Hill 1751: 155). Pomet discusses the origin of this property (only in the earlier editions, see footnote 14): A subtle matter, which is very mobile, is forced to move out the material through small holes through rubbing. Through its high mobility it overcomes air, attracts light things and when losing its mobility and retiring it takes these things with it. Because air follows the movement of the subtle matter things stick at the materials as long as the movement proceeds (Pomet 1717: 866-8).

"Amber" shares the precipitation into a "salt" of "acid spirit" obtained by distillation, the dissolubility in alcohol but not in water, the melting in the fire and inflammability with "bitumes" and "sulphurs" (Chambers 1728a: 74).

Possible chemical composition

The described materials correspond mainly with the modern term succinite or Baltic amber, because the main places mentioned are those, where Baltic amber is found. The soluble part of this resin is investigated in detail and can be used to distinguish it from other chemically and botanically related fossil resins (for example from France or Italy) (chapter 2.4).

A sample of Baltic amber was analysed for that investigation, with the results presented in chapter 4.4.1. The soluble part of the resin contains a typical monoterpene fraction with high amounts of camphor, fenchol and (iso)borneol. Succinic acid is not found. Characteristic constituents are di)monoterpanyl esters of succinic acid, diterpene acids with an isopimarane, pimarane and abietane structure, monoterpanyl esters of diterpene and dihydro-$\Delta 8$-agathic acids and a homologous alkane series assumingly derived from plant lipids. The relative amounts of these compounds changes, main constituents are the diterpene acids, monoterpenes and usually succinic acid. In this work, different coloured pieces from a mixed samples show a differing state of polymerisation. The state of maturation is necessarily different as well. The higher polymerisation rate, however, results in a differing dissolubility, which in turn influences the analysed chemical composition.

The composition of the polymeric fraction analysed by infrared spectroscopy is discussed in chapter 2.4. Basically, the steps of the maturation process degradation of exomethylene groups, rearrangement of double bonds to $\Delta 8$-position and succinylation are visible in the spectrum together with free carboxyl, hydroxyl- and methylene groups.

Chemical analysis

E/13 "Succinum Citrinum" was dissolved in all used solvents (methanol, methanol-chloroform and dichloromethane) solvents to a low extent. It was better soluble in methanol-chloroform and dichloromethane than in methanol. The best results were obtained with the methanol-chloroform extract. It was evaporated to dryness, the TMSH-solution was added and afterwards heated 10 minutes at 100°C.

In the methylated methanol-chloroform extract (Fig. 5.80), dimethylsuccinate, l-fenchone, fenchol, camphor and (iso)borneol are present. In the not methylated extract also bornylformate and –acetate are found (not shown). The material contains a very small sesquiterpene fraction (8 – 12 minutes), the compounds present only in traces could not be identified. Fenchyl- and bornylsuccinates (MS1 and MS3) are present in small amounts, no other terpanyl succinates are found. 1,2,3,4-tetrahydro-1,5,6-trimethyl-1-naphthalenecarboxylate (D5) is present in small amounts, in the not methylated extract also small amounts of abietatriene (A3) are present. The only degradation product present in significant amounts is 13-methylpodocarpatrien-18-oate (D11).

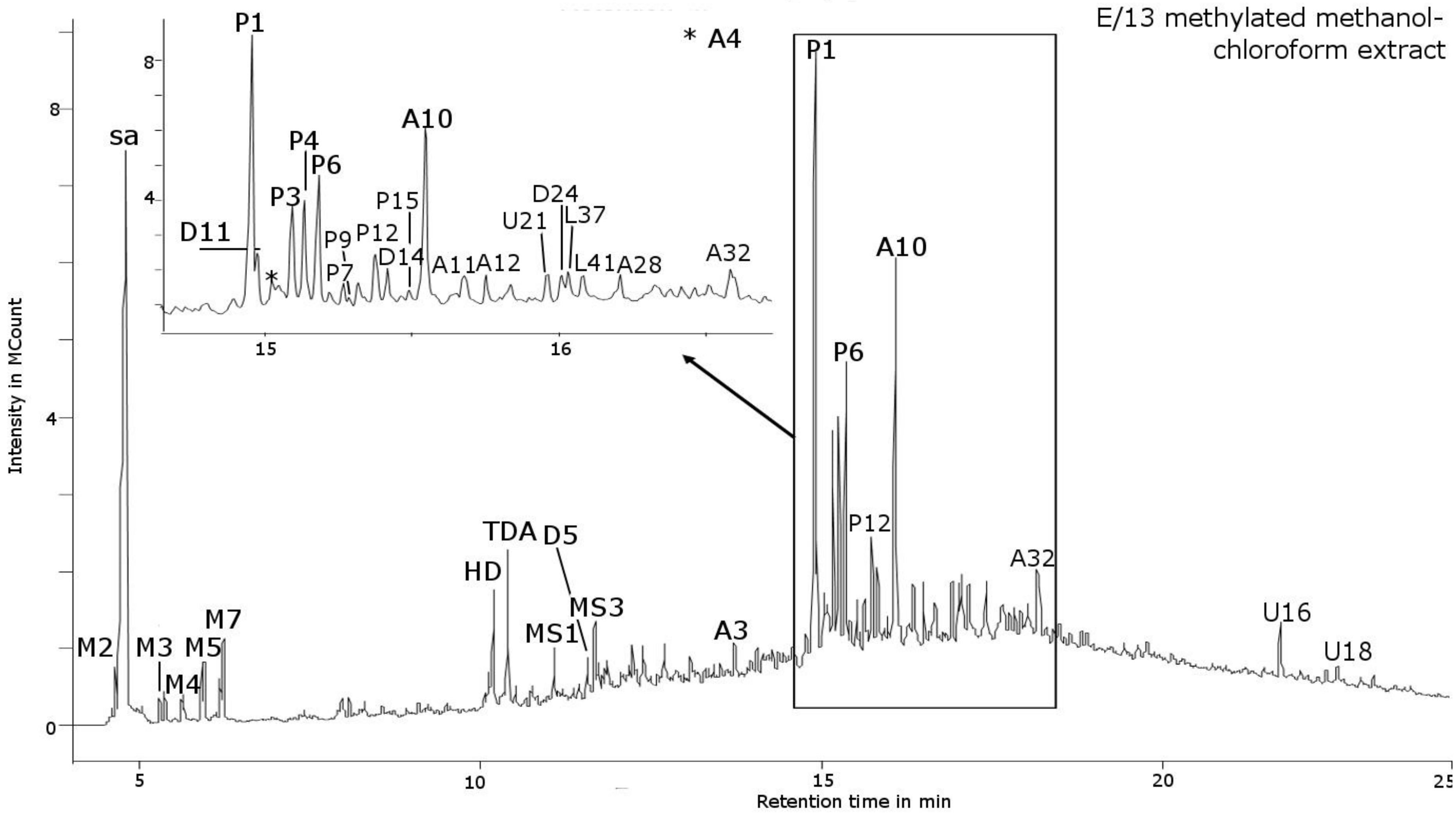
In the diterpene section high amounts (dihydro)Δ8-isopimarate, Δ8-pimarate, sandaracopimarate, isopimarate and dehydroabietate are present, together with smaller amounts of 5β-dehydroabietate, the dihydro derivatives of Δ8-pimarate, Δ7-pimarate and isopimarate, as well as abietate and another abietane acid (D14), the compounds D24 and U21. Small amounts of abietane aging markers are found: 15-hydroxy- and 7-oxo-dehydroabietate (A28 and A32). Dihyhdroagathate and its Δ8-isomer (L37 and L41) and agathate (L48) are present only in traces. The unidentified compounds U16 and U18 are reported in literature as dimeric units of the amber matrix (Islas et al. 2000). The compounds U21 and U16 are reported by Mills et al. for Baltic amber without identification (Mills et al. 1984/85).

Discussion

The composition of the soluble part is typical for Baltic amber with the characteristic monoterpene fraction, succinic acid, terpanyl succinic acids and high amounts of Δ8-isopimaric, sandaracopimaric and dehydroabietic acids together with double bond isomerized (iso)pimaranes and their dihydroderivatives. Additional labdanes with a (dihydro)agathic acid skeleton are present. The infrared spectrum was of very low transmittance and could not be used for further evaluation.

The composition is very similar to that found for E/15 "Succinum albam" (chapter 5.4.3), particularly the composition of the diterpene fraction and the relatively small amounts of monoterpanyl esters. Both materials also have some other compounds in common, the unidentified compound U_{21} and the dimeric matrix constituents U_{16} and U_{18}, whereas they are present in the better soluble E/15 in much higher amounts. Both contain oxygenated abietanes such as 7-oxo- and 15-hydroxy-dehydroabietic acids, which are not reported for Baltic amber until now. Koller et al. reports succinic acid only for decomposed cloudy outer layers of formerly clear Baltic amber samples (Koller et al. 1997c). This aging process seems to be typical for materials stored in collections and does not occur while the resin is still in its natural environment. Therefore, the high amounts of succinic acid are a result of a degradation process through the storage after excavation. Dehydroabietic acid is an oxidation product of abietic acid, which is present in the reference sample 4.3.6 in higher amounts. In the Vigani samples abietic acid is present in smaller amounts, mainly dehydroabietic acid is present. It is a degradation product of the storage as well.

A final conclusion is given in chapter 5.4.3.



Methylated methanol-chloroform extract (labels, see table 5.21)

Fig. 5.80 Gas chromatogram of E/13 "Succinum Citrinum" from the Vigani Cabinet, mono-, sesquit- and diterpene section (TIC)

Label	t_R	Name	Main mass fragments
M2	4.61	m-Cymene	53, 77, 91, **119**, 134
sa	4.82	Succinate, diME	55, 87, **115**, 146
M3	5.31	l-Fenchone	53, 69, **81**, 109, 152
M4	5.67	Fenchol	55, 67, 80, **81**, 93, 107, 121, 154
M5	5.96	Camphor	55, 67, 81, **95**, 108, 137, 152
M7	6.24	Borneol	55, 67, 79, **95**, 121, (154)
MS1	11.09	Fenchylsuccinate	55, 81, 87, **115**, 121, 136, 153, (268)
D5	11.58	1,2,3,4-Tetrahydro-1,5,6-trimethyl-1-naphthalenecarboxylate	91, 115, 128, 145, 158, **173,** 232
MS3	11.68	Bornylsuccinate	55, 81, 93, 95, 108, **115**, 121, 136, 153, (268)
A3	13.74	Abietatriene	67, 79, 93, 107, 121, 159, 173, 185, 237, **255**, (270)
P1	14.91	Δ8-Isopimarate	91, 185, **241**, 257, 269, 301, 316
D11	14.94	13-Methylpodocarpatrien-18-oate	91, 131, 145, 155, **211**, 227, 241, 271, 287, 301, 316
A4	15.04	5β-Dehydroabietate	91, 143, 157, 183, 211, **239**, 255, 273, 299, 314
P3	15.18	Δ8-Pimarate	105, 185, **241**, 257, 269, 301, 316
P4	15.27	Dihydro-Δ8-isopimarate	91, 187, **243**, 259, 271, 303, 318
P6	15.36	Sandaracopimarate	79, 91, **121**, 241, 257, 301, 316
P7	15.53	Pimar-8(14)-en-18-oate (dihydro-Δ8-pimarate)	79, 95, **121**, 159, 181, 219, 229, 289, 303, 318
P9	15.57	Pimar-7-en-18-oate (dihydro-Δ7-pimarate)	91, 121, 133, 159, **243**, 303, 318
P12	15.75	Isopimarate	91, 105, 121, 187, 201, 227, **241**, 256, 257, 287, 301, 316
D14	15.83	Unidentified diterpene acid, ME	91, 145, 159, 187, 227, **241**, 256, 257, 287, 301, 316
P15	15.98	Dihydroisopimarate	79, 93, 105, 121, 227, **243**, 259, 287, 303, 318
A10	16.09	Dehydroabietate	197, **239**, 199, 314
A11	16.34	Dehydroabietol	117, 159, 173, 185, 211, **253**, 271, 286
A12	16.51	Abietate	91, 105, 121, 185, 213, **241**, 256, 316
U21	16.93	Unidentified	91, 105, 121, 159, 173, 229, 237, **285**, 301, 345, 360
D24	17.02	Podopcarpatriene acid, oxygenated derivative	121, 159, 185, **225**, 240, 268, 300
L37	17.06	Dihydroagathate, diME	93, 107, **121**, 161, 217, 239, 257, 272, 304, 364
L41	17.17	Δ8-Dihydroagathate, diME	105, 119, **175**, 203, **235**, 257, 289, 304, 364
A28	17.42	15-Hydroxy-dehydroabietate	237, **255**, 273, 315, 330
A32	18.17	7-Oxo-dehydroabietate	187, 211, **253**, 269, 296, 313, 328
U16	21.73	Di- or polymeric matrix constituent	91, 105, 229, 289, **333**, 249, 361, 393, 408
U18	22.55	Di- or polymeric matrix constituent	105, **133**, 257, 375, 391, 403, 435, 450

Tab. 5.21 Compounds found in E/13 "Succinum Citrinum", sample analysed with temperature program Diterpenes 1, mass spectra references see appendix

5.4.2 E/14 Succinum flavan

Fig. 5.82 E/14 "Succinum flavan"

Fig. 5.81 Sampling of E/14

Description

The box is filled with small lumps of dark orange to brown and black colour similar to the compartment E/13 (chapter 5.4.1). They are more opaque and less cloudy at the surface compared to the compartment E/13.

Sampling

A sample of yellow lump (about 230 mg) was taken on 26 April 2007 (Fig. 5.82). Small yellow and opaque fragments were cut prior to analysis.

Vigani references

* Does not appear in MS Quns Vig.

* LECTURE NOTES UNDATED: 6

* LECTURE NOTES 1707: 12-14, 90

Contemporary literature

See chapter 5.4.1

Terminology

See chapter 5.4.1

Botanical and geographical origin

See chapter 5.4.1

Manufacture and trade

See chapter 5.4.1

Properties

See chapter 5.4.1

Possible chemical composition

See chapter 5.4.1

Chemical analysis

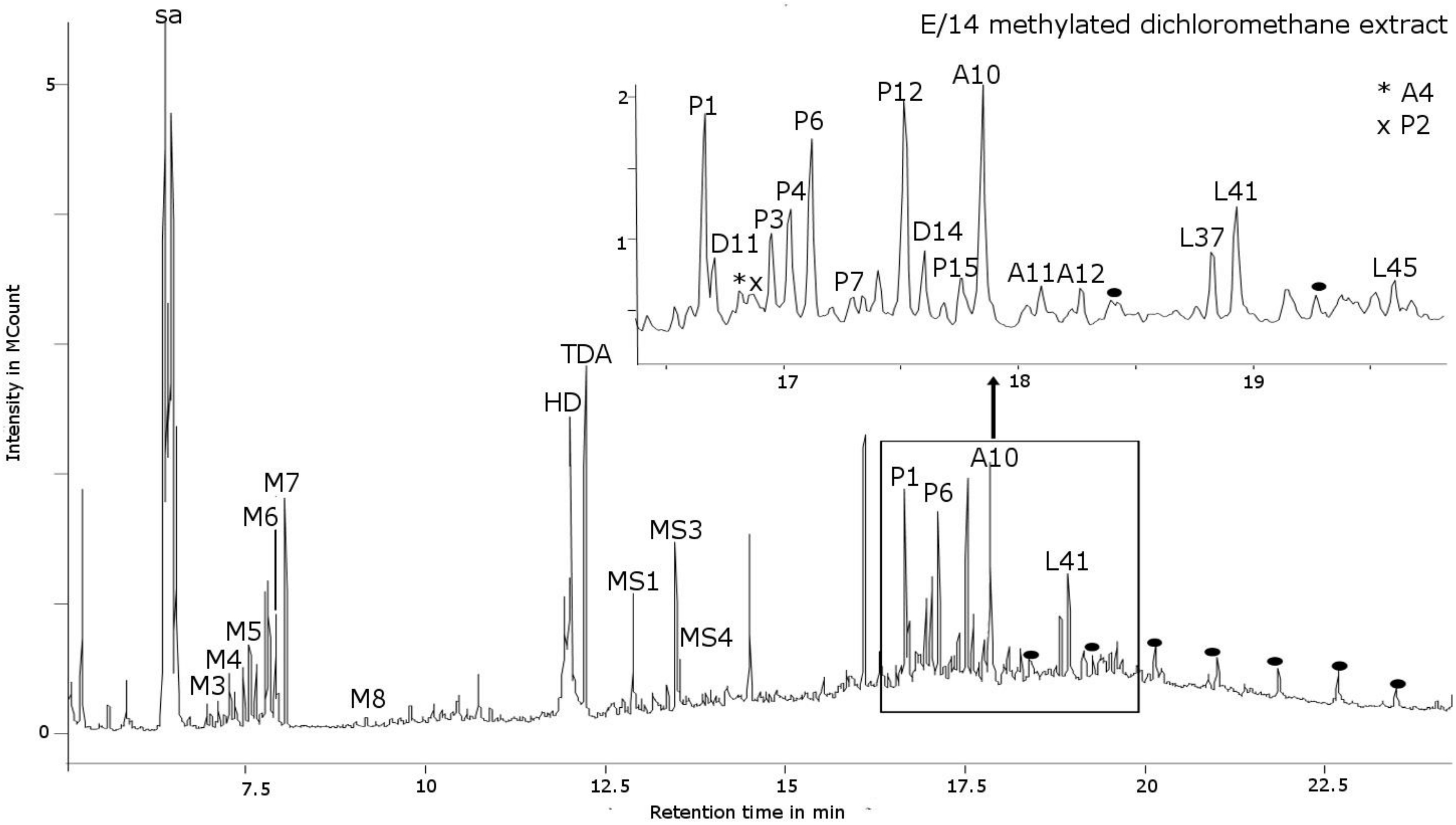
E/14 "Succinum flavan" was dissolved in all used solvents (methanol, methanol-chloroform and dichloromethane) solvents to a very low extent, with little differences between the different solvents. The methanol extract heated at 40°C for 30 min contains traces of monoterpanyl succinic acids (MS_2, MS_5, MS_6; Fig. 5.84a), which were destroyed during at longer heating time (24 hours at 40°C; Fig. 5.83b). Instead the dimonoterpanyl succinic acids and within the limits of the poor solubility also the monoterpanyl diterpenoates became more visible (dMS_1 – dMS_5, MD_2, MD_6; Fig. 5.83b). Apart from that the chromatogram of the extract heated for 24 hours some was of low intensity with some peaks missing and poor resolution (Fig. 5.83b).

The methanol-chloroform extract yield better intensities due to the concentration step included into the sample preparation (chapter 3.1.2). However, the heating of the extract mixed with TMSH caused a certain degradation and the diterpene fraction was nearly gone. Without heating the reaction mixture, the intensity was satisfying but the solubiliton properties properties proved to be different from that of the other solvents. Diterpene acids were dissolved much worse and with a prevalence to abietane compared to (iso)pimarane acids. Instead a homologous series of n-alkanes is present in significant amounts (Fig. 5.85). They are dissolved in the other solvents only in very small amounts (Fig. 5.83, Fig. 5.84a). Their main mass fragments are at m/z 57, 71, 85, 97, 111, 125, 139, 153, 167, 181 and 195. The series shows a Gaussian distribution with a slightly higher intensity for the peak eluting at 20.87 minutes, or lower intensity for the peak eluting at 20.06 minutes (Fig. 5.85a). No change is visible after methylation (Fig. 5.85b). The alkanes are, therefore, present as their natural methylester or do not possess a carboxyl group. No molecular ions are visible in the spectra, which are nearly identical. A similar series is reported by Czechowski et al., who report carbon numbers of C_{22} to C_{33}, maximising at C_{26} to C_{27} (Czechowski et al. 1996), and is present in the reference sample analysed in this work in small amounts as well (chapter 4.4.1; see also chapter 5.4.4).

The best results are obtained with the dichloromethane extract (Fig. 5.83). It contains dimethylsuccinate in high amounts, which cause a overleading of the ion trap and results in a split and unresolved peak. L-fenchone, fenchol, camphor, (iso)borneol and bornylacetate are also present. In the sesquiterpene fraction (8 – 12 minutes) only traces of unidentified compounds are present. Other constitutents of the material are monoterpanyl succinates (MS1, MS3 and MS4), dimonoterpanyl succinates (dMS1 – dmS5) and monoterpanyl diterpenoates (MD2 and MD6). Maturation products such as tetrahydronaphthalenes and abietatrienes are not present or only in small amounts (abietatriene, A8) (not shown). The only degradation product present in significant amounts is 13-methylpodocarpatrien-18-oate (D11).

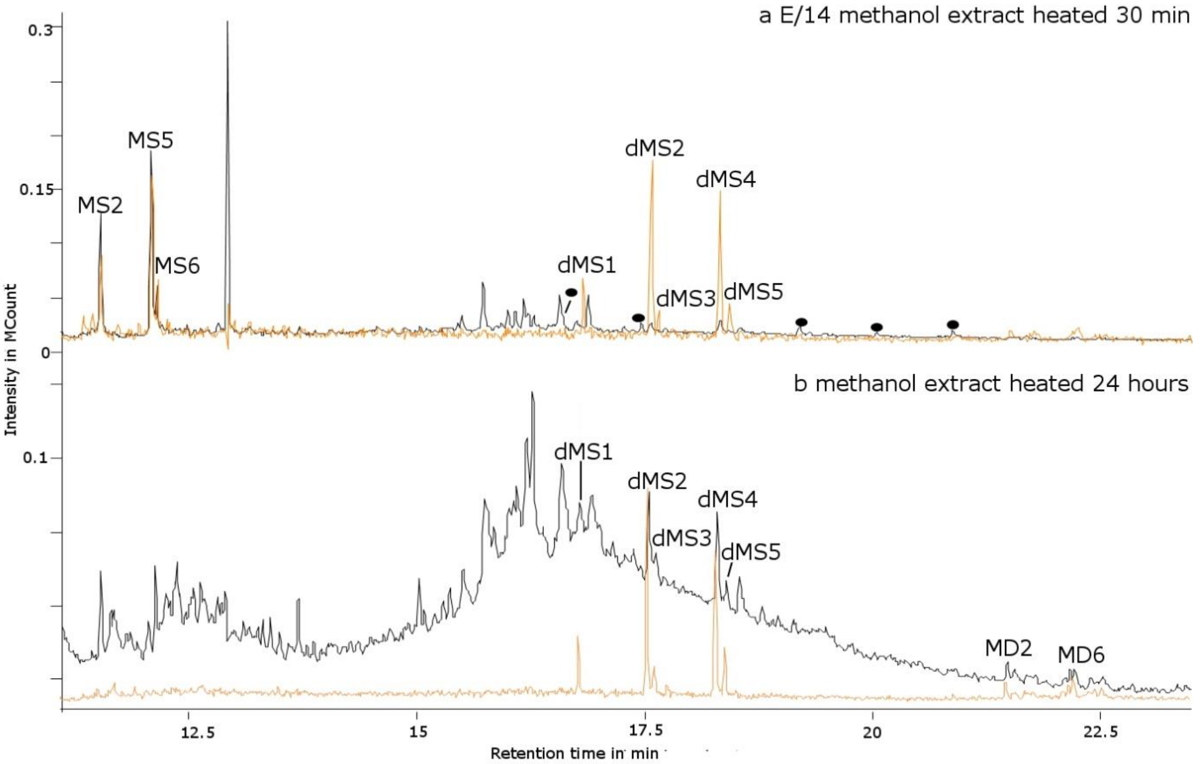
In the diterpene section (12 – 20 minutes) high amounts of Δ8-isopimarate, sandaracopimarate, isopimarate and dehydroabietate are present together with smaller amounts of Δ8-pimarate, dihydro-Δ8-isopimarate and dihydroagathate, its Δ8-isomer and agathate. Additionally, 5β-dehydroabietate, a pimaradienol (P_2), dihydro-Δ8-pimarate, an unidentified diterpene acid (D_{14}), dihydroisopimarate, dehydroabietol and abietate are present.

The infrared spectrum is shown in Fig. 5.86. It shows absorption of hydroxyl and hydroxymethylene groups (3448, 1,025 cm^{-1}), aliphatic structures (932, 2,871, 1,377 cm^{-1}, 1,455 cm^{-1}) and axial ester groups (1,717 and 1,164 cm^{-1}) (Hummel 1981: 424, 425, 428). The absorption at 1,717 cm^{-1} results from an unsaturated ester groups (Hummel 1981: 428). The Baltic shoulder is visible between 1,175 – 1,250 cm^{-1} (Wolfe et al. 2012). It results from a lack of free carboxyl (around 1240 cm^{-1}) and hydroxyl groups (1260 cm^{-1}). No peaks for exocyclic double bonds and terminal alkenes are visible (see chapter 5.4.3).



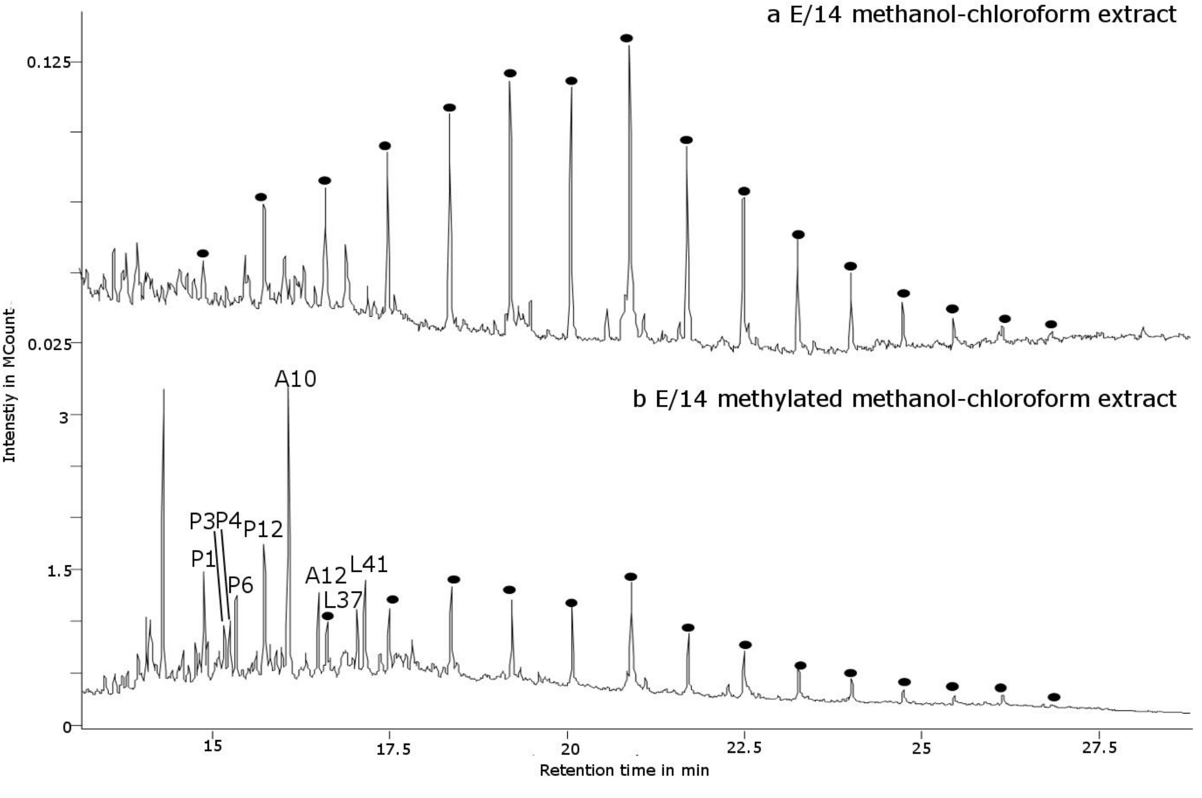
Methylated dichloromethane extract, peaks of the homologous series are marked with a dot (labels, see table 5.22)

Fig. 5.83 Gas chromatogram of E/14 "Succinum flavan" from the Vigani Cabinet, mono-, sesqui- and diterpene section (TIC)



a – methanol extract heated 30 min at 40°C and b – methanol extract heated 24 h at 40°C, peaks of the homologous series are marked with a dot (labels, see table 5.22)

Fig. 5.84 Gas chromatograms of E/14 "Succinum flavan", influence of the sample preparation, diterpene section (TIC – black, EIC at m/z 137 - orange)



a – methanol-chloroform extract and b – methylated methanol-chloroform extract, peaks of the homologous series are marked with a dot (labels, see table 5.22)

Fig. 5.85 Gas chromatograms of E/14 "Succinum flavan" from the Vigani Cabinet, homologeous series, di- and triterpene section (TIC)

Label	t_{R1}	t_{R2}	Name	Main mass fragments
sa		6.42	Succinate, diME	55, 87, **115**, 146
M_3		7.12	l-Fenchone	53, 69, **81**, 109, 152
M_4		7.27	Fenchol	55, 57, 67, 80, **81**, 93, 107, 121, (154)
M_5		7.56	Camphor(+)	55, 67, 81, **95**, 108, 137, 152
M_6		7.92	Isoborneol	55, 67, 79, **95**, 121, (154)
M_7		8.05	Borneol	55, 67, 79, **95**, 121, (154)
M_8		9.17	Bornylacetate	51, 67, 93, **95**, 121, 136, 154, (196)
MS_1		12.89	Fenchylsuccinate	55, 81, 87, **115**, 121, 136, 153, (268)
MS_2	11.54		Fenchylsuccinic acid	55, 80, **81**, 93, 101, 121, 136, 173, (254)
MS_3		13.47	Bornylsuccinate	55, 67, 81, 93, 95, **115**, 121, 136, (268)
MS_4		13.53	Isobornylsuccinate	55, 81, 93, 95, 108, **115**, 121, 136, 153
MS_5	12.09		Bornylsuccinic acid	55, 67, 80, 93, **95**, 108, 121, 136, 154, 236, (254)
MS_6	12.15		Isobornylsuccinic acid	55, 67, 93, **95**, 108, 11, 136, 175, 231, (254)
P_1	14.86	16.66	Δ8-Isopimarate	91, 185, **241**, 257, 269, 301, 316
D_{11}		16.71	13-Methylpodocarpatrien-18-oate	91, 131, 145, 155, **211**, 227, 241, 271, 287, 301, 316
A_4		16.83	5β-Dehydroabietate	91, 143, 157, 183, 211, **239**, 255, 273, 299, 314
P_2		16.86	Pimaradienol	105, **131**, 145, 155, 185, 225, 243, 288
P_3	15.16	16.95	Δ8-Pimarate	105, 185, **241**, 257, 269, 301, 316
P_4	15.24	17.03	Dihydro-Δ8-isopimarate	91, 187, **243**, 259, 271, 303, 318
P_6	15.32	17.11	Sandaracopimarate	79, 91, **121**, 241, 257, 301, 316
P_7		17.29	Pimar-8(14)-en-18-oate (dihydro-Δ8-pimarate)	79, 95, **121**, 159, 181, 219, 229, 289, 303, 318
P_{12}	15.72	17.51	Isopimarate	91, 105, 121, 187, 201, 227, **241**, 256, 257, 287, 301, 316
D_{14}		17.60	Unidentified diterpene acid, ME	91, 145, 159, 187, 227, **241**, 256, 257, 287, 301, 316
P_{15}		17.75	Dihydroisopimarate	79, 93, 105, 121, 227, **243**, 259, 287, 303, 318
A_{10}	16.07	17.84	Dehydroabietate	197, **239**, 199, 314
A_{11}		18.11	Dehydroabietol	117, 159, 173, 185, 211, **253**, 271, 286
A_{12}	16.48	18.26	Abietate	91, 105, 121, 185, 213, **241**, 256, 316
dMS_1	16.80		Difenchylsuccinate	67, **81**, 95, 121, 137, (390)
L_{37}	17.03	18.83	Dihydroagathate, diME	93, 107, **121**, 161, 217, 239, 257, 272, 304, 364
L_{41}	17.13	18.93	Δ8-Dihydroagathate, diME	105, 119, **175**, 203, **235**, 257, 289, 304, 364
dMS_2	17.55		Fenchylisobornylsuccinate	67, **81**, 95, 121, 137, 390
dMS_3	17.63		Fenchylbornylsuccinate	67, **81**, 95, 121, 137, (390)
L_{45}		19.59	Agathate, dME	79, 107, **121**, 189, 241, 271, 315, 347, 362
dMS_4	18.30		Dibornylsuccinate	57, 67, **81**, 95, 121, 137, (390)
dMS_5	18.42		Diisobornylsuccinate or Bornyl-isobornylsuccinate	57, 67, **81**, 95, 121, 137, (390)
MD_2	21.09		Isobornylisopimara-8,15-dien-18-oate	**81**, 95, 137, 175, 241, 287, 301, 396, 438
MD_6	22.22		(Iso)Bornylpimaradiene-18-oate	**81**, 95, 137, 255, 301, 350, 410, 438

Tab. 5.22 Compounds found in E/14 "Succinum flavan", t_{R1} - sample analysed with temperature program Diterpenes 1 and column A, t_{R2} – sample analysed with temperature program Diterpenes 3 and column A, mass spectra references see appendix

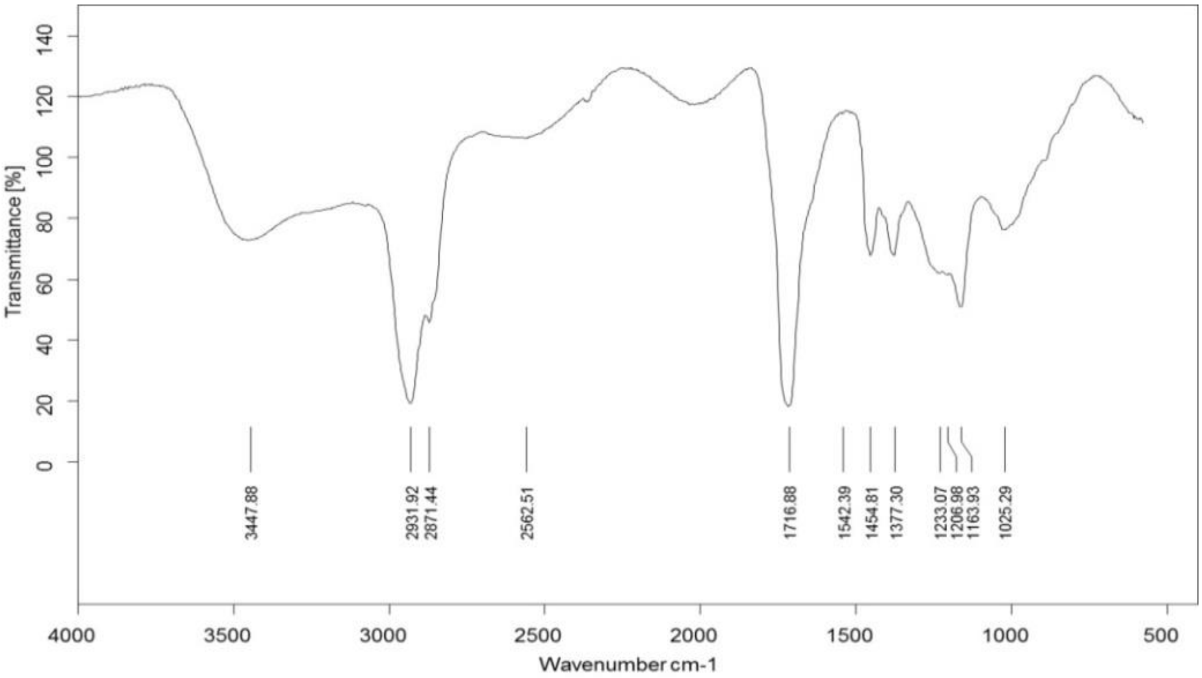


Fig. 5.86 Infrared spectrum of E/14 "Succinum flavan" from the Vigani Cabinet

Discussion

The composition of the soluble part is typical for Baltic amber with the characteristic monoterpene fraction, monoterpanyl succinic acids and high amounts of Δ8-isopimaric, sandaracopimaric, isopimaric and dehydroabietic acids together with double bond isomerized (iso)pimaranes and their dihydro derivatives. Additional labdanes with a (dihydro)agathic acid skeleton are present in significant amounts. The infrared spectrum shows the characteristic aliphatic ester compounds and the Baltic shoulder.

The composition is similar to that of the soluble part of E/16 "Succinum nigram" (chapter 5.4.4), particularly the composition of the diterpene fraction and the presence of the homologous n-alkanes. A similar distribution of homologous n-alkanes is reported for Polish ambers and is found in the reference sample. They originate from degraded plant lipids deposited with and incorporated into the resinous material. Czechowski et al. report a predominance for the C_{22} associated peak, which could not verified for E/14 due to lacking identification of the related peak (Czechowski et al. 1996). Despite the similarity of the soluble fractions, the infrared spectrum of E/14 differs significantly from that of E/16 "Succinum nigram", which is no Baltic amber.

The infrared spectrum of E/14 "Succinum flavan" is very similar to that of E/15 "Succinum albam" (chapter 5.4.3) (no spectrum was taken of E/13). E/15 "Succinum albam" however contains additional olefinic and exomethylene peaks (vinylide) and due to a slightly more intense absorption at 1246 and 2563 cm^{-1} more free carboxyl groups. E/14 "Succinum flavan" is of higher maturation compared to E/15 "Succinum albam". It also contains higher amounts of free succinic and dehydroabietic acids compared to the other amber samples from the Vigani Cabinet. Both compounds are products of a degradation occurred during the storage in the Cabinet (see chapter 5.4.1 'Discussion'). The monoterpene alcohols are incorporated into the polymer by esterificatrion with succinic acid (Mills et al. 1984/85), which makes free monoterpanyl succinic acids a product of degradation as well. The differing maturation state may be a possible explanation for the differing release of these compounds and the presence of oxygenated dehydroabietic acids in E/13 and E/15. When the E/14 "Succinum flavan" arrived in the collection, only small amounts of free abietic acids were present, because they are mainly incorporated into the polymer by acetylation with the hydroxyl groups of the polymer (Mills et al. 1984/85). During storage they were released from the material but not originally present as in the other two samples.

A final conclusion is given in chapter 5.4.3.

5.4.3 E/15 Succinum albam

Fig. 5.87 E/15 "Succinum albam"

Fig. 5.88 Sampling of E/15

Description

The box is filled with small lumps of different colour similar to the compartment E/14 (chapter 5.4.2). Additionally a big lump of dark red colour is placed in the middle of the compartment.

Sampling

A sample of whitish and yellowish opaque lump (about 800 mg) was taken on 26 April 207 (Fig. 5.10). Small fragments with a pale yellow and whitish surface but a dark yellow to orange interior were cut prior to analysis.

Vigani references

* MS Quns Vig. 4, folio 4, recto, as "Succ: Alb", 1 ounce at 1 shilling

* LECTURE NOTES UNDATED: 6

* LECTURE NOTES 1707: 12-14, 90

Contemporary literature

See chapter 5.4.1

Terminology

See chapter 5.4.1

Botanical and geographical origin

See chapter 5.4.1

Manufacture and trade

See chapter 5.4.1

Properties

See chapter 5.4.1

Possible chemical composition

See chapter 5.4.1

Chemical analysis

E/15 "Succinum albam" was dissolved in all used solvents (methanol, methanol-chloroform and dichloromethane) solvents to a low extent. The best results were obtained with the dichloromethane extract. Comparatively good results were obtained for the methanol-chloroform extract (not shown).

In the methylated dichloromethane extract (Fig. 5.89) dimethylsuccinate is present in high amounts, additionally p- and m-cymene, l-fenchone, fenchol, camphor and (iso)borneol are found. In the sesquiterpene fraction (8 – 12 minutes) several phenylpropanoid compounds are present (PP37-PP40), one of it identified as cumate. This is probably a contamination. Monoterpanyl succinates (MS1, MS3 and MS4) but no dimonoterpanyl succinates and monoterpanyl diterpenoates are present. The only maturation product present in significant amounts is 13-methylpodocarpatrien-18-oate (D11), 1,2,3,4-tetrahydro-1,5,6-trimethyl-1-naphthalenecarboxylate (D5) is present in small amounts.

In the diterpene section high amounts of (dihydro-)Δ8-isopimarate, sandaracopimarate and dehydroabietate are present together with smaller amounts of a pimaradienol, (dihydro)Δ8-pimarate and (dihydro-)isopimarate. Other constituents are 5β-dehydroabietate, dihydro-Δ7-pimarate, a dihydro-abietate (A8), an unidentified diterpene acid (D14), abietate and the compounds D24 and U21.

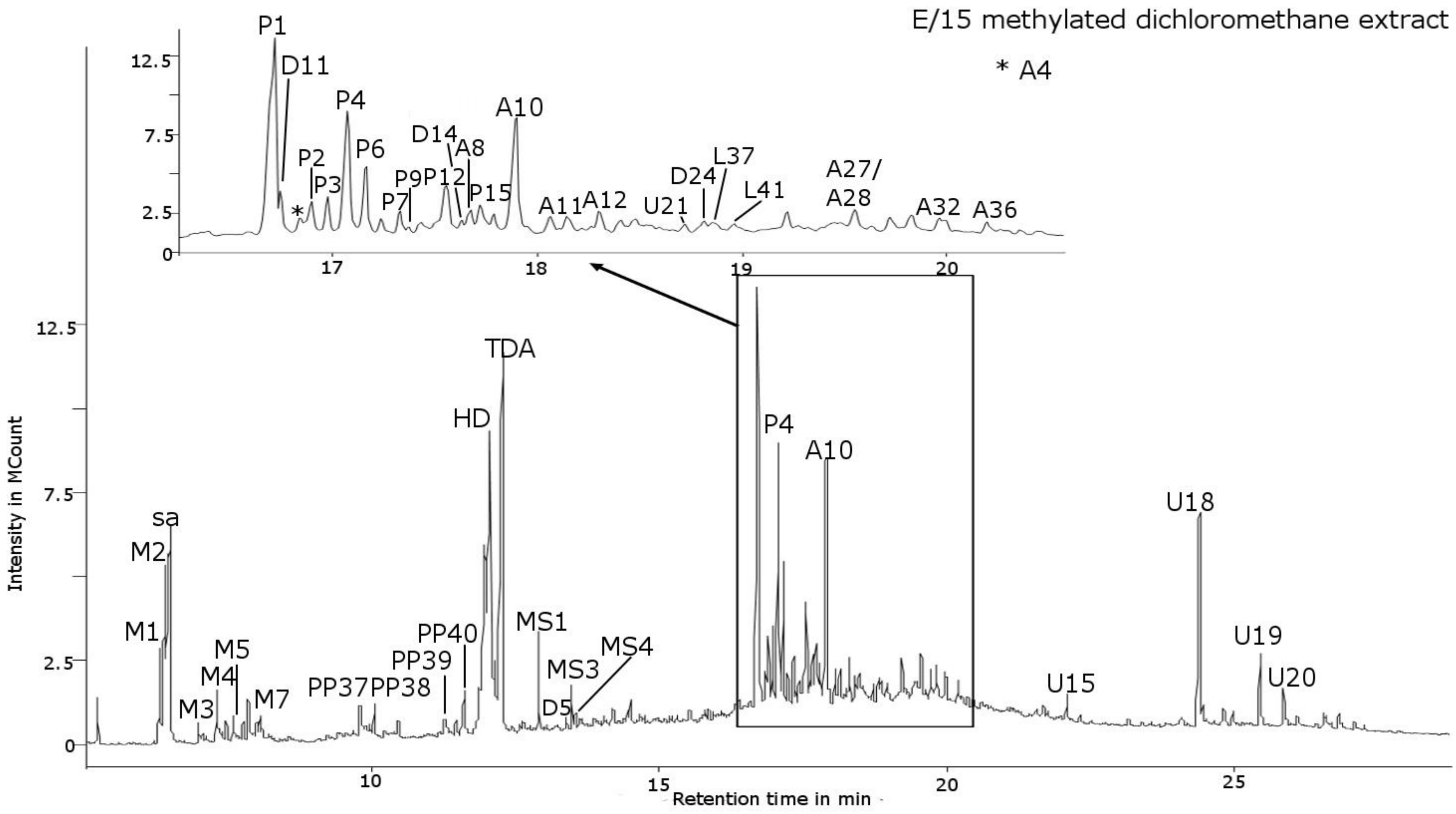
Dihydroagathate and its Δ8-isomer are present in small amounts. Small amounts of abietane aging markers are found: 15-hydroxy-, 7-oxo-dehydroabietates and (A27, A28, A32). The unidentified compounds U15, U18, U19 and U20 are reported in literature as di- or trimeric units of the amber matrix with masses between m/z 360 and 450 (Islas et al. 2001). U18 is also present in E/13.

The infrared spectrum is shown in Fig. 5.90. It shows adsorption of hydroxyl and hydroxymethylene groups (3,442, 1,024 cm^{-1}), aliphatic structures (2,932, 2,872, 1,378 cm^{-1}, 1,455 cm^{-1}) and axial ester groups (1,721 and 1,161 cm^{-1}) (Hummel 1981: 424, 425, 428). The Baltic shoulder between 1,175 – 1,250 cm^{-1} is present as well (Wolfe et al. 2012). It results from a lack of free carboxyl (around 1240 cm^{-1}) and hydroxyl structures (1260 cm^{-1}). Peaks at 3,080, 1,646 and 891 cm^{-1} originate from terminal alkenes and exocyclic double bonds. The adsorption at 1245 cm^{-1} and 2540 cm^{-1} from carboxyl groups (Hummel 1981: 425) are slightly more intense than in the spectrum of E/14 "Succinum flavan". The material contains higher amounts of free carboxyl groups and olefinic stuctures than E/14 "Succinum flavan". The latter indicates incomplete maturation, a higher amount of free carboxyl group incomplete polymerisation.

Discussion

This composition is typical for the soluble part of Baltic amber with the characteristic monoterpene fraction, monoterpanyl succinic acids and high amounts of Δ8-isopimaric, sandaracopimaric and dehydroabietic acids together with double bond isomerized (iso)pimaranes and their dihydroderivatives. Labdanes with an a (dihydro)agathic acid skeleton are present in small amounts. The infrared spectrum shows the characteristic aliphatic ester compounds and the Baltic shoulder.

The composition is very similar to that found for E/13 "Succinum Citrinum" (chapter 5.4.1), particularly the composition of the diterpene fraction and the relatively small amounts of monoterpanyl esters. Both contain the dimeric U18, E/15 additionally other related compounds U15, U19 and U20, whereas they are present in the better soluble E/15 in much higher amounts. Both samples share the presence of oxygenated abietanes such as as 7-oxo- and 15-hydroxy-dehydroabietic acids. As discussed for E/13 they are formed from dehydroabietic acid, which is released from the polymeric fraction during storage. This is a typical process found in amber samples from collections and supported by the high amounts of free succinic acid (see chapter 5.4.1, ‘Discussion’).



Methylated dichloromethane extract (labels, see table 5.23)

Fig. 5.89 Gas chromatogram of E/15 "Succinum albam" from the Vigani Cabinet, mono-, sesqui- and diterpene section (TIC)

Label	t_R	Name	Main mass fragments
M1	6.31	p-Cymene	53, 77, 91, **119**, 134
M2	6.38	m-Cymene	53, 77, 91, **119**, 134
sa	6.50	Succinate, diME	55, 87, **115**, 146
M3	7.11	l-Fenchone	53, 69, **81**, 109, 152
M4	7.31	Fenchol	55, 57, 67, 80, **81**, 93, 107, 121, (154)
M5	7.59	Camphor(+)	55, 67, 81, **95**, 108, 137, 152
M7	8.04	Borneol	55, 67, 79, **95**, 121, (154)
PP37	9.80	Unidentified	61, 77, 91, 119, 147, **163**, **178**
PP38	10.05	Cumate	77, 91, 119, 131, 147, **163**, 178
PP39	11.28	Unidentified	77, 91, 119, 163, **179**, 193, 208
PP40	11.61	Unidentified	77, 91, 105, 137, 163, **179**, 195
MS1	12.91	Fenchylsuccinate	55, 81, 87, **115**, 121, 136, 153, (268)
D5	13.38	1,2,3,4-Tetrahydro-1,5,6-tetramethyl-naphthalenecarboxylate	51, 83, 128, 143, 158, **173**, 185, (232)
MS3	13.48	Bornylsuccinate	55, 67, 81, 93, 95, **115**, 121, 136, (268)
MS4	13.55	Isobornylsuccinate	55, 81, 93, 95, 108, **115**, 121, 136, 153, (268)
P1	16.70	Δ8-Isopimarate	91, 185, **241**, 257, 269, 301, 316
D11	16.74	13-Methylpodocarpatrien-18-oate	91, 131, 145, 155, **211**, 227, 241, 271, 287, 301, 316
A4	16.84	5β-Dehydroabietate	91, 143, 157, 183, 211, **239**, 255, 273, 299, 314
P2	16.89	Pimaradienol	79, **91**, 105, 131, 161, 257, 273, 288
P3	16.97	Δ8-pimarate	105, 185, **241**, 257, 269, 301, 316
P4	17.07	Dihydro-Δ8-isopimarate	91, 187, **243**, 259, 271, 303, 318
P6	17.16	Sandaracopimarate	79, 91, **121**, 241, 257, 301, 316
P7	17.33	Pimar-8(14)-en-18-oate (dihydro-Δ8-pimarate)	79, 95, **121**, 159, 181, 219, 229, 289, 303, 318
P9	17.37	Pimar-7-en-18-oate (dihydro-Δ7-pimarate)	91, 121, 133, 159, **243**, 303, 318
P12	17.56	Isopimarate	91, 105, 121, 187, 201, 227, **241**, 256, 257, 287, 301, 316
D14	17.62	Unidentified diterpene acid, ME	91, 145, 159, 187, 227, **241**, 256, 257, 287, 301, 316
A8	17.67	Abiet-en-18-oate (dihydro-abietate isomer)	79, 91, 107, **121**, 215, 225, 239, 243, 259, 275, 303, 318
P15	17.73	Dihydroisopimarate	79, 93, 105, 121, 227, **243**, 259, 287, 303, 318
A10	17.89	Dehydroabietate	197, **239**, 199, 314
A11	18.15	Dehydroabietol	117, 159, 173, 185, 211, **253**, 271, 286
A12	18.29	Abietate	
U21	18.72	Unidentified	91, 105, 121, 159, 173, 229, 237, **285**, 301, 345, 360
D24	18.81	Podopcarpatriene acid, oxygenated derivative	121, 159, 185, **225**, 240, 268, 300
L37	18.86	Dihydroagathate, diME	93, 107, **121**, 161, 217, 239, 257, 272, 304, 364
L41	18.96	Δ8-Dihydroagathate, diME	105, 119, **175**, 203, **235**, 257, 289, 304, 364
A27	19.57	Δ16-demethyl-7-oxo-dehydroabietate (proposed)	155, 197, 211, 239, **253**, 313, 328
A28	19.55	15-Hydroxy-dehydroabietate	237, **255**, 273, 315, 330
A32	19.96	7-Oxo-dehydroabietate	187, 211, **253**, 269, 296, 313, 328
U15	22.09	Di- or polymeric matrix constituent	105, **133**, 295, 321, **377**, 392
U18	24.39	Di- or polymeric matrix constituent	105, **133**, 257, 375, 391, 403, 435, 450
U19	25.45	Di- or polymeric matrix constituent	91, 131, 229, 289, **375**, 391, 403, 435, 450
U20	25.85	Di- or polymeric matrix constituent	105, **121**, 133, **229**, 257, 289, 391, 435, 448, 476

Tab. 5.23 Compounds found in E/14 "Succinum flavan", sample analysed with temperature program Diterpenes 3 and column A, mass spectra references see appendix

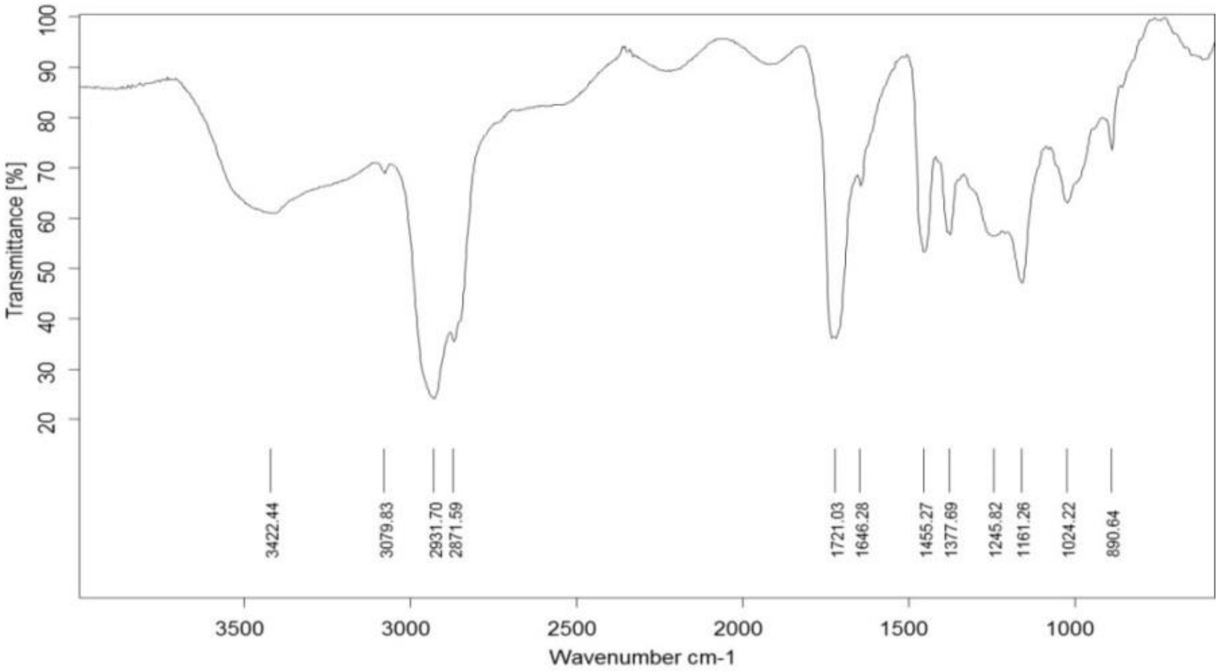


Fig. 5.90 Infrared spectrum of E/15 "Succinum albam" from the Vigani Cabinet

The infrared spectrum contains peaks from olefinic structures, a typical pattern for incomplete maturation. Due to the incomplete maturation higher amounts of free abietic acids were present, when the material arrived the collection. As a result, they were oxidated to dehydroabietic acid and further to smaller amounts of oxygenated at positions C-7 and C-15. A higher maturated amber contains higher amounts of dehydroabietic acid released from the esterified polymer, than oxygenated derivatives thereof (see chapter 5.4.2). Additionally, the infrared spectrum of E/15 shows more free carboxyl groups. Because the infrared spectrum of the whole resin is representative for the polymeric part (Stout et al. 1995), this indicates a indicates incomplete polymerisation. As a result, E/15 "Succinum album" has he hightest solubility of all amber samples from the Cabinet.

In summary, E/13 "Succinum Citrinum" and E/15 "Succinum albam" are Baltic amber with a lower maturation and in the case of E/15 lower polymerisation state than E/14 "Succinum flavan". E/14 in turn contains relatively high amounts of degraded lipids from incorporated plants parts. All three materials are Baltic amber due to the characteristic soluble fraction and infrared spectra. This is not necessarily the case for all pieces in the respective compartments, however. Vigani seems to have been handled them indeed as different sorts, because they were placed labelled according literature ("album sc. & flavum seu citrinum") in different compartments despite being nearly identical in appearance and as shown above also in chemical composition.

5.4.4 E/16 Succinum nigram

Fig. 5.91 E/16 "Succinum nigram"

Fig. 5.92 Sampling of E/16

Description

The box contains one big black lump. It is very hard, glossy and brittle similar to glass. Additionally, two smaller lumps, one red and one dark brown one, can be found in the compartment. They resemble the materials in the neighbouring compartments (E/13 – E/15).

Sampling

A sample of the big black lump (about 60 mg) was taken on 26 April 2007 (Fig. 5.92). Small black, brittle and hard fragments were cut from the sample prior to analysis.

Vigani references

* Does not appear in MS Quns Vig.

* LECTURE NOTES UNDATED: 6

* LECTURE NOTES 1707: 12-14, 90

Contemporary literature

Fine art materials

See chapter 5.4.1

Science

* DALE 1693: 54: "Succinum nigrum"

* POMET 1717: 789: "schwartze Carabe oder Agtstein", 1694: 85: "Ambre noir"

* JAMES 1747: 560: "Succinum nigrum"

* HILL 1751: 155: "Black Amber"

Encyclopaedias

* CHAMBERS 1728a: 75: "Black amber"

Terminology

A black sort of "amber" or "succinum nigrum" is mentioned together with "gagates" or "jet" by several authors. While some authors thought those materials to be identical (Dale 1693: 54; James 1747: 560; Savary des Brûslons, Savary 1748b: 1662), others only mention a black sort of "amber" resembling "jet" (Chambers 1728a: 75; Hill 1751: 155). According to Pomet black amber was "yellow amber deprived of its oil by subterranean heat" (Pomet 1717: 789-90). James describes a black and solid fossil, which is used as an alternative for the rare black amber, and dug out in the coal mines in England (James 1747: 592), which probably refers to a jet-like material. The terminology of "amber" in general is described in chapter 5.4.1.

Botanical and geographical origin

See chapter 5.4.1

Manufacture and trade

See chapter 5.4.1

Properties

"Black amber" can be distinguished from "gagates" by its higher hardness and lower inflammability. It also easily melts over fire, which is not the case with "gagates" (Hill 1751: 168). The properties of "amber" in general are described in chapter 5.4.1.

Possible chemical composition

The name black amber is mentioned in modern literature for stantienite (Yamamoto et al. 2006). A dichloromethane-methanol extract of this fossil resin contained several branched and cyclic diagenetic products, high amounts of homologous series of alkanoates (C_{12} to C_{32}) and alkanedioate (C_{12} to C_{27}). Some diterpenes (isopimarane, abietane, totarane) and triterpenes (oleanane, lupane, ursane and hopanes skeletons) were present as well. The alkan(edi)oates are thought to derive from degraded plant waxes or lipids, which were deposed together with the resinous material. This is a typical pattern of amber materials buried in inland geological layers such as brown coal or clay minerals.

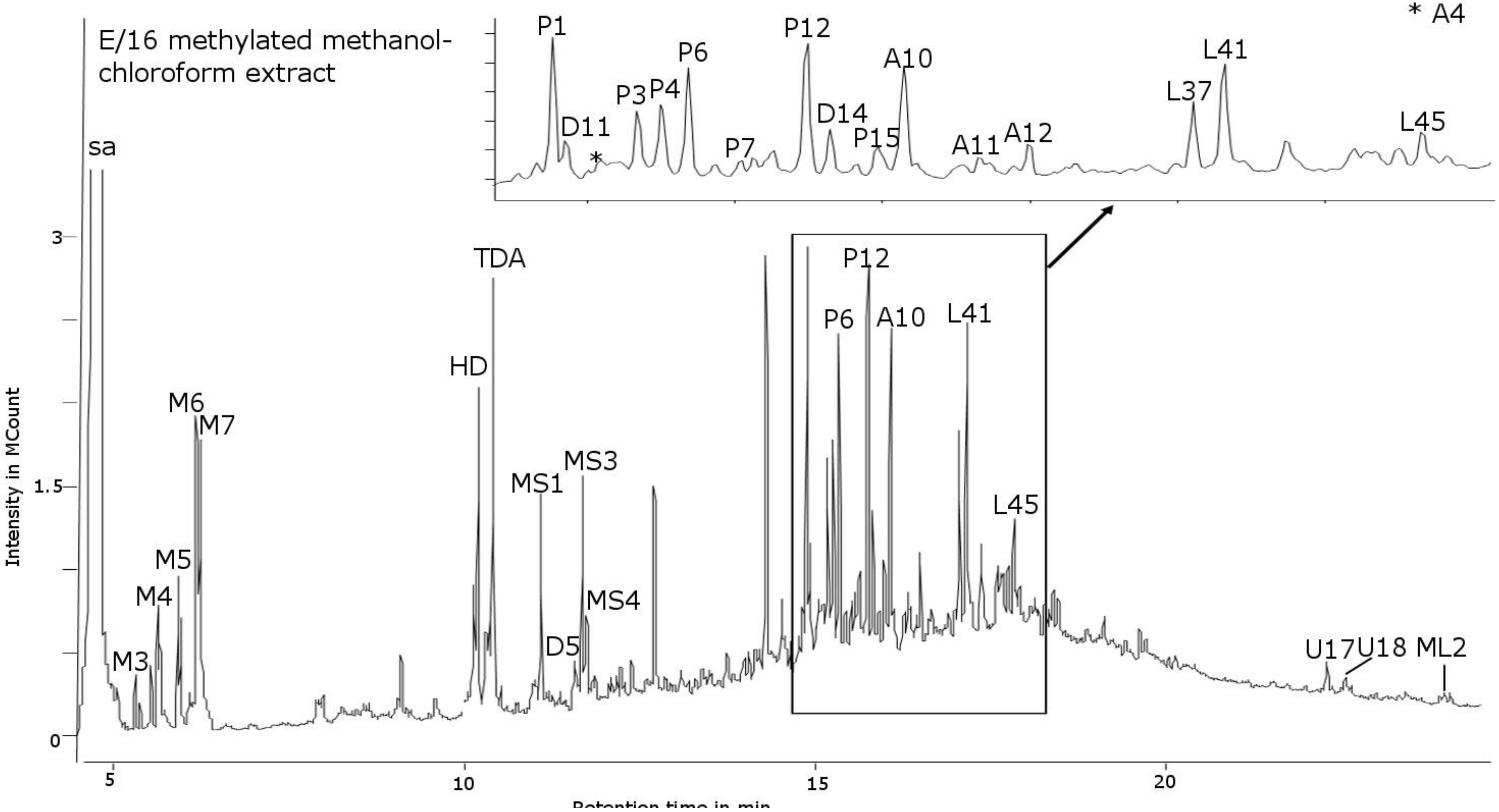
Chemical analysis

The material was not dissolved in methanol and dichloromethane. The methanol-chloroform extract showed a good intensity (Fig. 5.93). It contains high amounts of dimethylsuccinate and l-fenchone, fenchol, camphor and (iso)borneol. The material contains a very small sesquiterpene fraction (8 – 12 minutes), the compounds present only in traces could not be identified. Fenchyl- and (iso)bornylsuccinates (MS1 – MS3) are present in small amounts, as well as monoterpanyldihydro-Δ8-agathate (ML2). The only maturation product present in significant amounts is 13-methylpodocarpatrien-18-oate (D11), 1,2,3,4-tetrahydro-1,5,6-trimethyl-1-naphthalenecarboxylate (D5) is present in small amounts.

In the diterpene section high amounts of Δ8-isopimarate, sandaracopimarate, isopimarate and dehydroabietate are present together with smaller amounts of Δ8-pimarate, dihydro-Δ8-isopimarate, the unidentified compound D14, dihydroagathate and its Δ8-isomer. Other constituents are 5β-dehydroabietate, dihydro-Δ8-pimarate and –isopimarate, dehydroabietol, abietate and agathate. The unidentified compounds U_{17} and U_{18} are reported in literature as di- or trimeric constitutents of the amber matrix (Islas et al. 2000; see chapter 5.4.1, 5.4.3).

The material contains very small amounts of a homologous series of n-alkenes, which are visible only in the isooctane extract (Fig. 5.94). They have the same mass spectra and distribution as found for E/14 "Succinum flavan" in the methanol-chloroform extract (chapter 5.4.2, Fig. 5.85). The maximum of the series elutes at 20.87 minutes, which is identic with the pattern found in E/14.

The infrared spectrum is shown in Fig. 5.95. It shows absorption bands of hydroxyl and hydroxymethylene groups (3,391 and 1034 cm^{-1}) and aliphatic structures (2,925, 2,857, 1,375 cm^{-1}, 1,454 cm^{-1}). No ester peaks are present. Aromatic structures are visible at 1,611, 1,511 and 821 cm^{-1} (Hummel 1981: 283, 425). Adsorptions from carbonyl (1,695 cm^{-1}), hydroxyl groups (1,259 cm^{-1}) and ketones (1119 cm^{-1}) are present as well (Hummel 1981: 283).

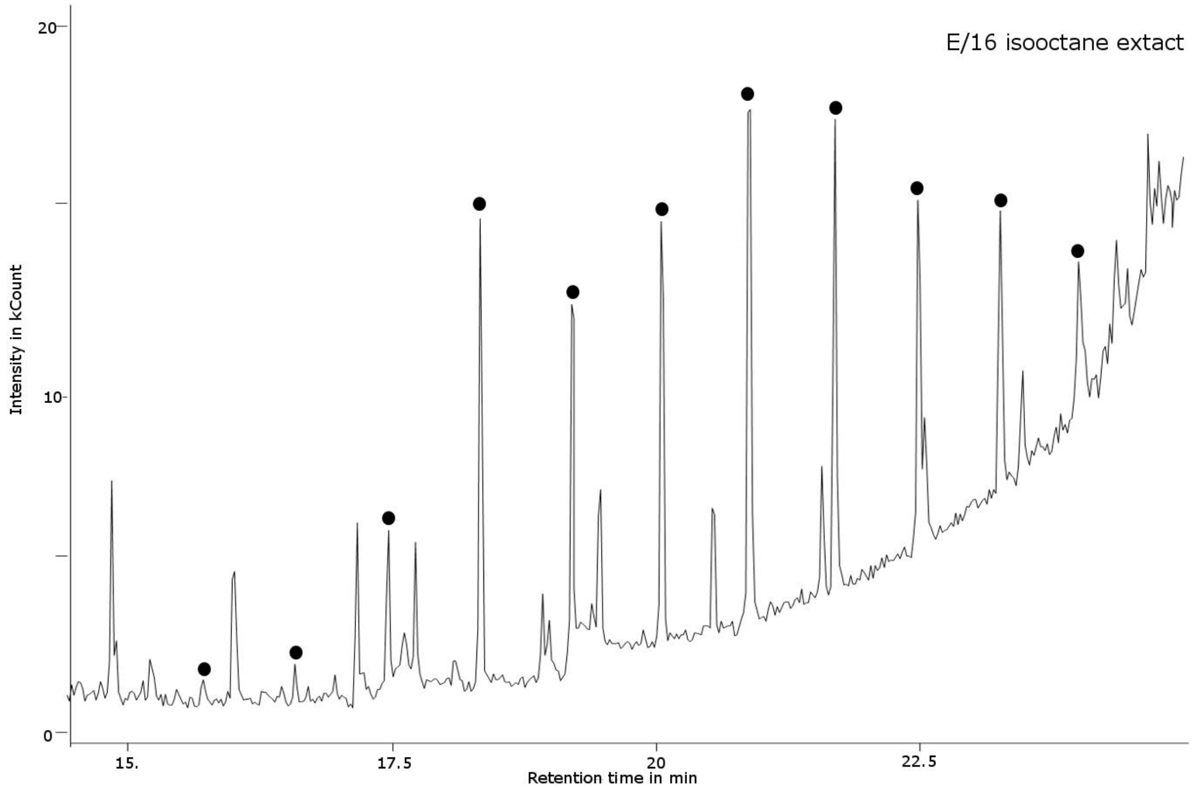


Methylated methanol-chloroform extract, the peak of succinate (sa) has a intensity of 13 MCount (labels, see table 5.24)

Fig. 5.93 Gas chromatogram of E/16 "Succinum nigram" from the Vigani Cabinet, mono-, sesqui- and diterpene section (TIC)

Label	t_R	Name	Main mass fragments
sa	4.83	Succinate	55, 87, **115**, 146
M3	5.32	l-Fenchone	53, 69, **81**, 109, 152
M4	5.64	Fenchol	55, 57, 67, 80, **81**, 93, 107, 121, (154)
M5	5.92	Camphor(+)	55, 67, 81, **95**, 108, 137, 152
M6	6.19	Isoborneol	55, 67, 79, **95**, 121, (154)
M7	6.25	Borneol	55, 67, 79, **95**, 121, (154)
MS1	11.10	Fenchylsuccinate	55, 81, 87, **115**, 121, 136, 153, (268)
D5	11.57	1,2,3,4-Tetrahydro-1,5,6-trimethyl-1-naphthalenecarboxylate	91, 115, 128, 145, 158, **173,** 232
MS3	11.68	Bornylsuccinate	55, 81, 93, 95, 108, **115**, 121, 136, 153, (268)
MS4	11.75	Isobornylsuccinate	55, 81, 93, 95, 108, **115**, 121, 136, 153, (268)
P1	14.91	Δ8-Isopimarate	91, 185, **241**, 257, 269, 301, 316
D11	14.94	13-Methylpodocarpatrien-18-oate	91, 131, 145, 155, **211**, 227, 241, 271, 287, 301, 316
A4	15.03	5β-Dehydroabietate	91, 143, 157, 183, 211, **239**, 255, 273, 299, 314
P3	15.17	Δ8-Pimarate	105, 185, **241**, 257, 269, 301, 316
P4	15.26	Dihydro-Δ8-isopimarate	91, 187, **243**, 259, 271, 303, 318
P6	15.34	Sandaracopimarate	79, 91, **121**, 241, 257, 301, 316
P7	15.52	Pimar-8(14)-en-18-oate (dihydro-Δ8-pimarate)	79, 91, 105, **121**, 181, 229, 289, 301, 318
P12	15.75	Isopimarate	91, 105, 121, 187, 201, 227, **241**, 256, 257, 287, 301, 316
D14	15.82	Unidentified diterpene acid, ME	91, 145, 159, 187, 227, **241**, 257, 287, 301, 316
P15	15.98	Dihydroisopimarate	79, 93, 105, 121, 227, **243**, 259, 287, 303, 318
A10	16.07	Dehydroabietate	197, **239**, 199, 314
A11	16.32	Dehydroabietol	117, 159, 173, 185, 211, **253**, 271, 286
A12	16.49	Abietate	91, 105, 121, 185, 213, **241**, 256, 316
L37	17.05	Dihydroagathate, diME	93, 107, **121**, 161, 217, 239, 257, 272, 304, 364
L41	17.15	Δ8-Dihydroagathate, diME	105, 119, **175**, 203, **235**, 257, 289, 304, 364
L45	17.82	Agathate, diME	79, 107, **121**, 189, 241, 271, 315, 347, 362
U17	22.28	Di- or polymeric matrix constituent	81, 105, 145, 229, 325, 355, **387**, 402, 415, 430, 447, 462, 488
U18	22.55	Di- or polymeric matrix constituent 80	105, **133**, 257, 375, 391, 403, 435, 450
ML2	23.96	Monoterpanylester of dihydro-Δ8-agathate	**81**, 95, 137, 175, 235, 271, 289, 331, 349, 426, (486)

Tab. 5.24 Compounds found in E/16 „Succinum nigram", samples analysed with temperature program Diterpenes 1 and column A, mass spectra references see appendix



Isooctane extract, peaks of the homologous series are marked with a dot (labels, see table 5.22)

Fig. 5.94 Gas chromatogram of E/16 "Succinum nigram" from the Vigani Cabinet, homologeous series, di- and triterpene section (TIC)

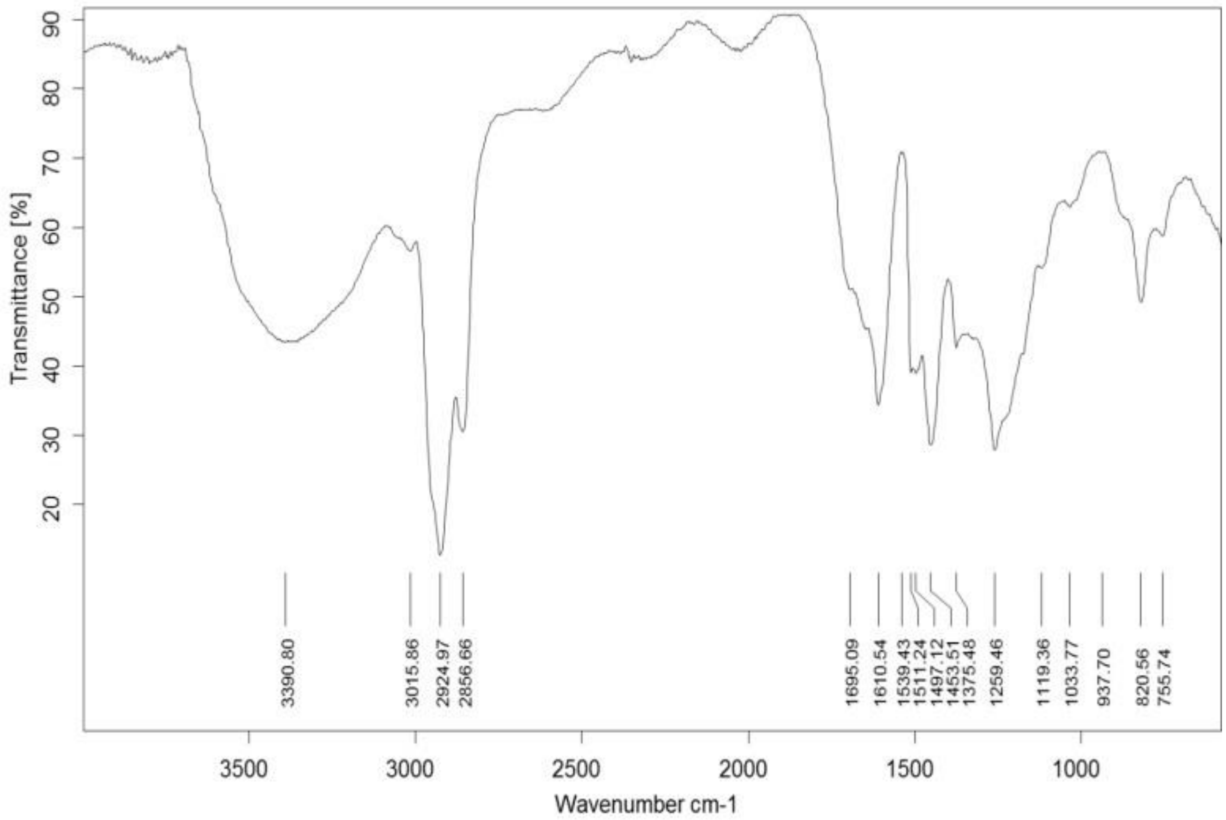


Fig. 5.95 Infrared spectrum of E/16 "Succinum nigrum" from the Vigani Cabinet

Discussion

The composition of the soluble fraction is typical for Baltic amber with the characteristic monoterpene fraction, monoterpanyl succinic acids and high amounts of Δ8-isopimaric, sandaracopimaric and dehydroabietic acids together with double bond isomerized (iso-)pimaranes and their dihydro-derivatives. Additional labdanes with a (dihydro-)agathic acid skeleton are present as well.

The composition of the soluble fraction is similar to that found for E/14 "Succinum flavan" (chapter 5.4.2), mainly for the composition of the diterpene fraction and the presence of the homologous n-alkane series. The relatively high amounts of succinic acid and dehydroabietic acid are the result of a degradation process occurred in the outer layer of the material while stored in the Cabinet, details see chapter 5.4.1. A possible explanation for the differing amounts of succinic and oxygenated abietane acids in the amber materials from the Cabinet is given in chapter 5.4.1.

Despite the composition of the soluble part is very similar to the other ambers from the Cabinet, the composition of the whole material significantly differs. The polymer makes up the main part of the resin, and as shown for all amber analysed in this work, only a very small part is soluble in the used solvents. The infrared spectrum of the whole material was found to be representative for the insoluble, hence polymeric, part (Stout et al. 1995). Based on the infrared spectrum, the polymer of E/16 "Succinum nigrum" is composed of an aliphatic, olefinic and aromatic hydrocarbon polymer with a high content of free hydroxyl groups. Particularly the non-aliphatic content is much higher than in the other ambers from the Cabinet. No esterification can be observed. Instead of succinylation isomerisation and oxidation seems to have been taken place.

The similarity to the spectrum of F/13 "L. Gagatis" (chapter 5.4.5) indicates a similar base structure of an aliphatic hydrocarbon polymer with partly aromatic structures. In contrary to F/13, E/16 shows a much higher content of oxygen bearing functional groups.

In summary E/16 "Succinum nigrum" is no Baltic amber because the characteristic crosslinking with succinic acid is not found. Despite the material contains succinic acid, it was not esterified and consequently is composed mainly of an aliphatic and olefinic hydrocarbon polymer. It is no stanetite and no other modern reports about black amber are found. It is however, at least partly a resin, and resinous compounds were incorporated into the polymer. To which extent the polymeric fraction was formed from a resinous or other plant matter, cannot be said without pyrolysis.

5.4.5 F/13 L. Gagatis

Fig. 5.97 F/13 "L. Gagatis"

Fig. 5.96 Sampling of F/13

Description

The box contains one big black lump. It is very hard and brittle. It is matte compared to the material in compartment E/16 (chapter 5.4.4)

Sampling

A sample (about 1 mg) was taken on 27 of April 2007 (Fig. 5.97). It was brittle and black.

* Vigani

* Does not appear in MS Quns Vig.

* Does not appear in LECTURE NOTES UNDATED

* Does not appear in LECTURE NOTES 1707

Contemporary literature

Fine art materials

* SALMON 1701: 555, 841-3: "Jet"

Sciences

* DALE 1693: 54: "Gagetes", "Jet"

* POMET 1717: 789: "Gagat", "Geest", "Jayet"; 1694: 85: "Karabé", "succin", "amber noir"

* LEMERY 1721: 477: "Gagates", "Geest", "Jays", "Jayet", "Agat"

* JAMES 1747: 560: "Gagates", "Succinum nigrum"

* HILL 1751: 168: "Gagates", "Jet"

Encyclopedias

* CHAMBERS 1728b: 371: "Jeat"

* SAVARY DES BRÛSLONS, SAVARY 1748b: 1662: "Jais", "Jayet"

Terminology

"Gagates" or "jet", French "jayet", is described as a mineral or "fossil or bituminous stone" (Dale 1693: 54; Pomet 1717: 789; Lemery 1721: 477[19]; James 1747: 560). The name probably derives from the river "Gaga(s)" near the city "Plagiopolis" in "Cilicia", a place already mentioned by Dioscurides (Lemery 1721: 477; James 1747: 561). It is formed of a "lapidisic or bituminous Juice in the Earth, in the manner of Coal" (Chambers 1728b: 371). It is but described a form of "amber jaune" deprived of its oil by subterranean fire as well. This oil would be "naphtha" or "Petroleum" than (Pomet 1717: 789; Lemery 1721: 477). The terminology of "amber" is described in chapter 5.4.1, that of "succininum nigrum" in 5.4.4.

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[19] Both Lemerys and Pomets "bitumineuse" was translated with "hartzigt" (Pomet 1694: 85; Pomet 1717: 789; Lemery 1716: 30; Lemery 1721: 477).

Manufacture and trade

The material is dug out from the earth, mentioned places are the Dauphine (Chambers 1728b: 371; Savary des Brûslons, Savary 1748b: 1662), Northern parts of England (Chambers 1728b: 371; James 1747: 592) and several other place in Europe such as Germany, Swedia, France (between St. Beaume and Poulon) and Ireland (Pomet 1717: 789; Lemery 1721: 477; Hill 1751: 169). Hill mentions it to be washed up by the sea in Italy and France as well as in England, where it is washed out the cliffs (Hill 1751: 169).

"Gagates" is confounded with "ampelites" and cannel coal (James 1747: 561; Hill 1751: 168).

Properties

"Gagates" is very hard, of a dark black colour, glossy and polishable (Pomet 1717: 789; Lemery 1721: 477; Chambers 1728b: 371; James 1747: 560; Savary des Brûslons, Savary 1748b: 1662). James describes a "kind of asphaltum" from the coal mines of England (James 1747: 592). It has a bituminous smell, is flammable and emits a black smoke when burned (Dale 1693: 54; James 1747: 560-1). Hill in contrary mentions a bright white flame, which burns a long time leaving only little ash behind (Hill 1751: 169). It splits very easily in horizontal direction and hardly in other directions (Hill 1751: 168). It has a bituminous and astringent taste and under the microscope many parallel thin plates laid upon each other are visible (Hill 1751: 168).

"Gagates" is distinguishable from "black amber" by its lower hardness and inflammability, while "amber" easily melts over fire (Hill 1751: 168).

Possible chemical composition

The chemical composition of jet is not discussed in this work in detail, because the material F/13 was chosen for analytical investigation mainly for comparison with E/16 "Succinum nigrum" due to their similar appearance and nomenclatorial connection (see chapter 5.4.1, 5.4.4).

Jet is a fossil hydrocarbon with a chemical composition similar to bituminous coal. It is carvable and polishable and was used mainly as a minor gemstone. The hydrocarbon is an insoluble complex organic polymer called kerogen with molecular weights upwards of 1.000 daltons. It originates from fossil wood of Araucariacean or Protopinacean origin under high compression in the presence of water and is found in geological layers of the Jurassic period (Black Jura in German and Lias in English mines). Salt water leads to hard jet, fresh water to softer jet. The material is very homogenous and significant amounts of sulphur are incorporated into the hydrocarbon structure, which is thought to be the reason for its stability (Weller, Wert 1993).

In pyrolysis-GC/MS jet shows mainly lignin-derived phenols and methoxy-phenols and n-alkane hydrocarbon (Watts et al. 1999).

Chemical analysis

The small black, brittle and hard fragment was not dissolved in any of the solvents.

The infrared spectrum is shown in Fig. 5.98. It shows adsorption of hydroxyl groups (3,407 cm^{-1}), aliphatic (2,924, 2,853, 1,374, 1,455 and 724 cm^{-1}) and aromatic (1,607 and 815 cm^{-1}) structures. The peak at 724 cm^{-1} results from long-carbon-chain structures. A small carbonyl group adsorption is present at 1,695 cm^{-1} (Hummel 1981: 283).

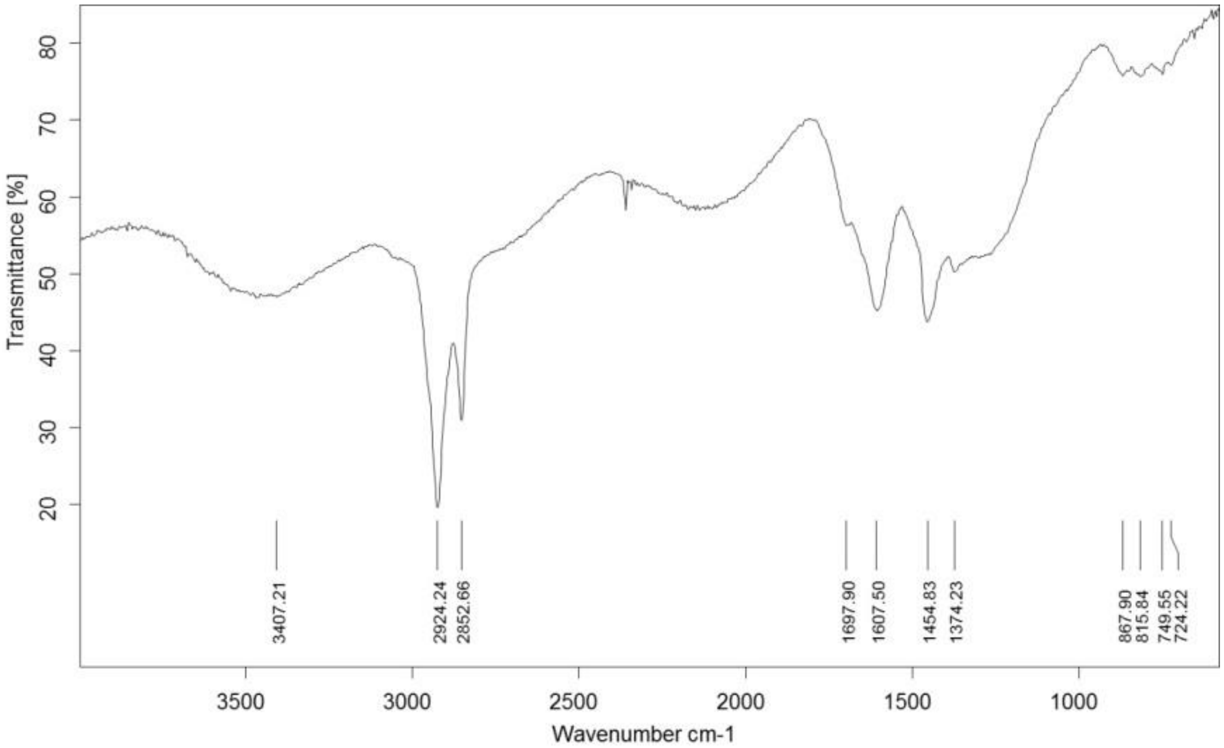

Fig. 5.98 Infrared spectrum of F/13 "L. Gagatis" from the Vigani Cabinet

Discussion

The material consists of an aliphatic, olefinic and aromatic polymeric hydrocarbon with only few functional groups. The infrared spectrum somewhat resembles that of E/16 "Succinum nigrum" (chapter 5.4.4), which contains the same aliphatic polymer but a higher content of oxygen containing functional groups. Additionally, E/16 "Succinum nigrum" shows adsorptions for p-substituted aromatic ring within a hydrocarbon chain (1,511 and 821 cm^{-1}), which are not present in F/13. Both materials show only small amounts of carboxyl groups.

6. CONCLUSIONS

The dissertation presented here was based on the assumption that the botanical taxonomy, the chemical composition and the terminology of natural resins are closely related. The question, whether chemotaxonomical data profiles provide a reasonable reference system for the identification of unknown resinous materials was raised. In order to answer this question, a review of present-day literature was conducted. It provided insights into the connection of taxonomy and chemical composition and into the limitations resulting from the complex nature of the resins' chemical compositions. Following this, a wide range of reference samples from botanical gardens and reference collections was analysed.

For some taxonomical groups, the correlation of taxonomy and chemical composition could be investigated in great detail by analysing reliable botanical reference samples. The analyses contributed systematic data for the differentiation of Pinaceae resins by pimarane acids and labdane alcohols. These resins are composed of high amounts of abietane acids in various aging states. A differentiation is possible by the relative amounts of pimaranes acids and the contents of neutral diterpenes such as labdane alcohols (epimanool, larixol, larixylacetate, abienols) and others (table 4.2). Pimaric acid serves as a marker for the adulteration with pine resin, while resins from *Picea*, *Abies* and *Larix* species can be distinguished according to the presence of the neutral diterpenes, *Picea* additionally by the lower amounts of sandaracopimaric acid compared to pimaric acid. Pimaric acid a characterstic compound of sapwood resins, which explains its absence in the blister resin of *Abies alba* Mill. and the cone resin of L*arix decidua* Mill. Despite some inconsistencies for *Larix* resins reported in literature (see chapter 4.1.4), *Abies* resins obtained not from the blister – such as reported occasionally in historical sources (Hill 1751: 710) – may contain pimaric acid, making a differentiation only possible by the composition of the neutral compounds. *Picea* and *Abies* resins contain differing compositions of abienols and related neutral compounds: *cis*-abienol is present in both *Abies* and *Picea*, but the composition of iso-abienol, abienol, Δ13-*cis*-neoabienol, *trans*-abienol and several unidentified diterpenes (D8, D10, L10), cembrene, cembrol and epimanoyloxide is different (see table 4.2). Resins from European *Larix* species contain epimanool, larixol and larixylacetate, while in some species belonging to the same section of the genus *Pinus* several labdane acids are typical.

The results of the chemotaxonomical investigations were applied to several commercially available materials called Venice and Strasbourg turpentine. There is a clear connection in literature to the resins of *Larix decidua* Mill. and *Abies alba* Mill., respectively (Mills, White 1999: 98; Koller et al. 1997a). However, several commercial samples of Venetian turpentine proved to have been mixed with colophony or made from pine resin. This is indicated by the presence or absence of the labdane alcohols and the presence of pimaric acid. Additionally, some of the German materials were labelled larch turpentine, which makes it a reasonable conclusion that the term Venetian turpentine is not connected unequivocally to larch resin, a finding which correspond with the historical situation (see below). The situation was similar for Strasbourg turpentine. Apart from its rarity, no pure materials could be obtained from German suppliers. A sample of an older material without pimaric acid but also with an ambiguous composition of labdanes is probably the pure resin of *Abies alba* Mill., but the product available now is a mixture of this resin with colophony. A sample from a collection labelled "fir resin" proved to be a pine resin or a mixture of pine with only very small amounts of fir resin. This leads to the conclusion that the composition of Strasbourg turpentine made from the silver fir (*Abies alba* Mill.) as well as the connection of the resin to the commercial material have still not been determined unequivocally (table 4.4, 4.5).

A second chemotaxonomical investigation was carried out for various resins called sandarac. This resin can originate from different botanical species. True sandarac from *Tetraclinis articulata* Mast. has a characteristic composition which makes it possible to distinguish it from juniper resins, and, according to literature data, very likely also from *Cupressus* resins (see chapter 2.1.2). Modern commercial sandarac is only partly suitable for a chemotaxonomical differentiation, because some materials contain several compounds not present in the resin of *Tetraclinis articulata* Mast, while the characteristic markers of the Sandarac cypress are missing. The origin of these compounds may be botanical or environmental, but their exact nature cannot be determined in the scope of this investigation.

Finally, commercial mastic and the resin of *Pistacia terebinthus* L. were compared in order to find differentiation criteria for the resins of the individual *Pistacia* species. In the resin of *Pistacia terebinthus* L., slightly decreased amounts of oleanane constituents compared to mastic and some additional compounds not found in modern as well as historical mastic are present. In a similar investigation (Assimopoulou, Papageorgiou 2005a; Assimopoulou, Papageorgiou 2005b), other differences were found. These were not confirmed in the analyses presented here. The reason for the different compositions found both in this work and in literature is unknown, and it remains open whether they are of botanical or environmental origin. Consequently, their usefulness as phytochemical markers is doubtful, even though the same differences are found in the historical samples from mastic and Pistacia turpentine.

The analyses presented in this work included several taxonomical groups for which influences by harvesting, manufacture, transport, and trade could not be ruled out as the analyses focussed mainly on commercially avaiblabe materials. It was therefore inevitable to include terminological considerations into the evaluation of the chemical data.

In the case of *Copaifera* resins, terminology, chemical composition and taxonomy could be investigated together. An assessment of the chemical composition of commercially available samples and of the different species was made based on literature data (see table 2.3). This assessment was complemented by further analyses. The diterpene composition of an additional species was added and several minor markers compounds investigated. According to these data, the trade to Europe of Copaiba balsam obtained from different species is a restricting factor for the availability of these different sorts of Copaiba balsam in Europe. The changing composition of materials of different age may be connected to these restrictions as well.

Copaifera resins can be distinguished from African genera of the Fabaceae by the presence of kauranes and high amounts of polyalthic and hardwickiic acids. The genera *Daniellia, Guibourtia* and *Tessmania* yield the so-called African legume copals. The investigation of these materials focussed on the connection between chemical composition and terminology, because the botanical sources of African copals are known only incompletely, and the names used are generic. The investigation revealed new insights into the chemistry of legume copals, mainly for the differentiation of Sierra Leone copal from other African copals. Apart from a deficiency in copalic acid reported before (White, Kirby 2001), Sierra Leone copals contain high amounts of C-18 oxygenated ent-labdane acids and labdanes (hydroxyl and methoxy groups), and C-15 oxygenated ent-labdane acids with the carboxyl group at C-18 instead of C-15, which are, if at all, present only in small amounts in the investigated Congo copals. Congo copals, in turn, are characterized by ent-labda-8(20)-en-15-oic acids, isomers thereof, labdanolic and kovalenic acids. A variety of additional compounds were identified based on their mass spectra and on data from literature (see chapter 4.2.2). A Zanzibar copal and a Copal americanum could also be attributed to *Hymeneae* resins based on their chemical composition and terminology. Together with the data from literature and the information from the historical sources, these data profiles provided a good basis for the investigation of Fabaceae resins from the Vigani Cabinet.

The last group of resins examined in the reference section were Burseraceae resins, which include a wide range of tropical and subtropical resins. As no botanical samples were available, the investigation was based on the connection of terminology and chemical composition. Phytochemical data are available from the literature, but remain fragmentary, and all materials share the commonality that their names were used as generic terms for resins from both the New and the Old World, and later also from Asia, regardless of their original geographical origin. American resins differ from Asian or African triterpene copals and elemis by the presence of low amounts of β-amyrin and higher amounts of 3α-β-amyrin, lupanes such as epi-lupeol, and 11-oxo derivatives of amyrins. Additionally, oxygenated non-acidic oleananes, ursanes, taraxastanes and lupanes may be present. The resin of *Amyris elemifera*, which belongs to the Rutaceae, is composed very similarly to *Bursera* resins and has been reported to yield copal or elemi resins (see chapter 2.3.3). The only exception among the American copals is *Protium copal* Engl., the resin of which has not been investigated so far. Its composition can only be derived by chemotaxonomical considerations from that of soft *Protium* resins. *Protium* (Asia, America) and *Canarium* (Asia, Africa) cannot be distinguished based on the present data, but they differ from other Burseraceae by high amounts of α- and β-amyrin, and characteristic compounds such as maniladiol, brein and tirucallane acids. Two African triterpene copals analysed for this work showed a highly characteristic composition and belong very likely to *Commiphora*. Although still fragmentary, these data proved to be very helpful for the identification of the materials from the Vigani Cabinet. Together with the analyses of the samples from the Vigani Cabinet, it was possible to propose a chemical composition for the majority of the materials listed in table 2.6.

Two groups of reference materials were chosen based on methodological considerations. The investigation of *Myroxylon* resins (Balsam of Peru and Tolu) was made independently from chemotaxonomical connections. Both materials have been studied in detail, but only rarely mass spectra are given. Therefore, the mass spectra of several unknown compounds found in modern reference samples were analysed. Several ester of (iso)benzyl-, dihydroconiferyl and cinnamic alcohols, ferulic, p-coumaric, benzoic and cinnamic acids could be proposed. Some of these compounds were identified in the historical samples as well.

A sample of Polish Amber was analysed by solvent extraction and GC-MS. No pyrolysis was applied, because literature indicates that most resins are well soluble in several organic solvents (Czechowski et al. 1996; Koller et al. 1997b; Yamamoto et al. 2006), and the solvent extraction scheme used in this work provided different solvents in case methanol was not sufficient (see chapter 3.1.2). This made it possible to investigate all samples within this work with the same sample preparation method. The soluble fraction of the reference amber sample was typical for Baltic amber and corresponded to literature data. Therefore, the same sample preparation was also used for the samples from the Vigani Cabinet, for which infrared spectroscopy was used in order to analyse the insoluble part of the resin. It was possible to identify three of the four materials in the Cabinet labelled as "succinum" as Baltic amber. Although the fourth, a black and glossy-brittle material labelled "succinum nigrum", showed the typical constituents in its soluble fraction as well, its infrared spectrum lacked the typical Baltic shoulder caused by the esterification of succinic acid. Fossil resins socialized with Baltic amber containing soluble but no esterified succinic acid are reported occasionally (Beck 1986). However, no similar European fossil resin is described in literature.

The reference analysis was made primarily as a basis for the investigation of the materials from the Vigani Cabinet. For three groups of resins, a botanical investigation was carried out and revealed new insights into their chemotaxonomy. The phytochemical reference system is very well suited for the identification of unknown materials.

From a methodological point of view, the materials from the Vigani Cabinet are references themselves. Consequently, chemical information from the Vigani samples in same helped to fill in the knowledge gaps that remained after the reference analysis was completed. In the case of *Pistacia terebinthus* L., the composition of the historical material is a further indication of differences between the species detectable with GC-MS. In the case of Burseracaea resins, the composition of the historical materials complemented the data profile as well: In addition to the Asian elemis, *Bursera* copals, other American *Bursera* resins and African copals from *Commiphora*, the Cabinet contains an American *Protium* copal (A/21), an African *Canarium* elemi (A/24) and two American *Bursera* tacamahaca (A/22, Z/1).

A second focus of the work was the information from a wide range of historical sources contemporary to Vigani. Several pharmaceutical, chemical and botanical works from the 17th and 18th century as well as encyclopaedic sources were consulted on terminology, botanical and geographical origin, manufacture, trade and properties of the materials traded at that time and found in the Cabinet. Multifarious information was compiled and contributed in a significant way to the historical-cultural and archaeological investigation of the samples and of natural resins in general. The historical classification and definition of "resin" and the connected "gum" influence the perception of resins until today. Additionally, the contemporary material classification is reflected in the drawers of the Cabinet.

At the time of Vigani, and favoured by the social developments of the time, a wide range of scientific studies was published, together with new standard and encyclopaedic works. As a result, it was possible to compile a complex mixture of information about the materials from the Vigani Cabinet. For the European materials, knowledge was quite comprehensive, while for exotic materials data were sometimes based reports that are 200 years old. Particularly in case of exotic plants, an individual tree was often described, while it is known today that several different species yield the related material. Apart from the lacking binominal nomenclature, the researchers often adopted endemic names, which were used by the natives for either the plant, various plants, or their resins (for example "jatoba", "icicariba", "copaiba" and "copal"). The compilation of information often revealed the historical development, for example for the "turpentines" and the development of the generic terms "copal", "anime" and "elemi" through language and trade. Materials from the Pacific regions are remarkably absent, while trade with America was frequent. This may be because the East Indian trade had just started or because the lack of knowledge about materials from that region. Only few hints that materials from Pacific regions appeared in Europe were found, and if they did so, it was under varying names and often not connected to that region. A soft "oriental copal" from "New Spain" or "Grandes Indes" is mentioned, which flows from the bark of the tree like "Vine yields it’s Water" (see chapter 5.3.3). Another "elemi verum" is described as a uniform white substance like wax with a smell of fennel (see chapter 5.3.4). Both descriptions resemble Manila elemi, which was in trade from the 14th century on, although under different names (Tschirch 1935a: 265). Without the historical information a definite identification result oftem would not have been possible, for example, for "Elemi", "Gum copal", "Gum animi" and " Venic. Turpent." (A/24, A/21, A/5, 1/11).

Based on these considerations and the chemotaxonomical analyses, what new insights on the materials from the Vigani Cabinet could be gained?

Conifer turpentines

The Vigani Cabinet contains seven so-called "turpentines", semi-liquid to liquid resins, six of which originate from conifer species. Based on the chemotaxonomical investigations of Pinaceae resins and information from historical sources about these widely used materials, a detailed picture of 17th and 18th century nomenclature of Pinaceae "turpentines" was obtained. It is characterized by high variability, great geographical differences and frequent adulterations. The main reason for this is the slow disappearance of the original "true turpentine" from the market and its replacement by local resins. At the time of Vigani, the term "Strasburg turpentine" was mainly used in England. The material was attributed to the silver fir and traded through Amsterdam. It became rare towards the middle of the 18th century. In continental Europe the material from the silver fir was mainly used as a substitute for the rare "true turpentine", from a *Pistacia* species. In this context it was also called "Venice turpentine". "Venice turpentine", on the other hand, was a generic name, used at different times for different materials. Because the name was originally a synonym for the "true turpentine", it was nearly synonymous to "fine turpentine" or "turpentine" of best quality. The name of the botanical source, "terebinth", and the place of its trade were transferred to high quality "turpentines". Substitutes were local coniferous resins from larch, fir, pine and spruce. The connection of the name to a geographically and botanically specific product disappeared during the 17th century, which in turn resulted in a shift in the botanical sources used for the production of "fine and common turpentines". Trees that were only used as a substitute before – larch and fir – became sources for "fine turpentines". This slow change in the material's properties was accompanied by frequent adulteration, in particular for the widely used "Venice turpentine". This situation is reflected in the materials found in the Cabinet: the "Terebin. Strasb." (1/8) is a *Pinus* resin, very likely an adulteration from southern France. Several other "turpentines" from the Cabinet are composed identically, including the (adulterated) "Venice turpentine" (1/10) and "Tereb E Chio" (1/13). Another "Venic. Turpent." (1/11) is a mixture of larch and fir resin. "Tereb E Chio" (1/13), which should be a *Pistacia* resin, is adulterated with pine, while the related "Cyprus turpentine" (1/14) is obtained from a *Pistacia* species, probably *Pistacia terebinthus* L. "Cyprus or Chios turpentine" were the contemporary names of the resin from the "terebinth", from which the name "terebinthina" is derived. At the time of Vigani, the botanical name was "*Terebinthus vulgaris* C.B.", which was classified as *Pistacia terebinthus* L. Because *P. atlantica* Desf. was described much later and not investigated in this work, it cannot be excluded as a botanical origin of historical Pistacia turpentine. Although several of the "turpentine" samples were adulterated, only one was a mixture, for which a high-priced resin (silver fir) was cut with a "common turpentine", in this case made from larch (1/10).

The samples from the Cabinet were presumably stored indoors and in the dark within the Cabinet. Aging characteristics of the "turpentines" were compared to light-aged reference samples. Dried-up materials from the Cabinet contained only small amounts of C-15 oxygenated but higher amounts of C-7 oxygenated abietane acids. 15-hydroxy-dehydroabietic acid is therefore an intermediate and is, according to the literature, further oxygenated to 7,15-dihydroxy-dehydroabietic acid (van den Berg et al. 2000). An apropriate dihydroxy-dehydroabietate was identified in several reference materials and samples from the Vigani

Cabinet. 7-oxo-dehydroabietic acid is present in high amounts in all-dried-up materials. Possible light-aging markers (A19, A27, A36, A37, A43) and 7-oxo-15-hydroxy-dehydroabietic acid are present in medium amounts as well. Samples taken from the bulk were less aged. This was also characteristic for the Pinaceae resins from the Cabinet: Although still sticky and with a resinous smell, they were all in an advanced aging state with significant amounts of aging markers from all oxidation states present. The main differences between dried-up and sticky samples were the relative amounts of the present aging markers. The only exception is "Venic. Turpent" (1/11), a mixture of European larch and silver fir resin. Both samples, taken from the bulk and from dried-up residuals, contained higher amounts of aging markers of oxidations state 3 and 4 but lower amounts of oxidation state 5 compared to the other conifer "turpentines" from the Vigani Cabinet. A similar phenomenon was observed for pure larch resins from the reference analyses, which indicates that different aging characteristics result from the presence of the larch resin.

Burgundy pitch

The investigation of Burgundy pitch or "Pix Burgundica" revealed a significant difference between literature and the investigation results. It must be noted that the repeated mentions of *Picea abies* Karst. as the botanical origin of modern Burgundy pitch very likely trace back to the original Burgundy pitch, which was, according to historical sources and the analysed material from the Vigani Cabinet, indeed made from that species, while modern materials originate from pines. The reason is a decline of the industry from the end of the 19th century on and its transfer to America (Langenheim 2003: 321). For both modern and historical Burgundy pitch, slight melting or heating is mentioned during production, which is also reflected in the chemical composition. A slightly isomerised abietane acid composition and low amounts of oxygenated acids are the result of a heating process, while removing the volatile fraction decreases the isomerisation process of the abietane acids.

"Sandaracha" or juniper resin

The Vigani Cabinet contains a "sandaracha" obtained from *Tetraclinis articulata* Mast., although a tree of this name or its basionym are not mentioned in the consulted sources. Instead, several "junipers" and "small cedars" were connected to "sandaracha" resin. Consequently, it is often simply called "juniper gum", which is, however, very likely a trade name. Due to the geographical origin of the Sandarac cypress, the right botanical source or its protionym would very likely only be mentioned in Portuguese and Arabian sources.

"Mastic and Pistacia turpentine"

Pistacia resins are represented by a "mastiche" (A/11) and a "Cyprus turpentine" (1/14). Both contain typical triterpenes with an oleanane, tirucallane and dammarane skeleton. Mastic is an old resin and has been in use since ancient times. "Therebintina" or "Cyprus turpentine" was apparently used as a "fine turpentine" for several high-quality purposes for a long time. Assumed it was harvested always at the same place, it is not apparent from the historical sources consulted in this work why it became rare during the 16th century. In contrast to mastic, a protection of its botanical source and supervision of the harvesting is not reported.

"South American balsam resins"

A Copaiba balsam from the Cabinet was obtained from a *Copaifera* species and imported from South-America. The type species of contemporary Copaiba balsam was *Copaifera officinalis* L. described by Linné some years after Vigani’s death. This is, however, very likely not the botanical source of the "Balsam Capivi" (1/4) found in the Cabinet. This supports the assumption that several different species of the genus *Copaifera* were described by Piso, Marcgrave and later Jacquin, which were merged into one by Linné despite being botanically different.

Other South American balsam resins present are two "Bals Peru" (1/31, 2/1) and one "Balsamum Tolutanum" (Z/17), the latter a solid material in a coconut shell. All were identified as the resin of *Myroxylon balsamum* var. *pereirae*, which is the source of Balsam of Peru. The trade in shells and gourds is mentioned in historical sources for both, a dry and solid sort of Balsam of Peru and for Balsam of Tolu, so the "Balsamum Tolutanum" was probably mistaken for Balsam of Tolu. A third sort, white Balsam of Peru, mentioned at the time of Vigani and onwards well into the 19th century, is not found in the Cabinet. Two botanical sources are mentioned for historical Balsam of Peru, but one of them, which was placed in South-America by contemporary authors, may be based on incorrect information. The material is only occasionally related to Peru, and if so, the region is mentioned as the origin of the material or its botanical source and not as a trading place.

"Copal, anime, elemi, and tacamahaca"

The Vigani Cabinet does not contain Asian conifer copals such as Manila or Kauri copal. African copals were unknown at the time of Vigani. There were, however, several African resins mentioned under differing names, including "anime", "cancanum" and "elemi". The Cabinet contains a "Gum Animi" (A/5), which, according to its chemical composition, belongs to the Fabaceae, and which is identical to what is nowadays called Sierra Leone copal. Additionally, both the East and the West African coast are mentioned as places of origin of the "oriental anime", and can be considered as the first places of origin of resins bearing this name. The name probably derives from Greek names for related materials from Africa. Later on, the name was transferred to South American materials of similar properties by the Portuguese, who called at West Africans ports in their East Indian trade. The most probable botanical origin of the related South American resin is *Hymenaea courbaril* L., which is, however, not found in the Cabinet. Other *Hymenaea* species may be potential botanical sources as well, which would explain the confusing contemporary descriptions of soft "copals" and hard "animes". Apparently, the term "anime" was transferred to American resins, where it began to overlap with resins also called "copal", a confusion, which was then transferred back to the old world, insofar as resins formerly called "anime" were now labelled "copals".

In contrast to the contemporaries of Vigani, at the beginning of the 20th century Tschirch derived the term "anime" from the African "elemi". The term is of old-world origin, originating from Greek "elaia" or "elea", which is derived from its presumed botanical source, an "olive-tree". The geographical origins of contemporary African "elemi" and "anime" partly overlap, and the botanical sources of both were unknown. Only the "olive tree" yielding "elemi" was described to some extent. However, "elemi aethiopicum" and "oriental anime" had differing properties, the former being soft and sticky, the latter rather hard and dry. The confusion of the two terms very likely occurred later in America, where they were used for several new resins which had properties similar to their old world analogues.

The connection is reflected in the modern terminology of American resins. Both elemi and the by now rarely used anime are now related to the same botanical genus, American soft *Protium* resins. This was not the case at the time of Vigani, when only "elemi" was clearly mentioned in connection with several South American species now classified into the genus *Protium*. Furthermore, the term "elemi" was transferred to Asian resins obtained from *Ca-*

narium species, which are composed very similarly to those of *Protium* species. An "Elemi" (A/24) was assigned to an African *Canarium* species because the historical information about the package of "elemi aethiopicum" corresponds to that from the Cabinet. As discussed above, *Canarium* and *Protium* resins are, however, nearly indistinguishable, and, based on the chemical composition, an American *Protium* species cannot be ruled out.

Resins called "copal" originated from America at the time of Vigani. The word is derived from the Nahuatl word for incense. The related trees are described by Hernandez as the copal-bearing trees ("copalliferae arbores"). In contrast to the modern Mexican copals purchased for this work the "Gum copal" (A/21) from the Vigani Cabinet shows a composition very similar to that of *Protium* resins. Therefore, at least one of Hernandez' copal-treesis a *Protium* species, which corresponds to modern references about *Protium copal* Engl., the only source of Mesoamerican copals from the genus *Protium*. Some of the others are *Bursera* species, which are the other main source of modern Mesoamerican copal resins. An anime resin found in the reference collection of the Academy of Fine Arts in Dresden was a *Bursera* resin as well, which confirms the mention of historical "anime" to one of the "copalliferae arbores". While the transfer of the old world terms "anime" and "elemi" to the new world was apparently at an advanced stage, this was not the case for "copal".

A resin that has nearly vanished today because it was mainly used for medical purposes is "tacamahaca". Neither the modern tacamahaca nor the two samples from the Cabinet originate from *Protium heptaphyllum* March., which is mentioned occasionally in modern literature as the botanical source. The botanical source of the samples from the Vigani Cabinet is a *Bursera* species (A/22, Z/1). The related tree is also mentioned to be used for the production of the resin in Madagascar. Later on, the term was transferred to several botanically different Asian resins. At the time of Vigani, however, only one tree, a *Bursera* species, was used for the production of different sorts of "tacamahaca",.

Amber

The Vigani Cabinet contains four materials labelled "succinum" and designated according to their different colours, although three are of the same appearance. Three of these four materials are Baltic amber, the fourth is a black material similar to "jet", to which it also has a terminological connection. However, the soluble fraction of this material was similar to Baltic amber, while its infrared spectrum lacked the Baltic shoulder. This was not the case for a "L. Gagatis" (F/13), which is the contemporary name of "jet". The terminological connection originates from the similar appearance and very likely from common deposits, but not from a chemical relation. Amber was at the time of Vigani thought to be a mineral, and was therefore placed in the same drawer as arsenic, sulphur and cinnebar. The different colours were indications for the quality.

In sum, the work presented here shed light on the historical dimension of the correlations between terminology, chemical composition and taxonomy, which in turn improves the identification of unknown resinous materials from different epochs and in mixtures.

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Appendix

Investigated materials from the Vigani Cabinet

Inv#	Transcription	Old inventory	Invoices
A/5	5. G. Anime	Gum Animi Exudation of Boswellia Frereana	Gum Annimi
A/11	II Mastiche	Mastiche A resin from the Lentisk-Pistacia Lentiscus L.	Gum Mastich
A/21	21. Gum Copal	Gum Copal. Resinous Gum from New Spain	Gum Copall
A22	22. Tacamahaca	Taccamahaca	Gum Taccemhac
A/23	23 Pix Burdundica	Pix Burgundica. Pinus Abies. Norway Spruce Fir.	Burg pitch
A/24	?4 ?m. Elemi	Gum Elemi. Resin from Canarium Commune	Gum Elemi
A/26	26. Sandaracha	-	Gum Juniper
E/13	Succinum Citrinum 13.	-	Succ: Citr
E/14	Succinum flavan 14	Succinum Slavon.	-
E/15	Succinum albam 15.	-	Succ: Alb
E/16	Succinum nigram 16.		-
F/13	13 L. Gagatis Lap.	Lap Gagati. Jet	-
Z/1	10. Tacamahaca	Taccanihacca Resin [later changed to Taccamahacca]	Tacamahacca opt.
Z/17	11 Balsam Tolutanum	Balsamum Tolutarum [later changed to Tolutanum]	Bals Tolu
1/4	Balsam Cipivi 2oz	Bals Capivi. 28	Bals Capivi
1/8	Terebin. Strasb. 2oz	Terebinth Strsb.	Tereb Strass
1/9	Tereb[..] Com 2oz	-	Com Tereb
110	Venice Turpentine 2oz	Venice turpentine.	Tereb venetiae
1/11	Venic Turpent. 2oz	Venice Turpentine.	Tereb venetiae
1/13	Tereb E Chio 1oz	Terebinth Chio.	Tereb E. Chio
1/14	Tereb i E Cypri [.]oz	-	Tereb Cypria
1/31	Bals Peruv (or: Peruo) 2[.]	Bals Peruv.	Bals Peru
2/1	1 Bals Peru	-	Bals peru
La2/7	not labelled	-	-

Annotated list of historical literature

The table lists most of the used historical sources used in chapter 5 with author(s), title, year of publication, which is not necessarily the year of the first edition, publisher and place of publication. It gives a short comment about the scientific background of the author(s) and the characteristics of the content or publication history of the related book. It does not aim a complete compilation of the used literature but a short annotation of charactistic features, which helps to understand the information given in chapter 5.

Author	Title	Year	Publisher	Place	Language	Notes
Aublet, Jean Baptiste Christian Fusée	*Histoire des plantes de la Guiane Francoise*	1775	P. F. Didot	London, Paris	French	French botanist and pharmacist; the book was based on a herbarium from French Guiana, it was published in two volumes, the second one with plates.
Bauhin, Casper	*Pinax theatri botanici*	1623	Sumptibus & typis Ludovici Regis	Basel	Latin	Bauhin was one of the pioneers of botany and concluded with a new development of botanical nomenclature, physiognomy and classification. He introduced many genera, which were later adopted by Linné.
Bauhin, Johann; Cherler, Heinrich	*Historia plantarum universalis*	1650 - 1651	Dominik Chabree & Franz Ludwig von Graffenried	Yverdon-les-Bains	Latin	Brother of Casper Bauhin, published a three volume compilation of botany.
Chambers, Ephraim	*Cyclopaedia, or, An universal dictionary of arts and sciences*	1728	J. and J. Knapton and [19] others	London	English	Creator of one of the first encyclopaedias, which was based on that of Harris (see below) and was in turn the basis for Diderot's and d'Alembert's *Encyclopédie*; in two volumes, some of the pages are double numbered in round and square brackets.
Dale, Samuel	*Pharmacologia seu maneductio ad Materiam Medicam*	1693	Samuel Smith & Benjamin Walford	London	Latin	English physician and botanist, was friend with John Ray; the first edition was published in 1693, the enlarged 4th edition with German, Dutch and French indices in 1739 in Leiden; in contrast to other authors, the book was not arranged after the materials, but the plants, from which these materials were derived.
Desfontaines, René Louiche	*Flora Atlantica*	1799	L. G. Desgranges	Paris	Latin	French botanist; after a two year expedition to Tunesia and Algeria he published the *Flora Atlantica* with about 300 species, which had not been described before; two volumes, both with plates.

Author	**Title**	**Year**	**Publisher**	**Place**	**Language**	**Notes**
Dodoens, Rembert	*Stirpium historiae pemptades sex sive libri XXX*	1616	Balthasar and Johannes Moretos	Antwerp	Latin	Flemish physician and botanist, also known as Rembertus Dodonaeus; the book is the Latin translation of his herbal *Cruydeboeck* from 1554, the first edition was published in 1583.
Dossie, Robert	*The handmaid to the arts*	1758	John Nourse	London	English	English scientist (chemistry, pharmacy, agriculture, arts), also an extensive writer and translator of medical works.
Dossie, Robert	*The elaboratory laid open*	1758	John Nourse	London	English	
Fragoso, Juan; Spachii, Israelis	*Aromatum, fructuum, et simplicium aliquot medicamentorum ex India utraque, et orientali et occidentali*	1601	Iodocus Martinus	Strasbourg	Latin	Garcia de la Orta’s book about drugs and medicine from India, *Colóquios dos Simples e Drogas e Cousas Medicinais da Índia*, from 1563, published in Goa, was translated by Fragoso into Spain, and by Spachii into Latin.
Geoffroy, Etienne-François; Bergier, Antoine	*Traité de la matiere medicale*	1743	Jean de Saint and Charles Saillant	Paris	French	French chemist, physician and pharmacist; based on his lectures the *Tractatus de Materia medica* was published 1741 posthum in 7 volumes. In 1743 it was translated into French. It contains analyses’ results obtained by distillation for each material.
Geoffroy, Etienne-Francois; Thicknesse, Ralph	*A treatise on foreign vegetables*	1749	Clarke, C. Davis, J. Wiston, S. Baker	London	English	A partial translation of the *Traité de la matiere medicale* by Thicknesse (1719–1790) covering only the exotic drugs.
Hernández, Francisco	*Nova plantarum, animalium et mineralium mexicanorum historia*	1651	Vitalis Mascardi	Rome	Latin	Spanish physician and naturalist; the results of the seven years expedition to New Spain were published posthumously in different compilations. Based on the edition of Nardo Antonio Recchi, Johannes Schreck and Fabio Colonna published an impression in Rom in 1648.

Author	Title	Year	Publisher	Place	Language	Notes
Hill, John	*A history of the Materia Medica*	1751	T. Longman ad [4] others	London	English	English writer, botanist and physician; his *History of the Materia Medica* is a comprehensive and detailed work on medicines and drugs from all over the world.
Jacquin, Nikolaus Joseph	*Enumeratio systematica plantarum*	1760	Theodorum Haak	Leiden	Latin	Austrian botanist and chemist; made a six year expedition to West India to collect exotic plants; the *Enumeratio* is a short work, in which various plants from the Caribbean islands are listed.
Jacquin, Nikolaus Joseph	*Selectarum stirpium Americanum Historia*	1763	Ex officina Krausiana	Vienna	Latin	Most of the plants mentioned in the Enumeratio (see above) are described more detailed, the second volumes with plates.
James, Robert	*Pharmacopoeia universalis*	1747	J. Hodges and J. Wood	London	English	English physician, also known for *A medicinal dictionary* (3 volumes).
Krünitz, Johann Georg	*Oekonomische Encyclopaedie*	1773-1858	Several	Several	German	German encyclopedist, physician and translator; he started the 242-volume work and completed 72 volumes thereof. The following volumes were written and published by different authors and publishers, see www. *kruenitz1.uni-trier.de.*
Lemery, Nicolas	*Dictionnaire ou Traité Universel des Drogues simples*	1714	Laurent D'Houry	Paris	French	French chemist and pharmacist; known for the development of an acid-base theory and the *Cours de Chymie* from 1675; the first edition of the *Traité universel des drogues simples* was published in 1697, the second edition in 1714.
Lemery, Nicolas; Richtern, Christoph, Friedrich	*Vollständiges Materialien-Lexicon*	1721	J. F. Braun		German	Translation of the third French edition Dictionaire ou traité universel des drogues simples published in 1717 in Amsterdam.
Lewis, William	*An experimental history of the materia medica*	1761	H. Baldwin	London	English	English physician and chemist; known for works about the application of chemistry to the improvement of the practical arts.

Author	Title	Year	Publisher	Place	Language	Notes
Linné, Carl von	*Species plantarum*	1753	Laurentius Salvius	Stockholm	Latin	Swedish botanist, zoologist and physician, also Carl Linnaeus; in 1735 he published a new system for classifying plants, the *Systema Naturae*. In 1753 a short description of plant species was published, which was linked by Linné to the 5th edition of the *Genera plantarum* published one year later, which made it the starting point of modern plant taxonomy; a second edition was published 1762, four additional editions followed.
Linné, Carl von	*Mantissa plantarum*	1767	Laurentii Salvii	Stockhom	Latin	Linné's disciples collected new plants according to his system, the Mantissa was a supplement of the 12th edition of the *Systema Naturae* containing many of those specimen.
Manget, Jean Jacques	*Pharmacopoea Schrödero-Hoffmanniana*	1687	Philipp Andrea	Cologne	Latin	Swiss physician (1652-1742), compiler of previous medical works; the book is a compilation of drugs and medicines based on the standard work of the German physician Johann Schröder (*Artzney-Schatz*)
Monardes, Nicolás; de L'Ecluse, Charles	*Simplicium medicamentorum ex novo orbe*	1579	Plantin	Antwerp	Latin	Spanish physician and botanist, also active as a trader; he described the goods arriving from the New world in three volumes, the first edition *Historia medicinal de las cosas que se traen de nuestras Indias Occidentales*, published in 1569, was translated into English by John Frampton and further into Latin by Charles de l'Écluse.
Miller, Phillipp	*The Gardeners Dictionary*	1731 to 1769		London	English	Scottish botanist; the Gardeners Dictionary was a widely cited work on plants cultivated in England

Author	Title	Year	Publisher	Place	Language	Notes
Piso, Willem; Marcgrave, Georg	*Historia naturalis Brasiliae*	1648	Francisus Hackius (1st) Ludovico and Daniel Elzevirios (2nd)	Leiden (1st) Amsterdam (2nd)	Latin	Dutch physician and German naturalist (also Georg Marggraf); the book compiles the results of the eight-years expedition to Brazil started in 1638, the second edition as *De Indiae utriusque re naturali et medica* in 1658, both editions resemble modern multiple authored work with separate contents and subtitles.
Plukenet, Leonard	*Phytographia*	1691-1692	T. Davies and [4] other	London	Latin	English botanist; compiled a herbarium covering 8.000 specimen and published within the *Phytographia* 2.700 drawings of rare and exotic plants in four volumes.
Plukenet, Leonard	*Almagestum botanicum*	1696		London	Latin	An alphabetical catalogue of about 6.000 plants.
Pomet, Pierre	*Histoire general des Drougues*	1694	Baptiste Loyson, Augustin Pillon, Estienne Ducastin	Paris, Palais	French	French pharmacist; first edition, a revised edition from 1935 was published in Paris. In 1717 a German translation titled *Der aufrichtige Materialist und Specerey-Händler* was published.
Ray, John	*Synopsis methodica Stirpium Britannicum*	1690	Samuel Smith	London	Latin	Important English botanist, introducted empirism into the botanical classification; the book is an overview over British plants.
Ray, John	*Historia plantarum*	1693	Samuel Smith, Benjamin Walford	London	Latin	The first edition was published in 1686 and 1688 (two volumes) and 1704 (volume 3, with plates), which was still unavailable when 1693 a new edition of the first two volumes was published.
Salmon, Guilielmus William	*Polygraphice. or The arts of drawing*	1701	Churchill & Nicholson	London	English	A self-educated English writer about medicine and pharmacy; the work also includes perfumery, make-up, prophecy and alchemy.

Author	**Title**	**Year**	**Publisher**	**Place**	**Language**	**Notes**
Savary des Brûslons, Jacques; Savary, Philémon-Louis	*Dictionnaire universel de commerce*	1723	Jacques Estienne	Paris	French	General inspector of the royal manufactures in Paris; the *Dictionnaire* was first published in 1723, the third edition in 1748, with translations into English and German.
Schröder, Johann	*Pharmacopoeia Medico-Chymica*	1644	Johann Gerlin	Ulm	Latin	German physician; published a widely distributed standard work on drugs with 14 editions in Latin, and translations into German, English and French.
Tschirch, Alexander	*Die Harze*	1935-1936	Bornträger	Berlin	German	German pharmacist and Professor for pharmacy in Bern; studied pharmacognosy, the *Harze* are a four volume work on a wide range of natural resins including several rare and exotic materials
Zwinger , Theodor	*Compendium Medicinae Universae*	1748	J. R. Thurnisios	Basel	Latin	Probably Theodor Zwinger the third, a Swiss physician; the book is oriented in content more towards the 17th century.

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Compound lists

In the following all compounds found in this work are listed according to their chemical structure (see also chapter 3.1.4). They are given with the label used in the work, their name, and main mass fragments. Labels ma0kred with an asterisks indicate compounds, for which a mass spectrum is given in the section below (‘Atlas of mass spectra’). For all identified compounds the used literature is given in square brackets and listed at the end of the section. The notation t_R indicate compouds, for which no mass spectrum is published, but the related mass spectrum of the methylated derivative and the relative retention time and elution order as well as similarities of the fragmentation pattern were used for identification. Finally, whenever necessary, the identification is commented.

Monoterpenes

Label	Name	Main mass fragments	Ref.	Comments
M1	p-Cymene	53, 77, 91, **119**, 134	[1]	
M2	m-Cymene	53, 77, 91, **119**, 134	[1]	
M3	l-Fenchone	53, 69, **81**, 109, 152	[1]	
M4	Fenchol	55, 67, 80, **81**, 93, 107, 121, 154	[1]	
M5	Camphor(+)	55, 67, 81, **95**, 108, 137, 152	[1]	
M6	Isoborneol	55, 67, 79, **95**, 121, (154)	[1]	
M7	Borneol	55, 67, 79, **95**, 121, (154)	[1]	
M8	Bornylformate	67, 93, **95**, 121, 136, (182)	[1]	
M9	Bornylacetate	93, **95**, 121, 136, 196	[1]	
M10	Unidentified	**71**, 79, 91, 100, 109, **111**, 126, 137, 147, 178	[1]	
M11	Unidentified	55, 69, **98**, **111**, 126, 168	[1]	
M12	α-phellandrene dimer	77, **92, 93**, 105, 119, 136, 159, 183, (272)	[54]	In [54] seven isomers are described, characteristic peaks are at m/z 92, 93, 136 and MW 272
M13	α-phellandrene dimer	77, 92, **93**, 105, 119, 136, 159, (272)	[54]	See M12
M14	α-phellandrene dimer	77, 92, **93**, 105, 119, 136, 157, 165, 227, 272	[54]	See M12
M15	α-phellandrene dimer	77, 92, **93**, 105, 119, 136,(272)	[54]	See M12
M16	α-phellandrene dimer	77, 92, **93**, 119, 136, 229, 257, 272	[54]	See M12
M17	α-phellandrene dimer	77, 92, **93**, 105, 119, 136, 157, 228, 272	[54]	See M12
M18	α-phellandrene dimer	81, 91, **92**, 93, 95, 105, 119, 137, 173, 185, 228,	[54]	See M12
M19	α-phellandrene dimer	77, 92, **93**, 105, 121, 136	[54]	See M12
M20	α-phellandrene dimer	77, 92, **93**, 105, 119, 136, 157	[54]	See M12

Sesquiterpenes

Note: Because it was not possible to determine the exact elution order of several sesquiterpene measured with different temperature programs, they were numbered according to the chapters, they are presented in.

Label	Name	Main mass fragments	Ref.	Comments
Chapters 4.2.1 and 4.4				
S1	α-Copaene	91, **105**, 119, 161, 204	[1]	
S2	β-Elemene	79, **93**, 105, 119, 147, 161, 189, 204	[1]	
S3	δ-Selinene	91, 105, 119, 133, 161, 189, **204**	[1]	
S4	Cyperene	79, 91, 105, 119, 133, 161, 189, **204**	[1]	
S5	trans-β-Caryophyllene	79, **91**, 93, 105, 133, 161, 204	[1]	
S6	Dihydro-ar-curcumene	91, 105, **119**, 179, 204	[23]	
S7	trans-α-Bergamotene	79, 93, **119**, 204	[1]	
S8	α-Humulene	79, 80, **93**, 105, 121, 204	[1]	
S9	γ-Muurolene	91, 105, 119, **161**, 204	[1]	
S10	β-Selinene	**79**, 93, 105, 119, 133, 161, 189, 204	[1]	
S11	Probably valencene	79, 93, **105**, 119, 161, 189, 204	[1]	
S12	β-Bisabolene	67, 79, **93**, 119, 161, 204	[1]	
S13	Unidentified sesquiterpene	79, 91, 105, 119, **161**, 189, 204	[1]	
S14	α-Selinene	79, 93, **105**, 119, 161, 189, 204	[1]	
S15	Calamenene	91, 115, 129, 144, **159**, 174, 187, 202	[1], [23]	
S16	Unidentified sesquiterpene	55, 82, 95, **111**, 123, 161, 179, 189, 204, 220	[1]	
S17	Cadina-1(10),6,8-triene	83, 131, 145, 159, **187**, 202	[1]	
S18	Palustrol	55, 67, 82, 93, **111**, 123, 133, 151, 161, 179, 204, 207, 222	[32]	
S19	δ-Cadinene	91, 105, 119, **161**, 204	[1]	

S20	Unidentified	67, 79, **93**, 105, 121, 161, 189, 204		
S21	Caryophyllene oxide	**79**, 91, 93, 105, 220	[1]	
S22	Unidentified sesquiterpene	67, 83, 95, 123, 161, **207**, 222	[1]	
Chapter 4.2.3				
S23	Cadina-3,9-diene (β-cadinene)	91, **105**, 119, 133, 147, 161, 189, **204**	[1]	
S24	Unidentified sesquiterpene	79, **91**, 105, 119, 133, 147, 161, 189, 204	[1]	
S25	Unidentified sesquiterpene	91, **105**, 107, 119, 133, 147, 161, 189, 204	[1]	
S26	trans-Nerolidol	67, 79, 81, **93**, 107, 121, 161, (222)	[1]	
Chapter 4.3.2				
S27	Elemol	59, 67, 79, **93**, 107, 119, 133, 161, 189, 204, (222)	[1]	
S28	γ-Eudesmol	59, 81, 91, 105, 119, 133, 147, **161**, **189**, 204, 222	[44]	
S29	β-Eudesmol	**59**, 79, 81, 93, 107, 121, 149, 161, 189, 204, 222	[1], [44]	
S30	Unidentified sesquiterpene	**59**, 79, 81, 93, 107, 121, 149, 161, 189, 204, 222		Probably eudesmol isomer
S31	Unidentified sesquiterpene	79, 93, 119, 146, **159**, 187, 202, 220		Probably a dehydro-eudesmol
S32	Unidentified sesquiterpene	79, 93, 105, 119, 133, **159**, 187, 202, 220		Probably a dehydro-eudesmol
S33	Unidentified sesquiterpene	59, 91, 105, 119, 131, **159**, 187, 202, 220		Probably a dehydro-eudesmol
S34	Unidentified sesquiterpene	59, **93**, 105, 121, 147, 159, 177, 187, 202, 220		Probably a isomer of eudesmol
S35	Unidentified sesquiterpene	**59**, 79, 91, 105, 119, 147, 162, 177, 187, 202, 220		Probably a isomer of eudesmol

Diterpenes and diterpenoids including compounds derived from diterpenes by degradation

Label	Name	Main mass fragments	Ref.	Comments
D1	1,5,6-Trimethyl-1,2,3,4-tetrahydro-naphthalene	91, 115, 128, 131, 145, **159**, 174	[1], [23],	
D2	1,1,5,6-Tetramethyl-1,2,3,4-tetrahydro-naphthalene	119, 131, 145, 159, **173**, 188	[23], [31], [32]	
D3	Unidentified diterpene	91, 115, 128, 131, 143, 145, 158, **173**, 186	[1]	
D4	1,2,3,4-Tetrahydro-1,5,6-trimethyl-1-naphthalenecarboxylate	91, 115, 128, 145, 158, **173,** 185, 232	[30], [31]	
D5	Unidentified diterpene	67, 79, 95, 107, 119, 135, **191**, 207, 222	[1]	
D6	Cembrene	79, **93**, 105, 119, 145, 229, 257, 272	[1]	
D7	Iso-cembrol	81, **93**, 107, 121, 147, 189, 229, 257, 272, 290	[1]	
D8	Unidentified	**67**, 81, 95, 109, 123, 135, 191, 207, 235	[2]	Probably a labda-13,14-8-ol: mass spectrum similar to abienols, no molecular ion or $[M-H_2O]^+$ visible; typical peaks at m/z 235, 207, 191 (loss of the side chain), 123 and109
D9	10,18-bisnorabieta-5,7,9(10,11,13)-pentaene	55, 67, 91, 96, 165, 181, 195, **223**, 238	[1]	
D10	Unidentified	81, 95, **109**, 121, 161, 217, 235, 245, 260, 278	[2], [36]	Probably a labda-11,13-dien-8-ol
D11	13-Methylpodocarpatrien-18-oate	91, 131, 145, 155, **211**, 227, 241, 271, 287, 301, 316	[23]	
D12	Unidentified diterpene acid	93, 133, **173**, **188**, 203, 241		
D13*	Unidentified diterpene acid, ME	95, 119, **175**, 235, 330	t_R	Methylester of D22
D14	Unidentified diterpene acid, ME	91, 145, 159, 187, 227, **241**, 256, 257, 287, 301, 316		
D15	Unidentified acid	133, 173, **188**, 203, 241, 330		
D16	Unidentified	107, 119, 138, **189**, 207, 305, 321, 336	[29]	Mentioned for Congo copal in [29]
D17	Probably ent-labda-8(20)-en-15,18-diol	95, 119, 133, **161**, 189, 207, 257	[19]	
D18	12-methoxy-podocarpa-8,9,12-trien-15-oate	159, 173, **227**, 239, 287, 302	[1]	

D19	Unidentified	81, 107, **121**, 161, 189, 257, 273, 330		
D20	Unidentified	95, 109, 135, **191**, 207, 289, 305, (320)	[28]	Very likely a labden-15-oate, no molecular ion present but probably at m/z 320 → no further functional group at ring A and B
D21	Unidentified	81, **93**, 107, 119, 133, 187, 220, 257, 305, 320		
D22*	Unidentified sandarac marker	**95**, 119, 133, 175, 220, 316	[3]	Mass spectrum without identification
D23	Unidentified sandarac marker	79, 93, **107**, 119, 135, 161, 187, 255, 315, 330	[3]	Mass spectrum without identification
D24	Podopcarpatriene acid, oxygenated derivative	121, 159, 185, **225**, 240, 268, 300	[1]	
D25	Unidentified	121, 233, 267, 287, **302**, 347, 362		
D26	Unidentified	91, **121**, 159, 189, 217, 271, 287, 314		

Abietanes

Elution order is reported in [3], [4] and [59]

Label	Name	Main mass fragments	Ref.	Comments
A1	18-Norabietatriene	117, 129, **159**,185, **241**, 256	[23]	
A2	19-Norabietatriene	117, 129, **159**,185, **241**, 256	[23]	
A3	Abietatriene	67, 79, 93, 107, 121, 159, 173, 185, 237, **255**, (270)	[30]	
A4	5β-Dehydroabietate	91, 143, 157, 183, 211, **239**, 255, 273, 299, 314	[23]	
A5*	Levopimarate	**92**, 105, **121**, 146, 187, 241, **316**	[1], [3]	
A6	Palustrate	**241**, 301, 316	[3]	
A7	Callitrisate	225, **239**, 285, 299, 314	[9]	
A8	Abiet-en-18-oate (dihydro-abietate isomer)	79, 91, 107, **121**, 215, 225, 239, 243, 259, 275, 303, 318	[1]	
A9	Tetradehydroabietate (didehydro-abietate)	197, **237**, 312	[58]	
A10	Dehydroabietate	**239**, 299, 314	[1], [58]	
A11	Dehydroabietol	117, 159, 173, 185, 211, **253**, 271, 286	[1], [23]	
A12	Abietate	185, 213, **241**, 256, 273, 316	[3]	
A13	Palustric acid	91, 133, 159, 187, 213, 241, **287**, 302	t_R	t_R in relation to the methylester A6
A14*	Levopimaric acid	**92**, 105, 131, 146, 187, 302	t_R, [3]	See text (chapter 4.1.1.1)
A15	Tetradehydroabietic acid (didehydro-abietic acid)	165, 195, **237**, 302	t_R, [58]	t_R in relation to the methylester A9, which is given in [58]
A16	7-methoxy-dehydroabietate	195, **237**, 253, 312, 344	[5], [6]	Methyl-15-dehydroabietate reported in [5]; $[M-CH_3]^+$, $[M-CH_3-CH_3OH]^+$, $[M-CH_3-CH_3OH-COOCH_3]^+$, [M-44] is missing, which is typical for the hydroxyl/methoxy group located at position C-15, cf. A23
A17	Neoabietate	121, **135**, 301, 316	[3]	

A18	Dehydroabietic acid	197, **239**, 285, 300	[3]	
A19*	7-methoxy-Δ6(7)-dehydrodehydroabietate	209, 227, **267**, 283, 327, 342	[1], [4], [18], [37]	Methoxyether of A32 (formed by methylation with TMAH) is reported in [4] and [18], as 7-methoxy-tetradehydroabietate in [37]
A20	Abietic acid	105, 131, 185, 213, 241, 259, 287, **302**	t_R	t_R in relation to the methylester A12
A21	Unidentified oxygenated abietane acid	227, **269**, 329, 344		
A22	7-hydroxy-dehydroabietate	121, 195, **237**, 253, 297, 312, 330	[1]	
A23	15-methoxy-dehydroabietate isomer	237, 269, 313, **329**, 344	[4], t_R	Mass spectrum resembles that of 15-methoxy-dehydroabietate reported in [4]; [M-H$_3$CO]$^+$ from methoxy group, [M-H$_3$CO-C$_3$H$_8$]$^+$ from propyl group → indicates a hydroxyl group is located at position C-15 and not C-7, cf. A16
A24	Oxygenated 7,13,15-abietatrien18-oate	121, 183, 239, **254**, 299, 314, 315, 329, 330	[1], [4]	
A25	Unidentified oxygenated abietane	169, 211, 225, 237, **267**, 295, 327, (342)		
A26	Unidentified abietane	163, 195, **237**, 255, 283, 297, 330		
A27*	Δ16-demethyl-7-oxo-dehydroabietate (proposed)	155, 197, 211, 239, **253**, 299, 313, 314	[1]	See text (chapter 4.1.1.2)
A28	15-hydroxy-dehydroabietate	255, 273, **315**, 330	[4]	
A29	Neoabietic acid	91, **135**, 148, 187, 241, 287, 302	t_R	t_R in relation to the methylester A17
A30*	7-methoxy-dehydroabietic acid (proposed)	181, 195, **237**, 283, 297, 315, 330	t_R	Fragmentation pattern correspond to that of A22: [M-CH$_3$-H$_2$O]$^+$, [M-CH$_3$-H$_2$O-HCOOH]$^+$, additionally [M-CH$_3$-CH$_3$OH]$^+$ is present at m/z 283, it is present in the unmethylated extracts, only → methoxyether of A22
A31	Unidentified abietane	107, 147, 229, 239, **289**, 331, 346		

A32	7-oxo-dehydroabietate	187, 211, **253**, 269, 296, 328	[1]	
A33	Unidentified	121, 199, 229, **241**, 257, 272, 289, 317, 332		
A34	Unidentified	91, 134, 185, 239, 254, 285, **300**		
A35*	7-hydroxy-dehydroabietic acid	145, 185, 195, **237**, 273, 299, 316	t_R	tR in relation to the methylester A22; fragmentation pattern corresponds to that of the methylester: $[M-H_2O]^+$, $[M-H_2O-CH_3]^+$, $[M- H_2O-CH_3-HCOOH]^+$ base peak
A36*	Unidentified hydroxy-dehydroabietate, probably a dihydroxy-compound	181, 195, 211, **249**, 264, 309, 324, 342	[18]	See text (chapter 4.1.1.2)
A37*	15-methoxy-Δ6(7)-dehydro-dehydroabietate (proposed)	213, 237, 251, **267**, 310, 311, 327, 342	[4]	Mass spectrum resembles that of A19; see text (chapter 4.1.1.2)
A38	Unidentified abietane	**187**, 225, 267, 285, 300		
A39*	15-hydroxy-dehydroabietic acid	131, 197, 237, 255, 283, **301**, 316	t_R	t_R in relation to the methylester A28: fragmentation pattern corresponds with that of the methylester: $[M-CH_3]^+$ base peak, $[M-CH_3-HCOOH]^+$, $[M-CH_3-HCOOH-H_2O]^+$
A40	7-oxo-Δ15(16)-dehydro-dehydroabietate	211, **251**, 266, 294, 326	[18], [58]	According to [58] the double bond is located at Δ5(6)
A41	Unidentified aging marker, oxygenated abietane	195, 211, **253**, 313, 328, **331**		
A42	7-oxo-dehydroabietic acid	211, **253**, 299, 314	[7], [58]	
A43*	Unidentified methoxy-dehydroabietate	59, 156, 212, 251, 255, 269, **311**, **315**, 329, 343, 358		Main peak at m/z 311 results from $[M-CH_3-CH_3OH]$
A44	Unidentified abietane	209, 239, 251, 253, **266**, 282, 310		
A45	Unidentified	185, 213, **241**, 269, 284, 301, 326, 344		
A46	7-oxo-15-hydroxy-dehydroabietate	187, 269, **329**, (344)	[4]	

(Iso)Pimaranes

Label	Name	Main mass fragments	Ref.	Comments
P_1	Δ8-Isopimarate	91, 131, 185, **241**, 257, 269, 301, <u>316</u>	[23]	
P_2	Pimaradienol	105, **131**, 145, 155, 185, 225, 243, <u>288</u>	[1]	
P_3	Δ8-pimarate	105, 185, **241**, 257, 269, 301, <u>316</u>	[23]	
P_4	Dihydro-Δ8-isopimarate	91, 187, **243**, 259, 271, 303, <u>318</u>	[1], [23]	
P_5	Pimarate	**121**, 241, 257, 301, <u>316</u>	[1]	
P_6	Sandaracopimarate	**121**, 241, 301, <u>316</u>	[3]	
P_7	Pimar-8(14)-en-18-oate (dihydro-Δ8-pimarate)	79, 95, **121**, 159, 181, 219, 229, 289, 303, <u>318</u>	[23]	
P_8	Sandaracopimarol	81, 91, 107, 121, 133, 147, 161, **257**, 273, <u>288</u>	[3]	
P_9	Pimar-7-en-18-oate (dihydro-Δ7-pimarate)	91, 121, 133, 159, **243**, 303, <u>318</u>	[1]	
P_{10}	Δ8-isopimaric acid	91, 105, 185, **241**, 269, 287, <u>302</u>	[23]	
P_{11}	Δ8-pimaric acid	91, 105, 159, 185, 241, 269, **287**, <u>302</u>	[23]	
P_{12}	Isopimarate	187, 227, **241**, 256, 287, <u>316</u>	[3]	
P_{13}	Dihydro-Δ8-isopimaric acid	91, 105, 133, 159, 187, 243, 271, **289**, <u>304</u>	[23]	
P_{14}	Pimaric acid	91, 107, **121**, 133, 241, 287, <u>302</u>	t_R	t_R in relation to the methylester P_5
P_{15}	Dihydroisopimarate	79, 93, 105, 121, 227, **243**, 259, 287, 303, <u>318</u>	[23]	
P_{16}	Sandaracopimaric acid	91, 107, **121**, 133, 241, 287, <u>302</u>	t_R	t_R in relation to the methylester P_6
P_{17}*	Methoxy-sandaracopimarate	91, 105, **121**, 159, 213, 239, 289, 299, <u>346</u>	[10]	Characteristic peaks at m/z 121 & 346 reported in [10], if only one hydroxyl group is present , MW at m/z 346 indicates methylation of both functional groups; correspond to the use of TMAH in [10], which methylates hydroxyl groups, see P_{19}
P_{18}	Isopimaric acid	91, 105, 131, 159, 187, 227, **241**, **287**, <u>302</u>	t_R	t_R in relation to the methylester P_{12}

P19*	Hydroxy form of sandaracopimarate	91, 105, **121**, 239, 255, 299, 314, 332	[10], t_R	Methoxyether see P17
P20*	12-acetoxy-sandaracopimarate	93, 105, **121**, 131, 239, 255, 299, 314, (374)	[10]	
P21*	12-acetoxy-sandaracopimaric acid (proposed)	91, 119, **134**, 157, 185, 239, 285, 300, 360	t_R	t_R in relation to the methylester P20

Phenolic abietatrienes

Label	Name	Main mass fragments	Ref.	Comments
Ph1	Methoxyether of phenolic abietatriene	189, 203, 215, 243, **285**, 300	[1]	
Ph2	Methoxyether of ferruginol	189, 203, 215, 243, **285**, 300	[1], [13]	See text (chapter 4.1.2)
Ph3	Methoxyether of totarol	**189**, 203, 215, **285**, 300	[1], [13]	See text (chapter 4.1.2)
Ph4	Unidentified phenolic abietatriene	175, 189, 201, **271**, 286		
Ph5	Totarol	175, 189, 201, 253, **271**, 286	[1], [14]	
Ph6	Unidentified phenolic abietatriene	159, 185, **202**, 213, 227, 269, 284		
Ph7	Ferruginol	175, **189**, 201, 253, **271**, 286	[1], [14]	
Ph8	Unidentified phenol (probably hinokinone)	197, 203, 215, **267**, 285, 300	[1]	
Ph9	Abieta-8,11,13-triene-one	197, **267**, 285, 300	[1]	
Ph10	Unidentified phenolic abietatriene	157, 199, **227**, 269, 284, 302	[1]	
Ph11	Unidentified phenolic abietatriene	157, 173, 199, 215, 243, **269**, 285, 300		
Ph12	Totarolone	215, 243, 257, **285**, 300	[1]	
Ph13	Methoxyether of sugiol	177, 219, 257, **299**, 314	[1]	
Ph14	Unidentified phenolic abietatriene	213, 243, **285**, 300	[1], [3]	
Ph15	Unidentified phenolic abietatriene	201, 213, 243, **285**, 299, 300	[1]	
Ph16	Unidentified phenolic abietatriene	175, 227, **269**, 287, 302		
Ph17	Hinokinol	199, 227, **269**, 302	[1]	
Ph18	Sugiol	203, 217, 243, **285**, 300	[1]	

Labdanes

Elution order is reported in [11], [12] and [29]

Label	Name	Main mass fragments	Ref.	Comments
L1	Epimanoyloxide	81, 177, 191, **257**, 275, (290)	[1]	
L2	Epimanool	**81**, 95, 137, 257, 272, (290)	[1], [17]	
L3	Manool	**81**, 95, 107, 121, 137, 161, 189, 229, 257, 272, 290	[1]	
L4	Δ13-*cis*-neoabienol	81, 95, 107, 121, **177**, 191, 290	[2]	
L5	iso-Abienol	81, 95, 109, **191,** 217, 235, 255, 272, 290	[2]	
L6	Abienol	81, 95, 109, **191,** 217, 235, 255, 272, 290	[2]	
L7	*cis*-Abienol	81, 95, **119**, 134, 163, 191, 257, 272, (290)	[2]	
L8	Unidentified labdane	79, 93, 105, **121**, 139, 159, 220, 246		
L9	*trans*-Abienol	81, 95, **119**, 134, 163, 191, 257, 272, (290)	[2]	
L10	Unidentified abienol	81, 95, 109, **191**, 217, 234, 255, 272, (290)	[2]	Mass spectrum identical with (iso)abienol
L11	Unidentified labdane	79, **93**, 105, 121, 33, 161, 189, 241, 246, 259, 274		
L12	Unidentified labdane	81, **91**, 107, 121, 133, 147, 161, 243, 257, 271, 286		
L13	*cis*-Communate	79, **121**, 175, 241, 301, 316	[1]	
L14	19-norlabda-8(20),3-dien-15-oate	81, 95, 107, 135, 191, 207, 215, 229, 257, **289**, 304	[11]	
L15	Cativate	95, **107**, 122, 191, 289, 305, 320	[1]	
L16	*trans*-Communate	79, 119, 175, **241**, 316	[1]	
L17*	Unidentified labdane acid, ME	105, 119, 133, **175**, 203, 235, 257, 316	[23], [24]	Δ8-double bond or rearranged, see text (chapter 4.2.2)
L18	Isomer of L14	**81**, 95, 107, 121, 135, 147, 189, 289, 304	[11]	
L19	Larixol	69, **109**, 119, 153, 187, 255, 273, 288, (306)	[3], [17]	
L20*	Unidentified labdane acid, ME of L29	**121**, 189, 241, 287, 301, 316	[29]	Mass spectrum without identification
L21	Unidentified labdane	81, 93, 107, **121**, 159, 173, 188, 213, 274, 290		

L22	Lambertianate	81, **121**, 189, 330	[1]	
L23	*cis*-Communic acid	**79**, 107, **119**, 175, 241, 287, 302	t_R	
L24	Probably communol	**81**, 93, 107, 119, 133, 147, 161, 175, 189, 257, 273, 288	[1]	
L25*	Labda-13-en-8-ol-15-oate	81, 109, 114, 135, 161, 189, **204**, 303, 318, 336	[20]	Mentioned as the CPP form of ent-labdanolate (eL17) in [20]
L26	Larixylacetate	79, 105, **153**, 185, **255**, 270, 288, 348	[4], [17]	
L27	Unidentified labdane acid, ME	79, 93, **121**, 161, 221, 290, 318, 350	[1]	Present in sandarac and Pinaceae resins, original non methylated compound is not found
L28	*trans*-Communic acid	**79**, 119, 175, 241, 287, 302	t_R	
L29*	Unidentified	81, 93, 107, **121**, 133, 159, 187, 241, 287, 302	[29], t_R	Cf. L20
L30	19-norlabda-4,8(20),13-trien-15-oate	81, 93, 121, **211**, 227, 287, 302	[11]	
L31*	Isocupressate	79, 93, 107, **121**, 241, 257, 301, 316, 333, 334	[15]	
L32	Lambertianic acid	81, 93, 107, **121**, 147, 161, 189, 255, 316	t_R	
L33	Unidentified	79, 93, **107**, 119, 135, 161, 187, 255, 257, 302, 315, 330		
L34*	Imbricatoloate (dihydroisocupressate)	79, 93, 107, **121**, 161, 276, 304, 336	[1], t_R	Mass spectrum of L46 in [1], t_R and similar mass spectrum indicate the methylester of L46
L35	Unidentified dicarboxylic labdane acid, diME	79, 93, 107, **121**, 175, 201, 211, 227, 287, 303, 315, 347, 362		
L36	Unidentified dicarboxylic labdane acid,di ME	79, 93, 107, **121**, 161, 189, 221, 287, 302, 347, 362		
L37	Dihydroagathate, diME	93, 107, **121**, 161, 217, 239, 257, 272, 304, 364	[1]	
L38*	Unidentified labdenoate, ME of L48	79, 93, 107, **121**, 189, 241, 257, 301, 319, 334	t_R	In relation to the non methylated compound L48
L39	Unidentified hydroxylabdanoate	79, 93, 105, **121**, 161, 273, 289, 316, 348		

L40	Unidentified dicarboxylic labdane acid, diME	79, 93, 107, **121**, 189, 287, 302, 347, (362)		
L41*	Δ8-Dihydroagathate, diME	95, 107, 121, 175, 203, **235**, 257, 289, 304, 349, 364	[23], [24]	Δ8-double bond or rearranged, see chapter 4.2.2
L42*	Isocupressic acid	79, 93, 107, **121**, 161, 207, 241, 287, 302, 320	[1]	
L43	Unidentified dicarboxylic labdane acid, diME	79, 93, 107, **121**, 175, 201, 211, 288, 303, 347, 362		
L44	Agathalate	79, 93, **107**, 121, 133, 147, 201, 229, 239, 289, 303, 314, 332	[11]	Mass spectrum corresponds with that reported in [11], but t_R is somewhat to low
L45	Agathate, diME	81, 93, 107, **121**, 189, 301, 347, 362	[23]	
L46*	Imbricatoloic acid	81, 93, 107, **121**, 161, 221, 276, 304, 322	[1]	Cf. L34
L47	Unidentified labdan-19-oate	91, 105, 121, 133, 175, **241**, 301, 314, 333	[1]	
L48*	Unidentified labdenoic acid	79, 93, 107, 121, 133, 147, 189, **241**, 259, 287, 305, 320		Cf. L38
L49	Agatholate	81, 93, **107**, 121, 243, 271, 303, 319, 334	[3], [12]	
L50	Unidentified labdane	79, 93, **107**, 119, 147, 237, 253, 315, 331, 345		
L51*	Dihydroagathic acid (proposed)	79, 93, 107, **121**, 161, 175, 290, 300, 318, 336	t_R	In relation to the t_R of the methylester L38
L52	Unidentified labdane acid	**82**, 93, 107, 121, 189, 211, 235, 301, (334)	[1]	Probably an agathic acid isomer
L53	Acetoxy-agatholate	79, 93, **107**, 135, 147, 241, 301, 316, 329, 344, 361, (376)	[11], [12]	
L54	Agathic acid	**82**, 93, 107, 121, 136, 161, 189, 288, 298, 319, 341		Found in conifer copals in methanol extracts, see chapter 4.1.3, t_R used to identify other labdanes acids, particularly in sandarac (chapter 4.1.2)
L55	Unidentified labdanoic acid	**82**, 93, 107, 121, 136, 161, 189, 288, 298, 319, 341		

Ent-labdanes

Elution order is reported in [22], [28] and [60]

Label	Name	Main mass fragments	Ref.	Comments
eL1	Endocyclic ent-labden-15-oate	95, 107, 121, **191**, 277, 305, 320	[21], [28]	Peak at m/z 191 results from the elimination of the side chain (chapter 4.2.2), peaks at 305 $[M-CH_3]^+$) and 277 ($[M-CH_3-CO]^+$, cf. eL8
eL2	Unidentified ent-labdane acid, ME	81, 95, 107, **121**, 135, 217, 244, 303, 318		
eL3	Iso-ozate	93, 107, **121,** 187, **241**, 257, 301, 316	[8]	
eL4	Unidentified ent-labdane acid, ME	**95**, 109, 135, 191, 277, 305, (320)	[21], [28]	Peak at m/z 191 results from the elimination of the side chain (chapter 4.2.2)
eL5	Unidentified ent-labdane acid, ME	**81**, 95, 121, 137, 177, 191, 277, 292, 305, (320)		Peak at m/z 137 typical for exocyclic double bond (chapter 4.2.2)
eL6	Eperuate	**81**, **95**, 121, 137, 177, 191, 305, 320	[3], [21]	
eL7	Unidentified ent-labdane acid, ME	79, 95, 107, **121**, 161, 191, 215, 262, 277, 305, 322		
eL8	Ent-labda-8-en-15-oate	**95**, 107, 121, 191, 277, 305, 320	[21]	
eL9	Unidentified ent-labdan-diol	**93**, 107, 257, 273, 288, (306)		
eL10	Labdanate	67, 81, 95, 109, **123**, 257, 275, 307, 322	[21]	
eL11	Unidentified ent-labdane acid, ME	67, 81, 93, **107**, 121, 135, 191, 207, 277, 305, 320		Probably an isomer of labda-8-en-15-oate
eL12*	Ent-labda-18-oate	79, **121**, 161, 215, 231, 247, 262, 275, 290, 322	[21], [28]	See text (chapter 4.2.2)
eL13	Isomer of ent-labda-8-en-15-	67, 79, **95**, 107, 121, 136, 191, 277, 289, 305, 320		Probably an isomer of labda-8-en-15-oate
eL14	18-Methoxy-nor-ent-labda-13(14)-en-15-oate (proposed)	**81**, 93, 107, 121, 149, 175, 291, 309, (324)	[28]	Methoxy form of eL27, see text (chapter 4.2.2)
eL15	Copalate	**81**, 95, 114, 121, 137, 243, 271, **303**, 318	[1]	
eL16	Daniellate	81, **121**, 189, 330	[1]	
eL17*	Probably ent-labda-13-en-8-ol-15-oate	81, **109**, 135, 161, 189, **204**, 243, 271, 303, 318, (336)	[20]	

eL18	Polyalthate	81, **121**, 189, 255, 330		
eL19*	19-Nor-ent-labda-8(20)-ene	81, **95**, 109, 123, 177, 277, 292	[28]	
eL20*	ent-Labda-8-ol-15-oate (ent-labdanolate)	81, **101**, 109, 121, 123, 177, 235, 305, 320, 338	[21], [22]	See text (chapter 4.2.2)
eL21*	15-methoxy-18-hydroxy-ent-labane	81, 95, 121, 149, 195, **277**, 290, 307, 322	[28]	Methoxy ether of eL31, see text (chapter 4.2.2)
eL22*	Unidentified	81, 93, 95, 101, **109**, 123, 161, 189, 217, 303, 318, 336		
eL23	Unidentified hydroxy-labdanoate	67, 81, **95**, 109, 123, 189, 207, 271, 303, 321, 336		m/z 303 originates from [M-CH$_3$-H$_2$O]$^+$
eL24*	18-Methoxy-ent-labda-8(20)-en-15-oate	93, 107, 121, 175, 223, **305**, 318, 335, 350	[28], [29]	Methoxy ether of eL33, see text (chapter 4.2.2)
eL25*	15-Methoxy-ent-labd-8(20)-en-18-oate	**121**, 161, 235, 290, 303, 318, 335, 350	[28]	Methoxy form of eL29, see text (chapter 4.2.2)
eL26	Unidentified ent-labdane	67, 79, 95, 107, 120, **189**, 243, 253, 271, 305		
eL27*	18-Hydroxy-nor-ent-labda-13(14)-en-15-oate (proposed)	**81**, 95, 107, 121, 135, 163, 277, 291, 304, 322	[28]	See text (chapter 4.2.2)
eL28	Unidentified hydroxy- or methoxy-ent-	95, **109**, 122, 135, 189, 221, 271, 305, 318		Probably the methoxy form of eL36, hydroxy-labda-7(8)-en-15-oate
eL29*	Hydroxy-ent-labd-8(20)en-18-oate	**121**, 161, 253, 276, 289, 304, 318, 336	[28]	See text (chapter 4.2.2)
eL30	ent-Pinifolate, diME	93, **121**, 161, 235, 304, 332, 364	[21], [57]	Mass spectrum resembles that of pinifolate given in [21], the enantiomeric form is reported by [57] for *Hymenaea* resins
eL31*	15,18-Dihydroxy-ent-labane	81, 95, 121, 149, 263, **277**, 290, 308	[28]	See text (chapter 4.2.2)
eL32*	Oxo-labda-13(14)-dien-15-oate	107, 139, 175, 203, 235, 286, 304, **332**	[28]	See text (chapter 4.2.2)
eL33*	18-hydroxy-ent-labda-8(20)-en-15-oate	81, 107, 121, 135, 175, 223, 291, **305**, 318, 336	[28]	See text (chapter 4.2.2)
eL34*	Hydroxy-ent-labda-8(20)-diene-15-oate	121, 135, **205**, 287, 303, 319, 334	[28]	See text (chapter 4.2.2)

eL35	Unidentified ent-labdane	**95**, 107, 121, 135, 149, 189, 207, 291, 305, 318, 331, 354		MW 354 is not sure
eL36*	18-hydroxy-ent-labda-7(8)-en-15-oate	95, **107**, 122, 149, 189, 207, 291, 305, 318, 336	[21], [28]	See text (chapter 4.2.2)
eL37*	Hydroxy-copalate	93, **107**, 119, 135, 175, 203, 225, 241, 269, 273, 301, 316, 319, (334)	[25], [26], [60]	The hydroxyl group is located at C-3 [60] and [62]
eL38	Unidentified ent-labdane	81, **95**, 121, 147, 180, 191, 217, 297, 329, 344		
eL39	Unidentified ent-labdane	109, **121**, 123, 135, 205, 235, 287, 303, 334		Probably labda-7,13-dien-8-oxo-15-oate
eL40*	8,18-Dihydroxy-ent-labda-15-oate (proposed)	95, 137, 163, **189**, 207, 304, 322, 354	[28]	See text (chapter 4.2.2)
eL41	Unidentified ent-labdane	79, 91, 107, 121, **135**, 205, 304, 332		
eL42	Unidentified ent-labdane	**81**, 95, 119, 131, 163, **173**, 201, 233, 281, 313, 328		
eL43*	Acetoxy-copalate	93, 107, 119, 135, 147, 175, 203, 225, 241, 269, 273, **301**, 316, (362)	[25], [26]	[25] and [26] refer to the enantiomeric labdanes; even though ent-labdanes are more probably, oxygenated copaiferic acids cannot be excluded completely; the acetoxy group is located at C-3 [60] and [62]
eL44	Unidentified ent-labdane	**79**, 81, 91, 93, 107, 121, 135, 147, 189, 203, 251, 289, 301, 319, 348		
eL45	18-Oxo-ent-labda-8(20)-en-15-oate isomer	95, **121**, 135, 163, 187, 205, 287, 303, 319, 334		Probably 18-oxo-labda-8(20)-en-15-oate
eL46	Unidentified ent-labdane	95, 109, 123, 137, 163, **189**, 207, 243, 286, 304, 322, 354		Probably an isomer of labda-8,18-diol-15-oate (eL40)
eL47	Unidentified ent-labdane acid, ME	79, 93, 107, 121, 135, 175, 189, 271, 318, 334, 352		Probably a hydroxy-oxo-labda-7(8)-en-15-oate
eL48	Unidentified ent-labdane	95, 107, 121, 135, 161, 189, 205, 243, 259, **285**, 300		
eL49	Unidentified ent-labdane	**79**, 81, 91, 93, 107, 121, 135, 147, 189, 203, 251, 289, 301, 319, 348		

Kauranes and clerodanes

Label	Name	Main mass fragments	Ref.	Comments
K1	ent-Kaur-16-ene	79, 91, **105**, 119, 213, 229, 257, 272	[1]	
K2	Kaur-16-en-19-oate	91, 131, 187, 213, **241**, 257, 273, 301, 316	[1]	
K3	Kauran-19-oate	81, 93, 109, 123, 149, 243, **259**, 286, 303, 318	[1]	
C1	Unidentified clerodane acid, ME	79, 91, 93, 95, **107**, 121, 135, 189, 243, 303, 318		See text (chapter 5.2.1)
C2	Kovalenate	95, 107, 120, **189**, 243, 253, 303, 318	[22]	
C3	Unidentified clerodane acid, ME	95, 107, 120, **189**, 243, 253, 303, 318		See text (chapter 5.2.1)
C4	Hardwickiate	96, **139**, 175, 203, 219, 235, 283, 299, 330	[1]	
K4	Probably an oxygenated kaurane	229, **255**, 289, 315, 330	[1]	
C5	Clerodan-15,18-oate, diME	79, 95, 121, 177, 187, 205, 237, 251, 307, 335, (366)	[22]	See text (chapter 5.2.1)
C6	Clerod-3-en-15,18-oate, diME	79, 105, 139, 175, 203, 235, 281, 313, **332**, (364)	[22]	See text (chapter 5.2.1)
K5	Unidentified kauranoate	79, 95, 121, 135, 205, 243, 259, **285**, 301, 317, 332	[1]	Probably an oxo-kaurenoate
C7*	12-Acetoxy-hardwickiate	81, 139, 173, 187, 201, **219**, 233, 281, 296, 328, 357, 408	[27]	

Phenylpropanoids

Note: Because it was not possible to determine the exact elution order of several phenylpropanoids measured with different temperature programs, they were numbered according to the chapters, they are presented in. Elution order is reported in [61].

Label	Name	MS	Ref.	Comments
Chapter 4.2.3				
PP1	Benzyl methyl ether	77, **91**, 121, 122	[1]	
PP2	Benzyl alcohol	77, **79**, 91, 108	[1]	
PP3	Benzoate	51, 77, **105**, 135, 136	[1]	
PP4	Benzoic acid	51, 77, **105**, 122	[1]	
PP5	Benzenepropanol (dihydrocinnamyl alcohol)	77, 91, 92, **117,** 118, 136	[1]	
PP6	Cinnamyl alcohol	77, 78, 91, **92**, 105, 115, 134	[1]	
PP7	Cinnamate		[1]	
PP8	Vanillin	81, 109, 123, **151**, 152	[1]	
PP9	Cinnamic acid	77, 91, 103, 131, **147**, 148	[1]	
PP10	Isomer of PP15	146, 165, **177**, 181, 193, 208	[1]	
PP11	Elemicin	79, 105, 133, 165, 177, 193, **208**	[1]	
PP12	Isoelemicin	79, 91, 105, 133, 165, 177, 193, **208**	[1]	
PP13	Vanillic acid	57, 71, 97, 125, 153, **168**	[1]	
PP14	Methoxyeugenol	77, 91, 103, 119, 131, 162, **194**	[1]	
PP15	Dihydroferulic acid	94, 122, **137**, 196	[1]	
PP16	Coniferyl alcohol	77, 91, 124, **137**, 180	[1]	
PP17	1,2-Dimethoxy-4-(3-methoxy-1-propenyl)benzene	77, 103, 131, 145, 146, **177**, 181, 208	[1]	
PP18	Benzylbenzoate	77,91, **105**, 167, 194, 212	[1]	
PP19	3,4-Dimethoxy-cinnamate	91, 147, 191, 207, **222**	[1]	
PP20	Ferulic acid	77, 105, 133, 179, **194**	[1]	

PP21	Cinnamylbenzoate	77, **91**, 103, 115, 131, 147, 178, 192, 220, 238		Mass spectrum similar to PP22, but PP21 is no main constituent
PP22	Benzylcinnamate	77, **91**, 103, 115, 131, 192, 220, 238	[1]	
PP23*	3-Phenylpropyl-3-phenylpropanoate	77, 91, 103, **117**, 118, 131, 280	[1]	See text (chapter 4.2.3, table 4.20)
PP24*	Benzylferulate	**91**, 145, 150, 161, 177, 207, 239, 266, 284	[1], [35]	
PP25	Cinnamylcinnamate	77, 103, 115, 117, **131**, 219, 264	[1]	
PP26*	Benzyl-p-coumarate	**91**, 120, 147, 208, 209, 236, 254		See text (chapter 4.2.3, table 4.20)
PP27*	Dihydroconiferylbenzoate, methoxy	77, 105, **137**, 150, 163, 300		See text (chapter 4.2.3, table 4.20)
PP28*	Unidentified	77, **105**, 131, 179, 284		See text (chapter 4.2.3, table 4.20)
PP29*	Isobenzylferulate	91, 145, 150, 161, 177, 207, 239, 266, **284**	[1], [35]	See text (chapter 4.2.3, table 4.20)
PP30*	Dihydroconiferylcinnamate, methoxy	103, **131**, 137, 150, 189, 326	[1]	See text (chapter 4.2.3, table 4.20)
PP31*	Unidentifed	103, **131**, 265, 298, 310		See text (chapter 4.2.3, table 4.20)
PP32*	Unidentified	139, 175, 189, **312**		See text (chapter 4.2.3, table 4.20)
PP33*	Unidentified	103, 131, 137, 163, **324**		See text (chapter 4.2.3, table 4.20)
PP34*	Unidentified	131, 137, **151**, 163, 312, 327, **358**		See text (chapter 4.2.3, table 4.20)
PP35	Eudesamin (pinoresinol, O,O-dimethyl)	151, **165**, 177, 219, 355, 386	[1]	
Chapter 5.4.3				
PP36	Unidentified	61, 77, 91, 119, 147, **163**, **178**		
PP37	Cumate	77, 91, 119, 131, 147, **163**, 178	[1]	
PP38	Unidentified	77, 91, 119, 163, **179**, 193, 208	[1]	
PP39	Unidentified	77, 91, 105, 137, 163, **179**, 195	[1]	

Triterpenes and triterpenoids including compounds derived from triterpenes by degradation and unknown triterpenes

Note: Because it was not possible to determine the exact elution order of all (unidentified) triterpenes measured with different temperature programs, they were numbered according to the chapters, they are presented in.

Label	Name	Main mass fragments	Ref.	Comments
Compounds present in *Pistacia* resins, elemi and copals, chapter 4.3.1 and 4.3.2				
T1	Unidentified	95, 135, 189, 207, **299**, 317, 327, 342, 360	[41]	Probably a nor-lupeol
T2	Unidentified	95, 135, **189**, 353, 368, 386?, 405, 420		
T3	Unidentified	107, 159, 257, 365, 383, **409**, 424		
T4	Unidentified	91, 119, 159, 255, 391, 409, **424**	[41]	Probably an olean-dien-ol
T5	Unidentified	**93**, 107, 121, 147, 205, 257, 311, 355, 409, 424		
T6	Unidentified	93, **109**, 189, 205, 313, 381, 409, 424		
T7	Unidentified	119, 213, 257, 297, 311, 365, 383, 393, **409**, 424		
T8	Unidentified	**93**, 107, 119, 175, **189**, 207, 297, 383, 393, 408, 426	[41]	Probably a olean-18-en-3-one
T9	3,8-Dihydroxypolypoda-13,17,21-triene	**81**, 107, 147, 175, 190, 203, 393, 408, 426, 444	[38], [39]	38, 39
T10	Unidentified	81, 105, 119, 173, 189, 241, 259, **393**, 411, 426	[41]	Probably a tirucall-ene
T11	Unidentified	239, 295, 391, **406**, 424		
T12	Unidentified	93, 121, 147, 175, **205**, 245, 313, 391, 409, 424		
T13	Unidentified	**93**, 121, 163, 189, 203, 313, 410, 426	[41]	Probably olean-18-en-3-one or lupen-3-
T14	Unidentified	81, 119, 133, 189, **203**, 262, 440, 468, 500		
T15	Unidentified	119, 151, 189, **219**, 391, 423, 467, 482		
T16	Unidentified	95, 109, 241, 259, **393, 411**, 426	[41]	Probably a tirucall-ene
T17*	Unidentified acetoxy-triterpene	93, 107, 175, **189**, 203, 216/218, 297, 393, 408, 453, 468	[1], [51]	Probably a lupane or taraxastane
T18	Unidentified	133, 189, **203**, 219, 262, 467, 482		

T19*	Unidentified	107, 147, 189, 203, **218**, 393, 408, 426, 439, 454		
T20*	Unidentified	107, 147, **189**, 203, 216, 229, 297, 341, 393, 408, 439, 454		
T21	Unidentified	147, 189, 203, **218**, 393, 439, 454		Isomer of T19?
T22	Unidentified	133, 187, 239, 299, 392, 406, **466**		
T23	Unidentified	95, 107, 121, 133, **189**, 207, 393, 408, **426**		
T24	Unidentified	132, 146, 187, **202**, 379, 393, 408, 426		
T25	Unidentified	119, 173, 189, **203**, 306, 391, **408**, 436		
T26	Unidentified	93, 121, 255, 273, 407, 423, **438**		
T27	Unidentified	**135**, 203, 218, 259, 285, 396, 409, 424, 466, 484		
T28	Unidentified	143, 205, 253, 381?, 389?, 399?, 407, 425, **440**		
T29	Unidentified oxy-genated oleanane or ursane	**135**, 217, **232**, 273, 285, 299, 410, 423, 438		Probably 11-oxo derivative of urs/olean-12- en-al , cf.T41
T30	Unidentified	67, 107, 121, **189**, 203, 377, 392, 395, 410		
T31	Unidentified	107, **189**, 203, 241, 367, 377, 395, 410, 428?		
T32	Unidentified	95, **109**, 135, 189, 207, 300, 313, 407, 426, 440, 454		
T33	Unidentified	67, **82**, 95, 135, 205, 245, 323, **341**, 359, 438		
T34	Unidentified	81, **107**, 133, **203**, 395, 409, 424, 438		
T35	Unidentified	95, 161, 175, 201, 217, 249, 381, **413**, 453, 485		
T36	Unidentified	105, 133, 175, 189, **203**, 232, 422, 440		
T37	Unidentified	119, **189**, 203, 219, 248, 262, 424, 438, 467, 482		
T38	Unidentified	135, 161, 217, 232, **257**, 273, 315, 407, 422, 440		
T39	Unidentified	**79**, 95, 105, 119, 147, 189, 205, 395, 409, 423, 438		
T40	Unidentified	67, **109**, 121, 147, 189, 203, 297, 339, 355, 468		

T41*	Unidentified oxy-genated oleanane or ursane	**135**, 232, 273, 395, 410, 423, 438		Probably 11-oxo derivative of urs/olean-12-en-al , cf. T29
T42	Unidentified	135, 175, 232, 273, 327, 407, **425**, 440		
T43*	Unidentified	**135**, 175, 232, 273, 407, 422, 482		Probably 11-oxo-olean/urs -12-en-3-acetate
T44	Unidentified	95, 149, **205**, 409, 424, 454?		
T45	Unidentified	107, 121, 135, **189**, 203, 367, 385, 439, 454, 472		
T46	Unidentified	81, 105, 133, 173, **203**, 421, 436, 453, 468		
T47	Unidentified	105, 133, **203**, 391, 409, 422, 440		
T48	Unidentified	**135**, 175, 232, 273, 383, 407, 422, 482		Probably 11-oxo-olean/urs -12-en-3-acetate
T49	Unidentified	109, 133, 203, 262, 325, 341, 369, **421**, 438, 452, 496		Present only in AS07, coelutes with Ur23, therefore is was not possible to determine whether it is identical with T50 or T51
T50	Unidentified	131, 159, 201, 215, 393, 408, **421**, 452		
T51	Unidentified	131, 173, 203, 215, 393, **421**, 437, 452		
T52	Unidentified	239, 371, 437, 496, **528**		
T53	Unidentified	109, 133, **203**, 393, 409, 421, 438		
T54	Unidentified	133, 203, 247, 436, **496**, 528		
T55	Unidentified	131, **145**, 159, 187, 203, 215, 393, 408, 421, 542		
T56	Unidentified	107, 121, 175, **189**, 367, 385, 439, 454, 472		
T57	Unidentified	131, **145**, 215, 246, 423, 454		
T58	Unidentified	95 133, **203**, 409, 447, 479, 494		
T59	Unidentified	95, 107, 121, 133, 147, 189, **203**, 245, 409, 440		
T60	Unidentified	133, **203**, 262, 467, 498		

T61	Unidentified	119, 161, 189, 248, 257, 317, 407, 449, **467**, 486, 499, 512, 544		
T62	Unidentified	95, 159, 203, 301, 407, 435, 449, **467**, 482		
Compounds present only in tacamahak, chapter 4.3.2				
T63	Unidentified	177, 189, 257, 311, 391, **409**, 424, 437, 452		
T64	Unidentified	105, 119, 173, 189, 203, 218, 257, **393**, 408		
T65	Unidentified	107, 189, **205**, 218, 245, 313, 391, 406, 409, 424		
T66	Unidentified	132, 163, 175, 191, **202**, 393, 408, 454		
T67*	Unidentified acetoxy-triterpene	107, 121, 147, 175, **189**, 203, 218, 229, 297, 393, 408, 453, 468	[1], [51]	Probably lupane or taraxastane skeleton
T68	Unidentified	173, 189, 202, 365, 393, **408**, 426		
T69	Unidentified	117, 132, **202**, 393, **408**		
T70	Unidentified	107, 173, 189, 202, 205, 393, **408**, 426	[1]	
T71	Unidentified	107, 147, 163, 175, **189**, 349, 377, 410, 452		
T72	Unidentified	117, 132, **202**, 377, 393, 437, 452		
T73	Unidentified	135, 159, 189, **203**, 232, 273, 407, 452, 470		
T74	Unidentified	133, **203**, 205, 216, 407, 414, 422, 468		
T75	Unidentified	133, **203**, 205, 216, 407, 414, 422, 468		
T76	Unidentified	107, 137, **189**, 203, 205, 216, 409, 424, 437, 452		

Dammaranes

Label	Name	Main mass fragments	Ref.	Comments
Da1	Mansumbione	**95**, 108, 121, 163, 205, 299, 314	[43]	
Da2	Mansumbinol	93, 108, 147, **190**, 203, 207, 383, 301, 316	[43]	
Da3	Mansumbiane	95, 108, 189, **205**, 301, 316	[43]	
Da4	Mansumbiane	95, 108, 119, 175, **189**, 207, 285, 300	[43]	
Da5	Hexakisnor-dammaran-3,20-	95, 135, 205, 273, 297, **315**, 325, 340, 358	[38], [39]	
Da6	Dammaradienone	109, 161, 175, 189, **205**, 218, 245, 313, 381, 409, 424	[39]	
Da7	Dammaradienol	93, 161, 175, **189**, 207, 315, 408, 426	[39]	
Da8	20,24-epoxy-25-hydroxy-3,4-seco-dammaren-3-oate (proposed)	107, 125, **143**, 371, 397, 411, 429, 473, (488)	[39]	Peaks for [M-CH$_3$]$^+$, [M-59]$^+$ and [M-77]$^+$ in the mass spectrum reported in [39] are more intense than in Da8
Da9	20,24-Epoxy-dammaran-3-one (proposed)	107, **143**, 205, 381, 399, 407, 425, **440**	[39], [52]	
Da10	Dammarenolate	81, 95, **109**, 149, 175, 215, 303, 343, 385, 411, 454	[39]	
Da11	20,24-epoxy-25-hydroxy-dammaran-3-one	107, 125, **143**, 161, 175, 205, 381, 399, 411, 443, (458)	[39]	
Da12	20,24-Epoxy-25-hydroxy-dammaran-3-ol	107, 125, **143**, 175, 191, 365, 383, 401, 445, 460	[39]	
Da13	Hydroxy-dammarenone (3-oxo-20-hydroxy-dammar-24-ene)	68, 81, 95, **109**, 205, 298, 311, 355, 409, 424, (442)	[38], [39]	
Da14	Hydroxy-dammarenol (3,20-dihydroxydammar-24-ene)	95, **109**, 135, 189, 207, 300, 313, 339, 357, 426, (444)	[39]	
Da15	3-Oxo-25,26,27-trisnor-dammarano-24,20-lactone	81, 95, 99, 107, 121, 135, **205**, 287, 315, 396, 414	[39]	
Da16	Unidentified dammarane	95, 149, **189**, 205, 369, 383, 409, 424, 452		

Tirucallanes

Label	Name	Main mass fragments	Ref.	Comments
Ti1	Hydroxy-Δ8-tirucallene	95, 241, 259, **393**, 411, 426	[39]	
Ti2	Tirucallone	109, 245, 257, 391, **409**, 424	[41]	
Ti3	Tirucallol	95, 241, 259, **393**, 411, 426	[39], [41]	
Ti4	Elemonate (proposed)	189, 257, 297, 311, 393, 421, **453**, 468	[39]	See text (chapter 4.3.2)
Ti5	3α-hydroxytirucall-8,24-dien-21-oate (α-elemolate) (proposed)	187, 281, 299, 377, 405, **437**, 455, 470	[47]	The peak at m/z 149 [47] is missing, see text (chapter 4.3.2)
Ti6	Unidentified hydroxytirucalladien-21-oate	119, 187, 241, 281, 299, 377, 405, **437**, 455, 470	[48]	[48] provides no mass spectra, but relative amounts of tirucallane acids present in Manila elemi, see text (chapter 4.3.2)
Ti7	3α-acetoxytirucalladien-21-oic acid	187, 281, 377, 405, **437**, 453, 497, 512	[48]	See text (chapter 4.3.2)
Ti8	3α-hydroxy-7,24-dien-21-oate (β-elemolate) (proposed)	187, 282, 378, 406, **437**, 455, 470	[47], [48]	
Ti9	Isomasticadienoate	95, 121, 159, 189, 257, 393, 403, 421, 435, **453**, 468	[39]	
Ti10	Epi-isomasticadienoloate	241, 378, 396, 406, 424, **437**, 455, 470	[40], [41]	
Ti11	Masticadienoate	95, 121, 159, 187, 257, 393, 403, 421, 435, **453**, 468	[39]	
Ti12	Acetoxy-isomasticadienolate	95, 187, 377, 405, 422, **437**, 453, 497,	[39]	
Ti13	Acetoxy-masticadienolate	95, 187, 377, 406, **437**, 497, (512)	[39]	

Lanostanes

Label	Name	Main mass fragments	Ref.	Comments
La1	Lanosterol	95, 187, 241, 259, **393, 411**, 426	[1], [38]	
La2	Lanost-8-en-ol-oate	95, 173, 301, 341, 427, 449, **467**, 482	[1]	Skeleton and position of the double bond identified by [1]; molecular ion at m/z 482 and the base peak at m/z 467 indicate a hydroxyl group

Oleananes

Because it was not possible to determine the exact elution order of all oleananes measured with different temperature programs, they were numbered according to the chapters, they are presented in.

Label	Name	Main mass fragments	Ref.	Comments
O1	3,4-Seco-28-norolean-12-en-3-oate	81, 119, 175, 189, **204**, 243, 355, 427, 442	[39]	
O2	28-Norolean-12,17-dien-3-one	81, 119, 189, 207, 229, 269, 393, **408**	[40]	
O3	Olean-9(11),12-dien-3-one	189, 255, 269, 408, **422**	[44]	
O4	3β-Methoxy-olean-12-ene	81, 95, 107, 189, **203**, 218, 393, 408, 425, 440	[1]	Methoxy ether of β-amyrin
O5	Olean-9(11),12-dien-3α-ol	159, 189, 255, 391, 409, **424**		Mass spectrum similar to that of O6
O6	Olean-9(11),12-dien-3β-ol	95, 119, 159, 255, 355, 391, 409, **424**	[1], [44]	
O7	Olean-10(11),12-dien-3-acetoxy	255, 295, 391, 424, 451, **466**	[1]	
O8	Nor-β-amyrone	79, 105, 175, 189, **204**, 395, 410	[39]	
O9	Olean-12-en-3α-ol (epi-β-amyrin)	95, 107, 119, 175 189, **203**, 218, 393, 411, 426		See text (chapter 4.3.2)
O10	β-Amyrone	203, 218, 424	[41]	
O11	Unidentified oleanen-ol	93, 105, 119, 161, 175, **189**, **204**, 397, 412	[1]	
O12	Olean-17-en-one	105, **163**, 175, 190, 395, 408, 424	[41]	
O13	β-Amyrin (olean-12-en-3β-ol)	189, **203**, 218, 393, 411, 426	[1]	
O14	Germanicene (olean-18-ene)	105, 134, 175, 191, **204**, 395, 410	[1]	
O15	28-Norolean-17-en-3-one	95, **163**, 175, 191, 377, 395, 410	[42]	
O16	17β-Hydroxy-28-norolean-12-en-3-one	91, 105, 132, 146, 173, 187, **202**, 393, 408, (426)	[38]	
O17	Moronate	119, 173, **189**, 203, 248, 262, 409, 468	[39]	
O18	Oleanonate	133, 189, **203**, 262, 393, 409, 468	[39]	
O19	Oleanonic aldehyde	105, 133, 175, **203**, 232, 311, 355, 409, 424, 438	[39]	
O20	Oleanolate	133, 189, **203**, 262, 395, 411, (470)	[1]	

O21	Isomer of maniladiol	175, 190, 201, **216**, 219, 234, 391, 409, 424, 442	[48], [49], [50]	According to [48] maniladiol and its isomer occur together
O22	Oleanolic aldehyde	105, 133, 175, **203**, 232, 311, 355, 409, 424, 440	[39]	
O23*	11-oxo-olean-12-en-3α-ol	**135**, 175, 217, 232, 273, 287, 407, 425, 440	[50]	
O24*	11-oxo-olean-12-en-3β-ol (11-oxo-β-amyrin)	**135**, 175, 217, **232**, 273, 407, 425, 440	[50]	
O25	Maniladiol	148, 160, 190, 201, **216**, 219, 234, 409, 424, 442	[48], [49], [50]	According to [48] maniladiol and its isomer occur together
O26	18α-Oleanonate	119, 133, 189, **203**, 262, 393, 453, (468)	[38]	
O27	17-Hydroxy-11-oxo-nor-β-amyrone	145, 161, 189, **216**, 257, 407, 422, 440	[39]	
O28	11-Oxo-oleanonate	119, 189, **217**, **257**, 276, 317, 407, 423, 435, 454, 467, 482	[38]	
O29	3-Oxo-6β-hydroxy-olean-12-en-28-oate	133, 189, **203**, 262, 391, 407, 466, 466, 484	[55]	
O30	Sumaresinolate	133, 189, **203**, 262, 425, 449, 468, 486	[55]	
O31	Oxo-oleanane	119, 147, 175, 189, 204, **217**, 233, 365, 407, 422, 435, 453, 468	[10]	
Compounds present only in African copals, chapter 4.3.2				
O32	Unidentified oleanane acid	133, **203**, 262, 421, 467, 480, 498	[1]	Probably a 2,3,23-trihydroxy-olean-12-en-28-oate

Ursanes

Label	Name	Main mass fragments	Ref.	Comments
Ur1	28-Nor-urs-12,17-dien-3-one	241, 269, 351, 375, 393, **408**	[40]	
Ur2	Urs-9(11),12-dien-3α-ol	159, 255, (395), 391, 409, **424**		
Ur3	Urs-9(11),12-dien-3-one	133, 159, 255, 269, 311, 389, 408, **422**		
Ur4	3β-Methoxy-urs-12-ene	119, 147, 161, 189, 203, **218**, 393, 408, 425, 440	[1]	
Ur5	Urs-9(11),12-dien-3α-ol	159, 255, (395), 391, 409, **424**	[44]	
Ur6	Urs-10(11),12-dien-3-acetoxy	255, 295, 391, 424, 451, **466**	[1]	
Ur7	Urs-9(11),12-dien-3β-ol	159, 255, 295, 391, 409, **424**		
Ur8	Nor-α-amyrone	105, 134, 175, 189, 191, **204**, 313, 395, 410	[39]	
Ur9	α-amyrone	107, 147, 189, 203, **218**, 409, 424	[1]	
Ur10	Urs-12-en-3α-ol (epi-α-amyrin)	107, 147, 189, 203, **218**, 393, 411, 426		See text (chapter 4.3.2)
Ur11	Urs-12-en-3β-ol (α-amyrin)	107, 147, 189, 203, **218**, 393, 408, 411, 426	[1]	
Ur12	3-acetoxy-14-nor-urs-12-ene	105, 134, 147, 175, 189, **204**, 439, 454	[1]	
Ur13	Urs-12-en-3β-acetate	79, 119, 147, 189, 203, **218**, 408, 453, 468	[1], [51]	
Ur14	Ursolic aldehyde (3-hydroxy-urs-12-en-28-al)	253, 271, 289, 407, 422, **440**	[39]	
Ur15	Ursonate	133, 189, **203**, 262, 393, 408, 453, 468	[39]	
Ur16	Ursonic aldehyde	133, **203**, 396, 414, 438	[39]	
Ur17	3-acetoxy-ursolate	133, 189, **203**, 262, 452, 512	[39]	
Ur18*	11-oxo-urs-12-en-3α-ol	105, **135**, 149, 175, 232, 273, 407, 425, 440	[50]	
Ur19	Isomer of brein	110, 151, 190, 219, **234**, 391, 409, 424, 442	[48], [49], [50]	According to [48] brein and its isomer occur together
Ur20*	11-oxo-urs-12-en-3β-ol (11-oxo-α-amyrin)	**135**, 175, 232, 273, 407, 425, 440		
Ur21	Ursolic aldehyde	133, **203**, 409, 422, 440	[39]	

Ur22	Brein	110, 151, 191, 207, 219, **234**, 409, 424, 442	[48], [49], [50]	According to [48] brein and its isomer occur together
Ur23	Unidentified ursonate	133, 203, 262, 409, 440, 498		
Ur24	Unidentified ursonate	133, 203, 440		
Ur25	Acetoxy-ursanoate	**133**, 165, 187, **203**, 219, 233, 262, 407, 422, 435, 450, 467, 482		
Ur26	Ursane acid	133, **203**, 262, 435, 467, 480, 498		
Ur27	Ursane	133, **203**, 262, 435, 467, 480		
Ur28	Ursane	133, **203**, 262, 456, 498		

Other pentacyclic triterpenes: hopanes, lupanes, taraxastanes, baueranes, friedelanes, and glutinanes

Label	Name	Main mass fragments	Ref.	Comments
Ho1	22-hydroxy-hopanone	**93**, 107, 121, 189, 205, 311, 355, 424	[1]	
Lu1*	Epi-lupeol	107, 135, **189**, 203, 207, 218, 229, 257, 393, 411, 426		See text (chapter 4.3.2)
Ba1	Epi-baurenol	95, 119, **229**, 241, 247, 393, 411, 426	[45]	
Gl1	Epi-glutinol or glutinol	95, 119, 229, 247, **259**, 274, 393, 408, 426	[53]	
Ba2	Baurenol	95, **229**, 241, 247, 393, 411, 426	[45]	
Lu2	Lupenone	107, 121, 147, 189, **205**, 313, 355, 409, 424	[1], [45]	
Ta1	Taraxasterol	93, 107, 121, 175, **189**, 207, 229, 393, 408, 426	[46]	
Lu3*	Lupeol	95, 107, 121,133, **189**, 207, 257, 393, 408, 426	[1], t_R	
Fr1	Friedelan-3-one	**107**, 125, 163, 191, 205, 218, 231, 273, 341, 411, 426	[1], [56]	
Lu4	3-Oxo-lup-20(29)-en-28-oate	119, 133, 173, **189**, 203, 249, 262, 393, 409, 437, 453, 468	[38]	

(Di)Monoterpanyl succinates, – diterpenoates and labdanoates

Label	Name	Main mass fragments	Ref.	Comments
MS1	Fenchylsuccinate	55, 81, 87, **115**, 121, 136, 153, (268)	[23]	
MS2	Fenchylsuccinic acid	55, 80, **81**, 93, 101, 121, 136, 173, (254)	[30]	
MS3	Bornylsuccinate	55, 81, 93, 95, 108, **115**, 121, 136, 153, (268)	[23]	
MS4	Isobornylsuccinate	55, 81, 93, 95, 108, **115**, 121, 136, 153, (268)	[23]	
MS5	Bornylsuccinic acid	55, 67, 80, 93, **95**, 108, 121, 136, 154, 236, (254)	[30]	
MS6	Isobornylsuccinic acid	55, 67, 93, **95**, 108, 11, 136, 175, 231, (254)	[30]	
dMS1	Difenchylsuccinate	67, **81**, 95, 121, 137, (390)	[23], [30],	
dMS2	Fenchylisobornylsuccinate	67, **81**, 95, 121, 137, 390	[23], [30]	
dMS3	Fenchylbornylsuccinate	67, **81**, 95, 121, 137, (390)	[33]	
dMS4	Dibornylsuccinate	57, 67, **81**, 95, 121, 137, (390)	[23], [33]	
dMS5	Diisobornylsuccinate or Bornylisobornylsuccinate	57, 67, **81**, 95, 121, 137, (390)	[33]	
MD1	Bornylisopimara-8,15-diene-18-oate	**81**, 95, 137, 175, 241, 287, 301, 396, 438	[33]	
MD2	Isobornylisopimara-8,15-dien-18-oate	**81**, 95, 137, 175, 241, 287, 301, 396, 438	[33]	
MD3	Unidentified monoterpanylditerpenoate	**81**, 95, 137, 215, 229, 275, 289, 301		Cf. MD7
MD4	Isobornylpimar-9(11)-en-18-oate	**81**, 137, 177, 193, 243, 271, 287, 289, 303, 377, (440)	[33]	
MD5	Isobornylpimar-7-en-18-oate	**81**, 137, 177, 193, 243, 257, 271, 289, 303, 440	[33]	
MD6	(Iso)Bornylpimaradiene-18-oate	**81**, 95, 137, 229, 275, 289, 301, 417, 438		Derived from MD5
MD7	Unidentified monoterpanylditerpenoate	**81**, 95, 137, 229, 257, 275, 289, 301, 377, 438		Cf. MD4
MD8	(Iso)Bornylpimaradiene-18-oate	**81**, 95, 137, 255, 301, 350, 410, 438		Derived from MD5
MD9	Bornyldehydroabietate	**81**, 95, 137, 173, 239, 285, 299, 436	[33]	
MD10	Isobornyldehydroabietate	81, 137, 173, 239, 285, 299, 436	[33]	
MD11	Isobornylabietate	81, 173, 255, **301**, 438	[33]	
ML1	Monoterpanylester of dihydro-Δ8-agathate	**81**, 95, 137, 175, 235, 271, 289, 331, 349, 426, (486)		See text (chapter 4.4.1)

ML2	Monoterpanylester of di-hydro-Δ8-agathate	**81**, 95, 137, 175, 235, 271, 289, 349, 426, (486)		See text (chapter 4.4.1)

Unidentified

Label	Name	Main mass fragments	Ref.	Comments
U1	Unidentified	55, 67, **82**, 93, 107, 121, 133, 161, 189, 222	[1]	
U2	Unidentified	79, 119, **175**, 189, 235, 245, 279, 304		Methylester of U7
U3	Unidentified	67, 81, 107, 119, 177, **243**, 261, 279		
U4	Unidentified	79, **95**, 105, 119, **189**, 207, 245, 302		
U5	Unidentified	105, 119, **133**, 175, 187, 213, 288		
U6	Unidentified	91, 105, 119, 133, **173**, 189, 221, 229, 287, 302		
U7	Unidentified	79, **107**, 121, 153, **175**, 235, 290		
U8	Unidentified	**91**, 107, 133, 185, 227, 241, 255, 288		
U9	Unidentified	91, 105, 121, 159, 173, 229, 237, **285**, 301, 345, 360		
U10	Unidentified	105, 131, **159**, 239, 259, 302		
U11	Unidentified	55, 67, 81, **95**, 107, 119, 135, 161, 189, 207, 277		
U12	Unidentified	81, **95**, 121, 189, 207, 229, 291, 305		
U13	Unidentified	91, 133, **189**, 249, 303		
U14	Unidentified	117, 128, **187**, 225, 267, 285, 300		
U15	Di- or polymeric matrix constituent	105, **133**, 295, 321, **377**, 392	[34]	
U16	Unidentified, probably di- or polymeric matrix	91, 105, 229, 289, **333**, 249, 361, 393, 408	[23]	
U17	Di- or polymeric matrix constituent	81, 105, 145, 229, 325, 355, **387**, 402, 430, 462, 488		
U18	Di- or polymeric matrix constituent	105, **133**, 257, 375, 435, 450	[34]	
U19	Di- or polymeric matrix constituent	91, 131, 229, 289, **375**, 391, 403, 435, 450	[34]	
U20	Di- or polymeric matrix constituent	105, **121**, 133, **229**, 257, 289, 391, 435, 448, 476	[34]	

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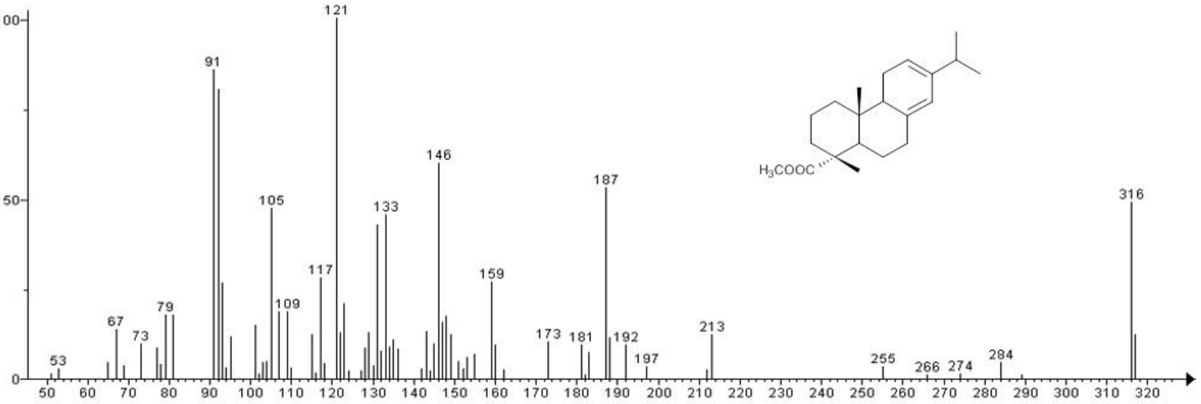
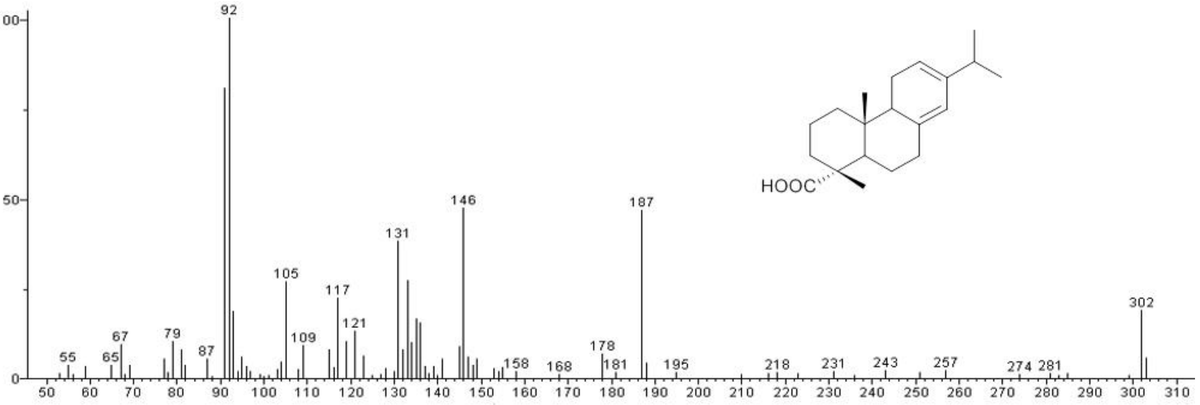
Atlas of mass spectra

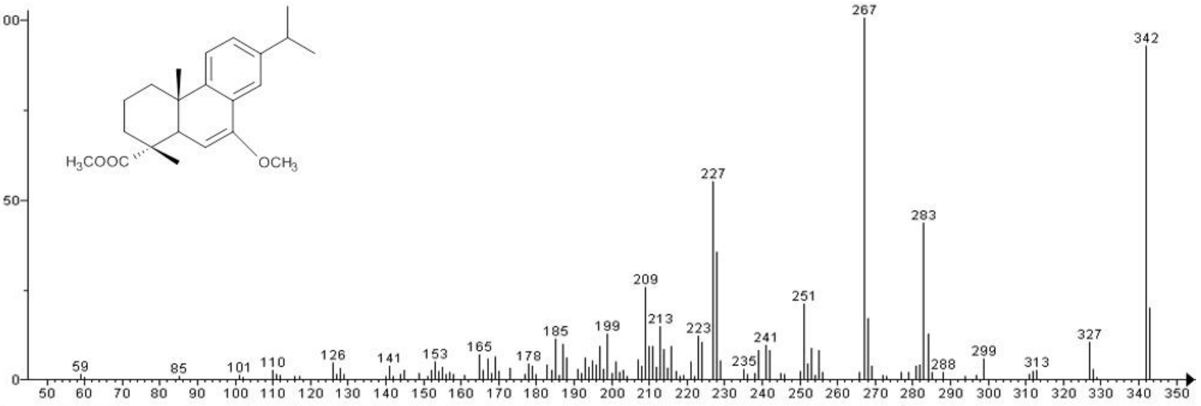
Mass spectra were obtained under electron ionisation conditions (70 eV). They were extracted with AMDIS after deconvolution. In some case this was not possible due to low intensities, then the related mass spectra were extracted with MS Data review. Peak labels refer to those used in the figures and tables in the related chapters and in the section above (‘Compound lists’). The mass spectra are presented in the order of their occurrence within the chapters of this work and refer to the single chapters Pinaceae, Cupressaceae, *Copaifera*, legume copals, *Myroxylon* and Burseraceae. The respective chapter can be found in the headlines.



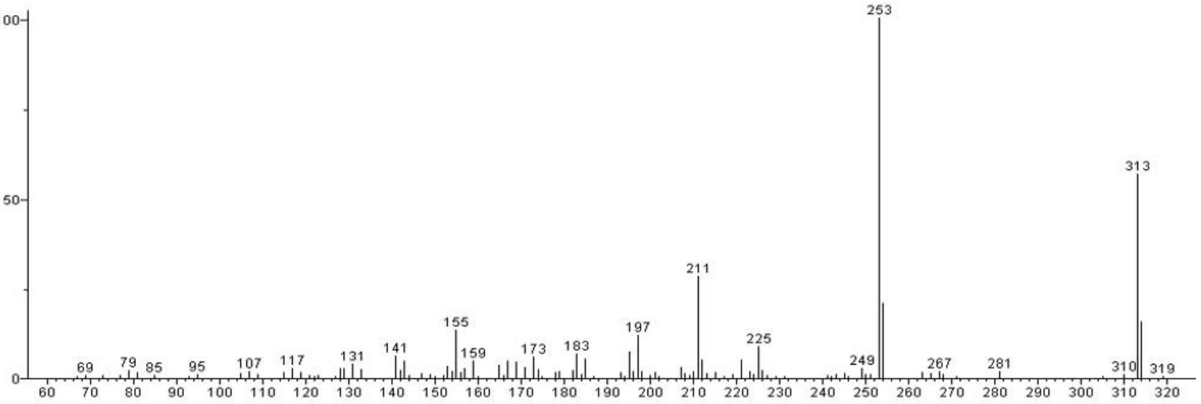
A5, Levopimarate



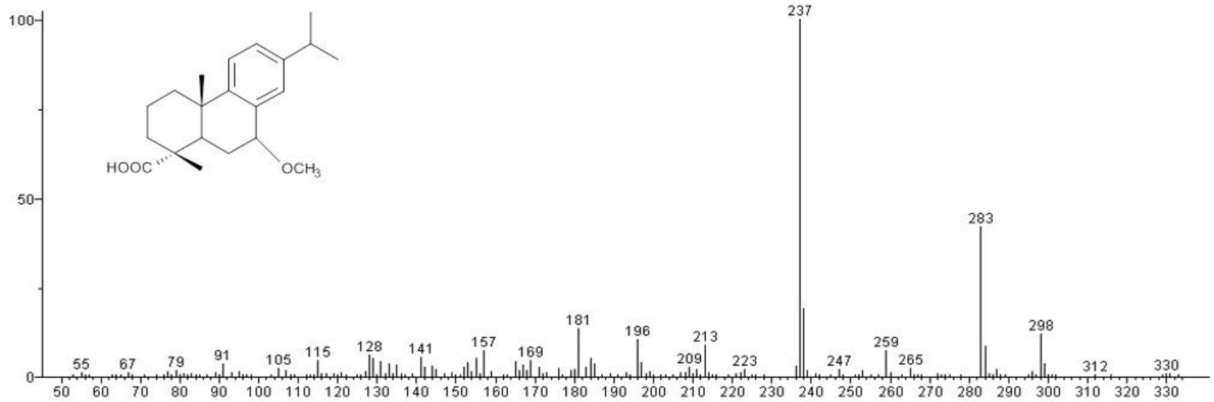
A14, Levopimaric acid



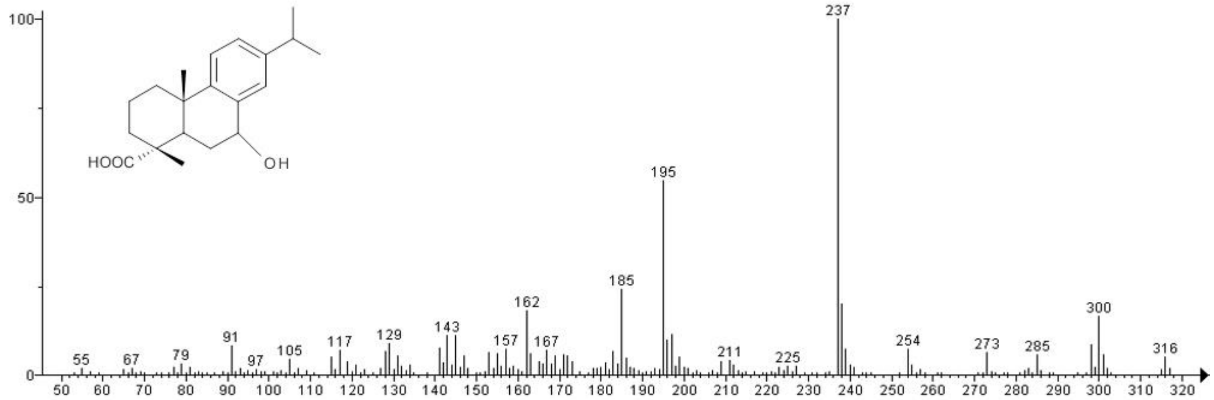
A19, 7-methoxy-Δ6(7)-dehydrodehydroabietate



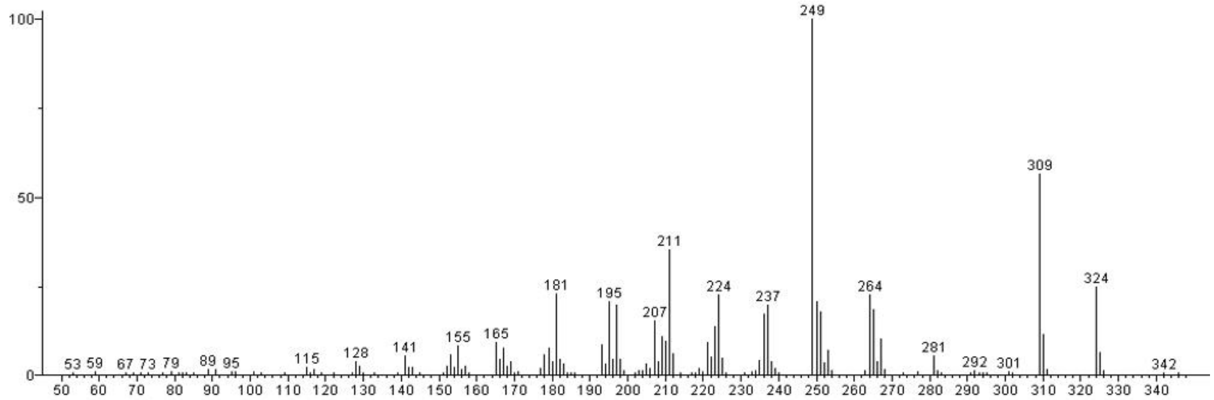
A27, Δ16-demethyl-7-oxo-dehydroabietate (proposed)



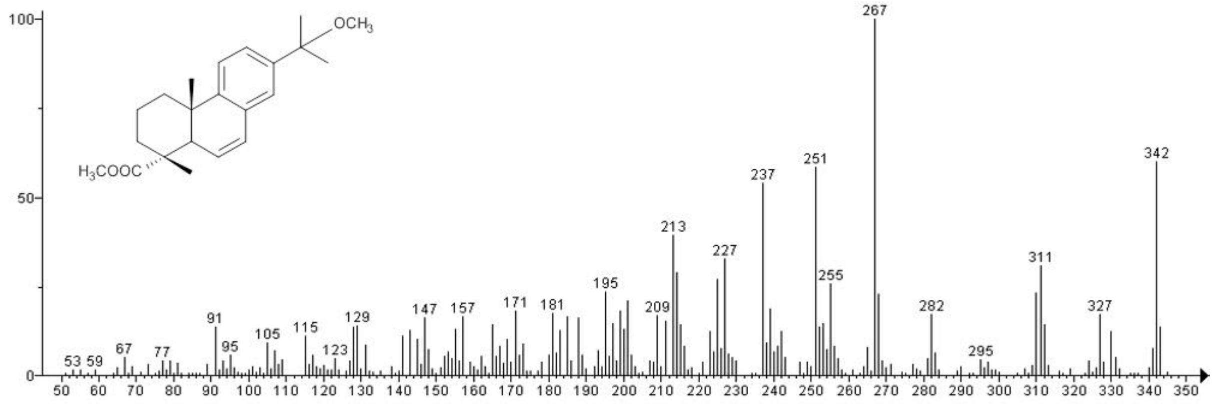
A30, 7-methoxy-dehydroabietic acid (proposed)



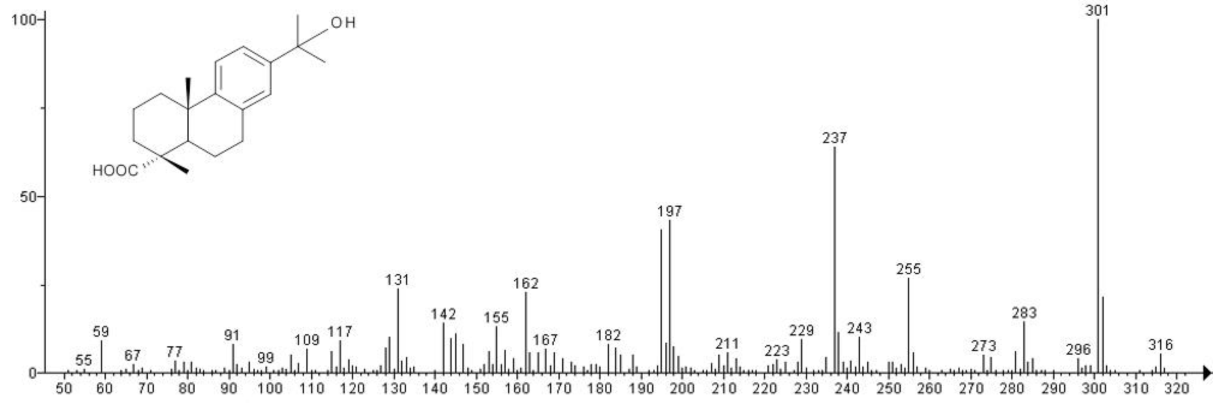
A35, 7-hydroxy-dehydroabietic acid



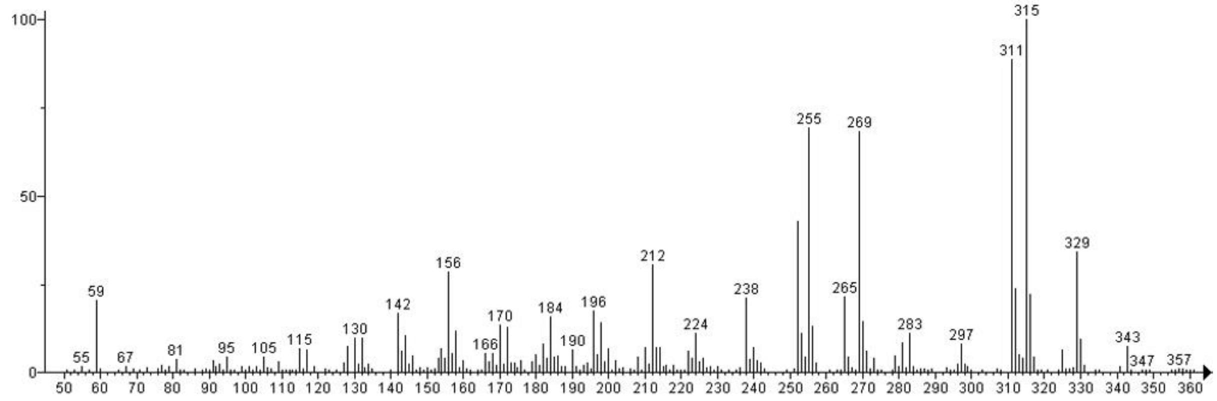
A36, Unidentified (di)hydroxy-dehydroabietate



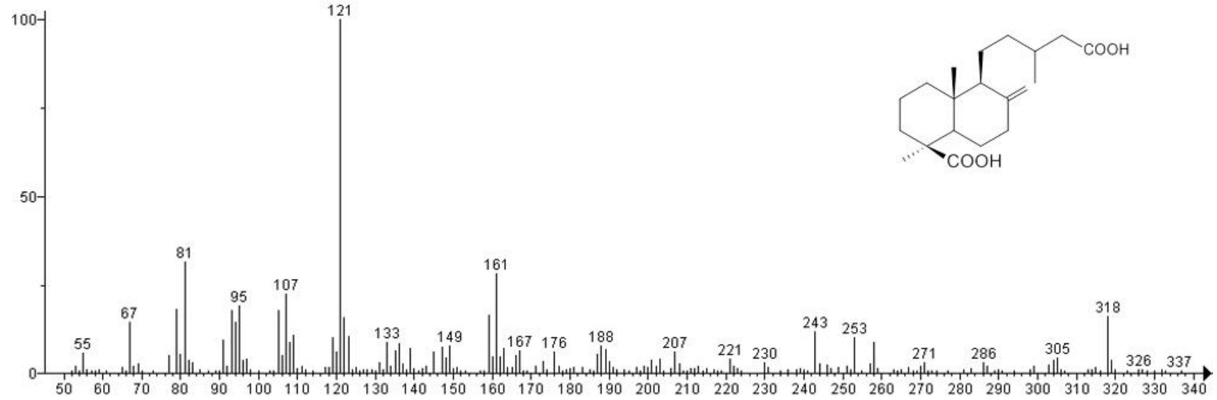
A37, 15-methoxy-∆6(7)-dehydrodehydroabietate



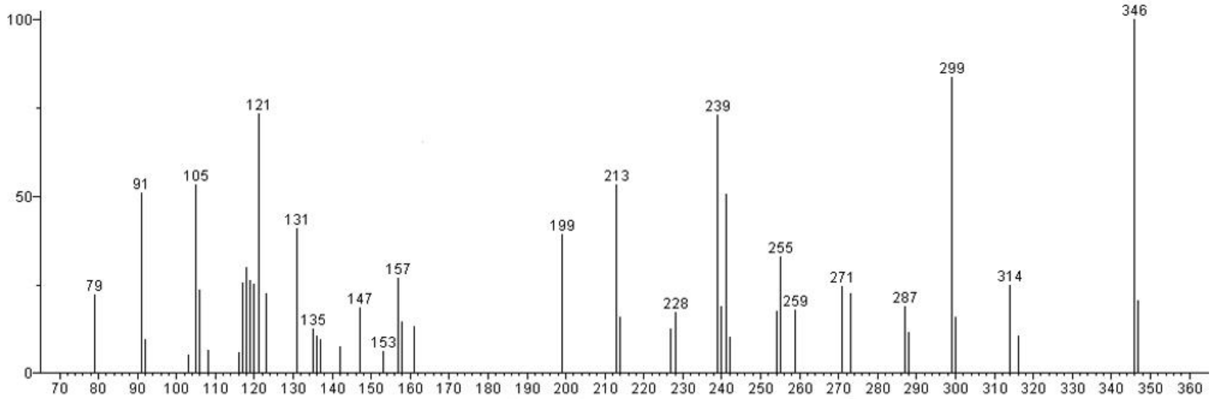
A39, 15-hydroxy-dehydroabietic acid



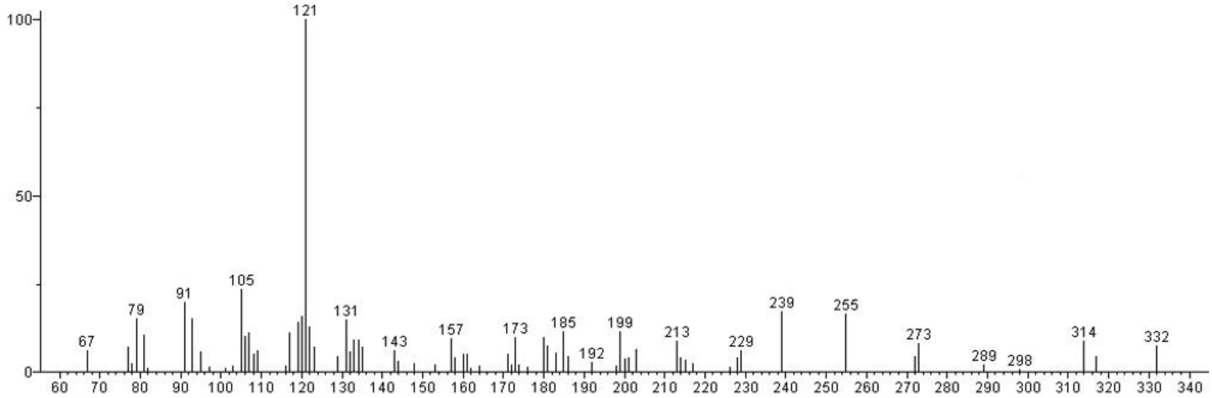
A43, Unidentified methoxy-dehydroabietate



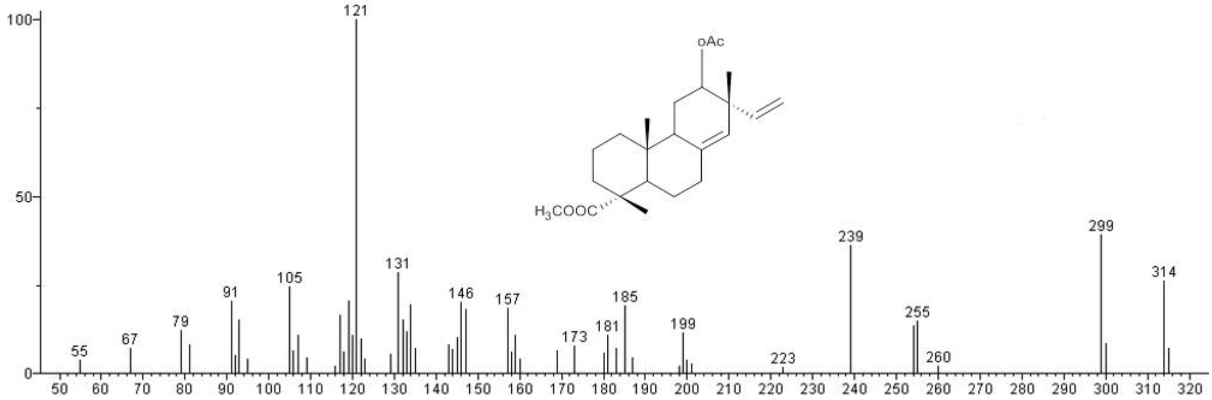
L51, Dihydroagathic acid (proposed)



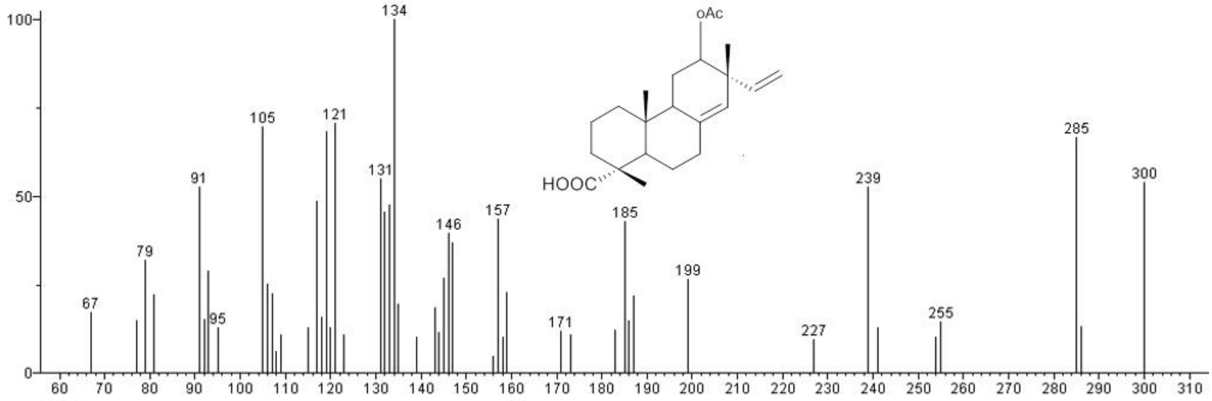
P17, Methoxy-sandaracopimarate, the position of the methoxy group is unknown



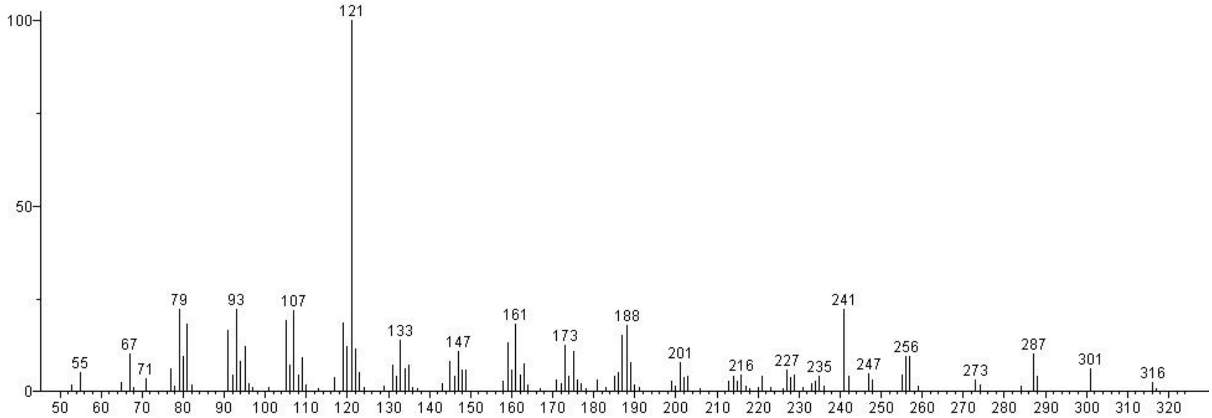
P19, Hydroxy form of sandaracopimarate, the position of the hydroxyl group is unknown



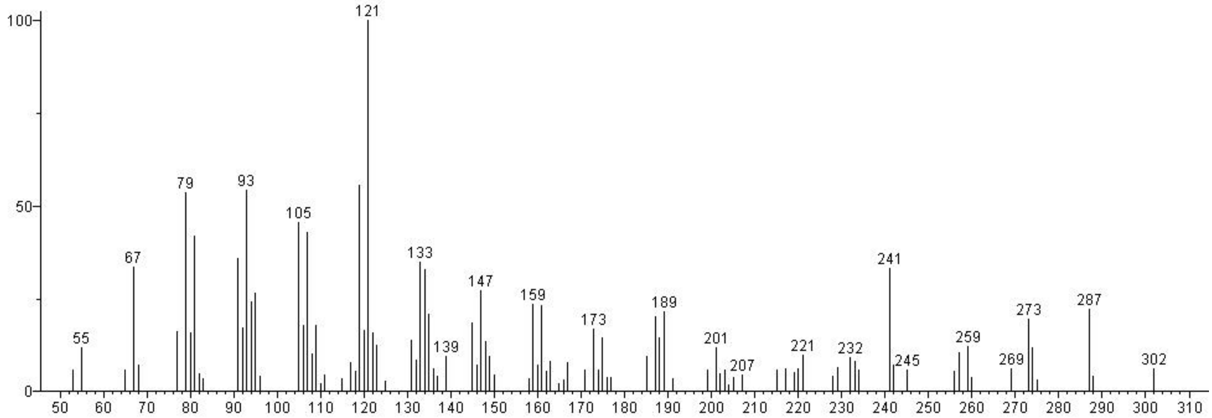
P20, 12-acetoxy-sandaracopimarate



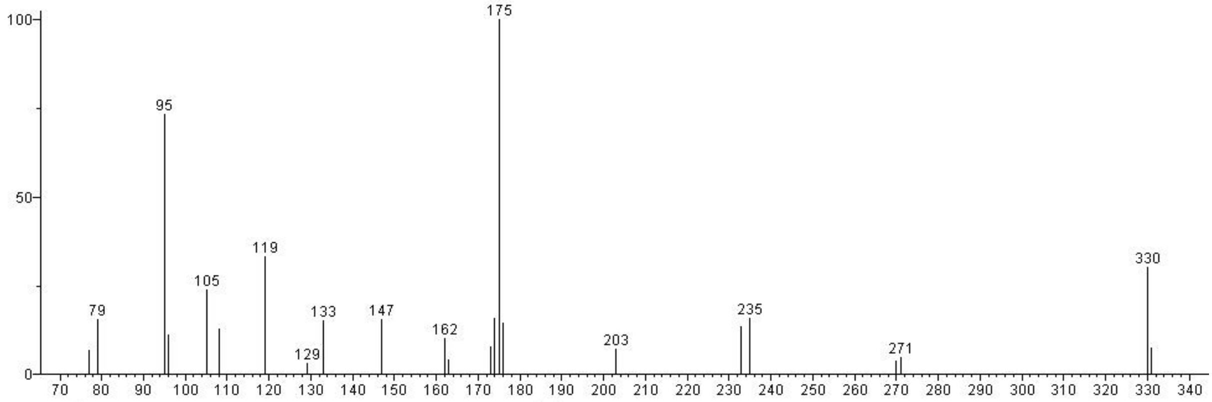
P21, 12-acetoxy-sandaracopimaric acid



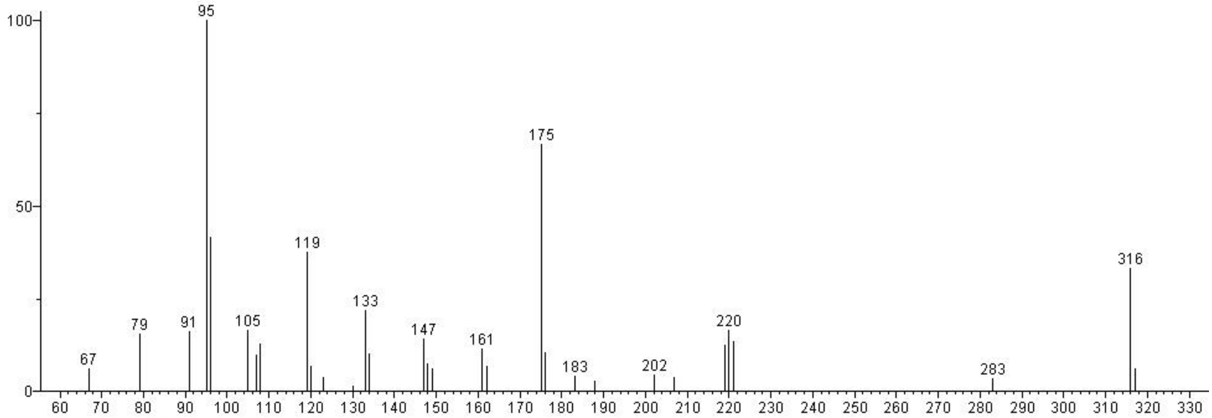
L20, Unidentified labdane acid, methylester of L29



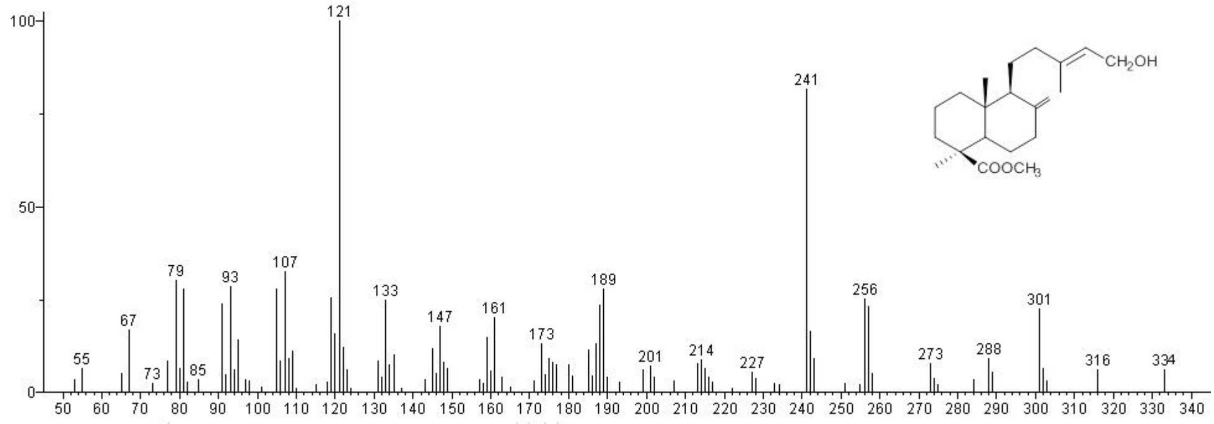
L29, Unidentified labdane acid



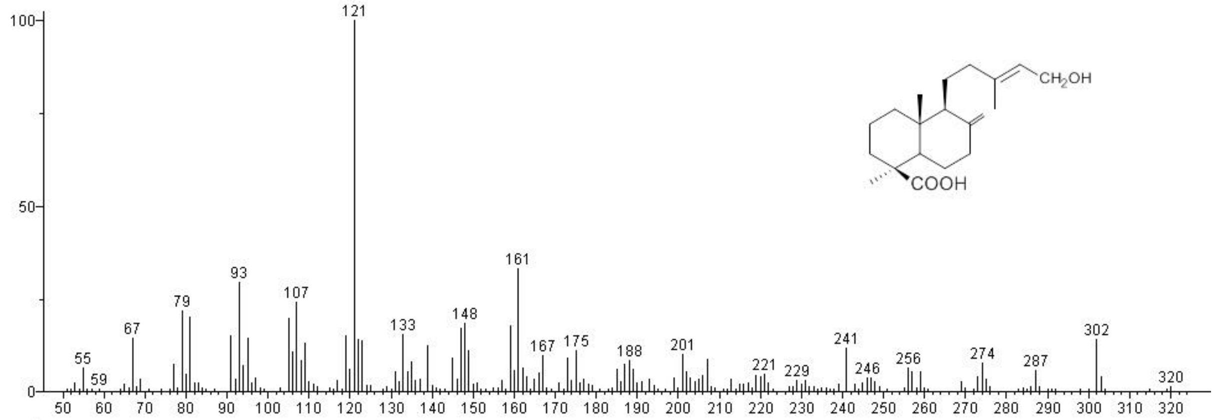
D13, Unidentified diterpene acid, methylester of D22



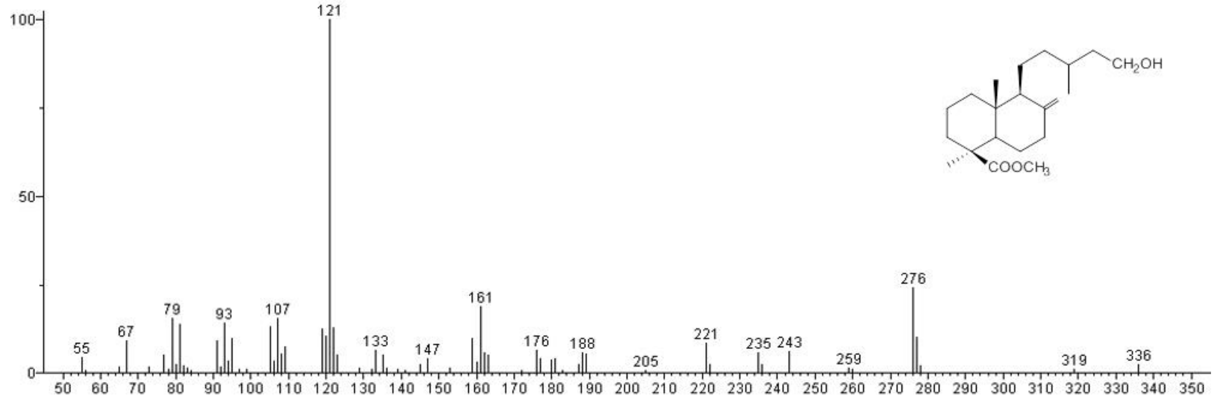
D22, Unidentified diterpene acid



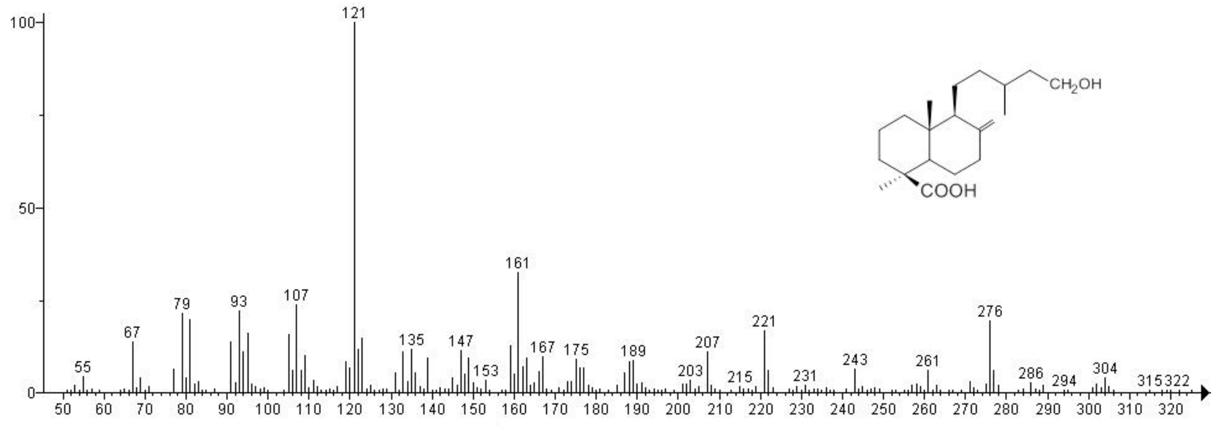
L31, Isocupressate



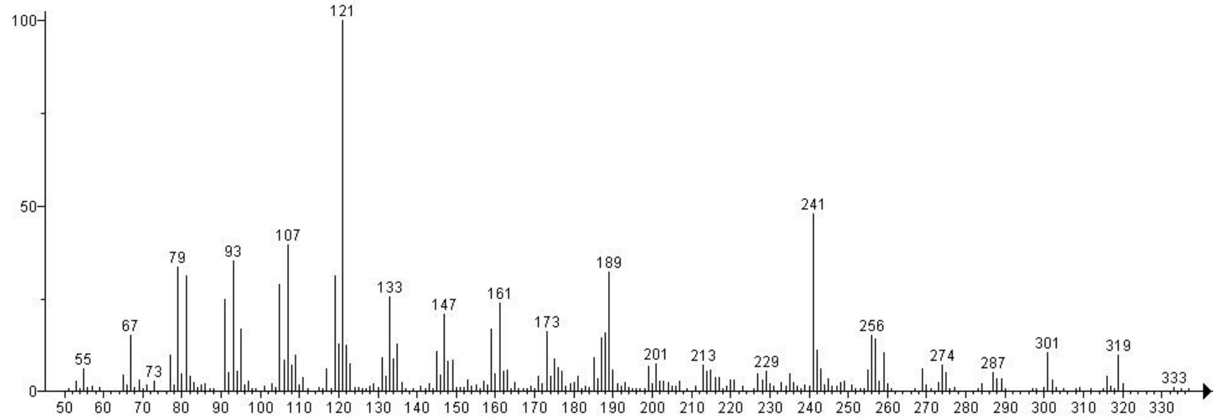
L42, Isocupressic acid



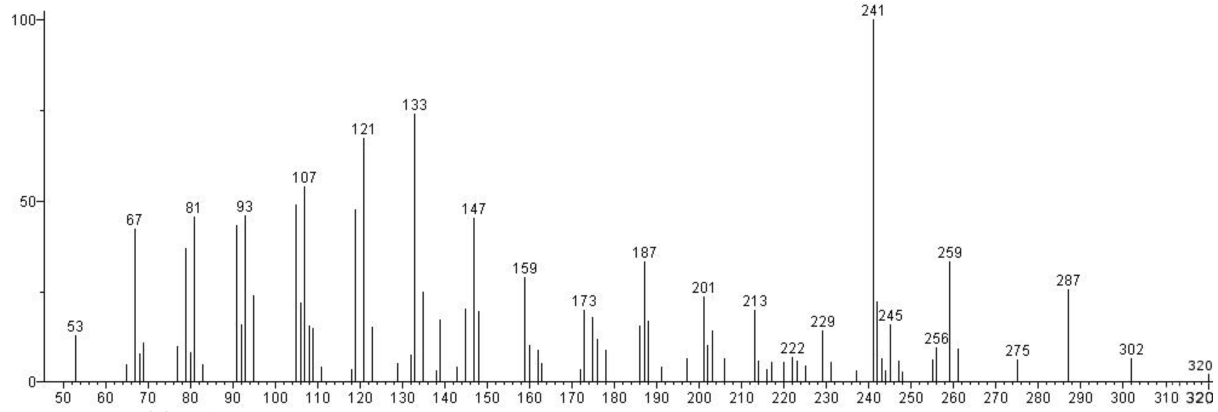
L34, dihydroisocupressate (imbricatoloate)



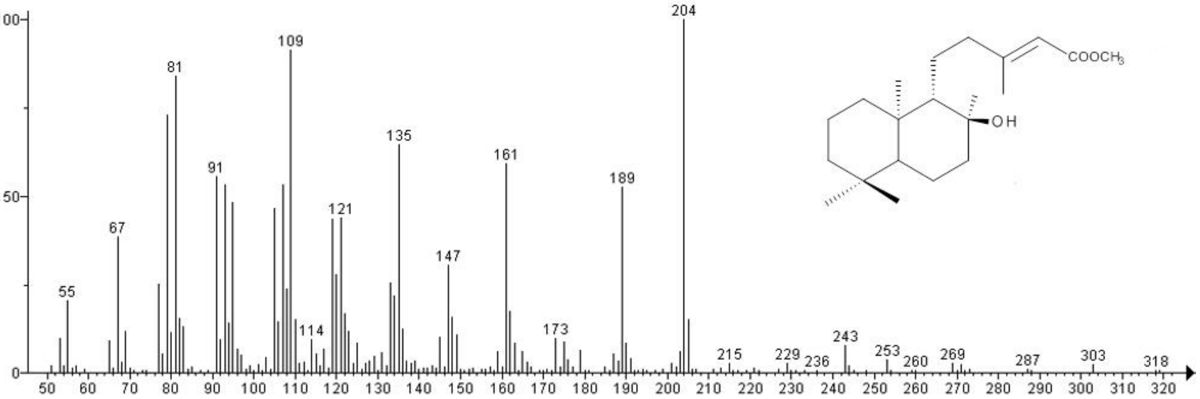
L46, dihydroisocupressic acid (imbricatoloic acid)



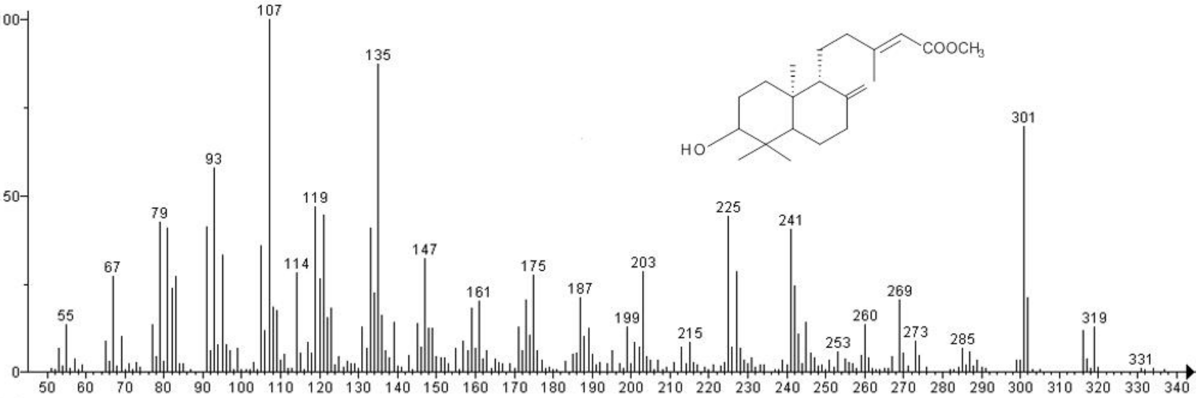
L38, Unidentified labdanoate, methylester of L48



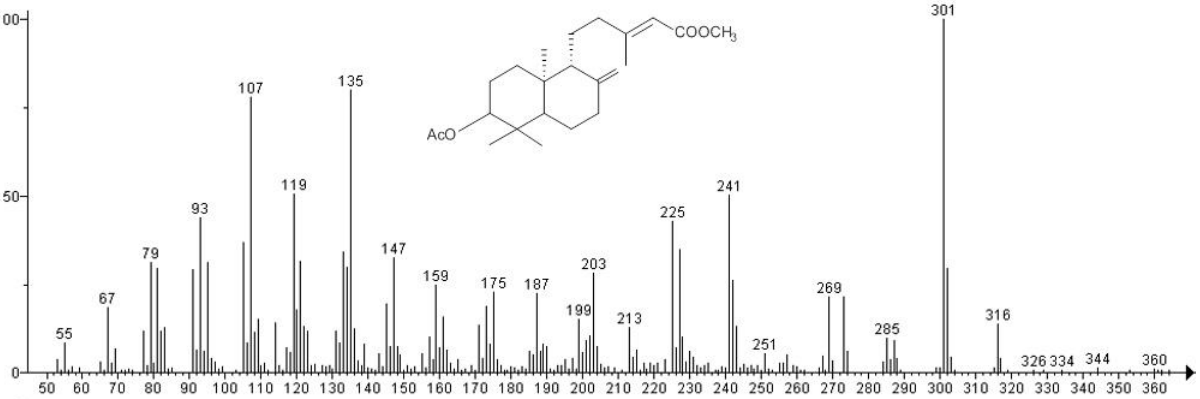
L48, Unidentified labdenoic acid



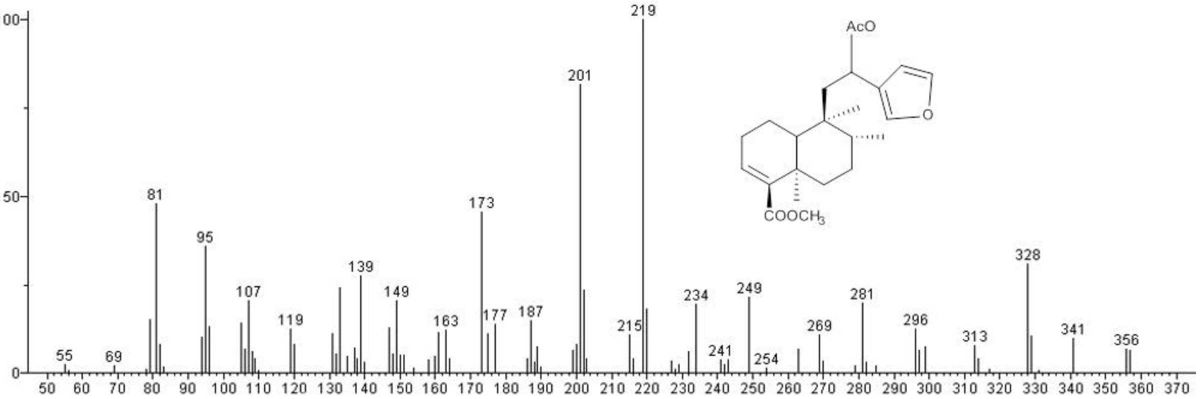
eL17, Ent-labda-13-en-8-ol-15-oate, MW at m/z 336 not present



eL37, 3-Hydroxy-copalate

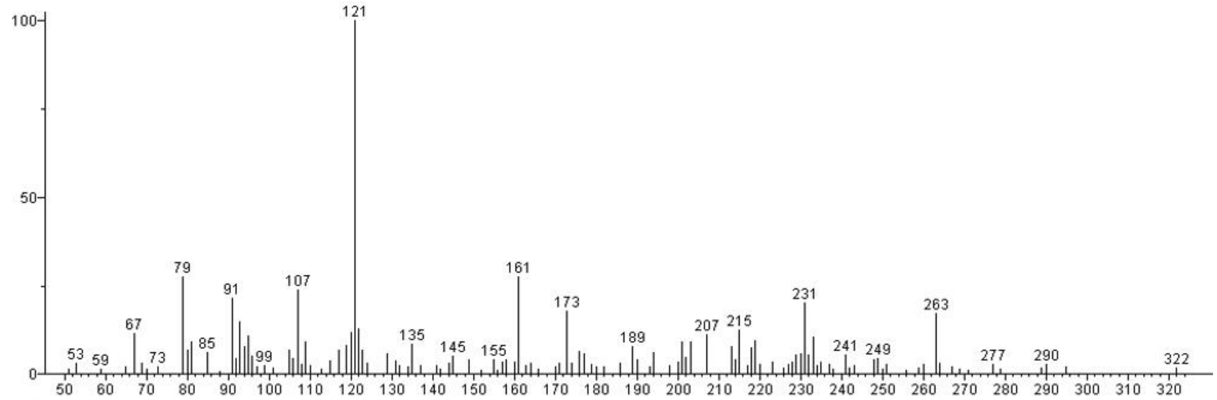


eL43, 3-Acetoxy-copalate

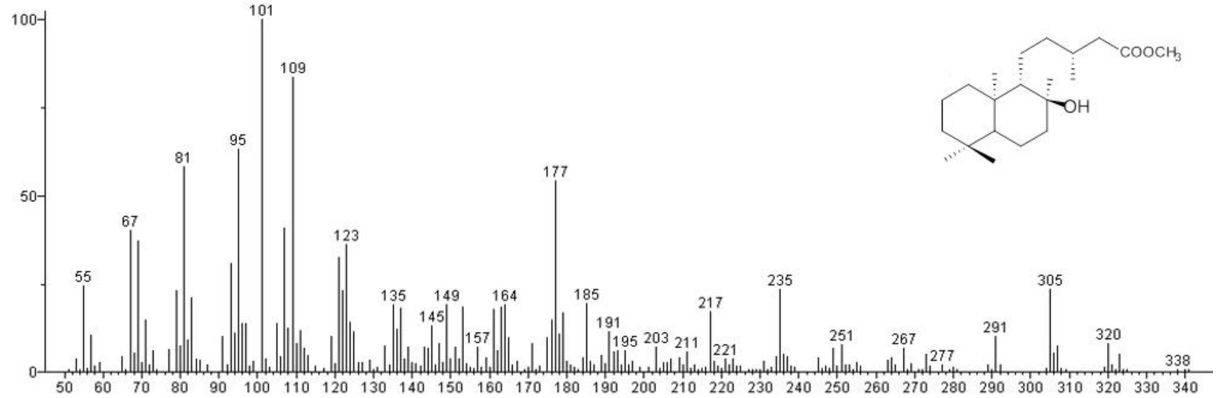


C7, 12-Acetoxy-hardwickiate

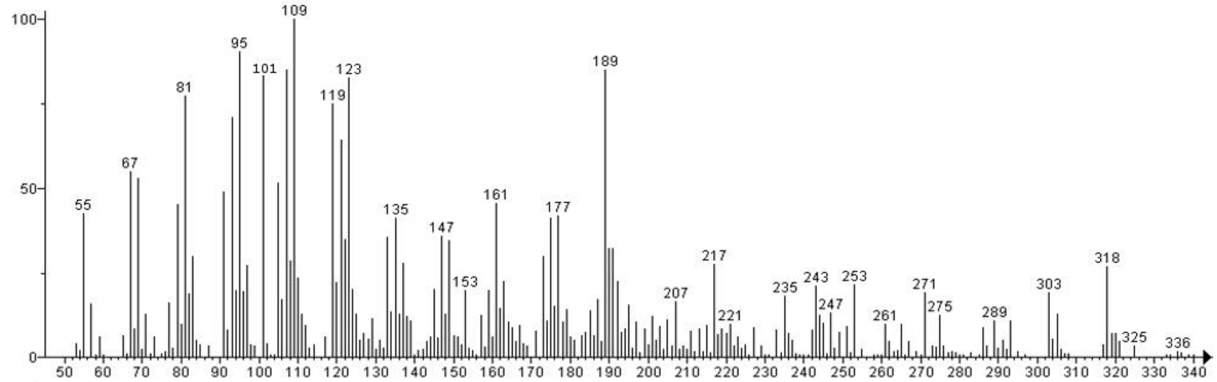
Congo copals



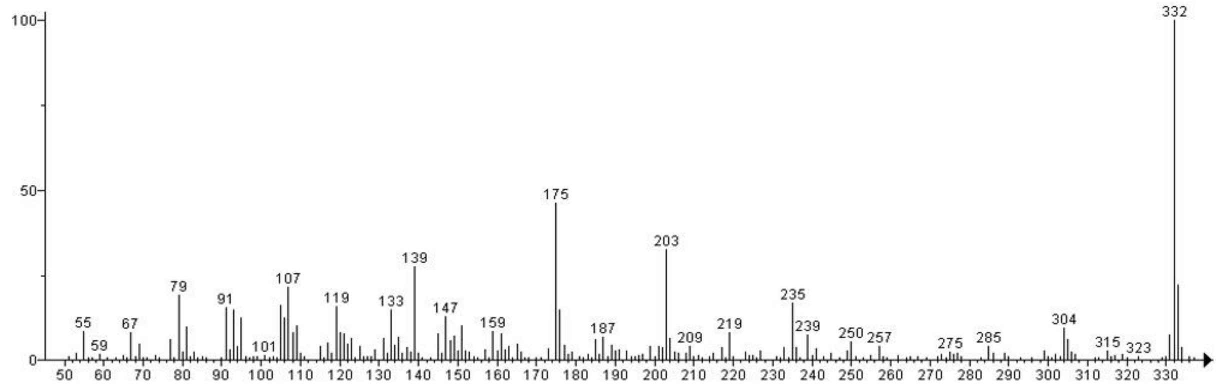
eL12, Ent-labdan-18-oate



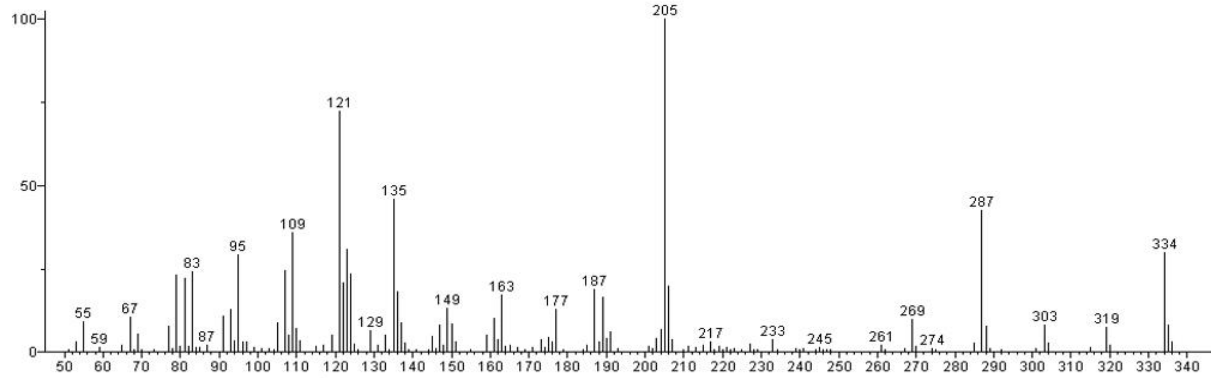
eL20, Ent-labda-8-ol-15-oate (ent-labdanolate)



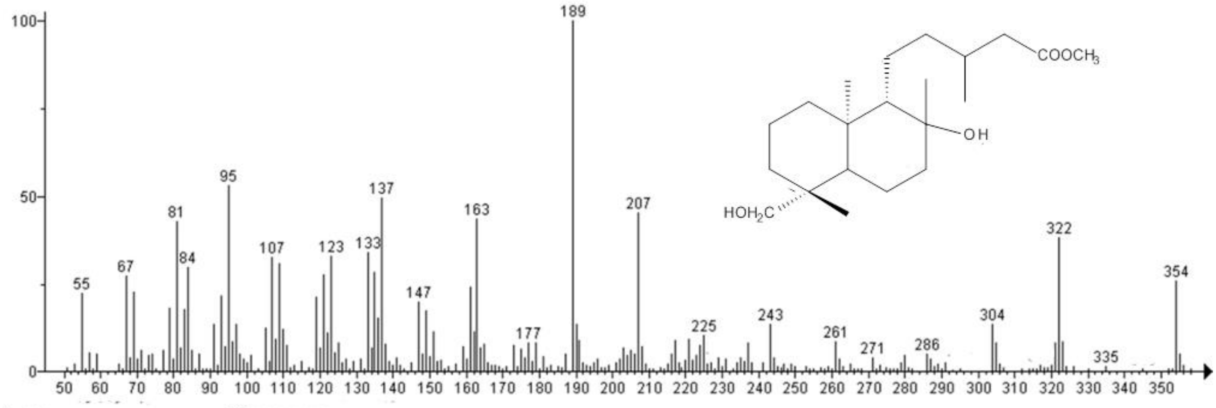
eL22, Unidentified ent-labdane acid



eL32, Oxo-ent-labda-13(14)-dien-15-oate, the position of the keto group is unknown

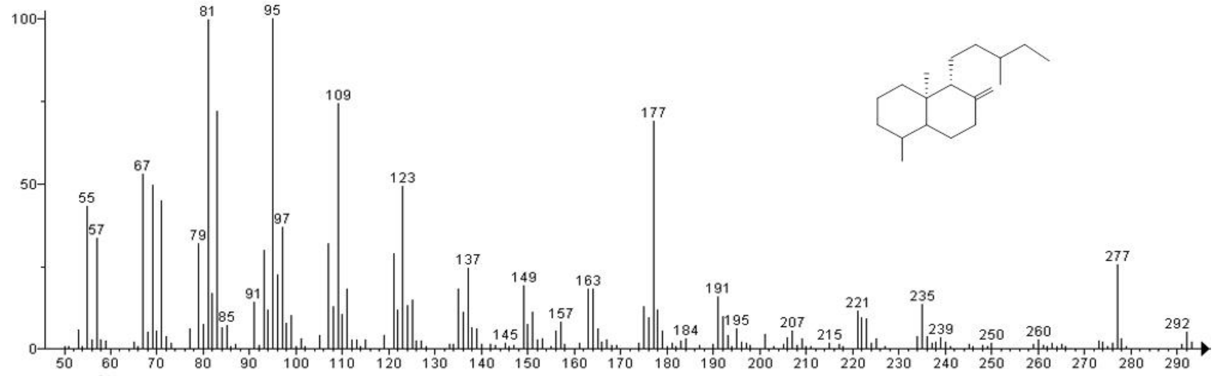


eL34, Hydroxy-ent-labda-8(20)-dien-15-oate, position of the hydroxyl group is unknown

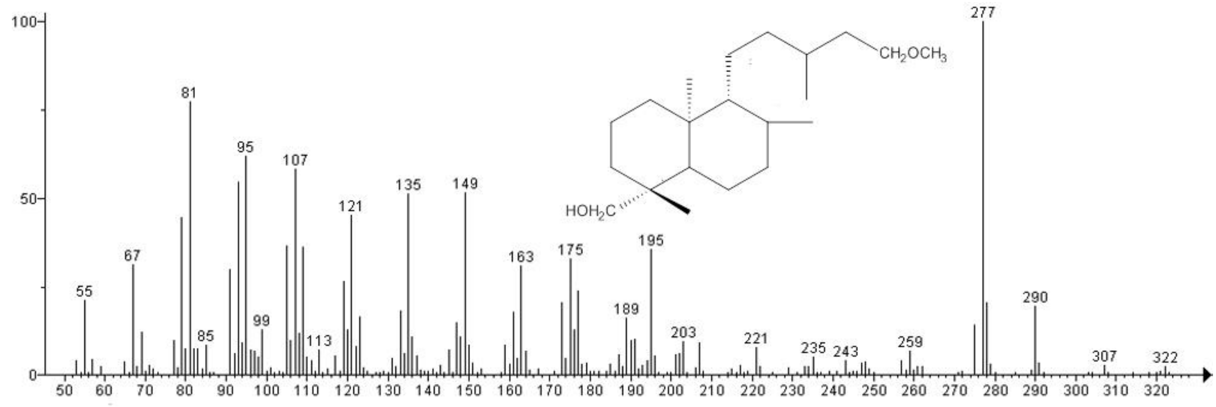


eL40 8,18-Dihydroxy-ent-labda-15-oate (proposed)

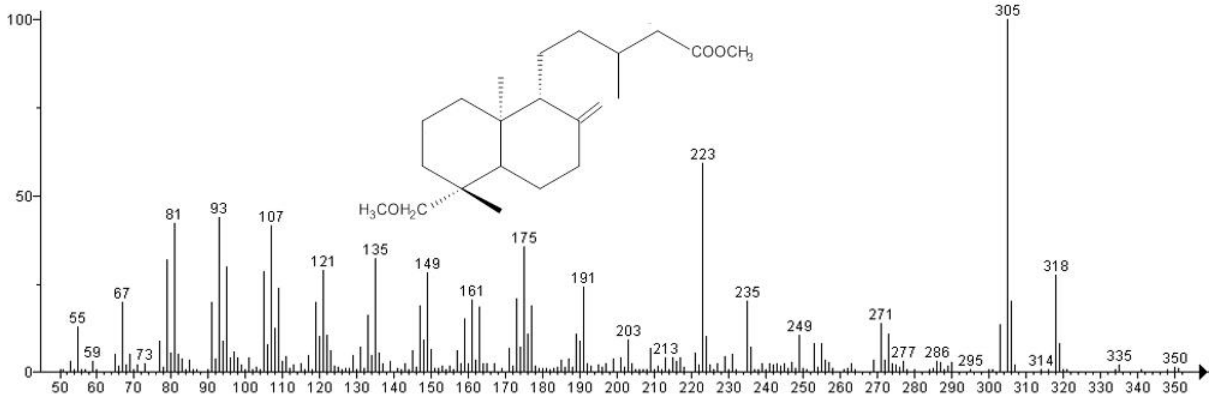
Sierra Leone copals



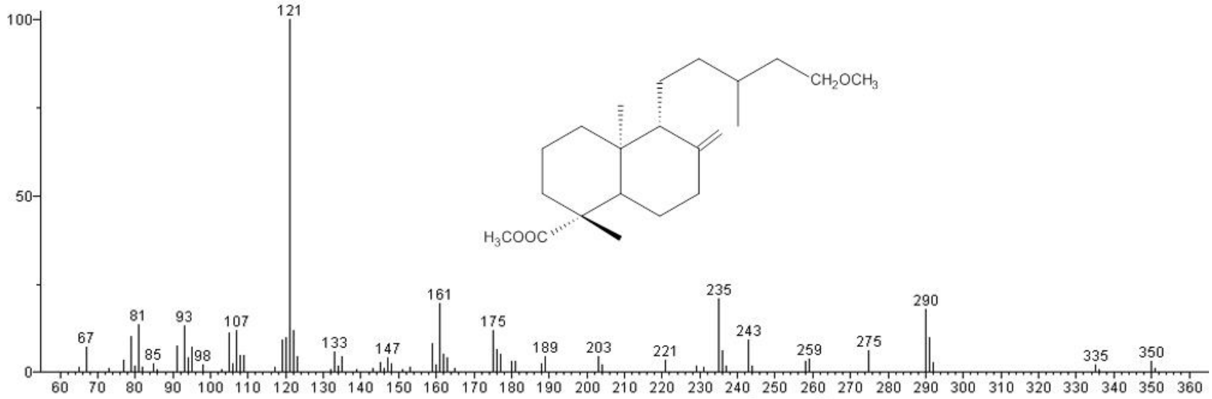
eL19, 19-Nor-ent-labda-8(20)-ene



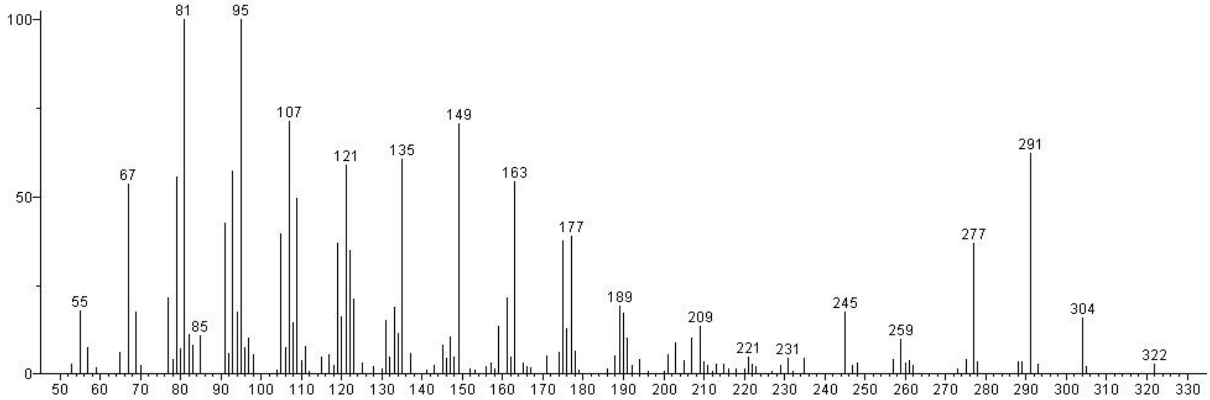
eL21, 15-methoxy-18-hydroxy-ent-labdane, methoxy ether of eL31



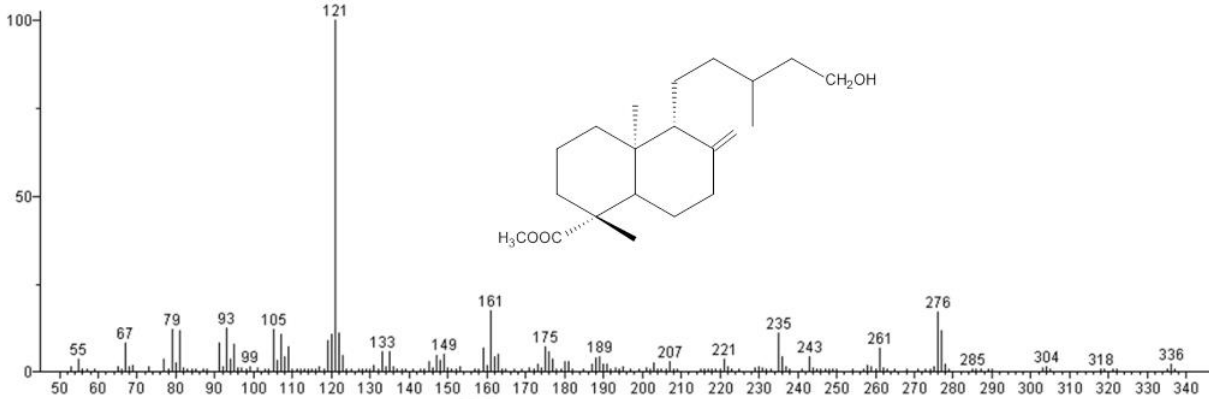
eL24, 18-Methoxy-ent-labda-8(20)-en-15-oate



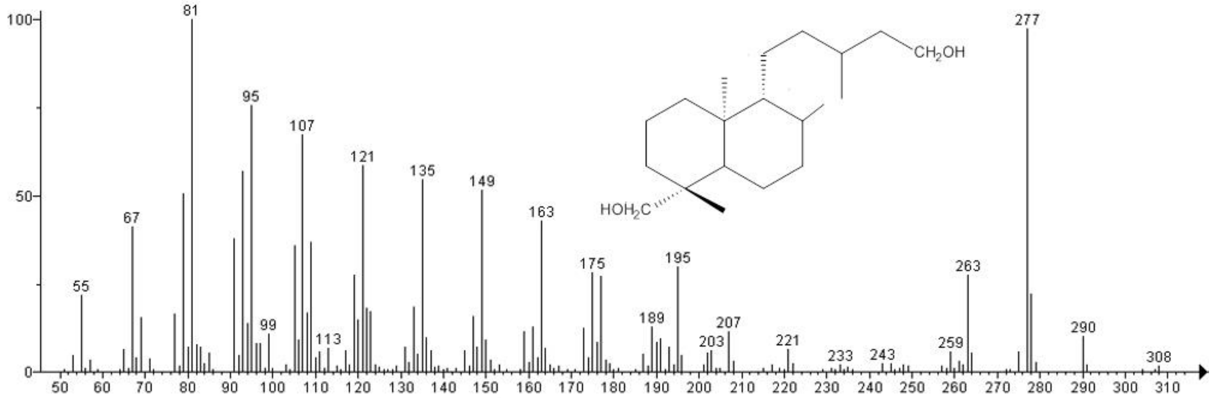
eL25, 15-Methoxy-ent-labda-8(20)-18-oate, methoxy ether of eL29



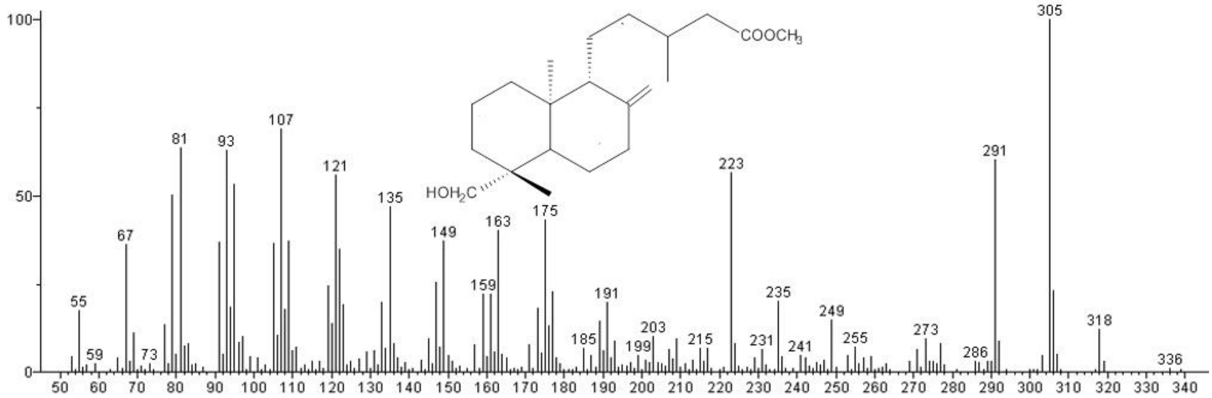
eL27, 18-Hydroxy-nor-ent-labda-13(14)-en-18-oate



eL29, 15-Hydroxy-ent-labda-8(20)-en-18-oate

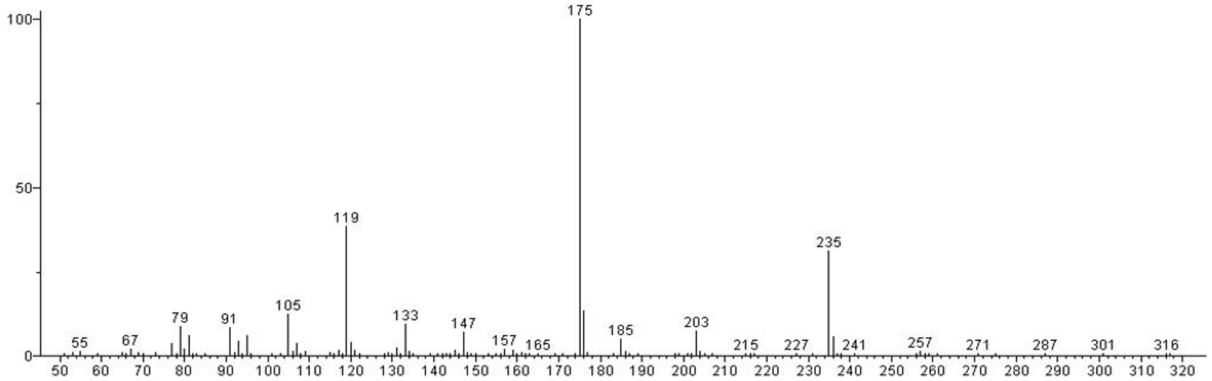


eL31, 15,18-Dihydroxy-ent-labdane

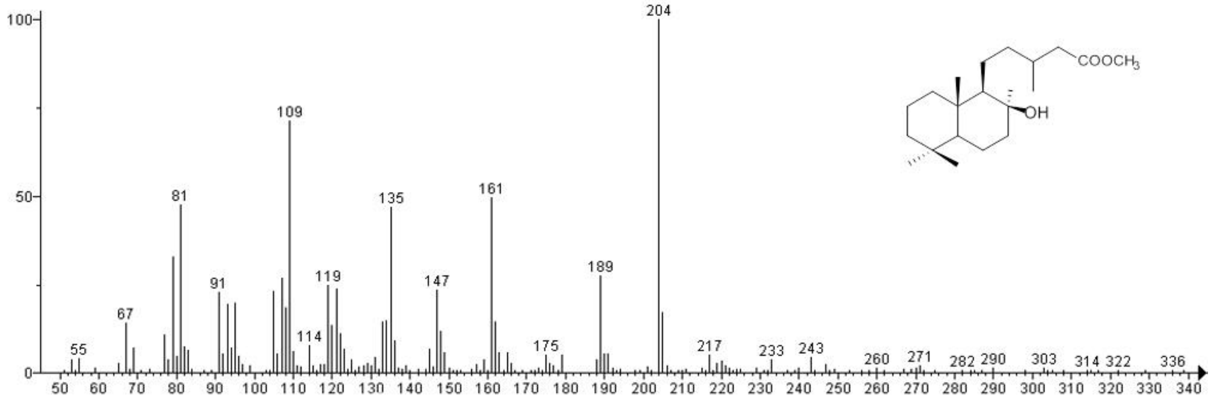


eL33, 18-Hydroxy-ent-labda-8(20)-en-15-oate

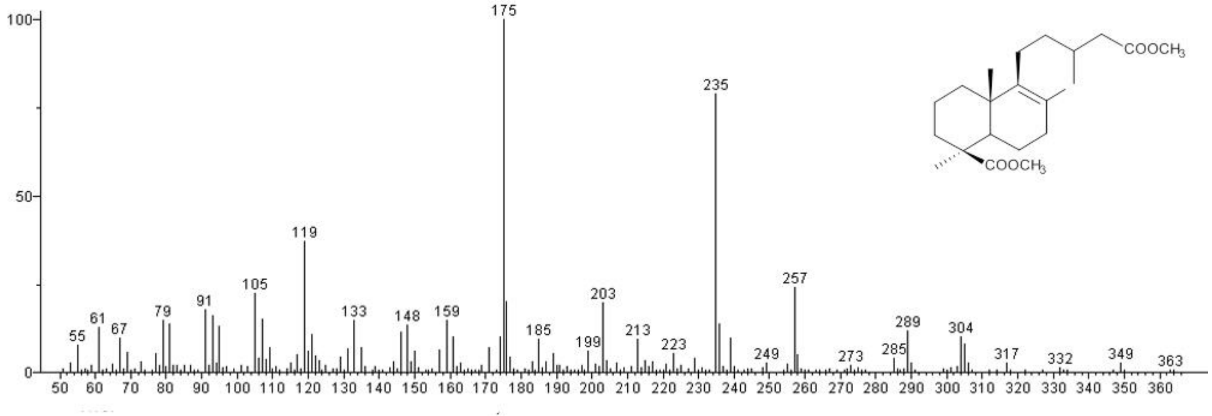
<u>Others</u>



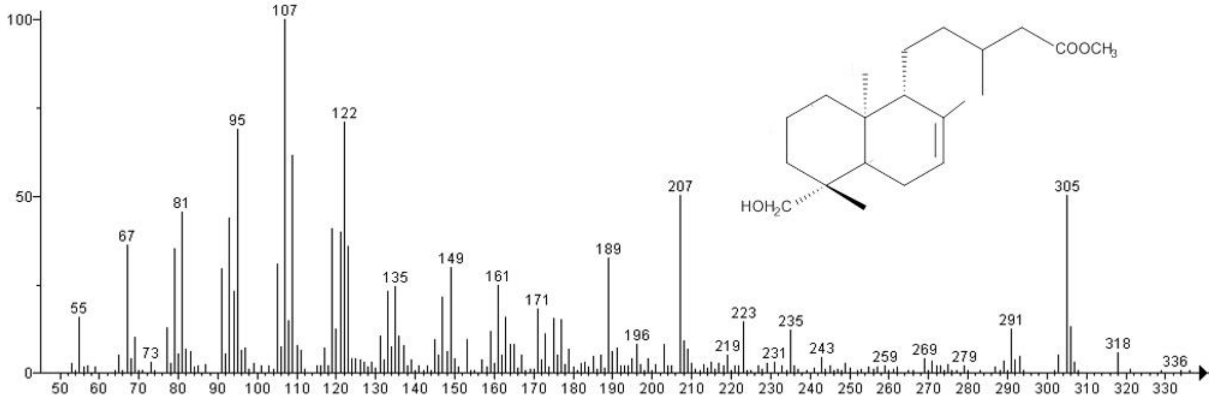
L17, Unidentified labdane acid, for possible structures see Fig. 4.20 and text



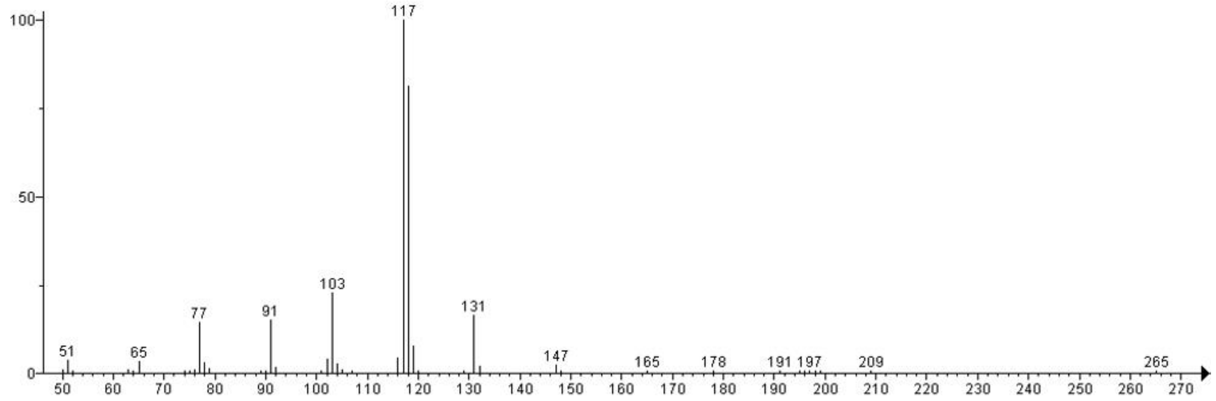
L25, Labda-13-en-8-ol-15-oate



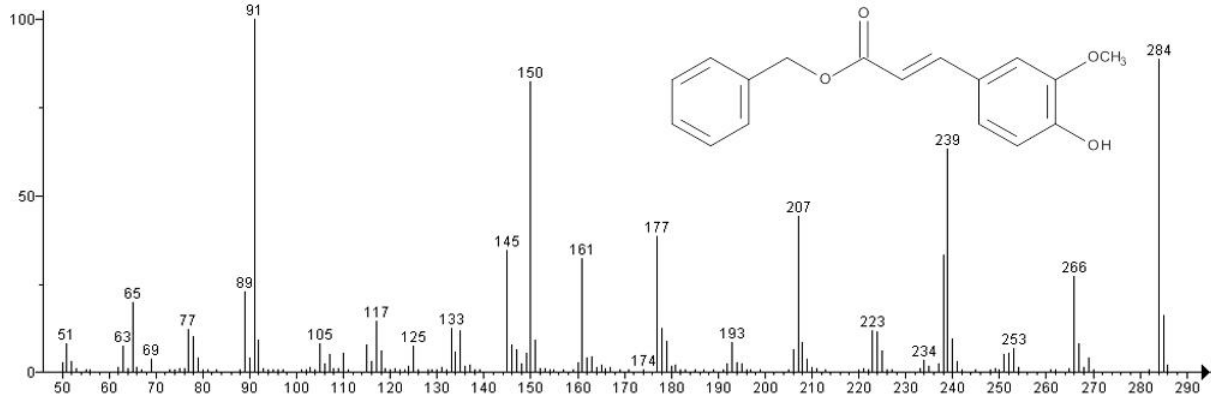
L41, ∆8-Dihydroagathate, diME



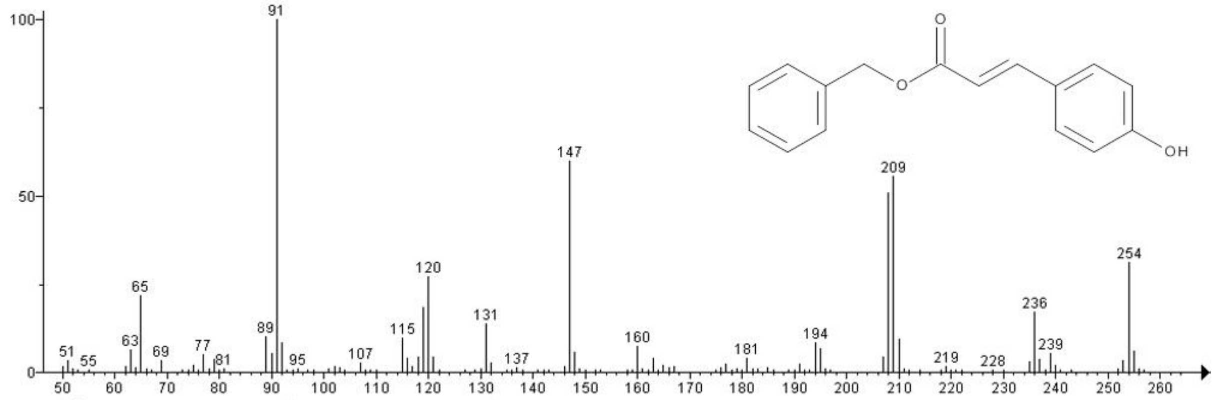
eL36, 18-Hydroxy-ent-labda-7(8)-en-15-oate



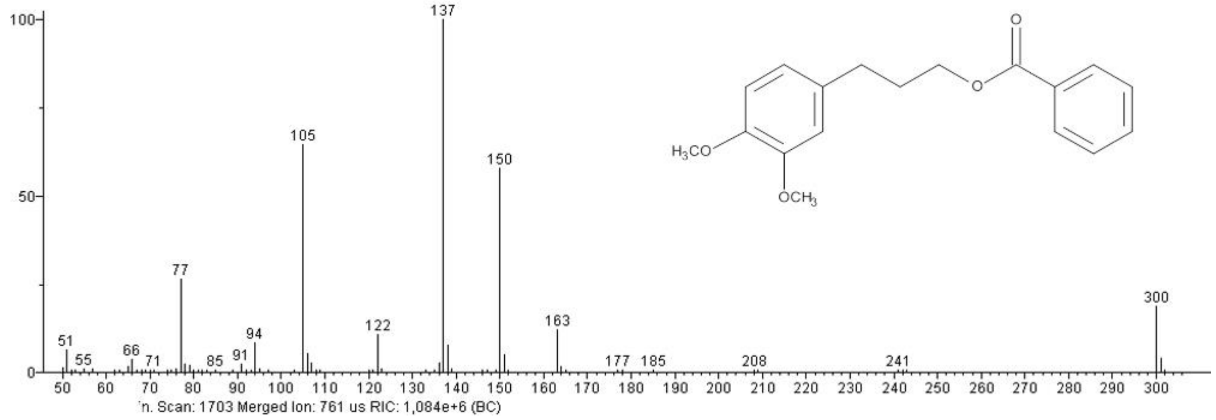
PP23



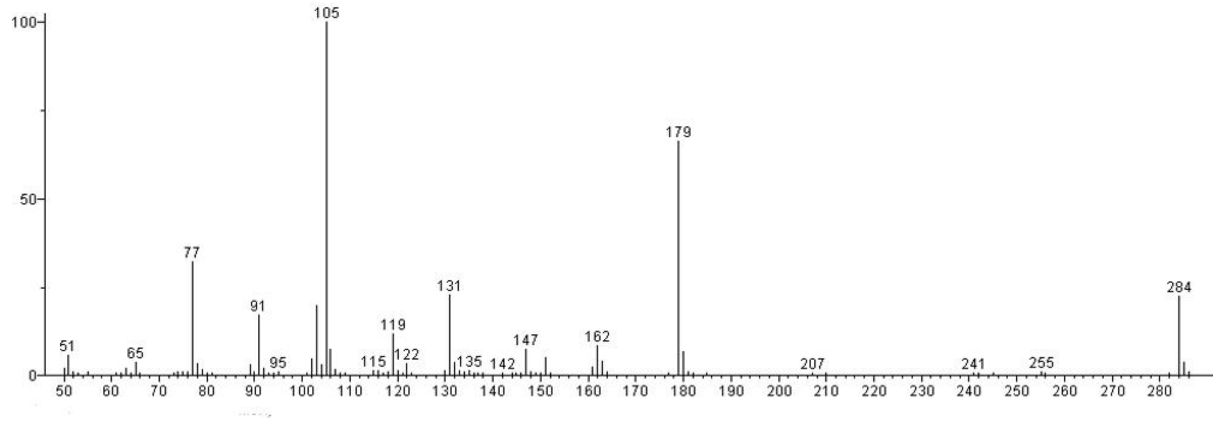
PP24, Benzyl-ferulate



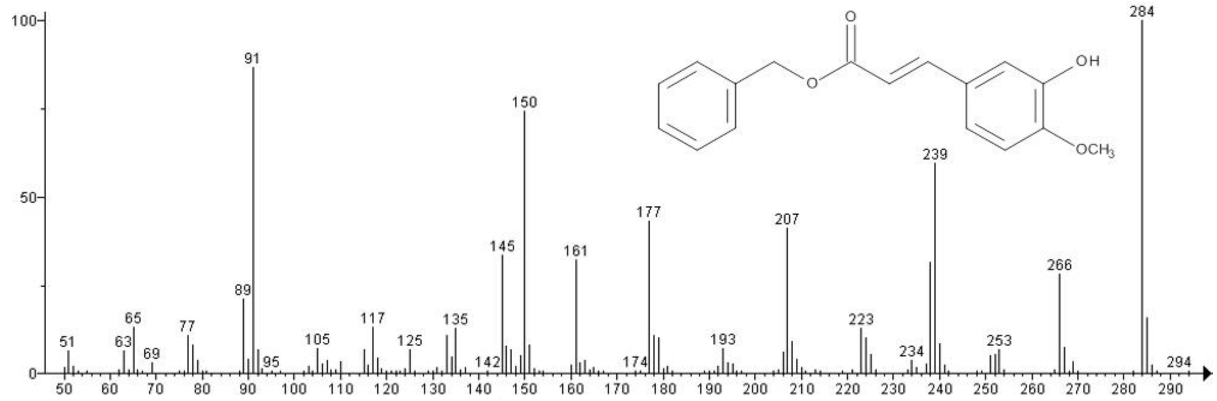
PP26, Benzyl-p-coumarate



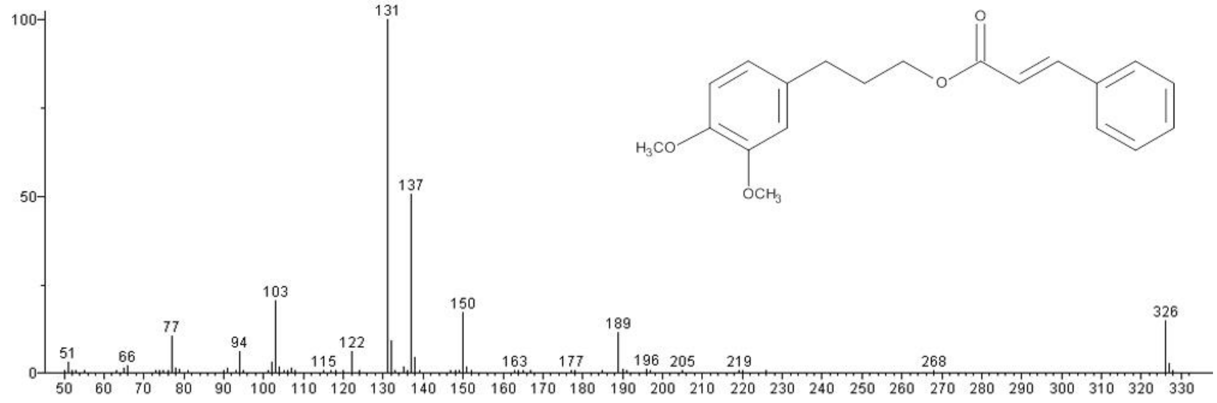
PP27, Methyl-dihydroconiferyl-benzoate



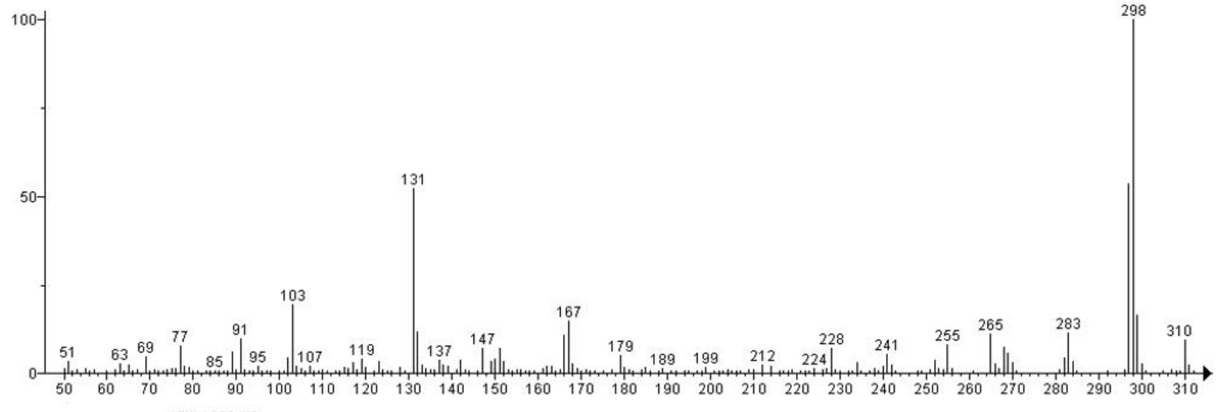
PP28



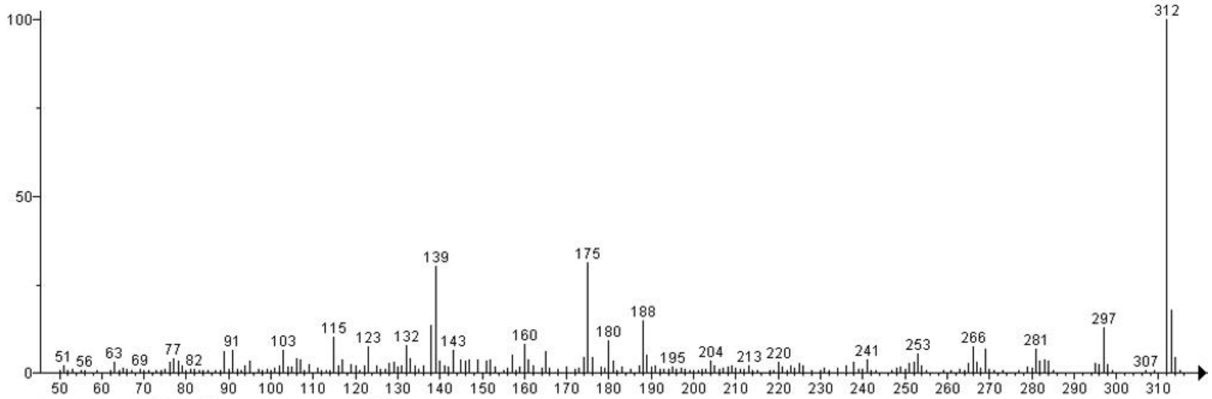
PP29, Benzyl-isoferulate



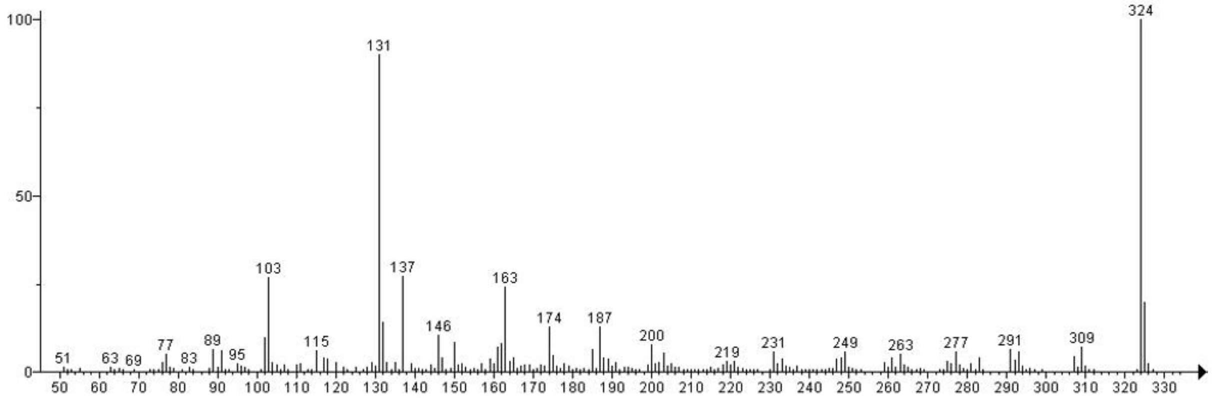
PP30, Methyl-dihydroconiferyl-cinnamate



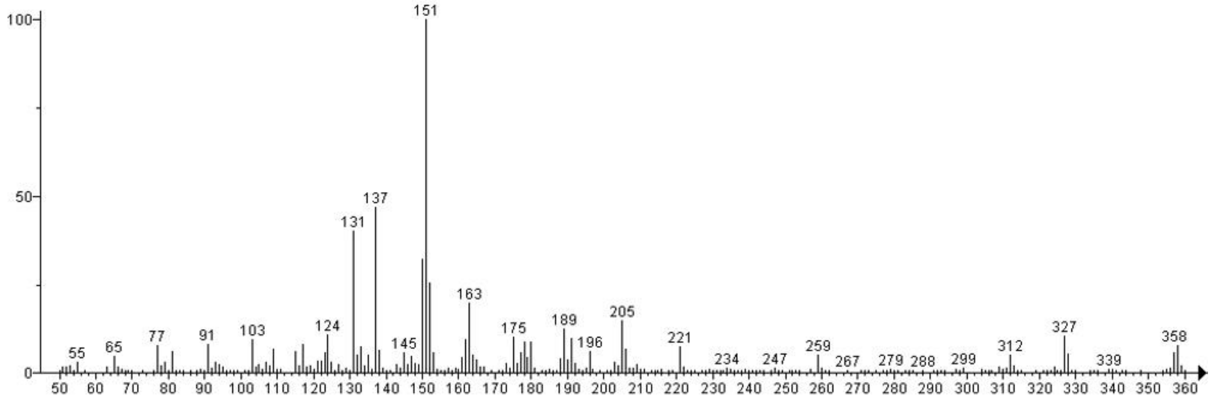
PP31



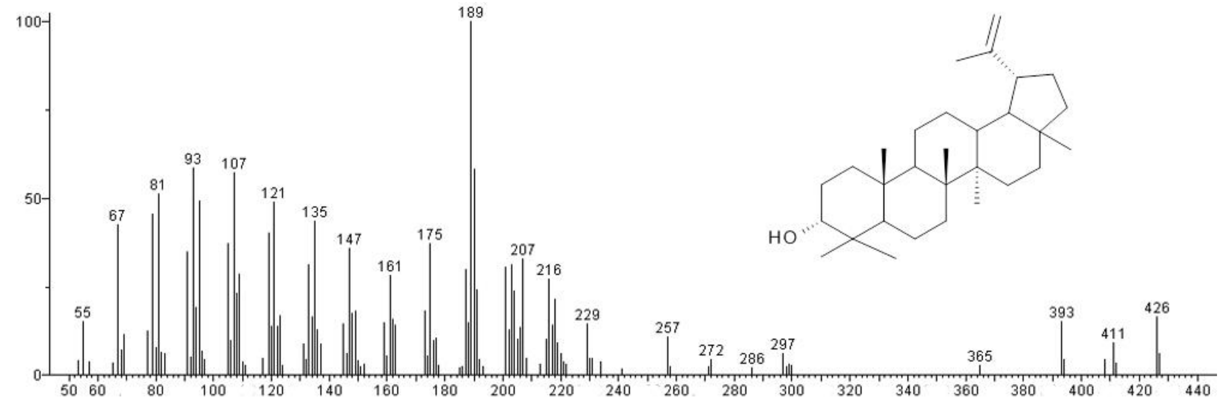
PP32



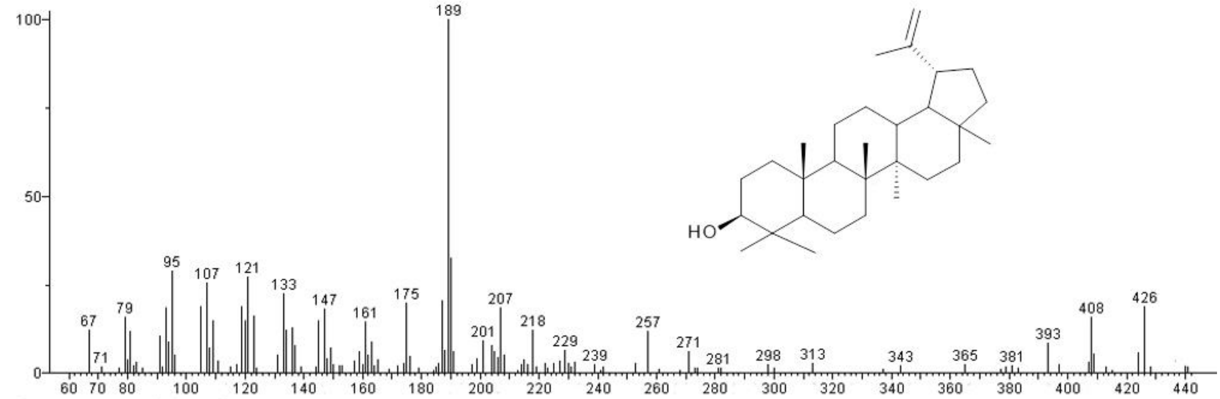
PP33



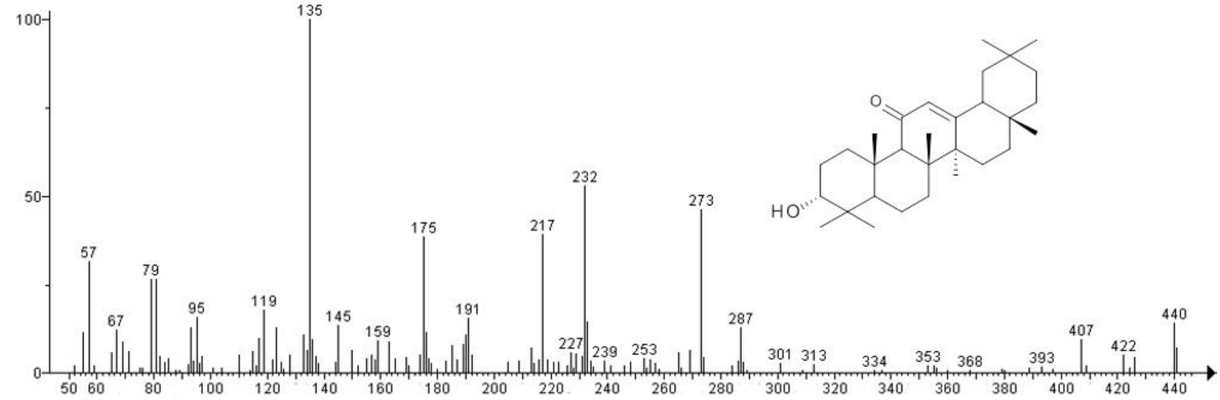
PP34



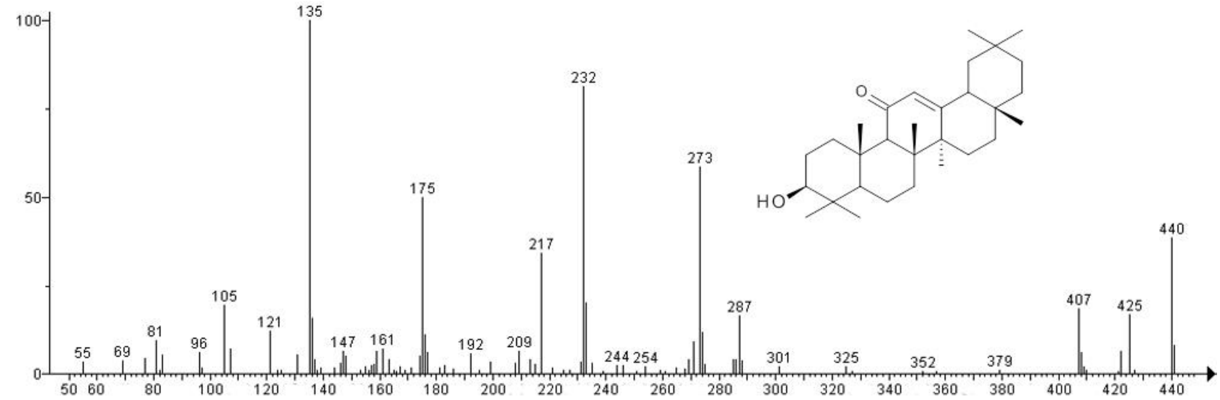
Lu1, Epi-lupeol



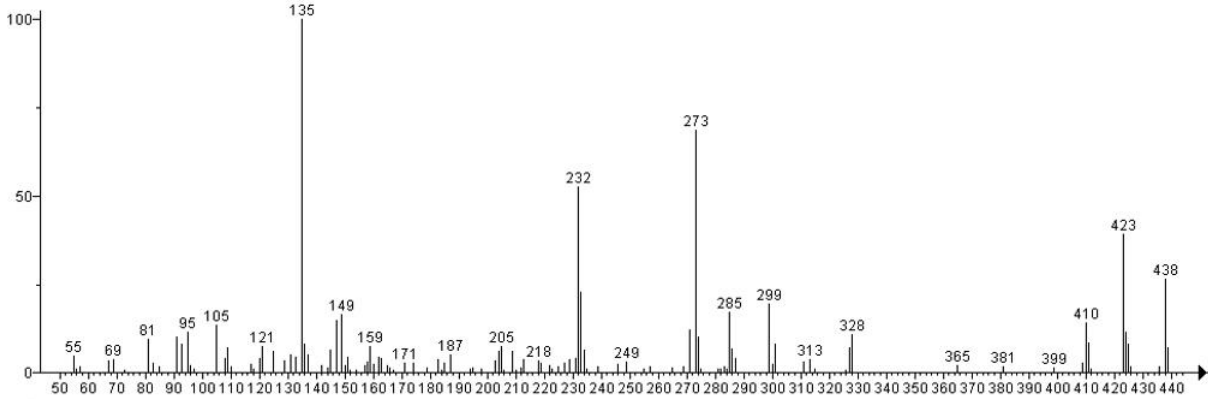
Lu3, Lupeol



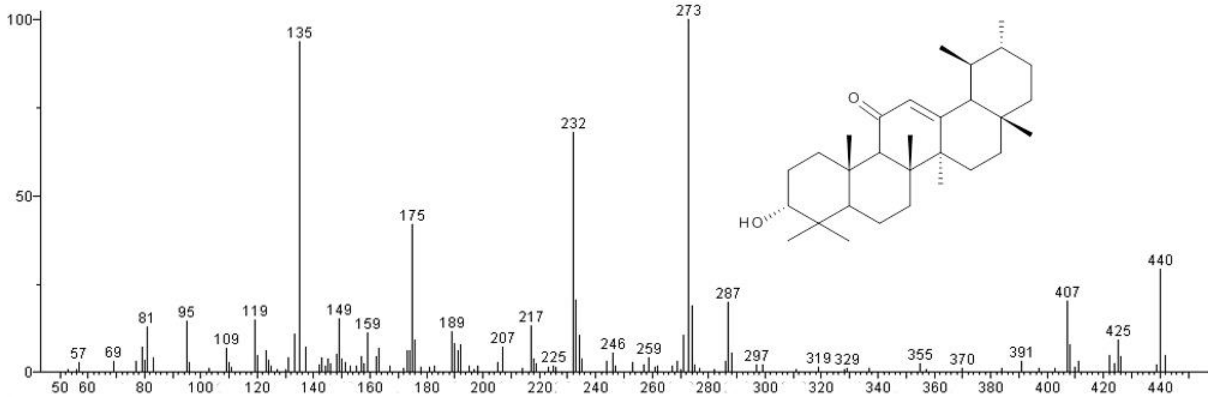
O23, 11-Oxo-olean-12-en-3α-ol



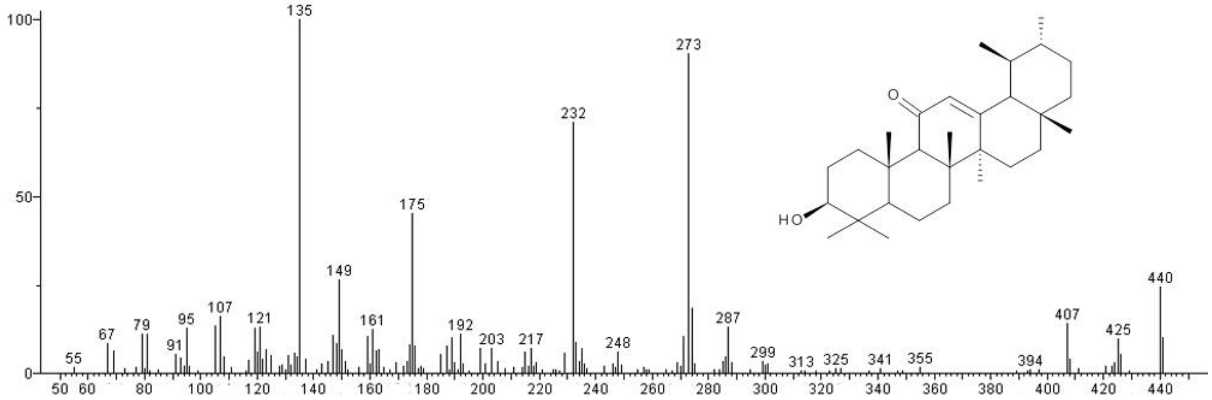
O24, 11-Oxo-olean-12-en-3β-ol



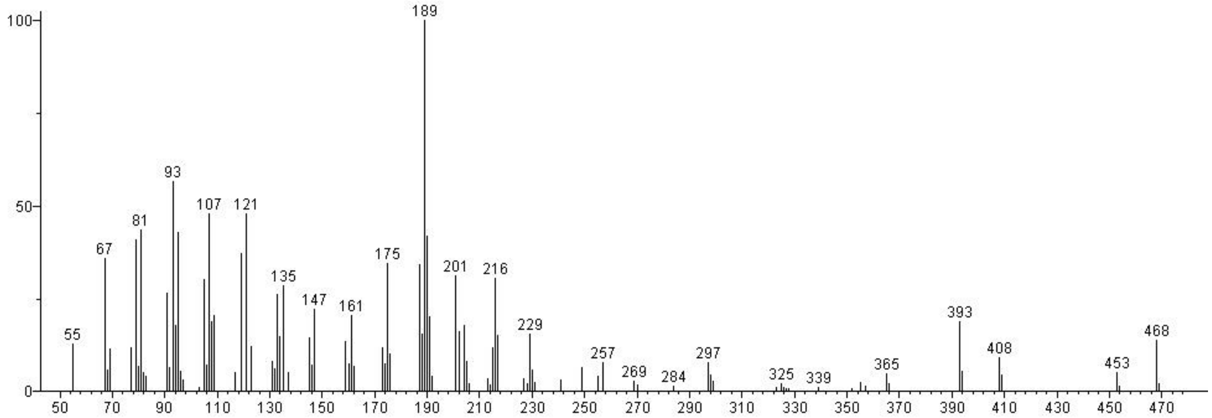
T41, Unidentified oxygenated triterpene



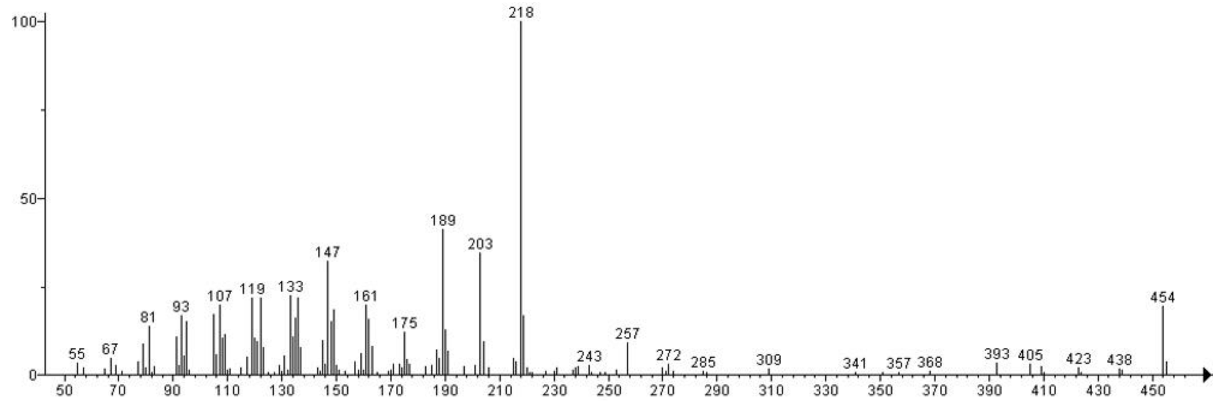
Ur18, 11-Oxo-urs-12-en-3⍰-ol



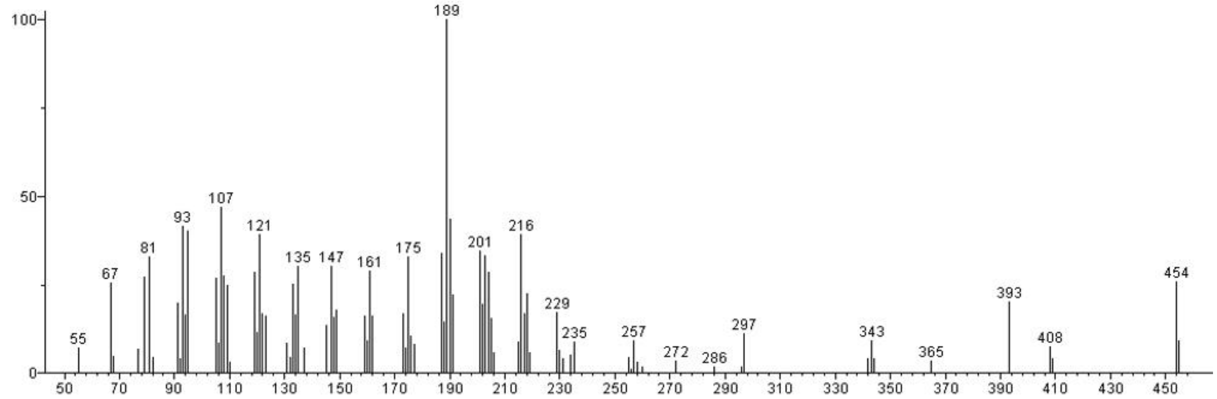
Ur20, 11-Oxo-urs-12-en-3⍰-ol



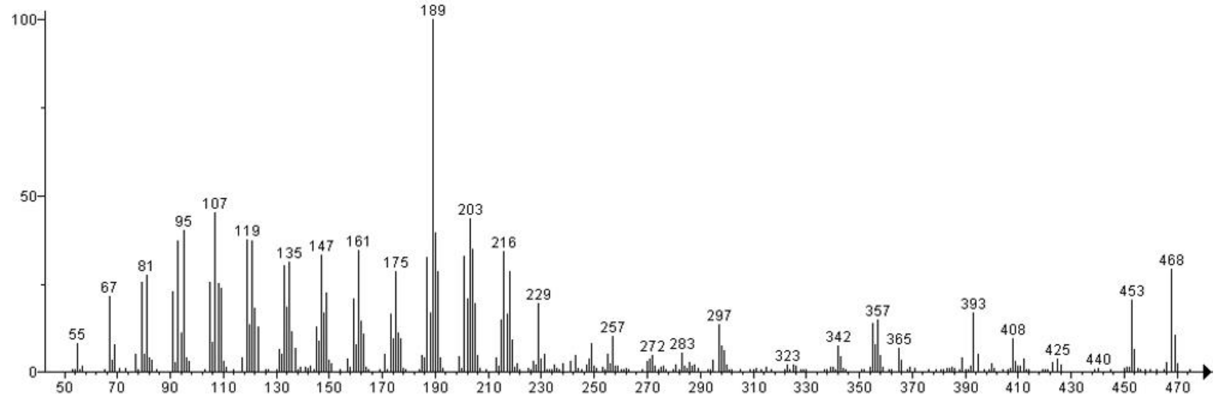
T17, Unidentified triterpene



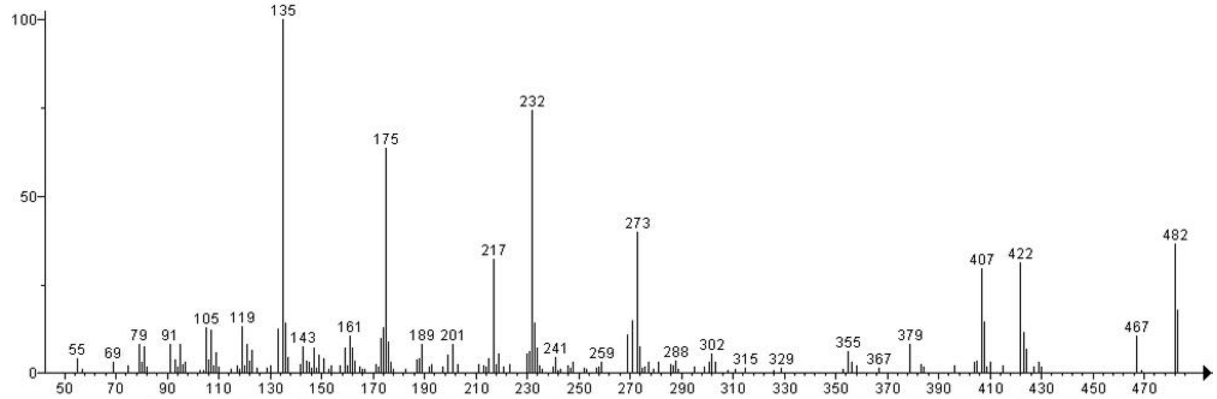
T19, Unidentified triterpene



T20, Unidentified triterpene



T67, Unidentified triterpene



T43, Unidentifed triterpene