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Chemical composition of essential oils of garlic (*Allium sativum* L.)

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Abstract

Six varieties of garlic grown in different geographical locations in Gujarat, India were analysed for their proximate composition including volatile oil content. Twenty nine compounds were identified in the volatile oils by gas chromatography and gas chromatography - mass spectrometry, among which 15 were new compounds hitherto not reported to be components of garlic. The relative concentrations of 13 major components in the volatile oils of all six varieties are also presented.

Key words : *Allium sativum*, essential oil, garlic.

Abbreviations

GC : Gas chromatography
GC-MS : Gas chromatography - mass spectrometry

Introduction

Garlic (*Allium sativum* L.) is used widely in food and pharmaceutical preparations. In India, Gujarat and Madhya Pradesh are major producers of garlic. Earlier reviews (Abraham *et al.* 1976; Whitaker 1976; Raghavan *et al.* 1983; Fenwick & Hanley 1985) provide exhaustive information on the chemistry of garlic. Data on essential oil, reducing sugars, protein and fibre (Artik & Poyrazoglu 1993) and proximate composition of garlic are also available (Abraham 1976). Yu *et al.* (1989) identified 28 volatile compounds by capillary GC and GC-MS analysis, of which 13 were reported for the first time. The volatile compounds suspended in the aqueous phase were also identified. Pino *et al.* (1991) employed high resolution GC, GC-MS and eluate sniffing and identified for the first time (Z)- and (E)-1-propenyl 2- propenyl disulphide (0.7 and 1.6% respectively), 1, 2, 3-trithi-4-ene (0.2%) and 2-propenyl tetrasulphide (0.3%). The volatile components of crushed garlic of Mediterranean origin were analysed by Mazza *et al.* (1992) and three compounds namely, methyl-(Z)-prop-l-enyl disulphide, allyl-(Z)- prop-l-enyl disulphide and allyl-(E)-prop-l-enyl disulphide were identified for the first time.

This paper deals with screening of six varieties of garlic grown in different

districts of Gujarat in India so as to find their suitability for processing and product development. Further, the chemical composition of the volatile oils obtained and the relative concentrations of the flavour constituents were computed.

Materials and methods

Proximate composition

Five geographical varieties of garlic namely, Rajkot, Gondal, Jamnagar, Junagadh and Amreli and one variety grown in Gujarat, were procured. The samples were kept in netlon bags and stored in a well ventilated room. The bulbs were broken with a wooden mallet for separating the cloves. The tight inner skin encasing each clove was removed without damaging the tissues of the garlic cloves. The samples were analysed for constituents like moisture, volatile oil, total ash, acid insoluble ash, reducing sugars, crude starch, crude fibre, crude protein and crude fat by standard methods (ASTA 1985; AOAC 1984)

Volatile oil

The volatile oil from fresh garlic was collected by hydrosteam distillation method (ASTA 1985) and dried over anhydrous sodium sulphate.

GC - MS analysis

GC-MS analysis was carried out for one of the garlic oil samples (Gondal) using a Shimadzu 17 GC coupled with a quadrapole MS (QP 5000). The conditions of analysis are as follows:

Column	: Fused silica capillary, SPB™-1
Column dimension	: 30 m x 0.32 mm i. d.
Film thickness	: 0.25 µm coated with poly dimethyl siloxane
Carrier gas	: Helium (1ml/min)
Split ratio	: 1:30
Injection port temperature	: 250°C
Detector block temperature (FID)	: 250°C
Oven temperature	: Programmed, 60°C (2) - 2°/min - 250°C (5)
Sample injection	: 1µl of 25 X in acetone.

GC analysis

The volatile oils of six garlic samples were analysed using a GC (Shimadzu GC 15 A) fitted with SS column (10'X 0.125"OD) filled with 10% SE 30 on Chromosorb W. Nitrogen was used as the carrier gas (30ml/min). The injection port and detector block (FID) were maintained at 200°C and 250°C, respectively. The column temperature was programmed as 75°C (2) - 4°/min - 220°C (8). The volatile oils were diluted (1 to 20) in acetone and 1µl was injected.

Results and discussion

The results of the proximate analysis of the six varieties of garlic are given in Table 1. Volatile oil is an important constituent determining the flavour quality of garlic. Volatile oil was maximum in two varieties namely, Gondal and Jamnagar. One of these was chosen for GC-MS analysis for identification of the flavouring components. The total ion chromatogram of the garlic oil (Gondal) is provided in Fig 1. Twenty nine compounds were identified (Table 2) based on the retention indices (Yu *et al.* 1994) and by matching the fragmentation patterns with those of the mass spectral data (NIST Library). Of

Table 1. Proximate composition of garlic varieties

Constituent	Variety					
	Rajkot	Gondal	Jamnagar	Junagadh	Amreli	Medicinal
Moisture	60.25	60.62	60.00	61.87	58.13	64.28
Volatile oil	0.65	0.85	0.87	0.79	0.76	0.73
Total ash	3.08	2.83	2.93	2.87	2.71	5.07
Acid insoluble ash	0.06	0.06	0.06	0.02	0.03	0.00
Reducing sugars	3.31	3.93	3.63	3.40	2.14	-
Crude starch	45.75	44.03	45.15	44.16	44.55	-
Crude fibre	6.41	8.87	7.10	9.52	7.56	14.60
Crude protein	20.15	23.98	20.82	22.23	18.75	22.97
Crude fat	2.10	2.15	2.00	1.78	2.42	3.60

All values are percentages (means of triplicate analyses) on dry weight basis
- Not carried out due to non availability of sample

those identified, 26 were organo sulphur compounds, 2 were monoterpenes and 1, an ester.

It is well known that when fresh garlic is macerated the cells are ruptured and the enzyme alliinase comes into contact with the precursor alliin (S-allyl cysteine sulphoxide) leading to the formation of sulphur containing di-, tri- and tetra sulphides. In recent studies (Mazza *et al.* 1992; Yu *et al.* 1994) it has been concluded that the possibility of involvement of other precursors, namely, methyl, propyl and prop-1-enyl cysteine sulphoxides cannot be ruled out.

In our study, we have identified 15 new compounds in garlic which are not hitherto reported. It is quite possible

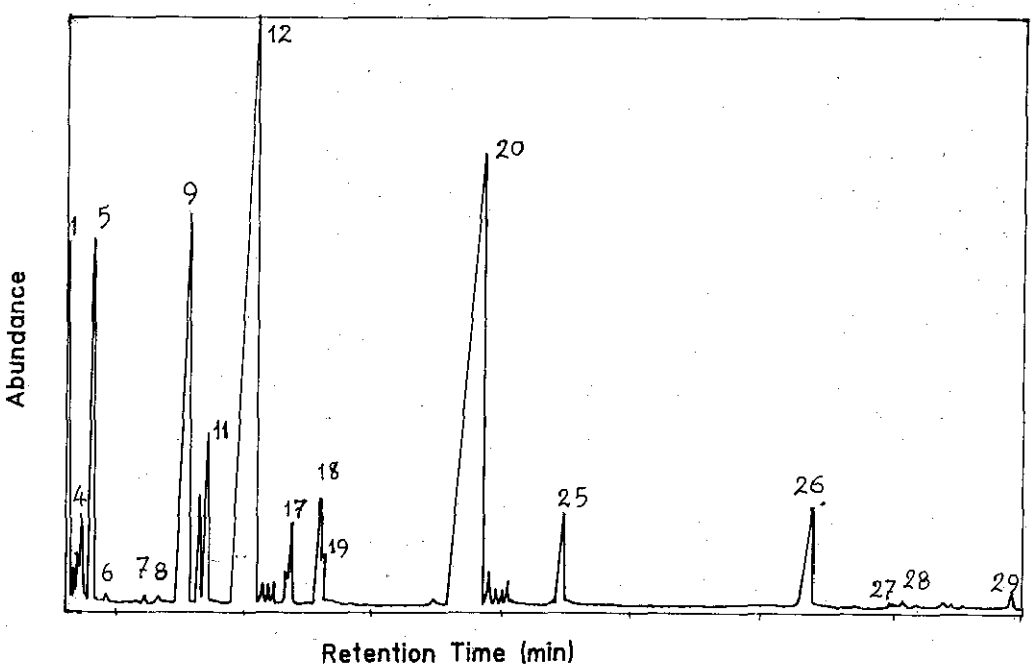


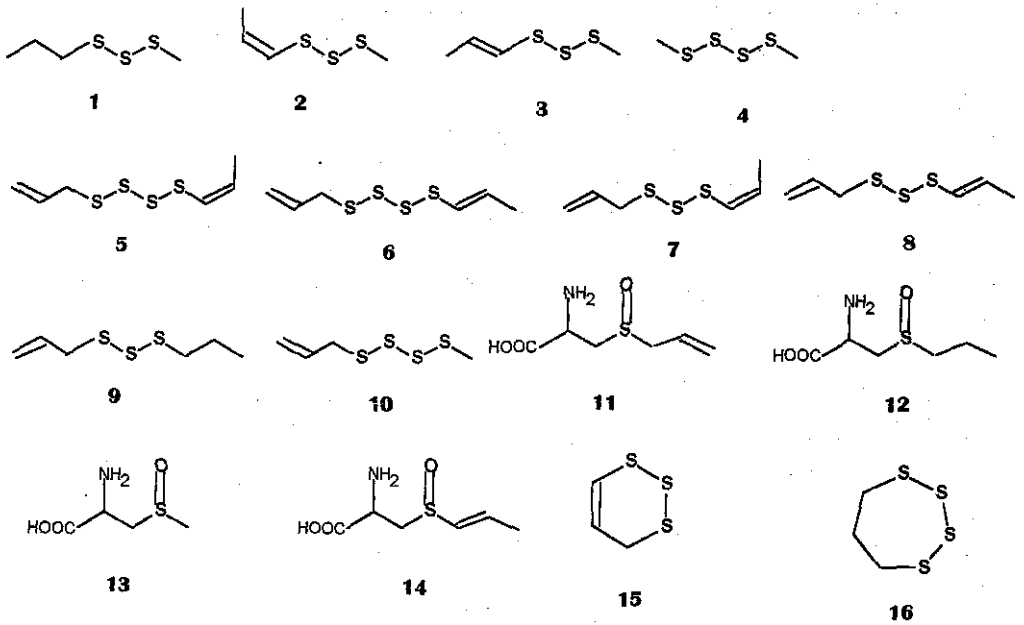
Fig. 1. GC-MS profile of garlic oil (Gondal)

Table 2. Identification of volatile components in garlic oil+

Peak No.	Ret. time (min.)	Compound	KI SPB-1	M+
1	3.05	Allyl methyl disulphide	903	120
2	3.28	Methyl (*Z*) prop-l-enyl disulphide	915	120
3	3.43	Methyl (*E*) prop-l-enyl disulphide	922	120
4	3.55	Dithia cyclopentane	928	104
5	4.03	Dimethyl trisulphide	949	126
6	4.55	Ocimene*	969	136
7	6.10	Limonene*	1021	136
8	6.63	Allyl propyl disulphide	1037	148
9	7.80	Diallyl disulphide	1069	146
10	8.20	Allyl (*Z*) prop-l-enyl disulphide	1079	146
11	8.48	Allyl (*E*) prop-l-enyl disulphide	1086	146
12	10.37	Allyl methyl trisulphide	1126	152
13	10.62	Methyl propyl trisulphide*	1130	152
14	10.90	Methyl (*Z*) prop-l-enyl trisulphide*	1139	152
15	11.08	Methyl (*E*) prop-l-enyl trisulphide*	1139	152
16	11.58	Trithia cyclo hexane*	1147	136
17	11.78	3-Vinyl-4H-1, 2-dithine	1151	144
18	12.90	2-Vinyl-4H-1, 3-dithine	1170	144
19	13.08	Dimethyl tetra sulphide*	1171	158
20	19.10	Diallyl trisulphide	1270	178
21	19.40	Allyl propyl trisulphide*	1275	180
22	19.68	Allyl (*Z*) prop-l-enyl trisulphide*	1279	178
23	19.95	Allyl (*E*) prop-l-enyl trisulphide*	1283	178
24	20.15	Tetrathiacycloheptane*a	1286	170
25	22.35	Allyl methyl tetra sulphide*	1322	184
26	31.83	Diallyl tetra sulphide	1472	210
27	34.92	Allyl (*Z*) prop-l-enyl tetra sulphide*a	1522	210
28	35.37	Allyl (*E*) prop-1-enyl tetrasulphide*a	1530	210
29	39.58	Cinnamyl tiglate*	1599	216

+ Gondal variety
* Reported for the first time
a Identified tentatively

that the new components identified in this study (Fig 2), namely, methyl propyl trisulphide (1), methyl (Z)-prop-l-enyl trisulphide (2) and its (E) isomer (3), dimethyl tetra sulphide (4), allyl (Z)-prop-l-enyl tetra sulphide (5) and its (E) isomer (6), allyl (Z)-prop-l-enyl trisulphide (7), and its (E) isomer (8), allyl propyl trisulphide (9) and allyl methyl tetra sulphide (10) might have formed from the corresponding unstable thiosulphonates through decomposition and rearrangement of alliin (S-allyl cysteine sulphoxide) (11), S-propyl cysteine sulphoxide (12), S-methyl cystine sulphoxide (13), S-(E)-l-propenyl cysteine sulphoxide (14) and their precursors y-glutamyl alkenyl cysteines as these are reported by Yu (1996) to be present in intact garlic. Two other sulphur volatiles, trithia cyclohexene (15) and tetra thia cycloheptane (16) might have formed from alliin. Limonene and ocimene might have formed in a monoterpene pathway, whereas cinnamyl tiglate shows the presence of



11 ⟶ 15,16

11,12 ⟶ 9

11,13 ⟶ 10

11,14 ⟶ 5,6,7,8

12,13 ⟶ 1

13 ⟶ 4

13,14 ⟶ 2,3

Fig. 2. Formation of new sulphur compounds from probable precursors in garlic

cinnamyl unit from shikimic acid metabolites and tiglyl unit from mevalonic acid metabolites. These observations are interesting and needs further confirmation.

Based on peak areas obtained through GC analyses of the six garlic oils, the relative concentration of 13 major components are computed (Table 3). It may be noted that the combined percentages of E and Z isomers of methyl prop-1-enyl disulphide and E and Z isomers of allyl prop-1-enyl disulphide are furnished in the table since they could not be resolved in the GC column under the conditions employed. It may also be noted that the di- and tri-sulphides together account for more than 90% of all the samples analysed and diallyl disulphide is the major character impact compound in garlic.

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Table 3. Relative concentrations of garlic oil constituents

Component	Ret.time (min)	Variety					
		A	B	C	D	E	F
Diallyl sulphide	6.628	2.43	2.08	1.39	2.41	1.15	1.25
Allyl methyl sulphide	8.328	11.96	10.86	8.28	11.41	7.32	4.44
Methyl (*Z*) prop-l-enyl disulphide and its (*E*) isomer	9.132	0.07	1.09	0.94	1.27	0.97	0.06
Dimethyl trisulphide	10.470	0.63	2.24	1.88	1.84	1.77	0.51
Diallyl disulphide	14.173	38.49	34.35	36.20	41.71	27.06	46.84
Allyl (*Z*) prop-l-enyl disulphide and its (*E*) isomer	14.897	4.66	5.24	5.84	5.28	7.20	5.36
Allyl methyl trisulphide	16.298	11.13	17.42	16.35	14.70	18.20	8.30
2-Vinyl-4H-1, 3-dithin	18.810	0.56	0.67	0.85	0.59	0.76	1.76
Diallyl trisulphide	22.133	29.34	24.70	27.36	19.93	34.05	30.57
Allyl methyl tetrasulphide	24.060	0.04	0.40	0.16	0.14	0.33	0.37
Diallyl tetrasulphide	29.890	0.66	0.91	0.74	0.69	1.16	0.52

A : Rajkot; B : Gondal; C : Jamnagar; D : Junagadh; E : Amreli; F : Medicinal

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