



Progress in Essential Oils

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Clary Sage Oil

A sample of clary sage oil was determined by Zani et al. (1991) to contain the following major components:

- myrcene (0.72 percent)
- limonene (0.26 percent)
- 1,8-cineole (0.30 percent)
- linalool (14.98 percent)
- linalyl acetate (60.88 percent)
- β -caryophyllene (2.37 percent)

Putievsky (1994) compared the major component composition of various plant parts of *Salvia sclarea* grown in Israel. The data obtained from this study is shown in T-1.

A supercritical CO₂ extract of the steam-distilled residue of *S. sclarea* was produced at 30°C under a pressure of 35

Mpa and a CO₂ flow rate of 5 L/h. This extract was determined by Liu et al. (2001) to contain sclareol (72.86 percent) as the major constituent.

Hudaib et al. (2001) compared the composition of clary sage oils produced from healthy plants and plants infected by the broad bean fava virus (serotype-BBWV-1) with a commercial sample of Russian clary sage oil. The data from the comparative analytical study is shown in T-2. As can be seen, the oil from infected plants was slightly richer in sesquiterpene hydrocarbons α -terpineol and sclareol; however, these differences were not large and could vary to this extent for oils from healthy plants within a single season. It is also unfortunate that the authors misidentified over 15 percent of the constituents listed in T-2.

Percentage composition of the main components of various plant parts of *Salvia sclarea* harvested during fall flowering

T-1

Compound	1	2	3	4
myrcene	t	2.4	2.2	1.5
γ -terpinene	t	0.6	0.7	0.3
p-cymene	t	1.5	1.5	0.7
linalool	8.4	32.0	40.3	36.1
linalyl acetate	t	44.1	25.9	36.3
β -caryophyllene	11.1	0.5	1.1	1.5
α -terpineol + α -terpinyl acetate	t	7.7	10.8	8.1
germacrene D ^a	70.2	-	-	-
neryl acetate	t	3.7	0.6	5.0
geranyl acetate	10.1	3.5	4.8	5.0
nerol	t	0.9	1.8	1.9
geraniol	t	2.9	4.2	3.1

1 – leaf oil; 2 – calyx oil; 3 – bract oil; 4 – peduncle oil; ^aalthough Putievsky noted that this was an unknown constituent, it has been changed to germacrene D because of this reviewer's own unpublished analysis of clary sage leaf oil; t = trace (<0.1 percent)

Percentage composition of clary sage oil produced from healthy and virus infected plants, and a commercial Russian oil

T-2

Compound	Healthy plant oil	Infected plant oil	Russian oil
α -pinene	0.02	0.02	0.12
camphene	0.01	0.01	0.02
sabinene	0.02	0.01	0.01
β -pinene	0.03	0.03	0.05
myrcene	3.29	2.08	0.68
α -phellandrene	0.05	0.03	0.12
α -terpinene	0.11	0.07	0.06
p-cymene	0.05	0.05	0.07
limonene	1.03	0.54	0.42
(Z)- β -ocimene	1.71	1.05	0.37
(E)- β -ocimene	2.96	1.89	0.78
γ -terpinene	0.09	0.06	0.04
myrtenol*	t	t	t
terpinolene	0.33	0.24	0.33
linalool	10.06	9.01	11.97
α -pyronene*	0.09	0.06	0.02
<i>cis</i> -dihydrocarvone*	t	0.01	0.01
borneol	0.03	0.05	0.01
terpinen-4-ol	0.01	0.02	0.04
α -terpineol	1.64	2.30	3.50
citronellol	0.16	0.06	0.36
terpinen-4-yl acetate*	0.13	0.21	0.35
linalyl acetate	55.72	54.40	42.75
(E)-anethole	-	-	2.04
isobornyl acetate	0.06	0.08	-
α -terpinyl acetate*	-	-	2.04
thymol	0.36	0.62	-
carvacrol	0.07	0.06	-
geranyl acetate	0.18	0.17	0.07
neryl acetate	1.11	1.27	0.98
α -copaene	2.06	2.33	1.00
β -bourbonene	0.34	0.49	0.13
sabinene hydrate acetate***	2.24	2.33	1.75
β -cubebene	0.50	0.55	0.29
α -gurjunene	0.28	0.37	0.18
β -caryophyllene	3.84	4.24	3.00
germacrene***	0.17	0.23	0.06
longifolene*	0.06	0.14	-
α -humulene	0.04	0.05	0.02
α -guaiene*	0.16	0.20	0.11
germacrene D	7.58	9.47	4.35
γ -muurolene	0.91	0.49	0.12
valencene	0.48	0.55	0.84
γ -cadinene	0.10	0.13	0.06
(E,E)- α -farnesene	0.19	0.18	0.19
longiborneol*	0.06	0.08	0.10
δ -cadinene	0.58	0.73	0.30
α -calacorene	0.01	0.04	t
spathulenol	0.06	0.17	0.19
caryophyllene oxide	0.26	0.60	0.35
(Z)- α -santalol*	0.13	0.20	0.05
α -eudesmol*	0.05	0.19	0.12
γ -eudesmol*	0.06	0.21	0.10
cuparene*	0.01	0.07	0.15

Compound	Healthy plant oil	Infected plant oil	Russian oil
lanceol acetate*	0.03	0.07	0.10
manool*	0.03	0.11	0.07
13-epi-manool*	0.02	0.05	0.03
sclareol	0.23	1.05	1.22

t = trace (<0.01 percent); *incorrect identity based on elution order; **correct isomer not identified

An oil of clary sage produced in the vicinity of Bassins (Switzerland) was subjected to fractional distillation by Van der Waal et al. (2002). The early fractions were then examined by sniffing the exit port of a preparative gas chromatograph; the odor-positive materials were then combined and further chromatographed. After removal of the solvent, the selected odor-positive fraction was subjected to GC/MS. The authors found that under the GC/MS conditions, linalyl acetate yielded 3,7-dimethylocta-1,3,6-triene and 7-methyl-3-methyleneocta-1,6-diene as elimination products. Unfortunately, these compounds eluted in the same region as a highly odorous compound and which masked the MS of the desired odorous compound. As a result, the authors decided to eliminate any free linalool and linalyl acetate from this odor-positive fraction by reduction with LiAlH_4 to reduce the linalyl acetate, followed by hydrolysis with ice water and extraction with diethyl ether. GC/MS of this linalool/linalyl acetate-free fraction revealed a highly odorous component, hexanol and (Z)-3-hexenol. The structural elucidation of this odor-rich compound was determined to be 1-methoxyhexane-3-thiol by spectroscopy. This identity was confirmed by synthesis. In addition, through asymmetric syntheses, the authors were able to determine that the naturally occurring enantiomer was (S)-(-)-1-methoxyhexane-3-thiol. Furthermore, its air threshold was measured and found to be 0.04×10^{-3} ng/L. This makes this compound one of the most powerful known odorants. The odor of 1-methoxyhexane-3-thiol was described as being herbaceous-green, alliaceous with a perspiration note. It was deemed to be key to the fragrance of clary sage flowers and freshly distilled clary sage oil.

Fiori et al. (2002) used HPLC followed by GC/MS to characterize α -pinene, β -pinene, limonene, (Z)- β -ocimene, (E)- β -ocimene, *cis*-linalool oxide (furanoid), terpinolene,

linalool, terpinen-4-ol, α -terpineol, (Z)-anethole, linalyl acetate, (E)-anethole, neryl acetate, α -copaene, geranyl acetate, β -caryophyllene, caryophyllene oxide, (Z)-sclareol oxide and sclareol in a commercial clary sage oil. In addition, genuine clary sage oils were obtained using soxhlet extraction (hexane) followed by steam distillation. From these oils, the author confirmed that all constituents identified in the commercial oil, including both (Z)- and (E)-anethole, were indeed natural constituents of clary sage oil.

Clary sage oils produced in the laboratory from wild growing flowering plants collected from Mt. Katara (central Greece) and Monodendri (northwest Greece) were analyzed by Pitarokili et al. (2002). The results of these GC/MS analyses can be seen in T-3.

Seeds from a Sicilian biotype of *S. sclarea* were grown in an experimental garden in Sparcia (Sicily, Italy) and harvested at both the full flowering stage and at the commencement of the fruit ripening stage. Inflorescences and leaves were separated from the plants harvested at each time; oils were produced from them in the laboratory by water distillation. Carrubba et al. (2002) analyzed the oils using GC and GC/MS. The analytical results obtained are summarized in T-4. It is interesting to note that the flower oils were rich in oxygenated monoterpenes (71.59-83.62 percent), while their sesquiterpene hydrocarbon content was 8.03-16.7 percent. In contrast, the leaf oils were devoid of oxygenated monoterpenes and rich in sesquiterpene hydrocarbons (91.11-94.62 percent). These results are somewhat similar to those of Putievsky (1994), although he found that the level of oxygenated monoterpenes exceeded 15 percent; the sesquiterpene hydrocarbon content was ca. 70 percent.

Kubeczka and Formacek (2002) used a combination of GC and ^{13}C -NMR to analyze an oil of clary sage. They found that the oil possessed the following composition:

- α -pinene (0.25 percent)
- camphene (0.06 percent)
- β -pinene (0.29 percent)
- sabinene (0.06 percent)
- myrcene (0.20 percent)
- limonene (0.51 percent)
- β -phellandrene + 1,8-cineole (0.15 percent)
- p-cymene (0.06 percent)
- trans*-linalool oxide* (0.40 percent)
- cis*-linalool oxide* (0.37 percent)

Compound	1	2	Compound	1	2
(Z)-3-hexenol	t	-	β -gurjunene	-	t
α -pinene	t	t	<i>trans</i> - α -bergamotene	-	t
benzaldehyde	-	t	aromadendrene	-	t
camphene	t	-	α -humulene	t	t
β -pinene	t	-	<i>cis</i> -muurolo-4(14),5-diene	t	t
myrcene	1.76	1.40	germacrene D	2.57	-
α -terpinene	-	t	valencene	0.39	0.49
p-cymene	t	t	epi-cubebol	t	t
limonene	0.62	0.54	bicyclogermacrene	-	t
1,8-cineole	-	t	α -muurolole	-	t
(Z)- β -ocimene	0.61	0.77	germacrene A	t	t
phenylacetaldehyde	-	t	(E,E)- α -farnesene	t	t
(E)- β -ocimene	0.75	1.31	δ -cadinene	t	0.53
γ -terpinene	-	t	α -calacorene	t	t
<i>cis</i> -linalool oxide*	-	t	1,5-epoxysalvia-4(14)-diene	t	0.44
terpinolene	t	0.59	(Z)-3-hexenyl benzoate	t	-
<i>trans</i> -linalool oxide*	-	t	germacrene D-4-ol	t	-
linalool	30.43	18.46	spathulenol	-	0.66
<i>cis</i> - β -terpineol	t	-	caryophyllene oxide	0.72	2.34
δ -terpineol	5.08	7.56	salvia-4(14)-en-1-one	-	0.44
δ -3-carene**	-	0.42	β -copaen-4 α -ol	t	t
nerol	t	1.24	β -oplophenone	t	t
geraniol	4.21	-	β -eudesmol	1.27	1.05
linalyl acetate	19.75	31.05	α -eudesmol	0.40	0.83
geranial	0.96	-	7-epi- α -eudesmol	t	-
geranyl formate	0.48	-	methyl 3-hydroxydodecanoate	0.27	-
α -cubebene	-	0.31	benzyl benzoate	t	-
neryl acetate	7.78	2.01	8,13-epoxy-15,16-dinorlab-12-ene	1.02	3.03
α -ylangene	-	t	farnesyl acetate***	0.50	0.47
α -copaene	-	1.67	manoyl oxide	0.35	1.07
geranyl acetate	12.10	4.45	13-epi-manoyl oxide	t	0.63
β -cubebene	-	0.52	manool	0.69	1.15
β -elemene	-	t	sclareol	3.53	5.55
β -caryophyllene	1.95	2.28			

1 – Mt. Katara plant oil; 2 – Monodendri plant oil; *furanoid form; **incorrect identification based on elution order; ***correct isomer not identified; t = trace (<0.01 percent)

α -copaene (0.39 percent)

camphor (0.68 percent)

linalool (18.62 percent)

linalyl acetate (69.93 percent)

β -caryophyllene + terpinen-4-ol (0.56 percent)

α -terpineol (0.70 percent)

α -terpinyl acetate (0.37%)

neryl acetate (0.26 percent)

geranyl acetate (0.49 percent)

nerol (0.06 percent)

geraniol (0.16 percent)

caryophyllene oxide (0.69 percent)

*furanoid form

E. Putievsky, *Factors influencing the yield and composition of essential oils. Section I: Genetics, morphogenesis and environment*. 4th Recontres Techniques et Economiques. Plantes Aromatiques et Medicinales. Edit., N. Verlet, p 103-115 ONIPPAM, Nyons (France) (1994).

B. Liu, W.-P. Chen, D.-J. Wang, W.-Q. Wang and Z.-A. Guo, *Extraction of Salvia sclarea Linn. residue by supercritical CO₂ and GC-MS analysis*. Xiangliao Xiangjing Huazhuangpin (Flavour Fragrance Cosmetics), **6**, 3-6 (2001).

M. Hudaib, M.G. Bellardi, C. Rubies-Autonell, J. Fiori and V. Cavrini, *Chromatographic (GC-MS, HPLC) and virological evaluations of Salvia sclarea infected by BBWV-1*. Il Farmaco, **56**, 219-227 (2001).

M. Van der Waal, Y. Niclass, R.L. Snowden, G. Bernadinelli and S. Escher, *1-Methoxyhexane-3-thiol, a powerful odorant of clary sage (Salvia sclarea L.)*. Helv. Chim Acta, **85**, 1246-1260 (2002).

F. Zani, G. Massimo, S. Benvenuti, A. Bianchi, A. Albasini, M. Melegari, G. Vauper, A. Bellotti and P. Mazza, *Studies on the genotoxic properties of essential oils with Bacillus subtilis rec-assay and Salmonella/Microsome reversion assay*. Planta Med., **57**, 237-241 (1991).

Compound	1A	1B	2A	2B
α-pinene	0.14	0.20	-	-
camphene	0.08	0.16	-	-
sabinene	t	0.10	-	-
β-pinene	0.19	0.32	-	-
myrcene	1.70	1.19	-	-
limonene	0.44	0.23	-	-
(Z)-β-ocimene	0.85	0.58	-	-
(E)-β-ocimene	1.46	1.01	-	-
terpinolene	0.40	0.24	-	-
linalool	28.91	25.65	-	-
terpinen-4-ol	0.06	0.07	-	-
α-terpineol	5.08	3.49	-	-
linalyl acetate	34.89	52.70	-	-
δ-elemene	0.09	0.06	0.40	0.39
α-cubebene	-	-	t	t
neryl acetate	0.90	0.63	-	-
α-copaene	0.54	0.24	5.26	5.78
geranyl acetate	1.75	1.08	-	-
β-bourbonene	t	t	t	0.07
β-cubebene	0.05	0.09	0.33	0.45
β-elemene	0.21	0.06	2.14	2.00
β-caryophyllene	1.82	1.43	5.90	5.65
β-gurjunene	0.08	0.03	0.20	0.22
aromadendrene	0.28	0.32	0.03	0.07
allo-aromadendrene	0.08	0.05	0.76	0.23
γ-gurjunene	t	t	0.05	0.05
γ-muurolene	0.12	0.10	0.87	0.31
germacrene D	10.56	3.92	68.85	67.72
viridiflorene	1.55	1.27	t	0.10
bicyclogermacrene	0.46	0.26	7.95	6.41
α-muurolene	0.11	0.03	0.10	t
β-bisabolene	0.59	t	0.17	0.10
δ-cadinene	0.18	0.17	1.50	1.56
cadina-1,4-diene	-	-	0.06	t
α-cadinene	-	-	0.05	t
spathulenol	-	-	0.76	0.93
α-muurolol	-	-	0.04	t
α-eudesmol	-	-	0.07	0.08
α-cadinol	-	-	0.45	0.39
valeranone	0.79	0.22	0.54	0.60
sclareol	0.10	0.06	0.31	0.57

1A – oil from flowers at full blooming stage; 1B – oil from flowers at fruit ripening commencement; 2A – oil from leaves at full blooming stage; 2B – oil from leaves at fruit ripening commencement; t = trace (<0.01 percent)

J. Fiori, M. Hudaib, L. Valgimigli, S. Gabbanini and V. Cavrini, *Determination of trans-anethole in Salvia sclarea essential oil by liquid chromatography and GC-MS*. J. Sep. Sci., **25**, 703-709 (2002).

D. Pitarokili, M. Couladis, N. Petsikos-Panayotarou and O. Tzakou, *Composition and antifungal activity on soil-borne pathogens of the essential oil of Salvia sclarea from Greece*. J. Agric. Food Chem., **50**, 6688-6691 (2002).

A. Carrubba, R. La Torre, R. Piccaglia and M. Marotti, *Characterization of an Italian biotype of clary*

sage (Salvia sclarea L.) grown in a semi-arid Mediterranean environment. Flav. Fragr. J., **17**, 191-194 (2002).

K.-H. Kubeczka and V. Formacek, *Essential oil analysis by capillary gas chromatography and carbon-13 NMR spectroscopy*. 2nd Edn., 315-319, J. Wiley & Sons, New York (2002).

Summer Savory Oil

An oil produced from *Satureja hortensis* L. grown in the vicinity of Baku (Azerbaijan) was found by Akhe-

Comparative percentage composition of an oil and extract of summer savory
T-5

Compound	Oil	Extract	Compound	Oil	Extract
α -thujene	1.20	0.24	p-cymene	2.59	1.25
α -pinene	0.84	t	limonene + β -phellandrene	0.47	t
camphene	0.07	-	(Z)- β -ocimene	0.22	-
sabinene	0.17	t	γ -terpinene	44.17	12.38
β -pinene	0.49	t	(E)- β -ocimene	0.40	0.65
myrcene	1.93	0.39	carvacrol	39.81	83.40
α -phellandrene	0.33	t	β -caryophyllene	1.39	t
α -terpinene	4.03	1.03	bicyclogermacrene	0.25	t

t = trace (<0.01 percent)

Percentage composition of two samples of summer savory oil
T-6

Compound	Sample 1	Sample 2	Compound	Sample 1	Sample 2
α -thujene	-	2.15	1,8-cineole	-	0.03
α -pinene	0.09	1.37	(E)- β -ocimene	-	0.18
camphene	-	0.15	γ -terpinene	7.61	52.91
sabinene	-	0.09	methyl chavicol	-	0.11
β -pinene	-	0.61	bornyl acetate	-	0.04
myrcene	0.43	3.68	carvacrol	77.55	14.34
α -terpinene	0.60	5.34	β -caryophyllene	0.74	2.57
p-cymene	4.21	8.57	α -humulene	-	0.11
limonene	0.53	0.53	β -bisabolene	-	2.36
β -phellandrene	-	0.34			

dova et al. (1983) to contain the following components:

α -thujene (1.1 percent)
 α -terpinene (0.6 percent)
 p-cymene (16.0 percent)
 linalool (26.0 percent)
 citronellol (0.6 percent)
 β -caryophyllene (2.5 percent)
 geraniol (1.2 percent)
 thymol (46.0 percent)

It should be noted that the oil of *S. hortensis* is generally rich in carvacrol, not thymol; however, the existence of thymol chemotypes is not unexpected.

Jean et al. (1992) compared the composition of an oil of *S. hortensis* L. produced by hydrodiffusion of fresh plant material with an extract of the same batch of plant material produced by microwave extraction using either hexane, toluene or carbon tetrachloride as the solvent (the authors did not specify which was used). Hydrodiffusion is a steam distillation process that works on the diffusion principle in which the steam is allowed to enter at the top of a plant charge and diffuse its way through the charge by gravity. It is supposed to diffuse oil from the oil glands by osmotic

pressure regardless of the type of glands (surface, subcutaneous or fat-rich ducts) onto the plant charge surface where it can be evaporated by the steam. The microwave extract was produced by immersing 15 g of fresh savory in a glass beaker containing 150 mL of organic solvent. This was placed in a conventional kitchen microwave (750 W, 2450 MHz) for a period less than 60 s. Afterwards, the mixture was filtered, and the solvent removed from the volatile concentrate (extract) by a conventional rotary film evaporator. The extract and oil were then subjected to analysis; the results of this can be found in T-5.

In 1995, Venskutonis analyzed a couple of samples of summer savory oil produced from plants raised in Lithuania. The two oils were quite different as can be seen from the results shown in T-6.

Gora et al. (1996) used a combination of GC and GC/MS to analyze an oil produced from a summer savory cultivator ('Saturn') that is commonly grown throughout Poland. The composition of the oil was determined to be as follows:

α -thujene (1.91 percent)
 α -pinene (1.50 percent)
 camphene (0.10 percent)
 sabinene (0.09 percent)
 myrcene (2.47 percent)
 β -pinene (0.79 percent)
 α -phellandrene (0.28 percent)
 α -terpinene (4.03 percent)
 limonene (0.34 percent)
 β -phellandrene (0.32 percent)
 p-cymene (6.24 percent)
 γ -terpinene (40.93 percent)
 linalool (t)
cis-sabinene hydrate (t)
 terpinen-4-ol (0.12 percent)
 borneol (t)
 α -terpineol (0.05 percent)
trans-dihydrocarvone (t)
trans-carveol (t)
 methyl carvacrol (0.06 percent)
 thymol (0.01 percent)
 carvacrol (39.28 percent)
 β -caryophyllene (0.82 percent)
 α -humulene (t)
 germacrene B (t)
 β -bisabolene (0.62 percent)
 β -sesquiphellandrene (t)
 α -bisabolene* (t)
 spathulenol (0.01 percent)

*correct isomer not identified; t = trace (<0.01 percent)

Palic et al. (1998) noted that the two major components of a selected strain of Balkan *S. hortensis* (oil yield 1.8 percent) were γ -terpinene (37.03 percent) and carvacrol (51.28 percent).

Esquivel et al. (1998) reported that the main components of a supercritical CO₂ extract of summer savory were γ -terpinene (ca. 30 percent) and carvacrol (ca. 45 percent). Examination of a lab distilled oil of *S. hortensis* grown in the vicinity of Ulaan-Baatar (Mongolia) was the subject of analysis by Shatar and Altantsetseg (2000). Their GC and GC/MS analysis of the oil revealed that it had the following composition:

α -pinene (3.2 percent)
 camphene (1.1 percent)
 β -pinene (0.6 percent)
 sabinene (0.1 percent)
 myrcene (2.8 percent)
 α -phellandrene (0.1 percent)
 α -terpinene (5.0 percent)
 limonene (0.6 percent)
 β -phellandrene (0.3 percent)
 1,8-cineole (t)
 (Z)- β -ocimene (0.1 percent)
 γ -terpinene (47.2 percent)
 p-cymene (3.5 percent)
 terpinolene (0.3 percent)
 1-octen-3-ol (0.1 percent)

trans-sabinene hydrate (0.1 percent)
cis-sabinene hydrate (0.1 percent)
 β -caryophyllene (0.5 percent)
 terpinen-4-ol (0.3 percent)
 α -terpineol (0.1 percent)
 borneol (0.1 percent)
 carvone (0.1 percent)
 T-muurolol (0.1 percent)
 carvacrol (33.6 percent)

t = trace (<0.1 percent)

Kubátová et al. (2001) used a technique called subcritical water extraction on coarsely grown, dried summer savory plant material to make an extract. The authors compared the extracts that were produced at different temperatures and times with a volatile concentrate produced by supercritical CO₂ and a water distilled oil of the same batch of dried plant material. The reason why subcritical water extraction is attractive as a technique is that the solubility of the oxygenated essential oil components have been found to be substantially more soluble in subcritical water, rather than supercritical fluid CO₂. A summary of the components found in the oil and various extracts can be seen in T-7. It can be realized from these results that the best overall yield of the oxygenated constituents was obtained when the subcritical water was held at 100°C; however, the extraction time was substantially longer.

Although the oil content of *S. hortensis* plants was found to increase 31 percent, and the total fresh herbage decrease 39 percent when grown in Iran under severe water stress, Bahar et al. (2002) determined that the oil composition did not change quantitatively anywhere near that extent as shown in T-8.

The seed oil of *S. hortensis* raised in Iran was analyzed by Ghannadi (2002) using a combination of GC and GC/MS. It was found to contain the following components:

hexanol (0.2 percent)
 heptanal (0.1 percent)
 α -thujene (0.2 percent)
 α -pinene (0.7 percent)
 camphene (0.1 percent)
 β -pinene (0.5 percent)
 p-menth-3-ene (t)
 myrcene (1.1 percent)
 α -phellandrene (0.2 percent)
 α -terpinene (2.1 percent)
 p-cymene (9.3 percent)
 β -phellandrene (0.5 percent)
 γ -terpinene (12.8 percent)
 terpinolene (0.2 percent)
 methyl benzoate (0.2 percent)
 linalool (0.2 percent)
 α -thujone (0.1 percent)
 borneol (0.1 percent)
 terpinen-4-ol (1.1 percent)
 α -terpineol (0.1 percent)
 myrtenol (0.2 percent)
 cuminaldehyde (0.3 percent)

Comparative concentration ($\mu\text{g/g}$) of constituents of *Satureja hortensis* in an oil, a supercritical fluid CO_2 extract and some subcritical water extracts

T-7

Compound	Oil (240 min) ^a	SFE (60 min)	Subcritical water extracts		
			100°C	150°C	175°C
p-cymene	407	551	126	104	154
γ -terpinene	97	112	22	17	25
thymol	830	862	864	690	665
carvacrol	1190	1180	1200	1140	1050
linalool	139	276	239	87	70
borneol	156	289	252	110	114
thymoquinone	22	498	506	277	176
β -caryophyllene	38	402	174	793	838

SFE = supercritical fluid CO_2 extract; ^atime of oil distillation or extraction

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Percentage composition of *Satureja hortensis* oil produced under different water stress conditions

T-8

Compound	Low water stress	Severe water stress	Compound	Low water stress	Severe water stress
α -thujene	1.6	1.9	(E)- β -ocimene	-	0.1
α -pinene	1.5	2.1	γ -terpinene	38.3	37.8
sabinene	0.2	0.3	piperitone	-	0.9
β -pinene	1.0	1.4	carvacrol	44.5	40.3
myrcene	1.8	2.7	thymyl acetate	0.7	1.2
α -phellandrene	0.3	0.4	β -caryophyllene	1.3	1.2
α -terpinene	5.1	5.4	bicyclogermacrene	0.4	0.4
p-cymene	2.2	2.7	β -bisabolene	0.4	0.5
limonene	0.6	0.7			

methyl carvacrol (0.5 percent)
 bornyl acetate (0.1 percent)
 thymol (0.3 percent)
 perillyl alcohol (0.1 percent)
 carvacrol (59.7 percent)
 eugenol (1.7 percent)
 carvacryl acetate (0.2 percent)
 α -copaene (0.1 percent)
 β -caryophyllene (1.2 percent)
 aromadendrene (0.1 percent)
 α -humulene (0.1 percent)
 germacrene D (t)
 β -bisabolene (1.1 percent)
 δ -cadinene (t)
 elemol (0.1 percent)
 germacrene B (0.1 percent)
 ledol (t)
 spathulenol (0.2 percent)
 caryophyllene oxide (0.4 percent)
 humulene epoxide I (0.2 percent)

t = trace (<0.1 percent)

nari region near Zara-Sivas (Turkey). The authors compared the analysis of the oil run both by GC/FID and GC/MS. The results of this comparison can be seen in T-9.

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Compound	GC/FID	GC/MS	Compound	GC/FID	GC/MS
α -thujene	0.8	0.8	terpinen-4-ol	0.3	0.3
α -pinene	2.6	3.0	pulegone	0.2	0.1
β -pinene	2.7	2.5	(E)-anethole	0.1	0.5
myrcene	1.7	1.4	thymol	29.0	28.9
α -phellandrene	0.2	0.3	carvacrol	26.5	26.1
α -terpinene	2.2	2.7	thymyl acetate	0.3	0.3
p-cymene	9.3	10.0	carvacryl acetate	0.1	0.1
β -ocimene*	0.1	0.1	β -caryophyllene	0.4	0.4
γ -terpinene	22.6	21.5	aromadendrene	0.1	0.1
terpinolene	0.1	0.1	bicyclogermacrene	0.1	0.2
borneol	0.3	0.3	β -bisabolene	0.2	0.1

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Mullilam Oil

Mullilam is an oil that is occasionally offered for sale in India. It is produced from the dried fruits (which are also used as a spice and are often used as a component of the spice blend garam masala) of a tall deciduous tree member of the Rutaceae family. The actual taxonomic origin of Mullilam is *Zanthoxylum rhetsa* DC. (syn. *Z. budrunga* Wall; *Z. limonella* (Dennst.) Alston).

Many years ago, Naves and Ardizio (1950) and Naves (1950) performed the first analyses of Mullilam oil. They reported that the oil was rich in sabinene with the other two major components being α -terpinene and terpinen-4-ol. In addition, minor quantities of β -phellandrene, 1,4-

cineole, cryptone, cuminaldehyde, decanal (and other aliphatic aldehydes) and phloroacetophenone dimethyl ether. All of these compounds were isolated and characterized by both derivatization and mpt measurements.

A few years later, Rao and Bhawe (1959) reported that they tentatively identified δ -terpinene, α -phellandrene, δ -3-carene, β -pinene, dihydrocarveol, terpinen-4-ol and carvotanacetone in the oil; however, their analysis was not very convincing.

Eight years later, Mathur et al. (1967) determined that sabinene was the major constituent of Mullilam oil with α - and β -pinene being the other major hydrocarbons. After a column chromatographic separation of the oil, the authors noted a white crystalline component, which they characterized as an oxidation product of sabinene. This oxidodiol was given the trivial name mullilamdiol (1,4-epoxy-p-menthane-2,3-diol).

Thappa et al. (1976) examined a crystalline substance that had precipitated during chromatography of an oil of *Z. budrunga*. By using synthesis and $^1\text{H-NMR}$ studies they characterized the material as 1S, 2S, 4S-trihydroxy-p-menthane.

Many years later, Paknikar and Kamat (1993) re-examined this mullilamdiol, and through synthesis and modern spectroscopic techniques (CI-MS and $^{13}\text{C-NMR}$), they were able to determine that mullilamdiol was in fact p-menthane-1 α , 2 β ,4 β -triol, an oxidation product of either terpinen-4-ol or sabinene.

Joy et al. (1986) subjected a lab-distilled oil of *Z. rhetsa* produced from mature fruits collected in the Western Ghats in Kerala to analysis using GC and GC/MS. The components found in the oil were as follows:

- α -pinene (10.0 percent)
- camphene (t)
- β -pinene (7.5 percent)
- sabinene (49.1 percent)
- myrcene (1.2 percent)
- α -phellandrene (0.2 percent)
- α -terpinene (1.9 percent)
- limonene (0.3 percent)

β -phellandrene (1.8 percent)
 γ -terpinene (3.7 percent)
p-cymene (2.5 percent)
terpinolene (0.9 percent)
terpinen-4-ol (14.1 percent)
 γ -cadinene[†] (0.4 percent)
 β -elemene (2.7 percent)
 β -caryophyllene (0.1 percent)
 α -terpineol (0.9 percent)
 α -farnesene[°] (0.2 percent)
 α -muurolol[°] (0.5 percent)
farnesol[°] (0.3 percent)

[°]correct isomer not identified

[°]tentative identification

[†]incorrect identity based on elution order

Shankaracharya et al. (1994) obtained dried fruits of *Z. rhetsa*; after cleaning the fruits were ground to produce a powder (500 μ size). Oils produced from the various origins by both steam and hydrodistillation were analyzed for the major constituents, which were found to range as follows:

α -pinene (3.18-7.55 percent)
 β -pinene (2.70-6.50 percent)
sabinene (35.73-67.73 percent)
 β -phellandrene + limonene (4.18-12.83 percent)
 γ -terpinene (0-4.34 percent)
terpinen-4-ol (3.17-13.42 percent)
 α -terpineol (0.58-1.91 percent)
 δ -cadinene (2.07-4.09 percent)

The authors also performed a more detailed analysis of one of the oils using GC/MS. It was found to contain the following components:

α -pinene (3.13 percent)
 β -pinene (1.29 percent)
sabinene (55.79 percent)
myrcene (2.06 percent)
 α -terpinene (1.42 percent)
limonene (0.75 percent)
 α -phellandrene[°] (t)
 β -phellandrene (2.93 percent)
 γ -terpinene (2.70 percent)
(E)- β -ocimene (0.59 percent)
p-cymene (0.77 percent)
terpinolene (0.67 percent)
 α -cubebene (0.34 percent)
trans-sabinene hydrate (1.18 percent)
 α -copaene (1.51 percent)
2,6-nonadienal[°] (1.64 percent)
 β -cubebene (0.75 percent)
cis-sabinene hydrate (0.91 percent)
linalool (0.67 percent)
linalyl acetate (0.15 percent)
 β -elemene (3.61 percent)
terpinen-4-ol (5.64 percent)
 α -terpineol (2.97 percent)
 β -selinene (1.11 percent)
germacrene B[°] (1.36 percent)
 α -farnesene[°] (0.15 percent)
 β -bisabolene (0.26 percent)
 α -selinene[°] (1.70 percent)

δ -cadinene (1.29 percent)
spathulenol (0.11 percent)
 α -cadinol (0.09 percent)
juniper camphor[†] (0.08 percent)

[°]correct isomer not identified

[°]incorrect identification based on elution order

[†]also known as selin-7(11)-4 α -ol

In 1998, Jirovetz et al. analyzed an oil of *Z. rhetsa* produced in the laboratory from dried seeds obtained from Kerala (India) using a combination of GC and GC/MS. The authors found that the oil possessed the following composition:

sabinene (47.12 percent)
 α -terpineol (7.73 percent)
terpinen-4-ol (6.61 percent)
 β -pinene (5.99 percent)
limonene (4.06 percent)
 α -pinene (3.87 percent)
 γ -terpinene (3.64 percent)
 α -terpinene (3.45 percent)
p-cymene (3.08 percent)
 β -phellandrene (2.11 percent)
 β -elemene (1.58 percent)
nonanal (0.89 percent)
linalool (0.76 percent)
myrcene (0.74 percent)
terpinolene (0.71 percent)
octanol (0.67 percent)
 β -caryophyllene (0.63 percent)
 γ -cadinene (0.57 percent)
camphene (0.55 percent)
 α -phellandrene (0.48 percent)
(E)- β -ocimene (0.42 percent)
 α -farnesene[°] (0.39 percent)
 δ -cadinene (0.33 percent)
1-hexen-3-ol (0.31 percent)
decanol (0.26 percent)
farnesol[°] (0.21 percent)
 γ -cadinol[°] (0.19 percent)
hexanoic acid (0.16 percent)
sabinene hydrate[°] (0.14 percent)
 α -muurolol (0.12 percent)
 β -cubebene (0.11 percent)
nonanoic acid (0.10 percent)
linalyl acetate (0.08 percent)
germacrene D (0.07 percent)
 δ -3-carene (0.05 percent)
 β -bisabolene (0.04 percent)
undecane (0.03 percent)
spathulenol (0.02 percent)
 α -selinene (0.02 percent)
germacrene B (0.01 percent)
 α -humulene (0.01 percent)

[°]correct isomer not identified

[°]incorrect identification based on elution order

More recently, Shafi et al. (2000) compared the composition of the leaf and seed oils of *Z. rhetsa* using GC and GC/MS. They identified more than 100 components in the leaf oil and over 70 in the seed oils,

although many of the constituents were present in levels of less than 0.1 percent. The leaf oil was found to contain:

heptane (3.5 percent)
 isoamyl alcohol (t)
 2-methylbutanol (0.2 percent)
 amyl alcohol (t)
 2-methyl-2-butanol (t)
 hexanal (t)
 octane (t)
 (E)-3-hexenol (0.1 percent)
 (E)-2-hexenal (t)
 (Z)-3-hexenol (0.1 percent)
 (E)-2-hexenol (t)
 hexanal (t)
 2-heptanone (t)
 (Z)-4-heptenol (t)
 heptanal (t)
 α -pinene (t)
 benzaldehyde (t)
 heptanol (t)
 hexanoic acid (t)
 sabinene (t)
 octenol^o (0.7 percent)
 6-methyl-5-hepten-2-one (0.3 percent)
 2,3-dehydro-1,8-cineole (t)
 6-methyl-5-hepten-2-ol (t)
 octanal (t)
 α -terpinene (t)
 p-cymene (t)
 limonene (t)
 β -phellandrene (0.1 percent)
 benzyl alcohol (t)
 o-cresol (0.2 percent)
 2,4,4-trimethyl-2-cyclohexen-1-ol (t)
 styrallyl alcohol (t)
 octanol (0.1 percent)
 acetophenone (t)
 p-cresol + m-cresol (0.2 percent)
 cis-linalool oxide^o (t)
 p-tolualdehyde
 4,4,6-trimethyl-2-cyclohexen-1-one (t)
 guaicol (0.1 percent)
 3,5-octadien-2-one^o (t)
 linalool (0.1 percent)
 6-methyl-3,5-heptadien-2-one (0.2 percent)
 6-hydroxy-2,2,6-trimethylcyclohexanone (t)
 2-phenethanol (0.1 percent)
 α -cyclocitral (t)
 cis-p-mentha-2,8-dien-1-ol (t)
 isophorone (0.1 percent)
 p-cymenene (t)
 p-tolyl alcohol (t)
 2-ethylphenol (t)
 benzyl cyanide (t)
 1,2-dimethoxybenzene (0.1 percent)
 2,5-dimethylphenol (0.1 percent)
 nonadienal^o (t)
 2-acetonyl-4-methyltetrahydropyran (t)
 benzoic acid (0.1 percent)
 4-ethylphenol (0.1 percent)
 α -terpineol
 safranal (0.2 percent)
 4-vinylphenol (0.5 percent)

β -cyclocitral (0.1 percent)
 cuminaldehyde (t)
 carvone (t)
 geraniol (t)
 piperitone (0.1 percent)
 β -homocitral^o (t)
 geranial (t)
 4-ethylguaicol (0.1 percent)
 2-undecanone (t)
 indole (t)
 2-methoxy-4-vinylphenol (0.4 percent)
 α -cubebene (0.3 percent)
 eugenol (0.2 percent)
 γ -nonalactone (t)
 dihydroeugenol (t)
 1,2,4-trimethoxybenzene (t)
 α -copaene (1.0 percent)
 methyl cinnamate^o (t)
 β -damascenone^o (0.1 percent)
 β -copaene (5.3 percent)
 β -elemene (0.4 percent)
 bourbonene^o (0.2 percent)
 vanillin (t)
 β -caryophyllene (9.6 percent)
 α -ionone^o (0.19 percent)
 aromadendrene (0.2 percent)
 geranyl acetone (1.2 percent)
 α -humulene (1.4 percent)
 γ -muurolene (0.3 percent)
 germacrene D (0.8 percent)
 β -ionone^o (t)
 pentadecane (0.9 percent)
 δ -cadinene (1.3 percent)
 dihydroactinodiolide (0.2 percent)
 dodecanoic acid (1.1 percent)
 nerolidol^o (0.4 percent)
 spathulenol (3.3 percent)
 globulol (0.2 percent)
 hexadecane (1.0 percent)
 isocaryophyllene oxide (12.7 percent)
 ledol (t)
 caryophyllene oxide (1.1 percent)
 cubenol (0.8 percent)
 heptadecane (2.9 percent)
 octadecane (2.9 percent)
 nonadecane (2.5 percent)
 eicosane (1.6 percent)
 heneicosane (0.9 percent)
 docosane (0.5 percent)
 tricosane (0.3 percent)
 tetracosane (0.2 percent)
 pentacosane (0.3 percent)
 hexacosane (0.5 percent)
 heptacosane (0.7 percent)
 octacosane (1.1 percent)
 nonacosane (1.5 percent)
 triacontane (1.5 percent)

^ocorrect isomer not identified

^ofuranoid form

t = trace (<0.1 percent)

In contrast, Shafi et al. found that the seed oil possessed the following composition:

2-heptanone (t)
 nonane (t)
 heptanal (t)
 tricyclene (t)
 α -thujene (0.5 percent)
 α -pinene (6.6 percent)
 camphene (t)
 sabinene (66.3 percent)
 β -pinene (6.4 percent)
 6-methyl-5-hepten-2-one (t)
 myrcene (1.4 percent)
 octanal (1.9 percent)
 α -phellandrene (0.1 percent)
 hexyl acetate (t)
 α -terpinene (0.4 percent)
 p-cymene (0.5 percent)
 limonene (0.2 percent)
 β -phellandrene (1.4 percent)
 1,8-cineole (0.1 percent)
 (Z)- β -ocimene (t)
 (E)- β -ocimene (0.2 percent)
 γ -terpinene (1.0 percent)
 octanol (0.7 percent)
 terpinolene (0.3 percent)
 2-nonanone (t)
 linalool (1.2 percent)
 nonanal (t)
 α -thujone (t)
 β -thujone (t)
 p-menth-2-en-1-ol^o (0.2 percent)
 pinocarveol^o (0.1 percent)
 p-menthadienol^o (t)
 octanoic acid (t)
 nonanol (t)
 terpinen-4-ol (3.5 percent)
 p-cymen-8-ol (t)
 α -terpineol (1.3 percent)
 methyl salicylate (0.1 percent)
 myrtenol (t)
 decanal (2.3 percent)
trans-piperitol (0.1 percent)
 nerol (t)
 cuminaldehyde (t)
 geraniol (t)
 linalyl acetate (t)
 piperitone (t)
 2-decenol^o (0.1 percent)
 decanol (0.2 percent)
 bornyl acetate (t)
 2-undecanone (t)
 isobornyl acetate (t)
 cuminyl alcohol (t)
 carvacrol (t)
 undecanal (t)
 α -cubebene (t)
 α -copaene (0.2 percent)
 β -copaene (0.2 percent)
 β -elemene (0.3 percent)
 dodecanal (0.3 percent)
 α -gurjunene (t)
 cryptone (t)
 β -caryophyllene (t)
 aromadendrene (t)
 2-dodecenal^o (t)
 α -humulene (t)

dodecanol (t)
 γ -muurolene (t)
 β -selinene (t)
 germacrene D (0.2 percent)
 α -selinene (0.1 percent)
 valencene (t)
 δ -cadinene (0.1 percent)
 spathulenol (t)
 isocaryophyllene oxide (0.1 percent)
 tetradecanal (0.1 percent)
 cubenol (t)
 heptadecane (t)

t = trace (<0.1 percent)
^ocorrect isomer not identified

A leaf oil of *Z. rhetsa* of Australian origin was the subject of analysis by Brophy et al (2000). The oil was found to contain:

α -pinene (0.7 percent)
 myrcene (t)
 α -terpinene (0.1 percent)
 γ -terpinene (0.2 percent)
 p-cymene (0.1 percent)
 terpinolene (0.1 percent)
 α -cubebene (1.6 percent)
 δ -elemene (1.2 percent)
 bicycloelemene (0.2 percent)
 α -copaene (5.4 percent)
 β -bourbonene (0.2 percent)
 β -cubebene (2.2 percent)
 α -gurjunene (0.9 percent)
 β -elemene (1.7 percent)
 β -caryophyllene (27.5 percent)
 aromadendrene (1.6 percent)
 allo-aromadendrene (0.9 percent)
 α -humulene (6.0 percent)
 viridiflorene (0.7 percent)
 germacrene D (18.4 percent)
 α -muurolene (0.9 percent)
 bicyclogermacrene (5.0 percent)
 δ -cadinene (4.3 percent)
 2-tridecanone (0.2 percent)
 caryophyllene oxide (0.8 percent)
 epi-globulol (0.3 percent)
 ledol (0.8 percent)
 cubeban-11-ol (0.6 percent)
 cubenol (2.0 percent)
 epi-cubenol (0.1 percent)
 globulol (0.5 percent)
 viridiflorol (0.3 percent)
 spathulenol (0.7 percent)
 T-cadinol (0.8 percent)
 T-muurolol (1.0 percent)
 α -muurolol (0.2 percent)
 α -cadinol (1.5 percent)

The pericarp oil of *Z. rhetsa* was found to be rich in oil (4.6 percent), whereas the seed contained only 0.5 percent oil. Mohan Rao (2000) reported that he analyzed the pericarp oil; however, he merely repeated an early analysis, which he co-authored with Shankaracharya et al. (1994).

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cis-linalool oxide* (0.1 percent)
 linalool (8.7 percent)
 linalyl acetate (0.1 percent)
 terpinen-4-ol (4.2 percent)
 α -terpineol (11.5 percent)
 α -terpinyl acetate (30.6 percent)
 neryl acetate (0.2 percent)
 geranial (0.3 percent)
 carvone (0.1 percent)
 geranyl acetate (0.8 percent)
 p-methylacetophenone (0.1 percent)
 nerol (0.1 percent)
trans-carveol (0.1 percent)
 geraniol (1.4 percent)
 p-cymen-8-ol (0.3 percent)
 (E)-nerolidol (0.4 percent)

*furanoid form

Menon et al. (1999) compared the composition of the free and bound volatiles of fresh green cardamom. They isolated the free volatiles by blending fresh green cardamom (2 kg) with water (2 L). After clarification of the mixture by centrifugation (18,000 rpm at 4°C), the supernatant aroma-rich liquid was separated by passing it through a pre-washed Amberlite XAD-2 column (50 cm x 1 cm) at a 2 mL/min rate. The column was further washed with water (1500 mL) to remove the sugars, proteins and free amino acids. Elution of the column with 500 mL of pentane/diethyl ether (1:1) removed the volatiles from the column. After careful solvent removal under vacuum, the volatile concentrate was subjected to GC and GC/MS analysis. The composition of the so-called free volatiles was found to be as follows:

3-hexenol* (0.2 percent)
 2-heptanol (t)
 α -thujene (0.1 percent)
 1-octen-3-ol (0.3 percent)
 sabinene (0.1 percent)
 β -pinene (1.9 percent)
 1,8-cineole (28.4 percent)
 γ -terpinene (1.7 percent)
 5-nonanone (1.6 percent)
trans-linalool oxide** (0.4 percent)
trans-sabinene hydrate (0.3 percent)
 myrcenol (0.2 percent)
 2-ethylphenol (0.7 percent)
 dihydrolinalool*** (t)
 β -terpineol* (0.1 percent)
 menthone (0.1 percent)
 isopulegol (0.1 percent)
 (E)-2-nonenal (t)
 isoborneol (0.1 percent)
 borneol (0.1 percent)
 α -terpineol (3.4 percent)
 dihydrocarveol* (2.5 percent)
 nerol (t)
 geraniol (3.7 percent)
 carvone oxide* (1.8 percent)
 safrole (t)
 (E)-cinnamyl alcohol (t)
 α -terpinyl acetate (21.3 percent)
 α -ylangene (0.7 percent)

Cardamom Oil

Casabianca and Graff (1996) determined that the enantiomeric distribution of linalool in Sri Lankan and Guatemalan cardamom oil was: (3S)-(+)-linalool (93 percent):(3R)-(-)-linalool (7 percent).

Rahman et al. (1999) used a combination of GC and GC/MS to analyze an oil produced from *Elettaria cardamomum* (L.) Maton fruit grown in Pakistan. The composition of the oil was found to be as follows:

α -pinene (0.5 percent)
 α -thujene (0.1 percent)
 β -pinene (0.1 percent)
 sabinene (0.8 percent)
 myrcene (0.6 percent)
 limonene (3.7 percent)
 1,8-cineole (30.7 percent)
 p-cymene (1.3 percent)
trans-linalool oxide* (0.2 percent)

(Z)-jasnone (t)
 β-bourbonene (t)
 epi-sesquithujene (t)
 isoeugenol* (t)
 β-caryophyllene (t)
 isoeugenol* (t)
 ethyl anisate (t)
 α-bergamotene* (t)
 α-cedrene (0.1 percent)
 β-farnesene* (t)
 α-humulene (t)
 methyl isoeugenol* (0.1 percent)
 valencene (t)
 germacrene D (t)
 α-muurolene (t)
 calamenene* (t)
 (Z)-nerolidol (t)
 elemol (t)
 helional*** (t)
 (E)-nerolidol (0.2 percent)
 caryophyllene alcohol (t)
 caryophyllene oxide (0.1 percent)
 cubenol (t)
 T-cadinol (t)
 α-cadinol (t)
 α-bisabolol (t)
 (Z,Z)-farnesol (t)
 (Z,E)-farnesol (t)
 α-eudesmol (t)
 (E,Z)-farnesol (t)
 (E,E)-farnesol (t)
 calamenone^a (t)
 vomifoliol^b (t)

t = trace (<0.1 percent)

*correct isomer not identified

**furanoid form

*** not a naturally occurring compound

^astructure unknown

^balso known as 6,9-dihydroxy-4,7-megastigmadien-3-one

5-octen-3-ol (0.4 percent)
 2-octanol (0.6 percent)
 1,8-cineole (0.2 percent)
 phenylacetaldehyde (0.3 percent)
 benzyl alcohol (0.1 percent)
 octanol (0.3 percent)
 1-nonen-3-ol (0.2 percent)
 cis-linalool oxide* (2.9 percent)
 trans-linalool oxide* (0.4 percent)
 tetrahydrolinalool** (1.9 percent)
 linalool (1.1 percent)
 myrcenol (0.4 percent)
 thymyl alcohol (0.7 percent)
 isopulegol (0.1 percent)
 isoborneol (0.1 percent)
 cis-linalool oxide*** (0.2 percent)

The glycosidically bound volatiles were eluted from the same column using methanol (500 mL). Once the methanol was removed under vacuum, the glycosidic extract was stabilized in a phosphate/citrate buffer (25 mL at pH 5.0). This mixture was then incubated at 37°C for 36 h after the addition of β-glucosidase (25 mg). At the end of the incubation period, the aglycones were extracted from the mixture using diethyl ether. Again, after careful solvent removal under vacuum, the released bound volatiles were subjected to GC and GC/MS analysis. The compounds identified as aglycones can be seen as follows:

isoamyl alcohol (1.5 percent)
 amyl alcohol (1.9 percent)
 3-methyl-2-pentanol (16.3 percent)
 2-heptanol (0.1 percent)
 (E)-2-hexenal (0.6 percent)
 benzaldehyde (0.3 percent)
 1-octen-3-ol (1.0 percent)

trans-linalool oxide^{***} (t)
 menthol (0.1 percent)
 terpinen-4-ol (0.1 percent)
 α -terpineol (6.2 percent)
 dihydrocarveol^{****} (0.3 percent)
trans-carveol (0.5 percent)
 nerol (t)
 anisaldehyde (0.1 percent)
 geraniol (1.1 percent)
 geranial (0.2 percent)
 p-menth-1-en-7-al (0.1 percent)
 cumyl alcohol (0.1 percent)
 (E)-anethole (0.1 percent)
 thymol (0.2 percent)
 carvacrol (0.1 percent)
 α -methyl cinnamaldehyde (0.1 percent)
 neric acid (t)
 isosafrole^{****} (3.8 percent)
 isoeugenol^{****} (0.2 percent)
 (Z)-nerolidol (0.3 percent)
 elemol (0.3 percent)
 (E)-nerolidol (6.7 percent)
 caryophyllene alcohol (0.4 percent)
 caryophyllene oxide (0.1 percent)
 globulol (0.8 percent)
 cedrene oxide^{****} (0.8 percent)
 ledol (0.3 percent)
 cedrol (1.4 percent)
 10-epi-cubenol (2.6 percent)
 cubenol (2.6 percent)
 T-muurolol (2.4 percent)
 (Z,Z)-farnesol (0.5 percent)
 (Z,E)-farnesol (4.0 percent)
 (E,Z)-farnesol (4.0 percent)
 (E,E)-farnesol (4.5 percent)
 vomifoliol (0.5 percent)
 dehydrovomifoliol (0.2 percent)
 1,8-dihydrovomifoliol (0.9 percent)

t = trace (<0.1 percent)

*furanoid form

**not a naturally occurring compound

***pyranoid form

****correct isomer not identified

In a follow-up paper, Menon (2000) repeated the results of the free volatiles. In addition, Menon also compared the oil produced from freshly harvested green cardamom fruit with an oil produced from commercially available cardamom. The comparative results of the analyses can be seen in T-10.

Although the main constituents of Indian cardamom oil were 1,8-cineole and α -terpinyl acetate, this latter compound was shown by Arora and Srinivas (2002) to be the most important flavor constituent of the oil. Furthermore, using chiral GC on a γ -cyclodextrin GC column, they showed that the natural α -terpinyl acetate was (4R)-(+)- form with an enantiomeric purity of 100 percent.

H. Casabianca and J.B. Graff, *Chiral analysis of linalool and linalyl acetate in various plants*. Rivista Ital. EPPOS, (Numero Speciale) 227-243 (1996).

Compound	FGCO	CCO	Compound	FGCO	CCO
isopropyl acetate	t	-	citronellyl acetate	0.5	-
1-penten-3-ol	t	-	geranyl acetate	0.1	-
heptane	0.2	-	α -copaene	1.2	0.1
isoamyl alcohol	t	-	β -bourbonene	0.3	t
amyl alcohol	t	-	epi-sesquithujene	0.9	t
3-hexenol*	t	-	isoeugenol*	0.1	t
hexanal	t	-	α -cubebene	0.3	-
4-heptanol	t	-	β -elemene	0.1	-
2-heptanol	t	-	β -caryophyllene	0.3	-
α -thujene	0.8	0.1	α -bergamotene*	0.3	-
camphene	t	-	β -farnesene*	0.2	0.2
sabinene	1.9	-	α -humulene	0.2	t
β -pinene	0.2	1.5	methyl isoeugenol*	0.3	t
myrcene	1.1	1.1	valencene	-	t
α -phellandrene	t	t	germacrene D	0.4	t
p-cymene	0.2	0.3	α -muurolene	0.3	0.2
1,8-cineole	29.3	28.5	β -selinene	0.2	-
γ -terpinene	0.5	0.3	calamenene*	0.9	0.1
1-nonen-3-ol	0.1	-	ar-curcumene	0.2	-
<i>trans</i> -sabinene hydrate	t	-	calamenene*	0.2	-
5-nonanone	t	-	β -sesquiphellandrene	1.0	0.1
<i>trans</i> -linalool oxide**	0.4	-	helional***	0.2	-
linalool	2.5	3.8	(E)-nerolidol	1.2	-
myrcenol	0.1	0.3	caryophyllenol*	0.2	1.5
2-ethylphenol	0.2	-	isocaryophyllene oxide	0.8	-
dihydrolinalool***	0.1	-	caryophyllene oxide	0.8	t
dihydrocarveol*	0.1	0.5	α -cedrene oxide	1.0	t
nerol	-	1.4	cedrol	0.1	t
geraniol	1.4	0.5	T-muurolol	0.1	t
geranial	0.7	0.1	T-cadinol	0.1	-
carvone oxide*	-	0.1	α -cadinol	t	t
carvacrol	0.1	-	α -eudesmol	t	t
(E)-cinnamyl alcohol	0.5	t	(Z,Z)-farnesol	-	t
anisyl formate	0.5	-	(Z,E)-farnesol	0.1	-
α -terpinyl acetate	25.0	29.0	(E,Z)-farnesol	0.2	-
neryl acetate	5.0	1.0	(E,E)-farnesol	0.3	-

t = trace (<0.1 percent)

*correct isomer not identified

**furanoid form

***not a naturally occurring compound

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