

Progress in Essential Oils

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Coriander Seed and Leaf Oils

In 1992, Nitz et al. used GC/MS to characterize the composition of a distilled oil of coriander and compare it with that of a supercritical fluid (SFC) extract of coriander. They found that the oil contained the following major compounds:

linalool (63%) γ-terpinene (9%) α-pinene (8%)

camphor (4%) geranyl acetate (2%)

limonene (4%)

In addition, a number of minor components of lower odor thresholds were also identified, including:

hexanal (0.07%)	2-octylfuran (0.03%)
heptanal (0.04%)	2-decylfuran (0.01%)
octanal (0.02%)	1-octen-3-one (0.01%)
nonanal (0.02%)	3-octen-2-one (0.01%)
undecanal (0.03%)	2,6-dimethylpyrazine (0.01%)
dodecanal (0.01%)	ethyl-dimethylpyrazine* (<0.01%
(E)-2-heptenal (0.02%)	furfuraldehyde (0.05%)
(E)-2-octenal (0.01%)	dihydroactinodiolide (0.02%)
(E)-2-decenal (0.07%)	safrole (0.11%)
(E)-2-dodecenal (0.03%)	4-vinylguaiacol (0.10%)
(E)-2-tetradecenal (0.05%)	4-vinylphenol (0.08%)
(E,E)-2,4-decadienal (0.01%)	dimethyldisulphide† (t)
2-pentylfuran (0.01%)	dimethyltrisulphide† (t)
2-hexylfuran (0.02%)	

*correct isomer not identified
† tentative identification
t=trace (<0.01%)</pre>

In contrast, the aroma-rich components that were identified in the SFC extract were:

hexanal (0.03%)	(E)-2-heptenal (0.08%)
heptanal (0.01%)	(E)-2-octenal (t)
octanal (t)	(E)-2-decenal (0.04%)
nonanal (t)	$(\mathrm{E,E})\text{-}2\text{,}4\text{-}decadienal}~(0.08\%)$
decanal (0.03%)	1-octen-3-one (t)
dodecanal (0.01%)	safrole (0.02%)

t=trace (<0.01%)

Three years later, Frank et al. (1995) reported that the main constituents of both lab prepared and commercial samples of coriander oil ranged as follows:

α-pinene (0.5-6.0%)
camphene $(<0.5\%)$
β -pinene (<0.5%)
sabinene (< 0.5%)
myrcene (0.2-0.8%)
limonene (1.3-6.3%)

γ-terpinene (2.7-7.7%) p-cymene (0.6-5.9%) terpinolene (<0.5%) linalool (68.4-87.5%) geranyl acetate (0.8-3.7%) geraniol (0.4-3.5%)

Table I. Percentage composition of commercial coriander oil adulterated with (+)- limonene and racemic linalool

	Genuine	Com	Commercial Oils		
Compound	Coriander Oil	1	2	3	
(4S)-(-)-limonene	50	38	12	7	
(4R)-(+)-limonene	50	62	88	93	
(3S)-(+)-linalool	10	33	27	34	
(3R)-(-)-linalool	90	67	73	66	

The authors also used both chiral GC analysis and GCisotope ratio mass spectrometry to determine adulteration in the commercial oil samples. For example, they determined that the enantiomeric ratios of limonene and linalool of the commercial samples were sufficiently different from the ratios expected for authentic oils to prove adulteration with (+)-limonene and racemic linalool as shown in Table I.

Diederischen (1996) screened 237 accessions of coriander and determined that the main fruit oil components varied as follows:

α-pinene (6.5-28.9%)	
γ-terpinene (0.7-35.4%)	geranyl acetate (1.3-12.4%)
camphor (0.4-6.3%)	geraniol (0.3-3.3%)
inalool (19.8-82.0%)	

Although the chirality of linalool in coriander oil is well known, Casabianca and Graff (1996) confirmed that it possessed the following enantiomeric distribution:

(3R)-(-)-linalool (10-14.5%) :
(3S)-(+)-linalool (85.5-90%)

In 1997, Anitescu et al. used GC/MS to analyze and compare the composition of a commercial sample of coriander oil purchased in Romania with a steam distilled oil and a lab prepared supercritical fluid extract of Romanian grown coriander. The results of this comparative study are summarized in Table II.

In 1997, Worku and Franz compared the composition of oils obtained from the leaves, stems and dried fruits of coriander. Their results, which were obtained from GC/MS analysis, are found in Table III.

The headspace volatiles of coriander seedling plants were collected on Porapak Q and analyzed by GC/MS by Valterova

Table II. Comparative percentage composition of two oils

and a superchilical fluid extract of contander				
Compound	Oil A	Oil B	SFE	
α-thujene	t	t	0.1	
α-pinene	3.3	2.3	2.8	
camphene	0.6	0.4	1.5	
sabinene	0.1	0.3	0.9	
β-pinene	1.0	0.3	0.9	
6-methyl-5-hepten-2-one	0.1	0.1	0.1	
myrcene	1.2	0.8	1.0	
δ-3-carene	1.1	0.3	0.3	
α-terpinene	0.1	0.1	0.1	
p-cymene	4.9	4.0	4.0	
limonene	2.4	2.3	2.7	
1,8-cineole	t	0.1	0.1	
γ-terpinene	4.6	3.5	3.5	
<i>cis</i> -linalool oxide†	0.6	0.2	0.4	
trans-linalool oxide†	0.8	0.3	0.4	
linalool	63.8	62.8	61.9	
camphor	5.5	5.6	5.6	
borneol	0.1	0.1	0.1	
menthol	t	0.1	0.1	
terpinen-4-ol	0.6	0.5	0.5	
p-cymen-8-ol	t	0.1	0.3	
(Z)-3-hexenyl butyrate	t	0.1	0.2	
α-terpineol	1.0	0.9	0.6	
<i>cis</i> -dihydrocarvone	-	0.1	0.1	
citronellol	0.1	0.3	0.2	
neral	0.1	0.1	0.2	
carvone	0.5	1.0	1.0	
geraniol	1.8	2.8	2.2	
geranial	t	0.1	0.2	
(E)-anethole	0.7	0.4	0.4	
thymol	t	0.1	0.1	
carvacrol	t	0.1	0.2	
geranyl formate	-	t	0.2	
eugenol	0.1	2.6	1.4	
neryl acetate	0.1	0.1	0.2	
geranyl acetate	1.0	1.8	2.4	
β-caryophyllene	t	2.1	0.8	
α-humulene	t	0.3	0.2	
eugenyl acetate	-	t	0.2	
caryophyllene oxide	t	t	0.2	
Oil A = commercial oil				

Oil B = steam distilled oil SFE = supercritical fluid CO₂ extract \uparrow = furanoid form t = trace (<0.1%)

et al. (1997). As this study was performed to determine the attraction of a specific insect to lay her eggs on the plant, the analysis was directed only towards the monoterpene hydrocarbons. Valterova et al. characterized the following monoterpene hydrocarbons in the headspace:

α-pinene (23.6%)	α -terpinene (44.8%)
β-pinene (11.1%)	limonene (5.5%)
δ-3-carene (10.8%)	$\beta\text{-phellandrene}\;(4.3\%)$

The authors also determined the enantiomeric distribution of the chiral hydrocarbons, with the exception of β -phellandrene, which they stated was too small to determine other than that the (-)-isomer predominated. The enantiomeric distribution of four other chiral hydrocarbons was as follows:

 $\begin{array}{l} (IS,5S)-(-)-\alpha-pinene \ (45\%): \ (IR,5R)-(+)-\alpha-pinene \ (55\%) \\ (IS,5S)-(-)-\beta-pinene \ (95\%): \ (IR,5R)-(+)-\beta-pinene \ (55\%) \\ (3S)-(-)-\delta-3-carene \ (0\%): \ (3R)-(+)-\delta-3-carene \ (100\%) \\ (4S)-(-)-limonene \ (61\%): \ (4R)-(+)-limonene \ (39\%) \end{array}$

A lab-distilled oil of coriander produced from coriander seed obtained from the spice shelf in the UK was analyzed by GC/MS by Tiziana Baratta et al. (1998). The oil composition was determined to comprise of the following constituents:

tricyclene (t)
α -thujene (0.1%)
α -pinene (8.5%)
camphene (0.9%)
sabinene (0.3%)
β -pinene (0.6%)
myrcene (0.9%)
α -terpinene (0.1%)
p-cymene (2.2%)
β -phellandrene (0.2%)
limonene (1.9%)
γ -terpinene (7.1%)
terpinolene (0.4%)

 $\begin{array}{l} \mbox{linalool} (66.3\%) \\ \mbox{camphor} (3.8\%) \\ \mbox{borneol} (0.6\%) \\ \mbox{terpinen-4-ol} (0.3\%) \\ \mbox{a-terpineol} (0.4\%) \\ \mbox{citronellol} (t) \\ \mbox{geraniol} (2.0\%) \\ \mbox{(Z)-anethole} (t) \\ \mbox{carvacrol} (t) \\ \mbox{pinocarvyl acetate}^{\circ} (t) \\ \mbox{geranyl acetate} (2.7\%) \\ \mbox{\beta-caryophyllene} (0.1\%) \end{array}$

*correct isomer not identified t=trace (<0.1%)

The compositions of a diethyle ther extract and a supercritical fluid CO_2 extract of coriander were compared with that of an oil by Feicke et al. (1998) using GC. The results of this study are shown in Table IV.

Also in 1998, Bandoni et al. compared the composition of coriander seed oil produced by water distillation (hydrodistillation) and steam distillation. As can be seen from the data presented in Table V, the oils were quite similar. The authors also compared the composition of coriander seed oils produced from plants grown in three different provinces of Argentina (Cordoba, Buenos Aires and Mendoza) with commercial oils and some oils produced in Russia. A summary of their results can be seen in Table VI. Finally, Bandoni et al. compared the composition of freshly prepared coriander oil with that of an aged oil as shown in Table VII.

The following year, Benyoussef et al. (1999) examined the composition of an oil and two extracts produced from

Table III. Effect of distillation process on oil composition of coriander

	Hydrodistilled	Steam Distilled
Compound	Oil	Oil
α-pinene	1.2	3.7
camphene	0.2	0.6
sabinene	0.1	0.1
β-pinene	0.1	0.4
myrcene	0.5	0.8
limonene	1.1	2.0
γ-terpinene	2.2	4.1
p-cymene	0.3	0.7
terpinolene	0.3	0.5
linalool	81.8	75.7
camphor	4.8	4.5
geranyl acetate	2.0	3.2
geraniol	3.2	2.0

Table IV. Comparative percentage composition of some coriander oils

	Argentinean	Russian	Commercial
Compound	Oils	Oils	Oils
a-pinene	1.0-2.7	3.9-4.8	2.7-6.5
camphene	0.1-0.4	0.6-0.9	0.5-1.2
sabinene	0.1-0.2	0.1-0.2	0.1-0.3
β-pinene	0.1-0.3	0.4-0.6	0.2-0.5
myrcene	0.4-0.5	0.6-0.8	0.6-1.0
limonene	0.9-1.1	2.4-5.1	1.8-2.6
1,8-cineole	0.1	0.1-0.2	0.1-0.2
γ-terpinene	2.8-5.0	3.3-4.4	4.1-5.1
p-cymene	0.3-1.5	1.7-3.0	0.7-1.7
terpinolene	0.2-0.3	0.4-0.5	0.5-0.6
nonanal	0-0.1	-	-
<i>cis</i> -linalool oxide†	t-0.2	0.2-0.4	t-0.2
trans-linalool oxide	† †-0.2	0.2-0.3	t-0.2
decanal	0-0.4	-	t-0.3
linalool	76.3-83.7	71.0-72.6	68.9-76.3
camphor	3.2-4.8	4.1-5.4	4.4-4.8
terpinen-4-ol	0.1-0.3	0.2-0.3	0.1-0.2
α-terpineol	0.3-0.6	0.4-0.9	0.3-0.4
geranyl acetate	0.8-2.0	2.4-3.9	2.6-3.8
geraniol	2.0-3.2	1.2-1.8	1.4-2.0
† furanoid form t=trace (<0.1%)			

Compound	Leaf Oil	Stem Oil	Dried Fruit Oil
nonane	0.1	-	-
α-pinene	-	-	0.9
camphene	-	-	0.2
β-pinene	-	-	0.1
myrcene	-	-	0.4
limonene	-	-	1.1
decanal†	0.6	0.3	-
β-phellandrene	-	-	0.1
p-cymene	0.3	0.3	0.3
γ-terpinene	-	-	1.0
linalool oxide*	0.6	0.3	-
α-terpinene‡	-	-	0.4
linalool	0.6	4.0	85.7
nonanal	0.4	0.3	-
(Z)-2-nonenal	0.1	-	-
decanal	27.3	-	-
camphor	-	-	6.2
<i>cis</i> -linalool oxide	0.4	-	-
(pyranoid)			
decanol	5.1	16.6	-
(E)-2-decenol †††	49.2	50.8	-
geraniol	-	-	t
undecanal	1.5	3.5	-
neral	-	-	0.1
sabinyl acetate*	-	-	0.1
(E)-2-undecenal	3.3	6.8	-
dodecanal	1.2	1.4	-
geranyl acetate	-	0.2	3.2
(E)-2-dodecenal	5.8	8.8	-
(E)-2-tridecenal	2.5	5.3	-
† should be octanal ‡ should be terpinolene ††† should be (E)-2-dece *correct isomer not iden t=trace (<0.1%)	enal tified		

coriander grown in Algeria. As can be seen from their results, which are shown in Table VIII, the hexane extract was very low in linalool and rich in myristic acid unlike the oil or the ethanolic extract. Also, it must be noted that the analyses were not very complete as only 86.2%, 68.6% and 78.8% were identified in the oil, hexane extract and supercritical fluid $\rm CO_2$ extract, respectively,

Tateo et al. (1999) determined that the content of camphor in coriander oil was 5.1-5.4%. Its enantiomeric distribution was found to be:

(IS)-(-)-camphor (86.3-87.6%) : (IR)-(-)-camphor (12.4-13.7%)

This same year, Cadwallader et al. (1999) examined a methylene chloride extract of *C. sativum* leaves (cilantro) that were freshly harvested and a second extract produced from cilantro leaves purchased at the grocery store using GC/MS and retention indices. Their results can be seen summarized in Table IX.

- S. Nitz, H. Kollmannsberger and M. Punkert, CO2 Hochdruckextraktian von Gewürzen. Chem. Mikrobiol. Technol. Lebensmitt., 14, 108-116 (1992).
- C. Frank, A. Dietrich, U. Kremer and A. Mosandl, GC-IRMS in the authenticity control of the essential oil of Coriandrum sativum L., J. Agric. Food Chem., 43, 1634-1637 (1995).
- A. Diederischen, Results of a characterization of a germplasm collection of coriander (Coriander sativum L.) in the Gatersleben gene bank. In: Proceedings International Symposium Breeding Research on Medicinal and Aromatic Plants. Edit., F. Pank, pp. 45-48, Bundesanstalt fur Züchtungforschung an Kulturpflanzen, Quedlinburg, Germany (1996).
- H. Casabianca and J. B. Graff, Chiral analysis of linalool and linalyl acetate in various plants. Rivista Ital. EPPOS, (Numero Speciale), 227-243 (1996).
- G. Anitescu, C. Doneanu and V. Radulescu, Isolation of coriander oil: Comparison between steam distillation and supercritical fluid extraction. Flav. Fragr. J., 12, 173-176 (1997).
- I. Valterova, G. Nehlin and A-K. Borg-Karlson, Hose plant chemistry and preferences in egg-laying Trioza apicalis (Homoptera, Psylloidea). Biochem., Syst. Ecol., 25, 477-491 (1997).
- T. Worku and Ch. Franz, Essential oil yield from different plant organs and various coriander accessions. In: Proceedings of 27th International Symposium on Essential Oils, Vienna 1996. Edits., Ch. Franz, A. Mathé and G. Buchbauer, pp. 333-336, Allured Publishing, Carol Stream, IL (1997).
- M. Tiziana Baratta, H. J. D. Dorman, S. G. Deans, D. M. Biondi and G. Ruberto, *Chemical composition, antimicrobial and antioxidative* activity of laurel, sage, rosemary, oregano and coriander essential oils. J. Essent. Oil Res., 10, 618-627 (1998).
- G. Fricke, H. Hoyer, R. Wermter and H. Paulus, Einfluss lipophiler Stoffe auf die mikrobiologische Hemmwirkung von Aromaextrakten am Beilspiel von Staphylococcus aureus. Arch. Lebensmittelhyg., 49, 107-111 (1998).
- A. Bandoni, I. Mizrahi and M. A. Juarez, Composition and quality of the essential oil of coriander (Coriandrum sativum L.) from Argentina. J. Essent. Oil Res., 10, 581-584 (1998).
- E. H. Benyoussef, R. Nbeddek, R. Belabbes and J. M. Bessiére, *Etude analytique des extraits des graines de coriander d'Algerie*. Rivista Ital., 28, 27-32 (1999).
- F. Tateo, M. Bonini, E. DeDominicis and V. Fumagalli, Update on enantiomeric composition of (IR)-(+)- and (IS)-(-)-camphor in essential oils by enantioselective gas chromatography. Anal. Commun., 36, 149-151 (1999).
- K. R. Cadwallader, R. Sarakarnul, S-P. Yang and T. E. Webb, Character impact aroma components of coriander (Coriandrum sativum) herb. In: Flavor Chemistry of Ethnic Foods. Edits., F. Shahid and C. T. Ho, pp. 77-84, Kluwer Academic/Plenum Publ., New York (1999).

Cassia Oil

In 1988 Frey used a technique of selective ion monitoring GC/MS to determine adulteration of cassis oil from China.

He determined that phenylpentadienal was an impurity in synthetic cinnamaldehyde of Chinese origin. As synthetic cinnamaldehyde is the common adulterant of cassia oil, if the amount of phenylpentadienal in an adulterated cassia oil can be determined, then the amount of adulteration with synthetic cinnamaldehyde can be accurately calculated. Frey was able to determine an adulteration level of as little as 2% synthetic cinnamaldehyde by quantifying the mass fragments m/e 158, 129 and 128.

More recently, Zhu et al. (1996) reported that synthetic cinnamaldehyde produced in China had the following composition:

benzaldehyde (0.95%)	eugenol (3.73%)
benzyl alcohol (16.26%)	(E)-cinnamyl alcohol (0.57%)
(Z)-cinnamaldehyde (0.97%)	phenylpentadienal (1.73%)
(E)-cinnamaldehyde (74.4%)	(E)-cinnamic acid (0.97%)

They also proposed that the addition of synthetic cinnamaldehyde to cassia oil could be determined from selective ion monitoring GC/MS using m/e fragments of 164 (to detect benzaldehyde), 158 (to detect phenylpentadienal) and 108 (to detect eugenol). In addition, Zhu et al. analyzed an authentic sample of cassia oil by GC/MS and found that it contained:

styrene (0.09%)	(E)-cinnamyl alcohol (0.04%)
benzaldehyde (0.74%)	α -copaene (0.13%)
camphene (0.03%)	coumarin (1.85%)
salicylaldehyde (0.17%)	(E)-cinnamyl acetate (0.20%)
2-phenethyl alcohol (0.37%)	(Z)-2-methoxycinnamaldehyde
acetophenone (0.08%)	(0.17%)
3-phenylpropanol (0.54%)	(E)-2-methoxycinnamaldehyde
borneol + 2-methylbenzofuran	(12.26%)
(0.12%)	nerolidol* (0.12%)
(Z)-cinnamaldehyde $(0.58%)$	(E)-2-methoxycinnamyl acetate
2-methoxybenzaldehyde (0.42%)	(0.06%)
2-phenethyl acetate (2.29%)	benzyl benzoate (0.07%)
(E)-cinnamaldehyde (78.60%)	

°correct isomer not identified

In 1994, Vernin et al. analyzed the headspace of ground cassia bark using GC/MS. They found that this headspace contained the following constituents:

α-pinene (0.10%)	borneol + α -terpineol (3.80%)
limonene (0.28%)	hydrocinnamaldehyde (0.69%)
p-cymene (0.82%)	2-phenethyl acetate (0.96%)
α -copaene (0.67%)	(Z)-cinnamaldehyde $(0.21%)$
benzaldehyde (23.80%)	2-phenethyl alcohol (0.24%)
linalool (0.05%)	2-methoxybenzaldehyde (0.82%)
bornyl acetate (0.62%)	(E)-cinnamaldehyde (39.50%)
linalyl acetate (0.44%)	(E)-cinnamyl acetate (0.24%)
salicvaldehvde (1.27%)	

The following year, Jayatilake et al. (1995) examined the composition of the oil produced from 25 samples of cassia bark. They found that the major components of the oils ranged as follows:

 $\begin{array}{ll} (E)\mbox{-cinnamaldehyde (92.0-98.0\%)} & cold \\ (Z)\mbox{-cinnamaldehyde (0.8-2.7\%)} & \alpha \\ \beta\mbox{-caryophyllene (0.4-3.6\%)} \end{array}$

 $\begin{array}{l} {\rm coumarin}\;(0.1\text{-}1.6\%)\\ \alpha\text{-ylangene}\;(0.1\text{-}2.7\%) \end{array}$

Table VI. Comparative percentage composition of aged coriander oil			
Compound	Typical Oil	Aged Oil	
α-pinene	1.0-6.5	2.3	
myrcene	0.4-1.0	0.1	
γ-terpinene	2.2-5.1	0.1	
p-cymene	0.3-3.0	3.8	
<i>cis</i> -linalool oxide†	0.1-0.4	4.9	
trans-linalool oxide†	0.1-0.3	4.3	
camphor	2.1-4.4	nd	
linalool	68.9-83.7	64.0	
nd = not determined † = furanoid form			

In addition, reduced amounts (amounts not given) of the following constituents were also identified in cassia bark oil:

β-phellandrene	δ-cadinene
3-phenylpropanal	benzaldehyde
(E)-cinnamyl alcohol	

Also in 1995, Ehlers et al. used HPLC to determine that the main constituents of Chinese cassia oil were:

(E)-cinnamyl alcohol (0.1-0.9%)	(E)-2-methoxycinnamaldehyde
(E)-cinnamaldehyde	(0.5-9.4%)
(68.2-71.9%)	(E)-cinnamyl acetate (5.6-6.0%)

The authors also analyzed a supercritical CO_2 extract of Chinese cassia. The components identified in three replicate extracts were:

(E)-cinnamic acid (t)	(E)-2-methoxycinnamaldehyde
(E)-cinnamyl alcohol (0.3%)	(1.4-4.6%)
(E)-cinnamaldehvde (73.9-74.4%)	coumarin (0.2-1.0%)

t=trace (<0.01%)

Miller et al. (1995) used solvent assisted supercritical fluid extraction, GC/MS analysis combined with principal component analysis to differentiate between cinnamon and cassia. The 12 constituents selected for the statistical analysis were benzaldehyde, benzyl benzoate, β -caryophyllene, caryophyllene oxide, cinnamaldehyde, cinnamyl acetate, cinnamyl alcohol, coumarin, eugenol, 2-methoxycinnamaldehyde, δ -cadinene and β -phellandrene. Miller et al. distinguished cinnamon from cassia by the presence of eugenol, absence of δ -cadinene, the lower amount of coumarin and the higher amount of benzyl benzoate. This use of principal component analysis was a bit surprising because it is relatively easy to differentiate between two oils because of differing minor component compositions.

Kwon et al. (1996) isolated salicylaldehyde from a bark extract of *C. Cassia*. Although this seems like just another constituent (salicylaldehyde), the authors determined that salicylaldehyde inhibited farnesyl protein transferase activity, which according to the authors is "an enzyme which Table VII. A comparison of the percentage composition of an oil, a diethyl ether extract and a supercritical fluid CO₂ extract of coriander

Compound	SDE	EXT	SFE
α-thujene	0.07	0.08	0.06
α-pinene	6.75	8.07	5.73
camphene	0.84	1.00	0.71
sabinene	0.37	0.45	0.28
β-pinene	0.51	0.62	0.47
myrcene	0.90	1.10	0.65
α-terpinene	0.04	0.05	0.04
p-cymene	1.13	1.27	0.89
limonene	1.93	2.35	1.90
γ-terpinene	6.63	8.23	7.27
trans-sabinene hydrate	0.07	0.08	0.10
linalool oxide (furanoid)*	0.13	0.04	0.09
terpinolene	0.53	0.51	0.54
linalool	59.02	63.33	63.48
camphor	3.30	3.49	3.43
citronellal	0.06	0.06	0.05
borneol	0.13	0.16	0.12
terpinen-4-ol	0.15	0.14	0.17
α-terpineol	0.25	0.24	0.29
citronellol	0.09	0.08	0.09
geraniol	2.18	2.22	2.51
geranial	0.07	0.03	0.08
(E)-anethole	0.03	0.04	0.03
neryl acetate	0.07	0.08	0.09
geranyl acetate	2.50	3.07	3.12
β-caryophyllene	0.07	0.08	0.10
sedanolide	0.04	0.04	0.04

SDE = simultaneous distillation/extraction

EXT - diethyl ether extract

SFE = supercritical fluid CO₂ extract *correct isomer not identified

catalyzes the transfer of the farnesyl group from farnesyl pyrophosphate into cysteine 186 at the C-terminal of the RAS protein". This process is considered to be mandatory and critical for promotion the RAS oncogene towards tumor formation. As a result, the authors believed that such farnesyl protein transferase inhibitors could lead to the development of effective tumor treatment therapeutic agents.

In 1998, Li et al. compared the composition of the leaf and bark oils of *C. cassia* grown in Yunnan province (China) using GC/MS as their method of analysis. A summary of the results of this study are shown in Table X. As can be seen from the results, there are some unexplained anomalies in the data; nevertheless, this is the first detailed analysis of *C. cassia* leaf oil that has appeared in the literature. An oil of *C. cassia* produced in China was subject to GC and GC/MS analysis by Li and Yuan (1999). The results of this analysis are as follows:

styrene (0.07%)	(E)-cinnamaldehyde (67.21%)
benzaldehyde (0.03%)	(E)-cinnamyl alcohol (1.02%)
p-cymene (0.98%)	eugenol (0.99%)
benzyl alcohol (0.02%)	α -copaene (0.23%)
salicylaldehyde (1.01%)	α -cubebene (0.11%)
phenylacetaldehyde (0.34%)	vanillin (0.30%)
benzyl formate (0.08%)	β-caryophyllene (5.58%)
acetophenone (0.06%)	benzofuran (0.34%)
2-pehnethyl alcohol (0.14%)	(E)-cinnamyl acetate (3.47%)
hydrocinnamyl alcohol (0.09%)	ethyl cinnamate (0.27%)
menthol (0.10%)	β -cubebene (0.07%)
2-phenethyl acetate (0.15%)	(E)-cinnamic acid (0.23%)
terpinen-4-ol (0.09%)	γ -cadinene (0.07%)
methyl salicylate (6.17%)	δ -cadinene (0.05%)
2-methylbenzofuran (0.13%)	(E)-2-methoxycinnamaldehyde
2-phenylpropanal (0.05%)	(7.40%)
benzylidenemalonaldehyde†	(Z)-nerolidol $(0.25%)$
(0.12%)	(9H)-fluren-9-ol † (0.06%)
2-methoxybenzaldehyde (0.93%)	adamantane † (0.22%)

 \dagger component identities require corroboration

The same analysis was also reported by Li et al. in 2000.

More recently, Gong et al. (2001) developed a new technique for the qualitative and quantitative analysis of two-dimensional data obtained from GC/MS analyses of cinnamon bark grown in four different geographic regions of China. The authors also used an iterative optimization procedure specially developed to resolve co-eluting peaks. They pointed out that the chemometric resolution techniques of data manipulation was a very promising tool for the analysis of complex samples. Unfortunately, they used cinnamon as the test material for these techniques without comparing the procedure with well-known analytical methodologies to show the value of this highly complex approach.

- C. Frey, Detection of synthetic flavorant addition to some essential oils by selective ion monitoring GC/MS. In: Flavors and Fragrances: A World Perspective. Edits., B. M. Lawrence, B. D. Mookherjee and B. J. Willis, pp. 517-524, Elsevier, Amsterdam (1988).
- G. Vernin, C. Vernin, J. Metzger, L. Pujol and C. Parkanyi, GC/MS analysis of cinnamon and cassia essential oils: A comparative study. In: Spices, Herbs and Edible Fungi. Edit. G. Charalambous, pp. 411-425, Elsevier, Amsterdam (1994).
- A. Jayatilake, S. K. Poole, C. F. Poole and T. M. P. Chichila, Simultaneous microsteam distillation/solvent extraction for the isolation of semivolatile flavor compounds from cinnamon and their separation by series coupled-column gas chromatography. Anal. Chim. Acta., 302, 147-162 (1995).
- D. Ehlers, S. Hilmerand S. Bartholomae, Hochdruckflüssig-chromatographische Untersuchung von Zimt-CO2-Hochdruckextrakten in Vergleich mit Zimtölen. Z. Lebensm. Unter Forsch., 200, 282-288 (1995).
- K. G. Miller, C. F. Poole and T. M. P. Chicila, Solvent assisted supercritical

fluid extraction for the isolation of semi-volatile flavor compounds from the cinnamons of commerce and their separation by seriescoupled column gas chromatography. J. High Resol. Chromatogr., 18, 461-471 (1995).

- M-S. Zhu, S. Liu, R-J. Lao and Y-L. Bu, GC/MS detection of synthetic cinnamic aldehyde added to cassia oil. Acta Pharm. Sinica, 31, 461-465 (1996).
- B-M. Kwon, Y-K. Cho, S-H. Lee, J-Y. Nam, S-H. Bok, S-K. Chun, J-A. Kim and I-R. Lee, 2-hydroxycinnamaldehyde from stem bark of Cinnamomum cassia. Planta Med., 62, 183-184 (1996).
- Z-Q. Li, L. Luo, R. Huang and Y-Q. Xia, Chemical studies of cinnamon, true plants from Yunnan province. Yunnan Daxue, Xuebao Ziran Kexueban, 20(Supl.), 377-379 (1998).
- L-L. Li and W-J. Yuan, *Cinnamon oil analysis by GC and GC/MS*. Fujian Fenxi Ceshi, 8, 1121-1125 (1999).
- L-L. Li and W-J. Yuan, *Cinnamon oil analysis by GC and GC/MS*. Yaowu Fenxi Zazhi, 20(2), 116-118 (2000).
- F. Gong, Y-Z. Liang, Q-S. Xu and F-T. Chau, Gas chromatography-mass spectrometry and chemometric resolution applied to the determination of essential oils in cortex Cinnamomi. J. Chromatogr., 905, 193-205 (2001).

Tea Tree Oil

In 1993, Southwell et al. measured the major component contents of tea tree oil produced in two regions of northeastern New South Wales (Australia). They found that the oils were rich in the following components:

α -pinene (2.5-2.8%)	terpinen-4-ol (39.0-42.0%)
α-terpinene (7.6-8.3%)	α -terpineol (3.3-3.5%)
1,8-cineole (4.1-5.3%)	sesquiterpenes (<5.0%)
γ-terpinene (18.4-18.9%)	

The following year, Butcher et al. (1994) examined the intraspecific variation in the leaf oils of *M. alternifolia*. They screened 109 trees found in 11 populations covering the natural range of tea tree in northeastern New South Wales. It was of interest to note that the oil yield ranged from 2.5-8.8% with lowest oil yields being found in oils rich in terpinolene. Butcher et al. found considerable variation in oil composition both between and within populations. There were oils that were rich in either terpinen-4-ol, 1,8-cineole or terpinolene. The oils could be divided into five forms, e.g.:

	Type	А	В	С	D
1,8-cineole	0.1-11%	36-48%	67-71%	30-36%	17-34%
terpinolene	nd	nd	nd	10-18%	28-57%
terpinen-4-ol	>30%	<30%	<30%	15-20%	1-2%

nd=no data

It was a shame that the authors did not publish their compositional data as they drew statistical conclusions from data to which the reader was not exposed.

Two years later, Southwell et al. (1996) determined that the 1,8-cineole content of tea tree oil was inversely proportional to the terpinen-4-ol content. They also noted that a 1,8-cineole content in the oil of greater than 15% was undesirable because of the concomitant decrease in the terpinen-4-ol content.

and two extracts of Algerian corlander				
Compound	Oil	Hexane Extract	Ethanol Extract	
α-pinene	0.1	-	t	
myrcene	0.2	-	0.5	
p-cymene	0.2	-	t	
γ-terpinene	0.6	-	t	
1,8-cineole	0.1	-	0.5	
linalool	70.2	5.4	62.6	
camphor	1.8	-	1.8	
terpinen-4-ol	0.5	-	0.3	
α-terpineol	0.3	-	t	
octanal [†]	2.2	-	1.5	
dodecane	0.5	t	0.2	
geranyl acetate	1.6	t	2.3	
dodecanal	0.5	-	0.3	
β-caryophyllene	0.2	t	0.2	
α-humulene	0.8	-	0.5	
nerolidol*	0.5	-	t	
myristic acid	5.9	63.2	7.8	

Table VIII. Comparative percentage composition of an oil

*correct isomer not identified +-trace (-0.1%)

*correct isomer not identified t=trace (<0.1%) † incorrect identification based on elution order

Table IX. Comparative composition of the volatiles of tw

cilantro sample extracts		
Compound	Store Bought Cilantro	Fresh Cilantro
(Z)-3-hexenal	2.20ª	-
(E)-2-hexenal	0.38	-
nonanal	0.13	-
(E)-2-nonenal	0.47	-
(E)-4-decenal	t	-
decanal	10.60	5.56
(E)-2-decenal	59.20	2.41
decanol	0.39	0.06
(E)-2-decenol	2.23	-
undecanal	0.23	0.35
(E)-2-undecenal	3.96	0.57
dodecanal	0.38	1.03
(E)-2-dodecenal	22.30	9.10
tridecanal	-	0.06
(E)-2-tridecenal	2.99	1.09
tetradecanal	0.18	-
(E)-2-tetradecenal	44.90	14.20
(E)-2-pentadecenal	6.49	4.65
(E)-2-hexadecenal	4.86	1.93
^a mg/g fresh wt. basis		t=trace (<0.1%)

Table X. Comp	arative percent	age compo	sition of the leaf and bark oils of Cinnamom	um co
compound	Leaf Oil	Bark Oil	Compound	Leaf Oi
-pinene	0.05-0.36	0.10-0.25	salicylaidenyde	0.05-0.42
ampnene	0.04-0.05	0.05-0.10		0.11-0.27
pinene	0.04-0.15	0.14-0.22	benzyl alcohol	t-0.05
iyrcene	0.02-0.03	t-0.10	acetophenone	t-0.1
-phellandrene	0.01-0.06	t-0.13	eugenol	0.04-0.06
nonene	0.13-0.24	0.14-0.29	(Z)-isoeugenol	0.14-0.28
8-cineole	0.05-0.08	0.06-1.07	(E)-cinnamyl acetate	4.50-12.50
3-careneț	0.03-0.05	t-0.07	γ-muurolene	t
cymene	0.11-0.19	0.04-0.18	anisaldehyde	0.58-1.02
amphor	0.07-0.15	0-0.08	2-phenethyl acetate	t-1.55
enzaldehyde	1.42-1.48	0.50-1.10	β-bisabolene	t-0.06
alool	0.11-0.23	0.08-0.16	β-bisabolol	t
rpinolene†	t	0-0.04	α-muurolol	0-0.08
caryophyllene	0.16-0.20	t-0.27	coumarin	0.03-0.08
numulene	t-0.03	0-0.15	(E)-cinnamic acid	0.80-2.48
elemene	-	t-0.06	(E)-2-methoxycinnamaldehyde	8.40-10.50
oborneol	0-0.20	0-0.27	hydrocinnamic acid	0.18-0.51
orneol	0.15-0.41	0.06-1.27	4-hydroxy-2-phenethyl alcohol	0-0.12
erpineol	t-0.10	0.07-2.05	caryophyllene oxide	0.15-0.17
raniol	t	0.08-0.31	patchoulene†	0.06-0.07
rvone	0.57-0.64	0-0.34	octanoic acid	t
methoxybenzaldehyde‡	0.08	0-0.12	3-phenylpropyl acetate	0.21-0.43
frole	-	t-0.20	nonanoic acid	t-0.10
elemene	0-t	0-0.41	guaicol	t
cadinene	t	t-0.13	(E)-cinnamyl alcohol	0.15
cadinene	-	t-0.10	(E)-ethyl cinnamate	0.11-0.27
drocinnamaldehyde‡	0.88-0.89	0-0.24	benzyl benzoate	0.07-0.15
nenylacetaldehyde	0.07-0.16	t-0.27	methyl alaninate†	t-0.05
ethyl eugenol	0.14-0.15	t-0.05	guaicyl cinnamate†	t
)-cinnamaldehyde	64.10-68.30	80.40-88.50	decanoic acid	t
copaene	0.41-0.49	0.23-0.68	undecanoic acid	0-0.05
/drocinnamaldehyde‡	0.67-0.83	0-0.22	dodecanoic acid	t-0.04
anillin†	t	t-0.10	benzoic acid	0.07-0.11

t=trace (<0.01%)

† misidentification based on elution order ‡ compounds listed twice

2-methoxybenzaldehyde‡

Bishop and Thornton (1997) evaluated the antifungal activity of tea tree oil. The oils that they screened contained the following major components:

 $\begin{array}{l} \alpha \text{-thujene} \ (0.8\%) \\ \alpha \text{-pinene} \ (2.3\%) \\ \beta \text{-pinene} \ (0.7\%) \\ \alpha \text{-terpinene} \ (0.8\%) \\ myrcene \ (9.0\%) \\ limonene \ (0.9\%) \end{array}$

 $\begin{array}{l} 1,8\text{-cineole}~(3.4\%)\\ \gamma\text{-terpinene}~(19.4\%)\\ p\text{-cymene}~(2.9\%)\\ terpinen-4\text{-ol}~(37.4\%)\\ \alpha\text{-terpineol}~(2.5\%) \end{array}$

0-0.12

0-0.10

Also in 1997, another oil of tea tree was screened for its cytotoxicity using human cell lines (Hayes et al. 1997). The main constituents of this oil were:

 $\begin{array}{l} \alpha \text{-pinene} \ (2.6\%) \\ \alpha \text{-terpinene} \ (8.6\%) \\ p \text{-cymene} \ (3.6\%) \\ limonene \ (1.2\%) \\ 1,8 \text{-cineole} \ (4.3\%) \end{array}$

salicylic acid

 γ -terpinene (19.2%) terpinolene (3.5%) terpinen-4-ol (39.3%) α -terpineol (3.0%)

t-0.10

0.10-0.20

The increasing use of tea tree oil has resulted in increase of undesirable side effects of its use such as allergic contact dermatitis and localized skin irritation (de Groot and Wayland 1992, Selvaag et al. 1994). In 1997, Southwell et al. screened a number of tea tree oil constituents for their skin irritancy. In addition to an initial oil screening, other components of the oil screened were α -pinene, β -pinene, α -terpinene, limonene, p-cymene, 1,8-cineole, γ-terpinene, terpinolene, terpinen-4-ol, α -terpineol, a sesquiterpene hydrocarbon fraction of the oil and a sesquiterpene alcohol fraction of the oil. Using 28 panelists for the initial oil-screening test, they found that three had a severe allergic reaction to tea tree oil. One panelist was found to exhibit a positive reaction to the α -terpinene, while all three had a positive reaction to the sesquiterpene hydrocarbon fraction, and only one had a reaction with the sesquiterpene alcohol fraction.

Three years later, Harkenthal et al. (2000) found that an oxidized tee tree oil possessed a sensitivity capacity greater than freshly distilled oil. Analysis of the oil revealed a crystalline oxidation product, which was characterized as p-menthan-1,2,4-triol, a degradation product that had been previously characterized in *M. linariifolia* oil (Jones et al. 1940), which was formed by the oxidation of terpinen-4ol. Additionally, Harkenthal et al. showed that ascaridole, another oxidation product, was also an imported allergen. Finally, the authors noted that beside p-menthan-1,2,4-triol and ascaridole, α -phellandrene, α -terpinene and terpinolene were also found to be allergens.

In 1998, Zhang and Gu analyzed an oil of *M. alternifolia* produced from leaves harvested from trees growing in the Guangdong Forestry Research Institute arboretum. Using GC/MS as their method of analysis the authors determined that the oil had the following composition:

α -pinene (0.72%)	aromadendrene (0.25%)
α -thujene (1.73%)	terpinen-4-ol (39.43%)
β -pinene (0.71%)	α -terpineol (2.81%)
sabinene (0.55%)	$\alpha\text{-muurolene}\;(0.56\%)$
myrcene (0.80%)	bicyclogermacrene (0.50%)
α -phellandrene (0.35%)	cis-piperitol (0.11%)
α -terpinene (9.44%)	δ -cadinene (1.81%)
limonene (1.74%)	nerol (0.55%)
β -phellandrene (1.49%)	p-cymen-8-ol (0.59%)
1,8-cineole (3.22%)	calamenene* (0.48%)
γ -terpinene (18.82%)	palustrol (2.19%)
p-cymene (2.91%)	cubebol (0.07%)
terpinolene (0.23%)	globulol (2.00%)
trans-p-menth-2-en-1-ol (0.33%)	viridiflorol (1.05%)

*collect isomer not identified

The following year, Cornwell et al. (1999) compared the major components of a methanolic extract of mature leaves of *M. alternifolia* with a steam-distilled oil also produced from mature leaves. A summary of their results can be seen in Table XI.

Also in 1999, Hethelyi et al. examined the composition of five samples of tea tree oil available in Hungary. They found that the oils ranged in composition as follows:

Table XI. Comparative main component
composition (%) of a methanolic extract and an
oil of Melaleuca alternifolia

	Methanolic	Steam-distilled
Compound	Extract	Oil
(+)-sabinene	0.43	trace
(-)-sabinene	0.27	trace
α-terpinene	4.88	8.99
p-cymene	0.80	1.77
γ-terpinene	17.00	19.50
1,8-cineole	4.44	4.73
terpinolene	2.60	3.41
(+)-terpinen-4-ol	30.62	27.43
(-)-terpinen-4-ol	16.49	14.77

A sample of tea tree oil was subjected to analysis by Reichling et al. (1999). Using a combination of GC and GC/MS this German commercial oil sample was found to contain:

α-thujene (1.09%)	terpinolene (3.74%)
α-pinene (2.76%)	2-phenethyl alcohol (15.26%)
sabinene (0.05%)	linalool (3.23%)
β-pinene (1.13%)	terpinen-4-ol (40.78%)
myrcene (0.62%)	α -terpineol (3.05%)
α-phellandrene (0.45%)	β -caryophyllene (0.34%)
α-terpinene (10.33%)	aromadendrene (1.46%)
p-cymene (3.36%)	allo-aromadendrene (0.45%)
1,8-cineole (3.81%)	β -bulnesene (0.20%)
γ-terpinene (19.45%)	viridiflorene (1.55%)

The occurrence of 2-phenethyl alcohol in this oil makes it very suspect. In this reviewer's view, this oil was adulterated.

This same year, Harkenthal et al. (1999) reported that a sample of Australian tea tree oil contained the following constituents:

α-thujene (0.90%)	limonene (0.88%)
α-pinene (2.30%)	γ -terpinene (21.67%)
β-pinene (1.10%)	terpinolene (3.59%)
myrcene (0.77%)	terpinen-4-ol (39.30%)
α -phellandrene (0.48%)	α-terpineol (2.62%)
α -terpinene (10.50%)	aromadendrene (0.63%)
p-cymene (2.00%)	viridiflorene (1.10%)
1,8-cineole (2.30%)	δ -cadinene (1.10%)

The authors also determined that this oil possessed strong antimicrobial properties.

Table XII. Comparative percentage composition of freshly distilled and aged tea tree oil		
Compound	Fresh Oil	Aged Oil
α-pinene	2.4	2.8
β-pinene	1.4	1.6
α-terpinene	11.2	5.2
p-cymene	2.0	11.5
1,8-cineole	3.9	3.9
γ-terpinene	21.0	13.7
terpinolene	3.5	2.8
terpinen-4-ol	37.6	35.0
α-terpineol	2.1	3.4
aromadendrene	0.7	0.8
viridiflorene	1.0	1.3
δ-cadinene	1.1	1.2

Hethelyi et al. (2000) repeated their 1999 analysis in a second publication.

Also in 2000, Harkenthal et al. compared the composition of freshly distilled tea tree oil with that of an oil of 2 months old that had been stored at room temperature at the end of the summer in Germany in natural light (on a windowsill). Over this two-month period the authors determined that the peroxide number had increased from 25-500ppm. A summary of this oil composition (shown in Table XII) reveals that the p-cymene content had drastically increased, whereas the contents of α -terpinene, γ -terpinene and terpinolene had decreased.

This same year, Griffin et al. used a couple of batches of tea tree oil supplied by one of the large distillers. They compared their oils with the ISO standard as shown in Table XIII. As can be seen, the standard is fairly wide thereby allowing four seasonal and clonal variations in planting stock from which the oil is obtained.

- T. G. H. Jones and H. C. Oakes, Crystalline solid formed in an oil of Melaleuca linariifolia. Univer. Queensland Papers 1 Chem., (18), 3pp, (1940); Chem. Abs. 36, 4967 (1942).
- A. C. deGroot and J. W. Weyland, Systematic contact dermatitis from tea tree oil. Contact Dermatitis, 27, 279-280 (1992).
- I. A. Southwell, A. J. Hayes, J. Markham and D. N. Leach, *The search for optimally bioactive Australian teatree oil*. In: *International Symposium on Medicinal and Aromatic Plants*. Edits., D. Palevitch and E. Putievsky, pp. 256-264, Internat. Soc. Hort. Sci., Galilee, Israel (1993).
- E. Selvaag, B. Erikson and P. Thune, *Contact allergy to tea tree oil and cross-sensitisation to colophony*. Contact Dermatitis, 31, 124-125 (1994).
- P. A. Butcher, J. C. Doran and M. U. Slee, *Intraspecific variation in leaf* oils of Melaleuca alternifolia (Myrtaceae). Biochem. Syst. Ecol., 22, 419-430 (1994).

- I. A. Southwell, J. Markham and C. Mann, Is cineole detrimental to tea tree oil? Perfum. Flavor., (215), 7-10 (1996).
- C. D. Bishop and I. B. Thornton, Evaluation of the antifungal activity of the essential oils of Monarda citriodora var. citriodora and Melaleuca alternifolia on post-harvest pathogens. J. Essent. Oil Res., 9, 77-82 (1997).
- A. J. Hayes, D. N. Leach, J. L. Markham and B. Markovic, In vitro cytotoxicity of Australian tea tree oil using human cell lines. J. Essent. Oil Res., 9, 575-582 (1977).
- I. A. Southwell, S. Freeman and D. Rubel, Skin irritancy of tea tree oil. J. Essent. Oil Res., 9, 57-52 (1997).
- Y-J. Zhang and F-Z. Gu, Study on the chemical composition of the essential oil from Melaleuca alternifolia. Linchan Hauxue Yu Gongye, 18(3), 74-76 (1998).
- C. R. Cornwell, D. N. Leach and S. G. Wyllie, *The origin of terpinen-4-ol in the steam distillates of Melaleuca argentea*, M. dissitiflora and M. Linariifolia. J. Essent. Oil. Res., 11, 49-53 (1999).
- E. Hethelyi, K. Korany, G. Hernadi, M. Palfine Ledniczky and J. Palinkas, Investigation of the chemotaxonomical varieties of tea tree (Melaleuca alternifolia) oils by GC and GC/MS techniques. Olag Szappan Kosmet. 48(4), 153-163 (1999).
- J. Reichling, M. Harkenthal and R. Saller, *Wirkung ausgewählter ätherischer Öle*. Erfahrungsheilkunde, 6, 357-366 (1999).
- M. Harkenthal, J. Reichling, H. K. Geiss and R. Saller, Comparative study on the in vitro antibacterial activity of Australian tea tree oil, cajuput oil, niaouli oil, manuka oil, kanuka oil and eucalyptus oil. Pharmazie, 54, 460-463 (1999).

Table XIII. Percentage composition of some samples of
tea tree oil and the ISO standard for it

Compound	Tea Tree Oil	ISO Standard
α-pinene	1.4-2.8	1.0-6.0
sabinene	0.4-0.7	t-3.5
α-terpinene	6.6-8.3	5.0-13.0
p-cymene	3.2-3.9	0.5-12.0
limonene	0.9-1.3	0.5-4.0
1,8-cineole	3.9-4.4	15.0 (max.)
γ-terpinene	16.3-20.0	10.0-28.0
terpinolene	3.0-3.6	1.5-3.0
terpinen-4-ol	37.1-44.4	30.0 (min.)
aromadendrene	1.4-1.5	t-0.7
δ-cadinene	1.3-1.4	t-8.0
globulol	0.4-0.5	t-3.0
viridiflorol	0.2-0.3	t-1.5)

E. Hethelyi, G. Takacs, M. Palfine Ledniczky and J. Domokos, Gas chromatographic investigation of the biologically active components of Melaleuca species and of natural cosmetic components containing tea tree oil. Olaj Szappan Kozmet., 49(1), 25-37 (2000).

Compound	Leaf Oil	Flower Oil
α-pinene	0.12-0.25	0.13-0.15
camphene	t-0.14	t-0.10
sabinene	0.41-0.87	0.48-0.66
β-pinene	0.13-0.19	0.12-0.14
myrcene + dehydro-1,		
8-cineole	t-0.23	t-0.12
p-cymene	0.18-0.29	0.16-0.21
limonene + 1,8-cineole	2.88-5.42	2.82-3.75
phenylacetaldehyde	t-0.13	0.12-0.13
2-methylbutyl 2-methyl-		
butyrate	t-0.18	0.37-0.45
α-thujone	10.79-16.10	9.04-10.78
β-thujone	1.09-2.21	1.03-1.06
trans-p-mentha-2,8-dien-1-ol	0.87-2.05	1.25-1.40
<i>cis</i> -p-mentha-2,8-dien-1-ol	0.45-0.92	0.48-0.50
<i>trans</i> -verbenol	t-0.17	t-0.16
pinocarvone	t-0.18	0.22-0.28
<i>cis</i> -dihydrocarvone	0.30-0.78	0.52-0.54
verbenone + <i>trans</i> -piperitol	0.48-0.78	0.13-0.19
trans-carveol	t-0.33	0.13
<i>cis</i> -carveol	0.19-0.38	0.20-0.33
carvone	51.83-68.01	59.50-61.67
cis-chrysanthenyl acetate	0.40-0.79	0.50-0.85
trans-carvone oxide	0.20-0.54	0.18-0.20
trans-carvyl acetate	0.11-0.45	0.19-0.30
<i>cis</i> -carvyl acetate	0.15-0.91	0.39-0.43
a-copaene	t-0.39	0.18-0.21
4-epi-cubebol	0.23-1.10	0.51-0.90
β-bisabolene	1.26-4.45	1.01-1.07
<i>cis</i> -calamenene	0.36-1.50	0.73-0.85
δ-cadinene	0.42-1.53	0.85-1.00
1-epi-cubenol	0.11-0.36	0.29-0.32
T-muurolol	0.34-2.19	2.16-3.77
selin-11-en-4a-ol	0.14-0.69	1.03-1.24
methyl isocosate	t-0.43	0.62-1.08
methyl 4-hydroxy-4,	0.13-0.43	0.80-1.80
5-dihydroisocosate		

- M. Harkenthal, B. M. Hausen and J. Reichling, 1,2,4-trihydroxymenthane, a contact allergen from oxidized tea tree oil. Pharmazie, 55, 153-154 (2000).
- M. Harkenthal, G. Layh-Schmitt and J. Reichling, Effect of Australian tea tree oil on the viability of the wall-less bacterium Mycoplasma pneumoniae. Pharmazie, 55, 380-384 (2000).

Balsamite or Costmary Oil

The oil of costmary is obtained from *Balsamita major* (L.) Desf. (syn. *Chrysanthemum balsamita* (L.) Baill. var *balsamita*; *Pyrethrum majus* (Desf.) Tzvelev. Occasionally it can be found as an item of commerce.

In 1979, Wolbis examined the composition of three morphotypes of *Chrysanthemum balsamita* L. Her findings can be found summarized in Table XIV.

Stroebel et al. (1987). analyzed an oil of *B. major* (carvone-type) and found that it contained the following components:

α-pinene	carvone
camphene	carvacrol
sabinene	bornyl acetate
β-pinene	trans-carvyl acetate
1,8-cineole	cis-carvyl acetate
limonene	α-terpinyl acetate
γ-terpinene	α-copaene
linalool	β-caryophyllene
α-thujone	(E)-β-farnesene
β-thujone	β-cubebene
trans-pinocarveol	zingiberene
citronellal	γ-cadinene
terpinen-4-ol	cadinol*
dihydrocarvone*	T-muurolol
cis-carveol	

° correct isomer not identified

Although the authors did not present any quantitative data, they did present a chromatogram which showed that the major components other than carvone were limonene, α -thujone, β -cubebene, γ -cadinene and T-muurolol.

The camphor-rich and carvone-rich chemotypes of *B. major* have been analyzed by GC/MS by Hanganu et al. (1995). The components identified in the camphor-chemotype were as follows:

camphene	borneol
1,8-cineole	menthol
(Z) - β -ocimene	carvone
α-thujone	bornyl acetate
β-thujone	isocaryophyllene
camphor (69.6%)	caryophyllene

In contrast, the carvone-rich chemotype was found to contain:

α-pinene	camphor (11.4%)
camphene	menthol
limonene	dihydrocarvone*
1,8-cineole	carvone (31.4%)
(Z)-β-ocimene	farnesol*
α-thujone (14.2%)	

°correct isomer not identified

As can be seen, the authors only listed quantitative data for components found in amounts exceeding 10%.

Two years later, Gleizez and Marculescu (1997) also analyzed oils of the two chemotypes of *B. major* produced from plants grown in Romania. Unfortunately, the authors also did not present any quantitative data. Also, this reviewer has eliminated some of the components purported to have been found based on prior knowledge of naturally occurring constituents. As a result, using GC/MS as their method of identification the camphor-chemotype was determined to contain:

camphene	β-bisabolene
p-cymene	borneol
limonene	bornyl acetate
1,8-cineole	hexadecanal
γ-terpinene	octadecanal
camphor	farnesol*
chrysanthenone	hexahydrofarnesyl acetone
verbenone	hexadecanoic acid
isoamvl isovalerate	

° correct isomer not identified

Furthermore, the authors found that the carvone-chemotype contained:

α-pinene	verbenol*
camphene	α-copaene
sabinene	cyperene
β-pinene	β-caryophyllene
myrcene	α-humulene
p-cymene	(E)-β-farnesene
limonene	zingiberene
1.8-cineole	γ-cadinene
γ-terpinene	spathulenol
α-thujone	(E)-nerolidol
dihydrocarvone*	T-muurolol
chrysanthenol*	(E,E)-farnesyl acetate
pinocarvone	hexahydrofarnesyl acetone
trans-pinocarveol	

*correct isomer not identified

Recently, Bylaite et al. (2000) compared the composition of the leaf and flower oils of *B. major* grown in Lithuania using GC and GC/MS. The results of these analyses are summarized in Table XV. In addition, the authors also characterized a number of trace constituents (<0.01%), which can be seen listed as follows:

α-thujene	2-phenethyl acetate
S-methyl pentathioate	bornyl acetate
benzaldehyde	α -terpinyl acetate
p-mentha-1,3,8-triene	δ-elemene
isoamyl butyrate	(Z)-jasmone
2-methylbutyl isobutyrate	β-caryophyllene
α-terpinene	α -muurolene
butyl 2-methylbutyrate	cubebol
3-methyl-2-butenyl 2-methyl-	trans-calamenene
butyrate	cadina-1,4-diene
trans-pinocarveol	(E)-nerolidol
cis-verbenol	spathulenol
borneol	caryophyllene oxide
p-mentha-1,5-dien-ol	trans-sesquilavandulol
terpinen-4-ol	β-eudesmol
trans-p-mentha-1(7),8-dien-2-ol	trans-sesquilavandulyl acetate
α-terpineol	6,10,14-trimethyl-2-pentadeca-
p-cymen-8-ol	none
cis-piperitol	methyl costate
methyl chrysanthemate	

Table XIV. Comparative percentage composition of the oils of three morphotypes of *Chrysanthemum balsamita*

Compound	Type 1	Type 2	Type 3
α-pinene	0.33-0.62	0.29-0.66	0.20-0.61
camphene	3.63-5.93	2.70-5.29	1.88-9.86
1,8-cineole	0.04-0.13	0.09-0.17	0.06-0.19
limonene	0.16-0.23	0.27-0.53	0.10-0.26
p-cymene	0.27-0.57	0.34-0.59	0.05-0.25
α-thujone	0.48-1.56	27.80-45.72	0.70-3.89
β-thujone	0-0.55	3.87-6.77	0-0.64
camphor	81.31-87.87	34.90-47.32	84.98-91.77
bornyl acetate	1.88-3.60	2.96-5.30	1.03-1.65
isoborneol	0.34-0.71	0.62-0.69	0-0.57
borneol	0.87-1.63	0.35-2.45	0.16-0.74
carvone	0.61-1.12	0.68-1.20	0-0.46

Finally, this reviewer (Lawrence) examined a lab-produced oil from plant material grown in North Carolina using GC and GC/MS. The main constituents of this oil were found to be:

α-pinene (0.3%)	p-cymene (0.3%)
camphene (0.2%)	α -thujone (5.9%)
β -pinene (0.3%)	β -thujone (0.7%)
sabinene (0.7%)	camphor (2.7%)
myrcene (0.2%)	carvone (60.6%)
limonene (3.1%)	β-bisabolene (2.0%
1,8-cineole (2.7%)	T-muurolol (1.9%)
γ-terpinene (0.2%)	

- M. Wolbis, Investigation of Chrysanthemum balsamita L. Studies of the volatile oil with consideration of the botanical characteristics of the taxon. Acta Polon. Pharm. 36, 707-714 (1979).
- A. Strobel, K. Knobloch and E. Ziegler, *Essential oils from Chrysanthemum balsamita L.* Z. Naturforsch. C. Biosci., 42, 502-506 (1987).
- D. Hanganu, A. Marculescu, R. Oprean, M. Tamas and H. Popescu, Identification of some compounds of the essential oil from Chrysanthemum balsamita L. (Asterceae). Clujul Med., 68, 244-247 (1995).
- M. Gleizez and A. Marculesu, Establishing the chemical composition of the chemical infraspecific taxons of Chrysanthemum balsamita L. Farmacia (Bucharest), 45(4), 53-59 (1997).
- E. Bylaite, R. Venskutonis, J. P. Roozen and M. A. Posthumus, *Composition* of essential oil of costmary (Balsamita major (L.) Desf.) at different growth phases. J. Agric Food Chem., 48, 2409-2414 (2000).

B. M. Lawrence, unpublished information.

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