Progress in Essential Oils

by Brian M. Lawrence, Consultant

Lime Oil

A commercially available distilled oil of lime was the subject of analysis by Inoma et al. (1989). The composition of the oil was found to be as follows:

α-pinene (1.05%)
camphene (0.70%)
sabinene (t)
β-pinene (1.41%)
myrcene (1.13%)
α-phellandrene (0.41%)
δ-3-carene (t)
1,4-cineole (2.90%)
p-cymene (2.39%)
1,8-cineole (4.52%)
limonene (45.26%)
(E)-β-ocimene (0.47%)
γ-terpinene (10.97%)
octanol (t)
terpinolene (8.60%)
linalool (t)
α-fenchyl alcohol (0.84%)
p-menth-3-en-1-ol (1.14%)
borneol (1.02%)
terpinen-4-ol (0.88%)
α-terpineol (8.55%)
decanal (1.39%)
neryl acetate (t)
geranyl acetate (t)
β-caryophyllene (1.02%)
α-berga motene* (t)
α-farnesene* (1.82%)
β-bisabolene (1.17%)

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

γ-terpinene (0.79%)
octanol (0.11%)
terpinolene (0.43%)
linalool (1.40%)
cis-limonene oxide (0.11%)
trans-limonene oxide (t)
isopulegol (t)
citronellal (0.10%)
terpinen-4-ol (2.01%)
α-terpineol (2.39%)
decanal (0.41%)
neral (5.30%)
geraniol (7.50%)
geranial (2.05%)
sabinyl acetate* (0.10%)
δ-elemene (0.44%)
neryl acetate (0.21%)
geranyl acetate (0.59%)
β-elemene (0.45%)
dodecanal (0.10%)
β-caryophyllene (0.84%)
α-bergamotene* (0.41%)
α-humulene (0.12%)
(Z)-β-farnesene (0.41%)
(E)-β-farnesene (1.48%)
α-elemene (t)
β-bisabolene (t)
(Z)-nerolidol (0.61%)
elemol (0.07%)
β-eudesmol (0.06%)
α-eudesmol (0.06%)
hexadecanoic acid (0.06%)

* correct isomer not identified
t = trace (0.01%)

Kaiser (1993) showed that the volatiles found in a hexane peel wash of Key lime were very different to that of a hexane peel extract. In particular, he found that key components (ca. 10%) in the peel wash volatiles were methyl *trans*-(Z)-jasmonate and methyl *cis*-(Z)-jasmonate (1:1 ratio).

Jantan et al. (1996) used a combination of GC on both polar and non-polar col–umns and GC/MS to examine the composition of a distilled oil from the peel of *C. aurantifolia* (Key lime) of Malaysian origin. The components found in this oil were:

α-thujene (0.07%)
α-pinene (1.45%)
camphene (0.16%)
β-pinene (28.44%)
octanal (t)
myrcene (1.00%)
α-phellandrene (0.08%)
δ-3-carene (0.48%)
α-terpinene (0.03%)
limonene (39.28%)
(Z)-β-ocimene (0.14%)
(E)-β-ocimene (0.47%)

Kubeczka (1997) compared the composition of the SPME headspace volatiles of cold-pressed lime oil with that of the oil. The results of this study are shown in T-1.

The composition of Tahitian (or Persian) lime oil (ex. *C. latifolia*) produced from fruit grown in Thailand were examined by Asano (1997). A summary of the analyses can be seen in T-2.

The peel oils of *C. aurantifolia* produced in Cameroon from lime cultivars obtained from Mexico, Tahiti and Lakeland, FL were subjected to analysis by Jazet-Dongmo et al. (1998). The analytical results obtained from these analyses can be found in T-3.

Haggag et al. (1998) analyzed an oil produced by cold pressing lime peel (ex. *C. aurantifolia*) obtained from fruit grown in Giza (Eqypt). The main components of the oil were found to be:

α-pinene (12.64%)
camphene (4.02%)
β-pinene (13.40%)
limonene (9.28%)

Comparative percentage composition of the oil and headspace volatiles of cold-pressed lime oil **T-1**

Compound	Oil	Headspace Volatiles
α-thujene	0.43	0.13
α-pinene	1.59	0.52
sabinene	1.54	0.91
β-pinene	8.66	4.74
myrcene	1.43	1.19
α-terpinene	0.28	0.20
limonene	55.74	52.17
(Z)-β-ocimene	0.07	0.16
(E)-β-ocimene	0.14	0.30
γ-terpinene	11.99	12.33
octanol	0.09	0.10
terpinolene	0.58	0.69
linalool	0.34	0.43
citronellal	0.06	0.12
α-terpineol	0.39	0.56
decanal	0.07	0.12
neral	1.42	3.29
geranial	2.33	5.16
neryl acetate	1.12	2.81
geranyl acetate	0.32	0.83
β-caryophyllene	0.60	1.30
trans-α-bergamotene	1.01	2.01
β-bisabolene	1.46	2.72
limettin	0.67	1.25
bergapten	0.27	0.20

p-cymene (0.91%)
citronellal (2.17%)
linalool (1.52%)
nerol (5.00%)
α-terpineol (4.08%)
citronellol (5.26%)
geraniol (2.74%)
thymol (1.09%)
carvacrol (1.07%)
eugenol (5.87%)

It should be noted that the phenol level of this oil is atypical. As a result, the analysis should be considered as being questionable.

The composition of the hydrocarbon fraction and the oxygenated fraction of Chinese lime peel extract (pentane/methylene chloride 1:1) was the subject of analysis of Yang et al. (1999). They found that the hydrocarbon fraction (87.22%) contained the follow–ing compounds:

α-thujene (0.55%)
α-pinene (1.98%)
camphene (0.04%)
sabinene (1.82%)
β-pinene (11.89%)
myrcene (1.60%)
α-phellandrene (0.05%)
α-terpinene (0.34%)
p-cymene (0.06%)
limonene (55.33%)
ocimene* (0.07%)
γ-terpinene (20.61%)
terpinolene (0.76%)
δ-elemene (0.05%)
β-elemene (0.04%)
α-cedrene (t)
β-caryophyllene (0.49%)
α-bergamotene* (1.20%)
β-farnesene* (0.11%)
α-humulene (0.04%)
γ-muurolene (0.06%)
α-farnesene* (0.15%)
β-bisabolene (1.85%)

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

In the oxygenated fraction (12.78%), the following compounds were characterized:

hexanal (t)
(Z)-3-hexenol (0.19%)
6-methyl-5-hepten-2-one (t)
octanal (0.04%)
hexyl acetate (t)
1,8-cineole (1.24%)
2,6-dimethyl-5-heptenal (t)
octanol (0.04%)
fenchone (t)
trans-limonene oxide (t)
nonanal (2.93%)
linalool (2.11%)
camphor (0.10%)
citronellal (0.75%)
borneol (0.16%)
terpinen-4-ol (0.59%)
α-terpineol (6.19%)
decanal (0.15%)
octyl acetate (0.02%)
citronellol (0.59%)
nerol (2.75%)
neral (15.89%)
piperitone (0.04%)
geraniol (3.64%)
geranial (25.01%)
perillaldehyde (0.40%)
decanol (0.09%)
thymol (0.01%)
bornyl acetate (0.07%)
perillyl alcohol (0.05%)
carvacrol (0.02%)
geranyl formate (t)
undecanal (0.10%)
(E,E)-2,4-decadienal (0.01%)
methyl geranate (0.07%)
α-terpinyl acetate (0.07%)
citronellyl acetate (0.15%)
neryl acetate (15.02%)
geranyl acetate (7.11%)
dodecanal (0.36%)
decyl acetate (0.04%)
tridecanal (0.06%)
undecyl acetate (t)
nerolidol* (0.07%)
tetradecanal (0.22%)
7-methoxycoumarin (0.85%)
pentadecanal (0.11%)
nootkatone (0.28%)

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

Dugo et al. (1999) compared the oxygen heterocyclic compounds of Key A and Key B lime and Persian lime oils, the results of which can be seen in T-4. The enantiomeric distribution of eight chiral components of both cold-pressed and distilled lime oils was also determined by Dugo et al. (1999 and 2001). A summary of their results can be seen in T-5.

Sawamura (2000) reported the results of his analysis of numerous oils of *Citrus* species. Within this study he examined the composition of *C. latifolia*, the results of which are summarized as follows:

α-pinene (2.98%)
camphene (0.05%)
β-pinene (11.59%)
sabinene (2.10%)
myrcene (0.01%)
α-phellandrene (1.41%)
α-terpinene (0.28%)
limonene (55.47%)
β-phellandrene (t)
(Z)-β-ocimene (0.05%)
γ-terpinene (14.50%)
p-cymene (0.05%)
terpinolene (0.60%)
octanal (0.01%)
nonanal (t)
trans-sabinene hydrate (0.08%)
δ-2-carene† (t)
δ-elemene (0.14%)
citronellal (0.04%)
decanal (0.03%)
linalool (0.31%)
cis-sabinene hydrate (0.06%)
α-bergamotene* (0.71%)
β-elemene (0.11%)
β-caryophyllene (0.35%)
terpinen-4-ol (0.04%)
undecanal (0.01%)
aromadendrene (0.03%)
β-santalene (0.02%)
α-humulene (0.04%)
citronellyl acetate (t)
(E)-β-farnesene (0.06%)

neral (1.73%)	carvone (0.01%)
δ-muurolene (0.02%)	geraniol (0.02%)
α-terpineol (0.35%)	dodecyl acetate (t)
germacrene D (0.07%)	(Z)-nerolidol (0.01%)
dodecanal (0.02%)	verbenol*† (0.01%)
geranial (5.14%)	hexadecanol (0.06%)
α-farnesene* (0.16%)	limonene dioxide (0.02%)
geranyl acetate (0.36%)	neryl acetone (0.02%)
citronellol (0.02%)	α-bisabolol (0.05%)
perillaldehyde (0.02%)	farnesal* (0.01%)
nerol (0.06%)	
germacrene B (0.13%)	

* correct isomer not identified
† incorrect identification based on elution order
t = trace (<0.01%)

Feger et al. (2000) compared the sesquiterpene hydrocarbon content of three different cold-pressed lime oils. A summary of their results can be seen in T-6.

Mitiku et al. (2001) noted that the four monoterpene hydrocarbons inherent in Tahitian lime oil were found to exist in the following amounts:

α-pinene (2.78-3.20%)	sabinene (2.09-2.53%)
β-pinene (12.62-13.00%)	limonene (49.39-52.20%)

The authors also found the enantiomeric ratios of the above four constituents were as follows:

(1R,5R)-(+-α-pinene (28.21-28.54%) : (1S,5S)-(-)-α-pinene (71.46-71.79%)
(1R,5R)-(+)-β-pinene (6.87-8.69%) : (1S,5S)-(-)-β-pinene (91.31-93.13%)
(1R,5R)-(+)-sabinene (18.67-19.29%) : (1S,5S)-(-)-sabinene (80.71-81.33%)
(4R)-(+)-limonene (97.12-97.57%) : (4S)-(-)-limonene (2.43-2.88%)

Pino and Rosado (2001) compared the distilled oils of Key lime (ex *C. aurantifolia*) and Persian lime (ex *C. tatifolia*) produced commercially in Banes (Western Cuba). A comparison of the oil compositions can be seen in T-7.

Feger et al. (2001) examined the germacrene content of both cold-pressed and distilled lime oils. The results of this analysis are shown in T-8.

Using high speed GC and GC/Time-of-Flight MS, (GC/TOFMS) Veriotti and Sacks (2001) found that a commercial oil of lime contained the following constituents:

pentane	camphene
1-methylcyclohexa-1,4-diene	1-methyl-4-(1-methylethyl)-cyclohexa-1,4-diene
nonane	β-pinene
ocimene*	myrcene
α-pinene	α-terpinene
2,3-dimethylcyclohexa-2,3-diene	terpinolene isomer*
sabinene	limonene
terpinen-4-yl acetate	*trans*-2,3-epoxycarane
cymene*	1-methyl-4-(1-methylethyl) -cyclohexa-1,3-diene
citronellal	citronellyl acetate
γ-terpinene	(E)-farnesene*
cis-limonene oxide	α-bergamotene*
2-methyl-1-nonen-3-yne	β-caryophyllene
terpinolene isomer*	(Z)-farnesene*
nonanal	ε-selinene
cinnamaldehyde	β-elemene
o-cymene	santalene*
linalool	isoledene
myrtenol	valencene
δ-3-carene	isoeugenol*
trans-limonene oxide	germacrene D
terpinen-4-ol	cadinene*
α-terpinyl acetate	10,12-octadecadiynoic acid
nerol	spathulenol
α-terpineol	

* correct isomer not determined

The components listed above are listed (according to the authors) in elution order from a DB-5 capillary column. It is obvious to this reviewer that (a) the authors know very little about essential oils, particularly citrus oils, (b) they have not paid any attention to the previously published data on lime oil composition and (c) they used a computer search to characterize their constituents. As a result, this paper should be ignored as the information on the oil composition is in error. It is hoped that such a weak manuscript will not deter essential oil scientists from examining the technique of GC/TOFMS.

Lota et al. (2002) compared the composition of the peel oils of various fruits known as lime. The fruit oils examined were *Citrus aurantifolia* (Christm.) Swing., *C. latifolia* Tan., *C. limettioides* Tan., *C. limonia* Ost., *C. karma* Raf. and *Microcitrus australasica* (F. Muell.) Swing.; however, it should be noted that commercial oils are only available from *C. aurantifolia* and *C. latifolia*. The composition of the peel oils produced from the two lime species noted above can be seen in T-9 and T-10.

Kubeczka and Formacek (2002) used a combination of capillary GC and ^{13}C-NMR to examine the composition of cold-pressed lime oil. The components identified in this oil were:

α-pinene (2.46%)	nonanal (0.04%)
α-thujene (0.42%)	δ-elemene (0.31%)
camphene (0.11%)	decanal (0.20%)
β-pinene (21.10%)	linalool (0.16%)
sabinene (3.06%)	*cis*-α-bergamotene (0.12%)
myrcene (1.26%)	*trans*-α-bergamotene (1.12%)
α-phellandrene (0.04%)	β-elemene (0.17%)
α-terpinene (0.20%)	β-caryophyllene (1.02%)
limonene (48.24%)	terpinen-4-ol (0.23%)
β-phellandrene (0.46%)	α-humulene (0.11%)
1,8-cineole (0.05%)	neral (1.36%)
(Z)-β-ocimene (0.12%)	α-terpineol (0.26%)
γ-terpinene (8.12%)	germacrene D (0.30%)
(E)-β-ocimene (0.33%)	neryl acetate (0.39%)
p-cymene (0.33%)	β-bisabolene (1.78%)
terpinolene (0.41%)	geranial (2.43%)
octanal (0.03%)	(E,E)-α-farnesene (1.03%)

Comparative composition (%) of lime extract oils produced in Thailand				T-2
Compound	**Menawa lime extract oil**	**Large Tahitian lime extract oil**	**Old Tahitian lime extract oil**	**Young Tahitian lime extract oil**
α-pinene	0.36	1.72	-	0.13
camphene	0.07	-	-	-
β-pinene	6.66	1.45	0.21	-
sabinene	0.39	0.24	0.15	0.08
myrcene	0.83	1.25	0.10	-
α-terpinene	0.60	0.50	1.27	0.92
limonene	41.10	42.69	63.99	56.62
1,8-cineole	0.61	-	-	-
γ-terpinene	7.56	21.74	1.28	0.68
p-cymene	1.04	2.44	0.11	0.27
terpinolene	1.61	1.21	0.12	0.27
limonene oxide*	0.11	-	-	0.10
decanal	0.73	-	0.32	0.21
trans-sabinene hydrate	0.12	0.52	-	0.46
linalool	1.42	0.65	0.44	1.30
terpinen-4-ol	0.32	1.36	0.92	0.44
undecanal	3.80	-	-	0.24
α-bergamotene* + β-caryophyllene	1.04	0.12	0.22	-
neral	5.42	5.58	8.53	12.99
α-terpineol	4.10	2.35	0.27	0.54
geranial	8.14	7.09	15.14	17.07
neryl acetate	0.49	0.44	0.56	0.89
β-bisabolene	1.83	-	-	-
geranyl acetate + α-farnesene*	4.19	0.14	0.56	0.46
nerol	0.31	2.51	1.65	1.86
geraniol	0.90	3.08	2.39	1.88

* correct isomer not identified

geranyl acetate (0.35%)
nerol (0.04%)
calamenene* (0.40%)
geraniol (0.05%)

* correct isomer not identified

In contrast, the authors found that the composition of distilled lime oil was as follows:

α-pinene (1.22%)
α-fenchene (0.19%)
camphene (0.49%)
β-pinene (1.95%)
2,6,6-trimethyl-2-vinyl-tetrahydropyran (0.21%)
myrcene (1.25%)
α-phellandrene (0.34%)
α-terpinene (2.07%)
1,4-cineole (3.00%)
limonene (47.56%)
β-phellandrene (0.34%)
1,8-cineole (1.79%)
(Z)-β-ocimene (0.21%)
γ-terpinene (10.71%)
(E)-β-ocimene (0.46%)
p-cymene (2.51%)
terpinolene (8.05%)
octanal (0.19%)
nonanal (0.08%)
δ-elemene (0.08%)
decanal (0.09%)
linalool (0.15%)
cis-α-bergamotene (0.06%)
terpinen-1-ol (0.97%)
α-fenchol (0.60%)
trans-α-bergamotene (0.81%)
β-elemene (0.07%)
β-caryophyllene (0.63%)
terpinen-4-ol (0.65%)
cis-β-terpineol (0.54%)
α-humulene (0.13%)
trans-β-terpineol (0.17%)
α-terpineol (5.38%)
γ-terpineol (0.77%)
borneol (0.47%)
β-bisabolene (1.78%)
(E,E)-α-farnesene (0.89%)
δ-cadinene (0.16%)
calamenene* (0.05%)
p-cymen-8-ol (0.16%)

* correct isomer not identified

Gancel et al. (2002) examined the volatile constituents found in the fresh peel of Mexican lime (*C. aurantifolia*). The components identified were as follows:

α-pinene (486)[a]
α-thujene (117)
camphene (17)
hexanal (1)
β-pinene (3731)
sabinene (513)
myrcene (213)
α-terpinene (22)
limonene (8778)
β-phellandrene (71)
1,8-cineole (6)
(E)-2-hexenal (<1)
(Z)-β-ocimene (31)
γ-terpinene (2361)
(E)-β-ocimene (67)
p-cymene (18)
terpinolene (70)
octanal (5)
nonanal (3)
citronellal (10)
decanal (22)
isopinocamphone (3)
linalool (62)
cis-α-bergamotene (17)
bornyl acetate (3)
trans-α-bergamotene (210)
β-caryophyllene (175)
terpinen-4-ol (5)
undecanal (5)
α-humulene (28)

Chemical composition (%) of three lime peel oils produced in Cameroon — T-3

Compound	Mexican cultivar oil	Tahitian cultivar oil	Lakeland cultivar oil
(Z)-3-hexenol	0.06	-	-
α-thujene	0.19	0.44	0.20
α-pinene	1.37	1.64	0.84
camphene	0.09	0.05	-
6-methyl-5-hepten-2-one	0.06	0.09	-
sabinene	1.44	1.28	0.14
β-pinene	15.65	11.18	0.91
myrcene	0.24	1.25	1.24
octanal	0.97	-	-
p-cymene	4.42	5.54	7.98
limonene	45.31	46.41	70.70
(E)-β-ocimene	0.24	0.10	0.21
γ-terpinene	3.54	12.54	4.13
trans-sabinene hydrate	0.10	-	-
octanol	-	-	0.25
linalool oxide* furanoid	-	-	0.13
terpinolene	0.32	0.63	0.25
linalool	0.82	0.74	2.18
α-pinene oxide	0.06	-	0.07
limonene oxide*	0.13	0.09	0.32
limonene oxide*	0.06	0.05	0.17
terpinen-1-ol	0.11	0.05	0.14
isopulegol	0.06	0.06	-
β-terpineol*	0.10	0.07	0.03
terpinen-4-ol	1.39	0.95	0.68
myrtenal	0.07	-	-
α-terpineol	2.04	1.47	1.67
p-cymen-8-ol	0.11	0.06	0.06
γ-terpineol††	0.30	0.11	-
verbenone	-	0.05	0.14
citronellol	-	0.05	0.04
neral	1.16	1.56	0.12
nerol	4.03	3.10	0.31
myrtenyl acetate	-	-	0.04
geraniol	1.49	1.55	0.26
geranial	5.21	3.89	0.39
decanol	-	-	0.03
geranyl formate	-	-	0.10
thymol	0.06	-	0.12
bornyl acetate	0.06	0.05	0.11
citronellyl acetate	0.08	0.05	-
δ-elemene	0.31	0.07	0.12
α-terpinyl acetate	0.13	1.56	0.30
undecanol	-	-	0.11
geranyl acetate	0.29	0.38	0.06
α-copaene	-	-	0.04
β-elemene	0.38	0.08	0.06
santalene*	-	-	0.04
β-caryophyllene	0.64	0.28	0.06
trans-α-bergamotene	0.66	0.56	0.55
(Z)-β-farnesene	0.09	0.05	0.08
α-humulene	0.11	-	-

Chemical composition (%) of three lime peel oils produced in Cameroon (continued) T-3

Compound	Mexican cultivar oil	Tahitian cultivar oil	Lakeland cultivar oil
allo-aromadendrene	-	-	0.04
dodecanol	-	-	0.17
germacrene D	0.55	0.06	0.03
α-selinene	0.10	-	0.06
bicyclogermacrene	0.20	-	0.18
(E,E)-α-farnesene	0.58	0.15	-
β-bisabolene	1.16	0.85	0.88
γ-cadinene	-	-	0.07
δ-cadinene	-	-	0.07
cadina-1,4-diene	0.41	-	-
elemol	-	-	0.05
nerolidol*	-	-	0.09
germacrene B	0.57	0.08	-
globolol	0.12	-	0.17
spathulenol	0.11	0.06	0.05
α-cadinene†	0.07	-	0.12
caryophyllene oxide	0.06	-	0.13
cubenol	-	-	0.14
γ-eudesmol	0.20	-	0.26
T-cadinol	0.16	-	0.15
β-eudesmol	0.33	-	0.53
(Z,E)-farnesol	0.11	0.06	0.07
β-sinensal	0.11	0.07	0.16
(Z,Z)-farnesol	0.08	-	0.09
(E,E)-farnesol	-	-	0.03

*correct isomer not identified
† incorrect identification based on elution order
†† the natural origin of γ-terpineol is in question

Oxygen heterocyclic components in lime oil T-4

Compound	Key A	Key B	Persian
bergamottin	3157-3283	3154	2221-3918
isoimperatorin	+	+	+
5-geranyloxy-7-methoxycoumarin	3065-4045	4093	1943-3780
methoxy psoralen	+	+	+
5-isopentyloxy-7-methoxycoumarin	+	+	+
cnidillin	25-35	24	5-8
citropten	491-632	484	326-569
8-geranyloxypsoralen	+	+	+
herniarin	86-96	74	339-594
bergapten	100-124	89	158-250
isopimpinellin	350-365	331	169-293
oxypeucedanin	-	144	210-328
oxypeucedanin hydrate	+	+	+

mg/100g oil lime

+ presence below 1 mg per 100 g of oil of lime

Enantiomeric distribution of selected compounds in lime oil

T-5

Enantiomer	Cold-Pressed Oils Key Lime Type A	Cold-Pressed Oils Key Lime Type B	Persian Lime	Distilled Lime
(1S,5S)-(-)-α-pinene	ND	ND	67.8	ND
(1R,5R)-(+)-α-pinene	ND	ND	32.2	ND
(1S,5S)-(-)-β-pinene	96.5-96.6	96.5	89.7-90.9	96.9-96.8
(1R,5R)-(+)-β-pinene	3.4-3.5	3.5	9.1-10.3	3.2-4.0
(1S,5S)-(-)-sabinene	84.8-84.9	84.7	76.6-81.8	-
(1R,5R)-(+)-sabinene	15.1-15.2	15.3	18.2-23.4	-
(4S)-(-)-limonene	2.6-2.9	1.8	0.4-2.7	5.5-8.7
(4R)-(+)-limonene	97.1-97.4	98.2	97.3-99.6	91.3-94.5
(3R)-(-)-linalool	70.2-71.5	70.0	54.4-69.3	49.8-50.0
(3S)-(+)-linalool	28.5-29.8	30.0	30.7-45.6	50.0-50.2
(4R)-(-)-terpinen-4-ol	70.5-70.8	70.5	75.1-81.4	55.0-57.7
(4S)-(+)-terpinen-4-ol	29.2-29.5	29.5	18.6-24.9	42.3-45.0
(4S)-(-)-α-terpineol	84.0-85.5	82.8	74.5-80.8	53.3-56.8
(4R)-(+)-α-terpineol	14.5-16.0	17.2	19.2-25.5	43.2-46.7
(3S)-(-)-citronellal	ND	ND	87.0	ND
(3R)-(+)-citronellal	ND	ND	13.0	ND

ND = not determined

Percentage composition of the sesquiterpene hydrocarbons found in three cold-pressed lime oils

T-6

Compound	Persian Lime	Key Lime Type A	Key Lime Type B
δ-elemene	t	0.05	0.03
β-elemene	0.02	0.07	0.05
cis-α-bergamotene	0.07	0.08	0.08
α-santalene	0.07	0.01	0.01
β-caryophyllene	0.48	0.95	0.89
trans-α-bergamotene	1.01	1.15	0.96
(E)-β-farnesene	0.10	0.11	0.10
epi-β-santalene	t	t	t
β-santalene	0.06	0.06	0.05
α-humulene	0.04	0.12	0.11
γ-curcumene	0.02	0.02	0.01
germacrene D	0.08	0.36	0.35
(Z)-α-bisabolene	0.12	0.12	0.10
β-selinene	0.01	0.03	0.03
(E,E)-α-farnesene	0.22	1.25	1.32
germacrene A	0.12	0.36	0.40
α-selinene	0.02	0.07	0.07
β-bisabolene	1.47	1.70	1.47
(Z)-γ-bisabolene	0.02	0.02	0.02
β-sesquiphellandrene	t	0.01	t
(E)-γ-bisabolene	0.01	0.01	0.01
germacrene C	0.11	0.53	0.52
7-epi-α-selinene	t	0.01	0.01
(E)-α-bisabolene	0.05	0.05	0.05
germacrene B	0.17	0.75	0.17

t = trace (<0.01%)

citronellyl acetate (1)	germacrene A (135)
(E)-β-farnesene (19)	geranyl acetate (80)
neral (271)	germacrene C (96)
(Z)-β-farnesene (16)	citronellol (10)
α-terpineol (95)	nerol (6)
germacrene D (122)	germacrene B (202)
α-selinene (23)	geraniol (35)
neryl acetate (13)	tetradecanal (3)
β-bisabolene (400)	hexadecanal (13)
geranial (429)	γ-eudesmol (8)
(E,E)-α-farnesene (248)	α-bisabolol (18)

[a] = mg/g (fresh weight)

S. Inoma, Y. Miyagi and T. Akieda, *Characterization of Citrus oil (mainly orange oil, mandarin oil, tangerine oil).* Kanzei Chuo Bunsekishoho, *29*, 87-97 (1989).

R. Kaiser, *Investigation of natural scents as a stimulation in perfumery.* Oral Presentation at Centifolia 93, Oct. 28-30, Grasse (1993).

I. Jantan, A. S. Ahmad, A. R. Ahmad, N. A. M. Ali and N. Ayop, *Chemical composition of some Citrus oils from Malaysia*. J. Essent. Oil Res., *8*, 627-632 (1996).

K-H. Kubeczka, *New approaches in essential oil analysis using polymer-coated silica fibres.* In: *Proceedings of 27th International Symposium on essential oils*. Edits., Ch. Franz, A. Mathé and G. Buchbauer, 139-145, Allured Publ., Carol Stream, IL (1997).

K-I. Asano, *Thailand in view of her agricultural products, particularly aromatic plants, spices and a number of citrus.* Koryo, *No. 195*, 53-64 (1997).

P. M. Jazet Dongmo, P. H. Amvam Zollo, F. Fekam Boyom. C. Menut, G. Lamaty and J. M. Bessiere, *Composition chimique des huiles essentielles de six espéces de Citrus cultivées au Cameroun.* Rivista Ital. EPPOS *(Numero Speciale)*, 156-162 (1998).

E. G. Haggag, S. M. A. Wahab, S. M. El-Zalabany, E. A. A. Moustafa, E. M. El-Kherasy and T. J. Mabry, *Volatile oils and pectins from Citrus aurantifolia (lime) and Citrus limonia (lemon).* Asian J. Chem., *10*, 828-833 (1998).

Percentage composition of germacrenes in various lime oils **T-7**

Germacrene type	Lime oil distilled	Key lime oil (A/B) CP	Persian lime oil CP
A	-	0.36-0.46	0.12-0.18
B	0.04-0.08	0.78-0.90	0.16-0.19
C	-	0.50-0.59	0.09-0.12
D	-	0.30-0.41	0.07-0.16

R-H. Yang, Q. Tao and J-L. Lin, *Volatile compounds in the peel oil of lime.* Wuxi Qinggong Daxue Xuebao (J. Wuxi Univ. Light Industry), *18(3)*, 80-83 (1999).

G. Dugo, K. D. Bartle, I. Bonaccorsi, M. Catalfamo, A. Cotroneo, P. Dugo, G. Lamonica, H. McNair, L. Mondello, P. Previti, I. Stagno d'Alcontres, A. Trozzi and A. Verzera,'*Advanced analytical techniques for the analysis of citrus essential oils. Part 3. Oxygen heterocyclic compounds: HPLC, HPLC/MS, OPLC, SFC, Fast HPLC analysis*. Essenz. Deriv. Agrum.,'69, 251-283 (1999).

G. Dugo, K. D. Bartle, I. Bonaccorsi, M. Catalfamo, A. Cotroneo, P. Dugo, G. Lamonica, H. McNair, L. Mondello, P. Previti, I. Stagno d'Alcontres, A. Trozzi and A. Verzera,'*Advanced analytical techniques for the analysis of citrus essential oils. Part 2. Volatile fraction: LC-HRGC and MDGC.* Essenz. Deriv. Agrum., *69*, 159-217 (1999).

M. Sawamura, *Volatile components of essential oils of the Citrus genus.* Recent Res. Develop. Agric. Food Chem., *4*, 131-164 (2000).

W. Feger, H. Brandauer and H. Ziegler, *Sesquiterpene hydrocarbons of cold-pressed lime oils.* Flav. Fragr. J., *15*, 281-284 (2000).

G. Dugo, L. Mondello, A. Cotroneo, I. Bonaccorsi and G. Lamonica, *Enantiomeric distribution of volatile components of citrus oils by MDGC.* Perfum. Flavor. *26(1)*, 20-35 (2001).

S. B. Mitiku, H. Ukeda and M. Sawamura, *Enantiomeric distribution of α-pinene, β-pinene, sabinene and limonene in various citrus essential oils.* In: *Food Flavors and Chemistry. Advances of the new Millennium*. Edits., A. M. Spanier, F. Shahidi, T. H. Parliament, C. Mussinan, C-T. Ho and E. Tratras Contis, 216-231, Royal Soc. Chem. Cambridge (2001).

J. A. Pino and A. Rosado, *Comparative investigation of the distilled lime oils (Citrus aurantifolia Swing. and Citrus latifolia Tanaka) from Cuba.* J. Essent. Oil Res., *13*, 179-180 (2001).

W. Feger, H. Brandauer and H. Ziegler, *Germacrene in Citrus peel oils.* J. Essent. Oil Res., *13*, 274-277 (2001).

T. Veriotti and R. Sacks, *High-speed GC and GC/Time-of-flight MS of lemon and lime oil samples.* Anal. Chem., *73*, 4395-4402 (2001).

M-L. Lota, D. DeRocca Serra, F. Tomi, C. Jacquemond and J. Casanova, *Volatile components of peel and leaf oils of lemon and lime species.* J. Agric. Food Chem., *50*, 796-805 (2002).

K-H. Kubeczka and V. Formacek, *Essential oils analysis by capillary gas chromatography and carbon-13 NMR spectroscopy.* 2nd Edn., 179-190, J. Wiley & Sons, NY (2002).

A-L. Gancel, D. Ollé, P. Ollitrault, F. Luro and J-M. Brillouet, *Leaf and peel volatile compounds of an interspecific Citrus somatic hybrid [Citrus aurantifolia (Christm.) Swing. + Citrus paradisi Macfayaden].* Flav. Fragr. J., *17*, 416-424 (2002).

Clove Oil

Zhu et al. (1995) reported that a sample of clove bud oil produced from plants cultivated in southern China contained the following components:

- 2-propenylphenol (0.12%)
- eugenol (85.07%)
- methyl eugenol (0.10%)
- β-caryophyllene (2.37%)
- α-humulene (0.28%)
- eugenyl acetate (9.45%)
- caryophyllene oxide (0.48%)

Comparative percentage composition of the distilled oils of *Citrus aurantifolia* and *C. latifolia* **T-8**

Compound	*C. aurantifolia*	*C. latifolia*
α-thujene	t	t
α-pinene	2.1	1.8
camphene	1.3	0.7
2,2,6-trimethyl-2-vinyl-tetrahydropyran	0.5	0.5
β-pinene	2.9	1.8
myrcene	2.1	2.6
1,4-cineole	2.0	1.8
p-cymene	1.6	1.5
limonene° + 1,8-cineole	40.4	55.6
(E)-β-ocimene	0.5	t
γ-terpinene	9.5	11.8
p-mentha-3,8-diene	t	t
α-p-dimethylstyrene	0.4	0.2
terpinolene	8.7	5.2
linalool	0.3	0.1
α-fenchol	1.4	1.1
terpinen-1-ol	2.3	1.9
cis-β-terpineol	2.2	2.2
isoborneol	t	t
trans-β-terpineol	t	0.1
borneol	1.4	0.3
terpinen-4-ol	1.9	1.3
α-terpineol	12.7	6.6
γ-terpineol†	1.6	0.4
trans-carveol	0.1	0.1
cis-carveol	0.1	0.2
carvone	0.1	t
δ-elemene	0.1	-
neryl acetate	t	0.5
geranyl acetate	0.1	0.1
cis-α-bergamotene	-	t
β-caryophyllene	0.7	0.1
trans-α-bergamotene	0.9	0.4
α-humulene	0.1	-
(E)-β-farnesene	0.1	t
β-santalene	-	t
β-chamigrene	0.1	t
(Z)-α-bisabolene	-	t
β-bisabolene	1.6	0.6

t = trace (<0.01%)
° major component of mixed peak
† the natural origin of γ-terpineol is in question

Comparative percentage composition of lime oils produced from *Citrus latifolia* **T-9**

Compound	1	2	3	4	5
α-thujene	0.6	0.6	0.7	0.4	0.4
α-pinene	2.3	1.4	2.4	1.7	1.3
camphene	t	t	0.1	t	t
β-pinene	12.2	11.6	13.7	12.1	11.1
sabinene	1.8	1.8	2.1	1.7	1.6
myrcene	1.3	1.3	1.3	1.1	1.1
α-phellandrene	t	t	0.1	0.1	t
α-terpinene	0.4	0.4	0.4	0.3	0.2
limonene	46.5	45.8	42.7	40.3	40.4
β-phellandrene	-	0.5	-	-	0.5
1,8-cineole	0.6	-	0.6	0.5	-
(Z)-β-ocimene	-	-	-	0.1	0.1
γ-terpinene	20.0	21.1	21.5	20.6	17.3
(E)-β-ocimene	0.1	0.1	0.1	0.1	0.2
p-cymene	0.4	0.2	0.3	2.0	5.3
terpinolene	0.8	0.9	0.9	0.8	0.7
octanal	t	-	-	-	-
6-methyl-5-hepten-2-one	-	-	-	-	t
allo-ocimene*	t	-	-	-	-
cis-limonene oxide	-	-	-	t	t
trans-limonene oxide	-	-	-	-	0.1
trans-sabinene hydrate	0.1	0.1	0.1	0.1	0.1
citronellal	t	0.1	0.1	0.2	0.2
decanal	t	t	0.1	t	t
linalool	0.4	0.4	0.4	0.5	0.5
linalyl acetate	t	t	-	-	-
trans-α-bergamotene	1.0	1.3	1.1	1.4	1.6
β-elemene	0.2	-	0.2	0.2	-
β-caryophyllene	0.5	0.4	0.3	0.4	0.5
terpinen-4-ol	t	t	t	0.1	0.1
undecanal	-	-	-	t	-
citronellyl acetate	-	-	-	0.1	-
(E)-β-farnesene	0.1	0.1	-	-	0.1
α-humulene	t	t	t	-	0.2
neral	1.6	1.7	1.6	1.9	2.3
α-terpinyl acetate	-	t	t	-	-
α-terpineol	0.4	0.4	0.5	0.5	0.6
germacrene D	0.1	0.1	0.2	0.1	t
β-bisabolene	1.5	1.9	1.6	2.1	2.4
neryl acetate	1.2	1.7	1.5	1.8	2.0
bicyclogermacrene	-	-	-	0.4	0.4
piperitenone	-	-	-	-	t
geranial	2.8	3.0	2.7	3.4	4.0
(E,E)-α-farnesene	0.4	0.3	0.3	-	-
geranyl acetate	0.7	0.9	0.7	2.2	2.4
nerol	-	-	-	t	t
geraniol	t	t	t	t	t
caryophyllene oxide	-	-	-	t	0.1
santal-10-en-2-ol	t	t	t	-	-
β-sinensal	0.1	0.1	-	0.1	-

The oils were obtained from the following cultivars: 1. El Kseur, 2. IAC, 3. Bearss, 4. DePerse, 5. Tahiti; t = trace (<0.1%)

Comparative percentage composition of lime oils produced from *Citrus aurantifolia*

T-10

Compound	1	2	3	4	5
α-thujene	0.4	0.5	0.3	0.2	0.3
α-pinene	1.2	1.4	2.1	1.1	1.7
camphene	t	0.1	0.1	t	0.2
β-pinene	6.1	14.7	19.2	14.7	15.3
sabinene	5.4	2.0	3.1	2.2	1.0
myrcene	1.5	1.2	1.2	1.1	0.8
α-phellandrene	t	-	t	t	0.1
α-terpinene	0.3	0.3	0.2	0.1	0.3
limonene	66.8	49.9	48.8	46.4	39.9
β-phellandrene	0.3	0.4	0.5	0.5	-
1,8-cineole	t	-	-	t	-.7
(Z)-β-ocimene	0.1	0.1	0.2	0.3	0.2
γ-terpinene	6.9	15.5	9.6	11.0	9.9
(E)-β-ocimene	0.3	0.2	0.3	0.5	0.4
p-cymene	2.3	1.3	0.6	0.2	5.2
terpinolene	0.4	0.6	0.4	0.4	1.1
octanal	t	-	t	0.1	t
nonanal	t	-	t	0.1	0.1
α-p-dimethylstyrene	-	-	-	-	0.1
cis-linalool oxide†	-	-	-	-	t
cis-limonene oxide	t	-	-	-	-
trans-limonene oxide	t	-	-	-	-
trans-sabinene hydrate	t	t	0.1	0.1	-
citronellal	0.1	0.3	0.1	0.1	t
decanal	-	-	0.1	0.3	0.1
linalool	0.4	0.2	0.3	0.3	1.4
trans-α-bergamotene	0.3	0.7	0.7	1.0	0.5
β-elemene	-	-	0.3	0.8	0.2
β-caryophyllene	-	0.2	0.4	0.5	0.4
methyl thymol	1.2	-	-	-	-
terpinen-4-ol	0.9	-	t	t	1.7
trans-p-menth-2-en-1-ol	t	-	-	-	0.1
citronellyl acetate	0.1	0.1	-	-	0.1
(E)-β-farnesene	-	-	0.1	0.1	t
α-humulene	t	-	0.1	0.1	-
neral	0.4	1.5	2.1	3.1	1.7
α-terpineol	0.6	0.3	0.3	0.3	4.7
germacrene D	0.1	0.2	0.3	0.5	0.1
dodecanal	-	-	-	t	-
β-bisabolene	0.4	1.0	1.3	2.1	0.8
neryl acetate	0.5	0.7	-	-	0.9
geranial	0.8	2.8	4.0	6.1	2.8
(E,E)-α-farnesene	-	0.4	1.0	1.9	0.6
geranyl acetate	0.6	2.1	0.5	0.8	1.8
citronellol	0.1	-	t	-	0.1
nerol	t	-	-	-	t
geraniol	0.1	-	t	t	0.3
caryophyllene oxide	-	-	-	-	t
santal-10-en-2-ol	-	-	t	-	-

The oils were obtained from the following cultivars: 1. Mexican. 2. Ambilobe, 3. Antillaise, 4. New Caledonia, 5. Kirk; t = trace (<0.1%)

In 1997, D'Alpaos et al. compared the composition of clove bud oil with a supercritical fluid CO_2 extract and a soxhlet extract of powdered clove buds. Unfortunately, the analysis of the oil was not detailed enough to determine whether its minor important odorous components were found in either of the extracts. The results of this study can be seen in T-11. This same study was published a second time by the same authors (Pallado et al. 1997).

Della Porta et al. (1998) analyzed the composition of a supercritical extract of clove buds produced at 90 bar and 50°C for 630 min. The results of this study were as follows:

benzaldehyde (t)
myrcene (t)
benzyl alcohol (t)
limonene (0.08%)
(Z)-β-ocimene (t)
cuminaldehyde (0.11%)
eugenol (65.87%)
methyl eugenol (t)
α-cubebene (0.09%)
α-ylangene (0.14%)
(E)-methyl isoeugenol (t)
gurjunene* (t)
β-caryophyllene (11.10%)
aromadendrene (t)
α-guaiene (t)
γ-humulene (t)
eugenyl acetate (19.00%)
α-humulene (1.32%)
allo-aromadendrene (t)
γ-muurolene (t)
germacrene D (0.18%)
β-selinene (t)
α-selinene (0.16%)
α-muurolene (0.15%)
α-farnesene* (0.36%)
δ-cadinene (t)
ledol (t)
spathulenol (0.73%)
viridiflorol (t)
benzyl benzoate (t)
aromadendrene epoxide* (t)
pentadecanol (0.09%)
aromadendrene epoxide* (t)
heneicosane (0.44%)
tetracosane (0.08%)
pentacosane (0.10%)

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

If the production conditions were increased to 200 bar at 50°C for 210 min and fractionated, the waxes were found to be:

pentadecane (t)
tricosane (t)
tetracosane (t)
pentacosane (0.20%)
hexacosane (0.08%)
heptacosane (4.05%)
octacosane (0.56%)
nonacosane (27.40%)
triacontane (1.94%)
hentriancontane (55.91%)
dotriacontane (1.02%)
tritriacontane (8.84%)

An oil produced from clove buds purchased in the UK was analyzed by Dorman et al. (2000) and found to contain the following major components:

methyl salicylate (0.28%)
eugenol (86.50%)
β-caryophyllene (5.58%)
α-humulene (0.66%)
eugenyl acetate (5.15%)
caryophyllene oxide (0.32%)

The main constituents of a clove bud oil used in an antifungal screening program by Delespaul et al. (2000) were as follows:

methyl salicylate (0.1%)
β-caryophyllene (2.6%)
α-humulene (0.3%)
eugenol (82.0%)
eugenyl acetate (14.0%)
caryophyllene oxide (0.7%)

Lee and Shibamoto (2001) studied the antioxi–dant properties of an oil of clove buds (dried) produced by steam distillation. The oil and water mixture was extracted with methylene chloride and the resultant oil was analyzed by GC/MS. Although they related their results on a weight/weight basis to the dried ground clove buds, they were calculated to be found in the oil in the following amounts:

2-heptanone (0.015%)
3-pyrrolidinol (0.004%)
2-heptanol (0.007%)
2-butenal* (0.007%)
2-methylpentanol (0.015%)
3(2H)-pyridazinone (0.011%)
1-acetoxy-2-propanone (0.593%)
1-acetoxy-2-propanol (0.015%)
methyl benzoate (0.011%)
benzaldehyde (0.007%)
ethyl benzoate (0.011%)
benzyl acetate (0.059%)
salicylic acid (0.121%)
benzyl alcohol (0.011%)
2-methyl-5-(1-methylethenyl)-cyclohexyl acetate (0.498%)
(E,E)-2,4-heptadienal (0.018%)
eugenol (89.271%)
(E)-isoeugenol (0.015%)
eugenyl acetate (8.623%)
2-(1,1-dimethylethyl)-2,5-cyclohexadien-1,4-dione (0.70%)
2,5-dimethylanisole (0.158%)
isophthaldehyde (0.462%)

This same year, Pino et al. (2001) analyzed the bud and leaf oils of *S. aromaticum* from trees growing at the experimental station in Havana (Cuba). The bud oil was found to contain:

3-methyl-3-butenol (t)
furfural (t)
(E)-2-hexenal (t)
ethyl 2-methylbutyrate (t)
(Z)-3-hexenol (t)
hexanol (t)
3-methyl-4-butenyl acetate (t)
2-heptanone (t)
2-heptanol (t)
methyl hexanoate (t)
benzaldehyde (t)
camphene (t)
6-methyl-5-hepten-2-one (t)
2-octanone (t)
myrcene (t)
ethyl hexanoate (t)
p-cymene (t)
2-heptyl acetate (t)
limonene (t)
(Z)-b-ocimene (t)
5-nonen-2-one (t)
trans-linalool oxide-furanoid (t)
2-nonanone (t)
linalool (t)
perillene (t)
benzoic acid (t)
terpinen-4-ol (t)
p-methylguaiacol (t)
methyl salicylate (t)
α-terpineol (t)
δ-elemene (t)
eugenol (69.8%)
β-caryophyllene (13.0%)
α-humulene (0.6%)
eugenyl acetate (16.1%)
humulene epoxide II (t)

t = trace (<0.1%)

Pino et al. also found that the composition of Cuban clove leaf oil was as follows:

furfural (t)
(E)-2-hexenal (t)
(Z)-3-hexenol (t)
hexanol (t)
2-acetylfuran (t)
benzaldehyde (t)
camphene (t)
6-methyl-5-hepten-2-one (t)
phenylacetaldehyde (t)
p-cymene (t)
limonene (t)
octanol (t)
cis-linalool oxide† (t)
2-guaiacol (t)
trans-linalool oxide† (t)
α-p-dimethylstyrene (t)
2-nonanone (t)
linalool (t)
perillene (t)
2-octyl acetate (t)
benzoic acid (t)
4-methylguaiacol (t)
eugenol (78.1%)
β-caryophyllene (20.5%)
α-humulene (1.1%)
(E)-β-farnesene (t)
germacrene A (t)
caryophyllene oxide (0.1%)
humulene epoxide II (t)
methyl linolenate (t)
phytol (t)

t = trace (<0.1%)
† furanoid form

An oil of clove that was analyzed by a combination of GC and ^{13}C-NMR by Kubeczka and Formacek (2002) was found to possess the following major components:

α-cubebene (0.1%)
α-copaene (0.2%)
β-caryophyllene (11.8%)
α-humulene (1.4%)
caryophyllene oxide (1.8%)
eugenol (84.4%)
eugenyl acetate (0.3%)

L-F. Zhu, Y-H. Li, B-L. Li, B-Y. Lu and W-L. Zhang, *Aromatic plants and essential oil constituents. Supplement 1*. South China Institute Botany, Chinese Acad. Sciences, Hai Feng Publ. Co., Peace Book Co., Hong Kong (1995).

M. D'Alpaos, P. Traldi, G. Tassinato and P. Pallado, *Extraction of essential oils and flavours with classic and supercritical techniques: a comparison*. Rivista Ital. EPPOS (*Numero Speciale-Agosto*), 200-207 (1997).

P. Pallado, G. Tassinato, M. D'Alpaos and P. Traldi, *Gas chromatography/mass spectrometry in aroma chemistry: a comparison of essential oils and flavours extracted by classical and supercritical techniques*. Rapid Commun. Mass Spec., *11*, 1335-1341 (1997).

G. Della Porta, R. Taddeo, E. D'Urso and E. Reverchon, *Isolation of clove bud and star anise essential oil by supercritical CO2 extraction.* Lebensm.-Wiss. Technol., *31*, 454-460 (1998).

H. J. D. Dorman, P. Surai and S. G. Deans, *In vitro antioxidant activity of a number of plant essential oils and phytoconstituents.* J. Essent. Oil Res., *12*, 241-248 (2000).

Q. Delespaul. V. G. de Billerbeck, C. G. Roques, G. Michel, C. Marquier-Vinuales and J. M. Bessière, *The antifungal activity of essential oils as determined by different screening methods.* J. Essent. Oil Res., *12*, 256-266 (2000).

K-G. Lee and T. Shibamoto, *Antioxidant property of aroma extract isolated from clove buds (Syzygium aromaticum (L.) Merr. et Perry)*. Food Chem, *74*, 443-448 (2001).

J. A. Pino, R. Marbot, J. Agüero and V. Fuentes, *Essential oil from buds and leaves of clove (Syzygium aromaticum (L.) Merr. et Perry) grown in Cuba.* J. Essent. Oil Res., *13*, 278-279 (2001).

K-H. Kubeczka and V. Formacek, *Essential oils analysis by capillary gas chromatography and carbon-13 NMR spectroscopy.* 2nd Edn., 81-85, J. Wiley & Saons, NY (2002).

Copaiba balsam oil

Using a combination of GC/MS and Kovats Indices, an oil of copaiba balsam oil was found to contain (Ramaswami et al. 1988):

α-copaene
α-cubebene
β-caryophyllene
β-bisabolene
δ-cadinene
β-elemene
α-humulene
α-gurjunene

In 1994, Koenig et al. examined the enantiomeric ratio of two sesquiterpene hydrocarbons in copaiba balsam oil. They found the following:

(+)-δ-cadinene (90%) : (-)-δ-cadinene (10%)
(+)-α-copaene (2%) : (-)-α-copaene (98%)

Stashenko et al. (1995) analyzed an oil of copaiba balsam (ex. *Copaifera officinalis*) produced from exudates of Colombian origin using both GC and GC/MS. The composition of the oil was determined to be as follows:

δ-elemene (1.59%)
α-ylangene (2.90%)
α-cubebene (1.99%)
α-copaene (20.73%)
β-cubebene (2.65%)
β-elemene (0.87%)
β-caryophyllene (24.70%)
trans-β-bergamotene (0.41%)
β-copaene (0.49%)
α-guaiene (0.25%)
α-humulene (2.67%)
germacrene D (2.30%)
allo-aromadendrene (1.79%)

T-11 Comparative percentage composition of clove bud oil and its extracts

Compound	Oil	$SFCO_2$	SOX
α-pinene	-	-	t
β-pinene	-	-	0.1
δ-3-carene	-	-	t
1,8-cineole	-	0.20	-
γ-terpinene	-	-	t
2-methylpentanal	-	t	-
linalool	-	t	t
camphor	-	0.12	-
benzyl acetate	-	0.09	0.18
terpinen-4-ol	-	-	0.19
methyl salicylate	-	0.11	0.19
linalyl acetate	-	0.21	t
thymol	-	-	t
eugenol	78.47	61.32	62.77
α-copaene	-	0.33	0.42
β-caryophyllene	13.50	18.95	27.80
α-humulene	1.42	2.81	3.91
γ-cadinene	-	0.08	0.13
ar-curcumene	-	-	0.05
bisabolene*	-	0.46	0.43
eugenyl acetate	6.61	14.18	2.69
β-farnesene*	-	-	0.04
caryophyllene oxide	-	0.75	0.48
benzyl benzoate	-	0.08	-

*correct isomer not identified
t = trace (<0.01%)
oil = hydrodistilled oil
$SFCO_2$ = supercritical fluid extract
SOX = soxhlet extract (solvent not noted)

β-guaiene† (0.47%)	γ-cadinene (5.51%)
α-selinene (4.07%)	δ-cadinene (7.71%)
γ-muurolene (1.24%)	calamenene* (0.21%)
α-muurolene (0.71%)	himachalene* (1.05%)
β-bisabolene (0.79%)	cedrol (4.83%)
β-selinene (1.53%)	cadalene (0.73%)
δ-guaiene‡ (0.93%)	β-bisabolol (1.06%)

* correct isomer not identified
† probably cis-isomer
‡ compound structure not fully elucidated

A sample of copaiba balsam oil was subjected to analysis by Moyler and Clery (1997). The components identified by retention indices (polar column) and GC/MS were as follows:

δ-elemene (1.8%)	*trans*-α-bergamotene (12.7%)
α-cubebene (0.9%)	β-caryophyllene (41.6%)
α-copaene (8.8%)	α-humulene (5.8%)
β-cubebene (0.5%)	
β-elemene (0.6%)	
cis-α-bergamotene (1.2%)	

A further 35 components (26.1% of the oil) were noted as being present in the oil although they were not identified.

Cascon and Gilbert (2000) compared the composition of the exudates (oleoresins) of three Brazilian *Copaifera* species (*C. multijuga* Hayne, *C. guianensis* Desf. and *C. duckei* Dwyer), which might be used as a raw material source for copaiba balsam oil. The results of their analyses can be seen in T-12. From these results, it is evident that only *C. multijuga* could be a source of commercial copaiba oil.

S. K. Ramaswami, P. Briscese, R.J. Gargiullo and T. von Geldern, *Sesquiterpene hydrocarbons: From mass confusion to orderly line up*. In: *Flavors and Fragrances: A World Perspective.* Edits., B.M. Lawrence, B. D. Mookherjee and B. J. Willis, 951-989, Elsevier Science Publ., B.V., Amsterdam (1988).

W. A. Koenig, A. Rieck, I. Hardt , B. Gehrcke, K-H. Kubeczka and H. Muhle, *Enantiomeric composition of the chiral constituents of essential oils. Part 2. Sesquiterpene hydrocarbons.* J. High Resol. Chromatogr., *17*, 315-320 (1994).

E. Stashenko, H. Wiame, S. Dassy, J. R. Martinez and T. Shibamoto, *Catalytic transformation of copaiba (Copaifera officinalis) oil over zeolite ZSM-5.* J. High Resol. Chromatogr., *18*, 54-58 (1995).

D. A. Moyler and R. A. Clery, *The aromatic resins: Their chemistry and uses*. In: *Flavors and Fragrances*. Edit., K. A. D. Swift, pp. 96-115, Royal Soc. Chem., Cambridge, UK (1997).

V. Cascon and B. Gilbert, *Characterization of the chemical composition of oleoresins of Copaifera guaienesis Desf., Copaifera duckei Dwyer and Copaifera multijuga Hayne*. Phytochemistry, *55*, 773-778 (2000).

Fennel Oil

Using chiral GC as the method of analysis, the enantiomeric ratio of α-phellandrene in fennel oil was found by Casabianca (1996) to be as follows:

(4R)-(+)-α-phellandrene (100%) : (4S)-(-)-α-phellandrene (0%)

Percentage composition of the oleoresins of *Copaifera multijufa, C. guainensis* and *C. duckei*			T-12
Compound	***C. multijuga***	***C. guainensis***	***C. duckei***
α-copaene	2.1	0.6	-
β-caryophyllene	60.3	4.7	6.2
trans-β-bergamotene	2.0	7.2	3.4
β-selinene	-	1.5	7.3
α-selinene	-	-	4.5
β-bisabolene	-	2.1	8.9
δ-cadinene	1.6	-	-
caryophyllene oxide	t	19.1	-
kaur-16-en-19-oic acid	-	17.5	19.8
kauran-19-oic acid	-	0.9	-
copalic acid	11.0	1.4	4.8
polyalthic acid	-	10.6	27.7
hardwidkiic acid	-	11.0	-
3-acetoxycopalic acid	6.2	-	-

In 1997, Baser et al. found that fennel oil produced from fruits collected in Uzbekistan contained as major constituents:

limonene (0.78%)
γ-terpinene (0.39%)
fenchone (8.03%)
methyl chavicol (3.24%)
(E)-anethole (87.33%)

Kubeczka (1997) compared the oil composition and headspace of bitter fennel fruit. A summary of his results can be seen in T-13. The relative amounts of monoterpene hydrocarbons in small fennel plants was the subject of study by Valterova et al. (1997). As a result of this analysis, the following components were characterized:

α-pinene (2.4%)
camphene (0.1%)
β-pinene (0.3%)
sabinene (0.5%)
δ-3-carene (0.2%)
myrcene (64.4%)
α-terpinene (0.2%)
limonene (11.0%)
β-phellandrene (6.1%)
(Z)-β-ocimene (0.7%)
γ-terpinene (10.5%)
p-cymene (1.9%)
terpinolene (0.4%)
allo-ocimene* (1.5%)

*correct isomer not identified

The authors also determined that the enantiomeric ratio of three of the hydrocarbons was as follows:

(1R,5R)-(+)-α-pinene (96.0%) : (1S,5S)-(-)-α-pinene (4%)
(4R)-(+)-limonene (92%) : (4S)-(-)-limonene (8%)
(4R)-(+)-β-phellandrene (99%) : (4s)-(-)-β-phellandrene (1%)

Also in 1997, Kruger and Zeiger examined the major components found in a hexane extract of the 41 accessions found in the German gene bank of *F. vulgare* and compared the results with those obtained from an SPME analysis of the headspace of ground dried fruit. A summary of the range of data obtained can be seen in T-14.

Kartnig et al. (1998) compared the composition of lab-distilled and commercial fennel oils, the results of which can be seen in T-15. The authors pointed out that bitter and sweet fennel oils were not differentiated so that the fenchone contents ranged widely. They also noted that the occurrence of dillapiole and myristicin in some commercial oils was indicative of adulteration perhaps with fennel root oil. Also, the occurrence of high levels of α-pinene, α-phellandrene and limonene and lower levels of α-terpineol, longifolene, β-caryophyllene and α-humulene in some commercial oils were indicative of further oil adulteration. Finally, the occurrence of foeniculin as a fennel oil was indicative of adulteration with star anise oil.

The following year, Kruger and Hammer (1999) re-reported the same results as were presented by Kruger and Zeiger two years earlier. In addition to presenting these results, the authors examined the data in greater detail and subdivided them into four chemotypes as shown below:

Chemotype 1. (eight samples): α-pinene (ca. 5%), limonene (ca. 2%), fenchone (ca. 10%), methyl chavicol (>50%), (E)-anethole (20%).

Chemotype 2. (30 samples): α-pinene (ca. 5%), limonene (ca. 2%), fenchone (ca. 20%), methyl chavicol (ca. 2%), (E)-anethole (>60%).

Chemotype 3. (three samples): α-pinene (ca. 8%), limonene (ca. 2%), fenchone (ca. 30%), methyl chavicol (ca. 40%), (E)-anethole (not detected).

Chemotype 4. (one sample): α-pinene (<1%), limonene (>40%), fenchone (ca. 30%), γ-terpinene + terpinolene (ca. 20%).

Borazani et al. (1999) collected samples of fruit of *F. vulgare* var. *vulgare* from plants indigenous to Israel. The authors analyzed the hexane extracts from their collections obtained from across Israel and, as expected, found some chemical variations in the extracts as shown in T-16. Although the data presented in T-16 represents 11 populations (five in the North and six in the South), they have been grouped according to the similarity of extract composition.

Fennel oils of Italian origin were produced in the laboratory from dried fruit (seed) from 10 separate samples. Three of these samples were collected in southern central Tuscany and one from a high mountain close to the coast while six others were obtained commercially from natural food stores. Using GC/MS as the method of analysis, Miraldi (1999) compared the composition of the oils. The results of this study have been

T-13 Comparative percentage composition of the headspace and oil of *Foeniculum vulgare*

Compound	Headspace	Oil
α-pinene	11.69	2.99
camphene	1.31	0.31
sabinene	0.53	0.14
β-pinene	0.82	0.22
myrcene	1.39	0.38
α-phellandrene	0.53	0.15
p-cymene	1.83	0.76
limonene + β-phellandrene	5.82	1.71
1,8-cineole	1.10	0.33
γ-terpinene	0.82	0.25
fenchone	44.35	26.36
nonanal	2.49	0.04
camphor	0.69	0.76
methyl chavicol	2.91	3.68
anisaldehyde + (Z)-anethole	2.16	3.68
(E)-anethole	17.43	55.15
(E)-anethole epoxide	1.73	0.05
p-methoxy-phenylacetone	0.81	0.22

T-14 Percentage compositional range of the major components of the fennel gene bank in Germany

Compound	Extract	SPME
α-pinene	1.05-25.87	0.87-20.93
myrcene	0.73-4.06	0.36-3.26
limonene	1.55-14.90	1.98-23.85
fenchone	2.14-27.40	2.06-28.38
methyl chavicol	2.00-73.15	2.66-72.93
(E)-anethole	0-82.70	0.40-79.60

partially combined for ease of presentation and can be seen summarized in T-17.

Also in 1999, Bellomaria et al. analyzed oils produced from *F. vulgare* ssp. *vulgare* collected from different locations [Rocca Varano and Sentino (Camerino), Grotte (Fabriano) and Colle Truscino (L'Aquila)] in Italy. The oils examined were produced from plants harvested at different growth stages; the analyses of which can be seen summarized in T-18. The authors also examined one other oil produced from plants collected in the vicinity of Pano Lefkara (Cyprus) and found that it possessed the follow–ing composition:

α-thujene (0.1%)
α-pinene (2.7%)
camphene (0.2%)
β-pinene (0.2%)
sabinene (0.3%)
myrcene (5.4%)
limonene (1.7%)
1,8-cineole (1.2%)

Comparative percentage composition of lab -distilled and commercial samples of fennel oil		T-15
Compound	**Lab-distilled Oils**	**Commercial Oils**
α-pinene	0.5-3.7 (1.81)[a]	0.7-11.7 (3.84)[b]
camphene	0-0.3 (0.13)	0-0.6 (0.17)
sabinene	t-0.3 (0.11)	0-0.2 (0.05)
β-pinene	0-0.2 (0.10)	0-3.6 (0.63)
myrcene	0.1-1.0 (0.55)	0-4.0 (0.98)
α-phellandrene	0-0.4 (0.21)	0-13.0 (2.53)
δ-3-carene	0-t (0)	0-1.1 (0.10)
α-terpinene	0-t (0)	0-0.2 (0.02)
p-cymene	t-0.9 (0.21)	0-3.1 (0.65)
limonene	0.9-4.4 (2.07)	0.7-34.9 (8.29)
1,8-cineole	0-1.2 (0.31)	0-2.7 (0.37)
γ-terpinene	0.2-1.0 (0.61)	0-2.9 (0.53)
terpinolene	0-0.1 (0.03)	0-1.2 (0.14)
fenchone	2.1-29.3 (16.18)	0.4-19.7 (12.0)
linalool	0-t (0)	0-0.9 (0.16)
camphor	0-0.6 (0.31)	0-0.5 (0.20)
terpinen-4-ol	0-t (0)	0-0.2 (0.02)
α-terpineol	0 (0)	0-1.9 (0.35)
methyl chavicol	2.2-14.0 (3.74)	0.2-7.4 (2.92)
carvone	0-0.4 (0.04)	0-0.9 (0.04)
(Z)-anethole	0-0.2 (0.06)	0-3.6 (0.45)
anisaldehyde	0-1.8 (0.51)	0-2.0 (0.50)
(E)-anethole	58.7-86.9 (69.10)	16.2-82.0 (63.12)
anisketone†	0-0.3 (0.03)	0-0.7 (0.13)
longifolene	0 (0)	0-0.9 (0.06)
β-caryophyllene	0 (0)	0-2.0 (0.18)
α-humulene	0 (0)	0-0.3 (0.02)
germacrene D	0-t (t)	0-0.3 (0.03)
myristicin	0-t (0)	0-0.5 (0.03)
dillapiole	0-t (0)	0-7.9 (0.55)
foeniculin	0 (0)	0-1.0 (0.13)

a = average of 21 lab-distilled oils
b = average of 24 commercial oils
† p-methoxybenzyl methyl ketone

(Z)-β-ocimene (0.5%)
γ-terpinene (1.5%)
p-cymene (3.4%)
terpinolene (0.1%)
fenchone (14.0%)
α-fenchyl acetate (0.2%)
α-fenchyl alcohol (1.3%)
camphor (0.3%)
β-caryophyllene (0.1%)
methyl chavicol (65.8%)
(Z)-anethole (0.4%)
(E)-anethole (0.1%)
carvacrol (0.3%)

Braun and Franz (1999) examined the quantitative quality criteria for bitter fennel oil sold in Germany. They found that the compounds that varied the most in the 12 oils that they analyzed were anethole, fenchone, methyl chavicol (often called estragole, particularly in Europe), α-pinene and limonene. In 11 of the oils, these constituents varied as follows:

anethole (23.8-78.2%)
fenchone (3.5-23.4%)
methyl chavicol (1.4-6.8%)
α-pinene (1.5-8.4%)
limonene (1.6-35.8%)

The variations in other oil components were found to be:

β-pinene (0.2-3.9%)
sabinene (0-0.3%)
δ-3-carene (0-0.5%)
myrcene (0.4-4.3%)
α-phellandrene (0.2-8.7%)
p-cymene (0.3-2.8%)
β-ocimene* (0-1.6%)
γ-terpinene (0.2-0.8%)
(Z)-anethole (t-0.4%)

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

Furthermore, Braun and Franz found that the most striking change in bitter fennel oil was the oxidation of anethole to p-anisaldehyde. The found that careful oil isolation by water distillation of the ground fruit for one hour resulted in the production of an oil that was devoid of

Comparative percentage composition of hexane extracts of *Foeniculum vulgare* var. *vulgare* indigenous population in Israel **T-16**

Compound	Northern Populations 1 (1)[a]	2 (1)	3 (5)	Central and Southern Populations 4 (5)	5 (1)
α-pinene	3.29	3.26	1.85-2.32	1.48-2.43	0.91
camphene	0.60	0.17	0.2-0.33	0.15-0.29	0.10
sabinene	0.35	0.32	0.31-0.34	0.21-0.29	0.11
β-pinene	1.65	0.76	0.50-0.58	0.09-0.37	0.05
myrcene	2.04	1.36	1.30-1.41	0.83-1.24	0.61
α-phellandrene	0.54	0.36	0.25-0.32	0.19-0.29	0.13
p-cymene	0.04	0.06	0.04-0.67	0.06-0.36	0.09
limonene	6.67	3.15	6.44-8.62	3.97-8.53	4.50
γ-terpinene	1.48	1.03	1.26-1.82	1.36-1.79	1.46
fenchone	25.61	22.12	16.76-19.30	13.21-19.73	9.15
allo-ocimene*	-	0.16	0-0.23	0.11-0.22	-
camphor	0.61	0.47	0.36-0.50	0.32-0.51	0.21
methyl chavicol	39.54	63.28	8.07-28.40	21.19-46.74	8.53
α-fenchyl acetate	0.02	0.01	t-0.23	0.02-0.03	0.01
(Z)-anethole	0.02	t	0-0.08	0.03-0.14	0.19
p-anisaldehyde	-	-	0-1.13	0-0.08	-
(E)-anethole	17.38	3.31	39.73-55.76	29.15-48.88	73.81
germacrene D	0.12	0.16	0.09-0.34	0.09-0.21	0.12

[a] number of populations analyzed
* correct isomer not identified
t = trace (<0.01%)

Comparative percentage composition of oils produced from fennel fruit of different origins in Italy **T-17**

Compound	Wild Collections 1	2 (2)[a]	3	Commercial Samples 4 (2)	5 (4)
α-pinene	0.4	0.2-0.7	1.0	0.6-1.5	0.2-1.2
β-pinene	-	t	t	t	t-0.6
sabinene	t	t	0.1	t	t-0.2
myrcene	t	t-0.4	t	0.4-0.7	0-2.2
α-phellandrene	t	t	t	t	t-0.5
limonene	4.5	0.6-1.6	0.1	t	t-22.4
1,8-cineole	-	t-0.5	1.2	2.3-3.4	t-8.3
γ-terpinene	0.2	t-0.2	t	t	0-t
p-cymene	0.2	t	t	t	0-t
fenchone	2.3	5.4-10.4	0.7	1.0-2.4	2.4-6.9
camphor	-	0-t	t	t-0.4	0-0.9
methyl chavicol	8.2	69.3-75.0	1.4	2.6-2.9	67.1-93.9
(E)-anethole	81.6	16.3-19.0	94.6	88.1-90.6	1.4-3.6
anisaldehyde	2.6	0.1	0.7	1.6-2.3	t-0.1
eugenol	0.1	t-0.1	t	0-0.1	0-t
apiole	t	0-t	0.4	t-0.2	t-0.1

t = trace (<0.1%)
[a] number of samples

p-anisaldehyde; thereby confirming that it did not occur naturally. However, they found that if they increased the distillation time to 4 h, anisaldehyde was formed at a level of 0.3%. Of the oils analyzed, the anisaldehyde content ranged from 0.1-1.9%. Similar and even higher increases in anisaldehyde were observed for fennel oil stored at 25°C for three months. As a result of this study, the authors concluded that a good quality bitter fennel oil should have the following composition:

(E)-anethole (55.0-75.0%) (Z)-anethole (<0.3%)

Comparative percentage composition of oils produced from *Foeniculum vulgare* ssp. *vulgare* harvested at different growth stages from different locations in Italy

T-18

Compound	Vegetative Plant Oil	Flowering Plant Oil	Fruit Oil	Stem Oil
α-thujene	0-0.1	-	-	-
α-pinene	0.9-2.1	1.2-2.1	2.0-2.3	1.1-8.5
camphene	0.1-0.3	t-0.1	0.2	t-0.1
β-pinene	0.1-0.7	0.1-0.2	0.1	0.1-1.1
sabinene	0.2	0.2-0.3	0.4	t-0.2
α-phellandrene	-	0-0.4	-	-
myrcene	13.4-38.2	4.3-24.9	3.5-4.1	2.7-4.2
limonene	1.5-15.9	1.9-6.1	1.7-3.5	1.1-1.2
1,8-cineole	1.6-4.0	1.4-2.5	1.4-1.5	1.0-1.2
(Z)-β-ocimene	0.2-0.7	0.3-0.6	0.1	0.2-0.8
γ-terpinene	0-0.1	1.7-2.4	0.6-0.8	-
p-cymene	2.0-12.5	0.6-7.0	1.0-1.1	5.8-6.1
terpinolene	0.1-0.2	0.1-0.2	0.1	-
fenchone	6.6-10.4	5.0-10.4	18.4-19.7	7.0-8.2
α-fenchyl alcohol	0-0.2	0-0.4	0-0.3	0-0.6
camphor	0.1-0.2	0.1-0.3	0.3-0.4	0.3-0.5
linalool	0-0.1	-	-	-
linalyl acetate	0-0.2	-	-	-
bornyl acetate	0-0.1	0-1.4	-	-
β-caryophyllene	0-0.1	0-0.2	-	0.1
methyl chavicol	22.0-57.6	51.0-64.3	59.8-65.0	64.3-64.7
α-terpineol	0-0.1	0-0.2	-	0-0.3
bicyclogermacrene	-	0-0.1	-	t
carvone	-	0-1.0	-	0.2-0.4
(Z)-anethole	0.1-0.9	0.1-0.6	0-t	0.6-1.0
(E)-anethole	1.5-12.7	0.9-10.3	3.2-7.5	1.6-3.4
γ-cadinene	0-0.1	-	-	-
calamenene*	0-t	0-0.1	-	0-0.1
caryophyllene oxide	t-0.2	0-0.2	-	0.1-2.3
anisyl alcohol	-	-	-	0.2-0.5
cedrol	0-0.1	0-0.2	-	-
thymol	0-0.7	t-0.3	-	0.4
carvacrol	0-0.3	0-1.1	-	0.1-0.5
2,4-dimethylundecanol	0-0.1	0-0.2	-	0.1-0.6
anisaldehyde	-	0-0.2	-	0-0.1
farnesol*	0-0.2	0-0.2	-	0.1-0.2
isobutyl phthalate†	0-0.3	0-0.1	-	-

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

methyl chavicol (<5.0%)
α-pinene (2.0-8.0%)
limonene (1.0-5.0%)
α-pinene/limonene ratio (>1.0)

Finally, they also found that the remaining oil sample not included in the quantitations listed above was a chemotype; the main oil components being:

α-pinene (1.8%)
limonene (30.7%)
fenchone (1.7%)
methyl chavicol (61.5%)
(E)-anethole (0.5%)

Simándi et al.(1999) compared the major components found in fennel oil with those found in a supercritical fluid CO_2 extract, a hexane extract and an ethanolic extract of ground fennel seed. The results of this study can be seen in T-19.

Garcia-Jimenez et al. (2000) collected bitter fennel plants from two populations in Aranjuez and Santander (Spain) and separated the leaves, stems and seeds (dried) fruit prior to separate distillation so that each of the oils from different plant parts could be analyzed. The results of these analyses are presented in T-20.

Shatar and Altantsetseg (2000) used GC and GC/MS to analyze a fruit oil of *F. vulgare* produced in Mongolia. The oil was found to possess the following composition:

α-pinene (8.7%)	camphor (0.5%)
camphene (0.1%)	β-caryophyllene (0.2%)
β-pinene (0.8%)	terpinen-4-ol (0.1%)
sabinene (0.4%)	β-farnesene* (0.1%)
myrcene (1.2%)	methyl chavicol (2.0%)
α-phellandrene (9.6%)	α-terpineol (t)
α-terpinene (0.1%)	germacrene D (0.5%)
limonene (13.4%)	carvone (t)
β-phellandrene (1.0%)	δ-cadinene (0.1%)
1,8-cineole (0.6%)	(E)-anethole (51.3%)
(Z)-β-ocimene (2.4%)	methyl eugenol (0.1%)
γ-terpinene (1.2%)	anisaldehyde (0.1%)
p-cymene (0.5%)	methyl isoeugenol* (0.1%)
terpinolene (0.2%)	carvacrol (t)
nonanal (0.1%)	α-cadinol (0.1%)
fenchone (1.6%)	apiole (0.1%)
α-thujone (0.1%)	isophytol (t)
β-thujone (0.1%)	phytol (0.5%)

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

Also in 2000, Ruberto et al. screened the plant oils of two accessions of *F. vulgare* collected from two locations in eastern Sicily for their antioxidant and antimicrobial properties. In addition to finding that the oils demonstrated comparable antioxidant capacities to α-tocopherol and BHT, they found that the oils contained the following constituents:

2-hexenal* (0.06-0.12%)	fenchone (8.06-8.67%)
α-thujene (0.06-0.10%)	terpinolene (0.58-0.85%)
α-pinene (8.49-14.20%)	linalool (0.02%)
camphene (0.17-0.21%)	camphor (0.09-0.11%)
sabinene (0.21-0.40%)	terpinen-4-ol (0.12-0.33%)
β-pinene (0.59-1.11%)	methyl chavicol (52.93-57.67%)
myrcene (2.09-3.15%)	α-fenchyl acetate (7.12-11.05%)
α-phellandrene (0.08-0.09%)	α-fenchyl valerate (0.03-0.10%)
δ-3-carene (0-0.18%)	piperitone (0.07-0.15%)
α-terpinene (0.04-0.08%)	(E)-anethole (0.09-0.11%)
p-cymene (0.29-1.00%)	germacrene D (1.82-1.94%)
limonene (3.08-6.52%)	δ-cadinene (0.06-0.07%)
(Z)-β-ocimene (0.09-0.51%)	geranyl butyrate (0.04-0.20%)
(E)-β-ocimene (0.07-0.11%)	
γ-terpinene (0.16-0.36%)	

*correct isomer not identified

Ehlers et al. (2000) examined the major constituents of fennel fruit (seed) oil and compared it with a supercritical CO_2 extract of the same batch of seed from three different sources. In addition to comparing the oils and extracts, they also compared the GC results of some components with those obtained from HPLC analyses — even though GC is the most favored method of analysis for volatile materials. The main constituents found in the oils and extracts of the three origins (Germany, United States and India) can be seen in T-21. A conclusion that can be drawn from the results is that the oils were richer in the more toxic (Z)-anethole than the CO_2 extract [(Z)-

T-19

Comparative percentage composition of oil and extracts of *Foeniculum vulgare*

Compound	Oil	Hexane Extract	Alcohol Extract	SFE Extract
α-pinene	2.53	0.90	t	0.98
β-pinene	0.46	0.44	t	0.52
limonene	3.23	1.58	0.55	1.21
fenchone	17.38	17.31	14.03	15.71
methyl chavicol	5.30	3.54	3.37	3.14
(E)-anethole	64.21	71.38	70.93	77.55

T-20

Percentage comparison of oils of various plant parts of *Foeniculum vulgare* of Spanish origin

	Leaf Oil		Stem Oil		Seed Oil		
Compound	1	2	1	2	1	2	3
α-thujene	0.1	0.3	0.4	0.3	0.1	t	t
α-pinene	7.4	6.6	9.7	14.4	3.2	3.2	1.9
camphene	0.6	0.5	0.4	0.6	0.6	0.6	0.6
sabinene	0.1	0.2	0.4	0.2	0.5	0.2	0.7
β-pinene	1.6	2.3	6.7	5.3	0.6	1.0	1.3
myrcene	3.3	3.0	2.5	4.3	1.3	2.2	2.5
α-phellandrene	9.4	27.2	24.3	31.4	2.4	7.8	3.5
p-cymene	2.6	5.6	11.5	5.2	1.1	0.8	0.5
(Z)-β-ocimene	-	0.6	1.2	1.2	-	0.3	0.7
limonene	25.3	18.0	11.6	15.0	7.3	7.2	5.7
(E)-β-ocimene	0.1	0.1	-	t	-	-	t
γ-terpinene	0.1	0.1	1.0	0.1	1.8	0.2	0.7
trans-sabinene hydrate	-	-	-	-	-	t	0.1
fenchone	19.4	18.3	9.1	17.5	22.4	34.4	24.6
cis-sabinene hydrate	0.8	0.1	0.3	0.4	-	1.9	0.4
α-fenchyl alcohol	-	-	0.1	-	-	-	0.1
β-fenchyl alcohol	0.1	-	t	-	-	-	t
camphor	0.2	0.1	0.3	0.2	0.4	0.7	0.5
terpinen-4-ol	0.1	-	-	t	0.1	0.1	t
methyl chavicol	12.3	12.1	1.5	-	2.9	1.2	54.9
(Z)-anethole	0.2	0.2	-	-	-	-	-
p-anisaldehyde	-	-	0.1	-	-	-	-
(E)-anethole	10.9	4.5	17.4	3.3	54.9	38.1	0.9

t = trace (<0.1%); all samples were from Aranjuez except seed oil 3, which was from Santander

T-21

Percentage composition of the main components in the oil and CO_2 extract of fennel seed of different origins

	German		American		Indian	
Compound	Oil	Extract	Oil	Extract	Oil	Extract
α-pinene	2.5	2.6	1.0	2.6	-	-
limonene	2.2	2.8	1.1	1.6	5.1	3.9
fenchone	28.2	28.6	15.1	16.4	10.4	8.7
methyl chavicol	2.1	2.1	2.7	2.6	2.9	2.2
(Z)-anethole	0.8	0.7	0.14	0.09	0.25	0.11
(E)-anethole	60.5	60.4	68.6	70.2	66.9	63.8
p-anisaldehyde	0.19	0.02	0.89	0.07	4.20	0.30

Percentage composition of the oils of thirteen accessions of Italian *Foeniculum vulgare*

	Par	Bol	Pes	Fir	Liv	Anc
α-pinene	0.75	7.21	5.02	0.90	3.82	0.84
camphene	0.19	0.09	0.20	0.18	0.19	0.17
sabinene	0.23	0.25	0.26	0.31	0.24	0.27
β-pinene	0.10	1.01	0.53	0.11	0.42	0.09
myrcene	1.79	1.94	2.02	2.08	1.68	1.68
α-phellandrene	30.76	15.67	28.66	39.53	24.78	33.75
hexyl acetate	0.11	0.24	0.24	0.25	0.09	0.18
δ-3-carene	0.03	0.02	0.03	0.15	0.05	0.03
p-cymene	2.03	2.12	1.71	1.12	0.62	0.91
limonene	5.00	3.24	4.80	6.81	3.94	5.09
(Z)-β-ocimene	0.32	0.50	0.89	0.32	0.50	2.29
(E)-β-ocimene	t	0.03	0.03	0.02	0.02	0.09
γ-terpinene	0.39	0.27	0.13	0.95	0.47	1.13
fenchone	10.96	8.02	11.22	7.56	9.84	10.70
camphor	0.12	0.11	0.13	0.08	0.10	0.14
terpinen-4-ol	0.09	0.06	0.09	0.06	0.08	0.07
methyl chavicol	23.98	24.45	43.10	40.76	50.52	35.02
trans-carveol	0.51	0.19	t	t	t	0.11
carvone	0.58	0.33	0.14	0.05	0.16	0.31
p-anisaldehyde	0.07	0.22	t	t	t	t
(E)-anethole	22.09	42.26	6.19	0.83	0.90	4.08

t = trace (<0.01%); Par = Parma, Bol = Bologna, Pes = Pesaro, Fir = Firenze, Liv = Livorno, Anc = Acona, Mac = Macerata, Nap = Napoli, Bar = Bari, Bri = Brindisi, Tar = Taranto, Cal = Caltanisetta, Cat = Catania

Percentage composition of fennel oil produced in different regions of China

Compound	Neimonggol	Ningxia	Guangdong	Beijing	Shanghai
α-pinene	0.59	0.58	0.64	0.60	1.09
sabinene	0.35	0.38	0.44	0.34	0.40
myrcene	0.20	0.23	0.27	0.22	0.30
α-phellandrene	0.10	0.10	0.14	0.04	0.05
limonene	9.81	8.28	8.66	9.97	9.90
(E)-β-ocimene	0.41	0.56	0.72	0.32	0.18
γ-terpinene	1.90	1.71	1.98	1.57	1.09
fenchone	3.64	1.87	2.04	5.10	12.04
(E,E)-allo-ocimene	0.13	0.19	0.08	0.11	0.15
methyl chavicol	3.32	6.30	7.35	6.17	5.58
carvone	0.47	0.57	0.22	0.66	1.20
p-anisaldehyde	0.41	0.11	0.02	1.52	1.35
(E)-anethole	73.98	77.44	75.31	71.90	64.80
(E)-isodillapiole	0.06	0.08	0.10	0.04	0.03
α-copaene	0.04	0.05	0.11	0.04	-
p-methoxyphenyl acetone	0.86	1.13	1.20	0.85	0.31
germacrene D	0.02	0.04	0.06	0.03	-
(E)-methyl isoeugenol	0.01	0.02	0.02	0.02	-
1-methoxy-4-(1-methyl propyl)benzene†	-	0.04	0.05	0.08	-
butyl benzensulphonamide†	0.03	0.05	0.06	0.05	0.02

† unusual constituent, possibly incorrect identification

T-22

Mac	Nap	Bar	Bri	Tar	Cal	Cat
1.80	21.28	1.25	23.19	13.81	26.54	24.02
0.12	0.10	0.04	0.09	0.05	0.14	0.11
0.43	0.44	0.39	0.37	0.34	0.38	0.47
0.23	2.39	0.16	2.49	1.67	2.61	2.66
1.72	2.59	1.48	3.12	1.38	2.83	2.74
36.75	18.12	82.07	7.57	9.09	1.97	0.31
0.29	0.27	0.06	0.30	0.18	0.22	0.38
0.04	t	0.02	3.40	1.64	3.49	0.05
0.85	0.24	2.23	0.90	0.59	0.38	0.19
7.36	2.69	11.35	3.34	1.74	3.38	22.68
1.79	0.48	0.04	0.72	0.60	1.61	1.80
0.06	t	t	0.04	0.05	0.10	0.07
0.36	0.26	0.97	0.33	0.49	0.58	0.83
2.21	2.37	1.70	3.38	2.16	4.58	1.80
t	0.05	0.04	t	0.03	0.07	0.09
0.11	0.10	0.07	t	0.08	0.09	0.11
45.47	49.35	0.15	38.96	52.17	46.98	8.78
t	t	t	t	0.14	0.03	0.24
0.14	t	0.06	0.09	0.08	0.18	3.80
t	t	-	t	0.13	0.05	0.13
4.35	0.14	0.26	11.57	15.26	2.53	28.31

T-23

Shangxi 1.	Shangxi 2.	Sichuan	Baoding	Xingjiang
0.96	0.83	0.43	0.80	0.56
0.41	0.45	0.30	0.36	0.37
0.46	0.27	0.17	0.41	0.19
0.12	0.15	0.10	0.12	0.10
9.48	8.74	7.14	9.71	7.87
0.33	0.62	0.47	0.24	0.55
1.45	1.94	1.38	1.75	1.52
8.64	2.43	1.77	8.78	1.52
0.08	0.23	0.09	0.08	0.10
6.99	6.31	6.39	5.29	5.44
0.22	0.02	0.05	-	0.02
0.01	0.01	0.13	0.05	0.22
68.55	76.82	78.34	71.28	74.42
0.06	0.04	0.04	0.04	0.08
0.08	0.03	0.04	0.02	0.07
0.75	0.21	0.43	0.41	0.78
0.04	0.05	0.04	0.02	0.05
0.02	0.02	0.02	-	0.03
0.01	0.12	0.16	-	0.09
0.07	0.06	0.03	0.04	0.05

Comparative percentage composition of four fennel oils **T-24**

Compound	Hungarian	Spanish	Rectified	Sweet
α-thujene + α-pinene	11.73	15.86	0.73	1.95
β-fenchene	0.03	0.09	0.02	0.06
α-fenchene	0.04	0.07	-	-
camphene	0.49	0.70	0.06	0.20
β-pinene	1.63	4.15	0.06	0.59
sabinene	0.27	0.21	0.22	0.10
δ-3-carene	0.15	0.32	-	0.16
myrcene	1.80	3.13	0.11	0.87
α-phellandrene	3.48	10.88	-	1.96
α-terpinene	0.05	0.08	-	0.03
limonene	10.33	28.58	5.72	21.03
1,8-cineole + β-phellandrene	1.61	3.44	0.27	0.51
(Z)-β-ocimene	0.42	1.28	0.04	0.29
γ-terpinene	1.28	0.36	0.10	0.31
(E)-β-ocimene	0.11	0.41	0.02	0.10
p-cymene	0.87	1.34	1.65	0.68
terpinolene	0.17	0.21	0.01	0.13
fenchone	14.65	11.80	9.04	7.99
camphor	0.21	0.13	0.20	0.16
linalool	0.01	0.01	-	0.35
terpinen-4-ol	0.04	0.08	-	0.23
methyl chavicol	2.34	1.44	5.07	2.28
α-terpineol	0.18	0.51	-	0.10
(Z)-anethole	0.16	0.08	0.24	0.73
(E)-anethole	47.59	14.48	67.30	58.12
anisaldehyde	0.24	0.08	6.98	0.97
anethole epoxide	0.03	-	0.88	0.12

anethole is ca. 15 times more toxic than (E)-anethole]. Also, p-anisaldehyde, an oxidation product of anethole, was lower in the CO_2 extract than in the oil. As a result, the authors considered that fennel CO_2 extracts were of better quality and less toxic than the steam distilled oils.

Piccaglia and Marotti (2001) analyzed oils produced from 13 different accessions of *F. vulgare* grown in an experimental garden near Bologna. The original accessions came from thirteen Italian locations of different latitudes from the Parma region (44°48ˡ N) to Catania in Sicily (37°30ˡ N). The results of the analyses are shown in T-22. As can be seen, most of the oils contained methyl chavicol as the major constituent. The oil originating from plants collected in Bari was the most unusual being rich in α-phellandrene.

The GC/MS analysis of the oils of fennel fruit produced in 10 different areas in China was the subject of a study by Wu et al. (2001). The results of this study can be summarized in T-23.

More recently, Kubeczka and Formacek (2002) used a combination of GC and ^{13}C-NMR to analyze four fennel oil samples (Hungarian, Spanish, rectified and sweet). A summary of these results can be seen in T-24.

H. Casabianca, *Méthodes analytiques axées sur l'énantiomérie avantages-inconvénient-limites*. Rivista Ital. EPPOS, (*Numero Speciale*), 205-219 (1996).

K. H. C. Baser, T. Özek, Kh. R. Nuriddinov, A. M. Nigmatullaer, K. Kh. Khadzimatov and Kh. N. Aripov, *Essential oils of Mediasia macrophylla (Regel et Schmalh.) Pimen and Foeniculum vulgare Mill. from Uzbekistan.* J. Essent. Oil Res., *9*, 249-250 (1997).

K-H. Kubeczka, *New approaches in essential oil analysis using polymer-coated silica fibers.* In: *Proceedings of 27th International Symposium on Essential Oils, Vienna 1996*, p. 139-146, Allured Publ., Carol Stream, IL (1997).

I. Valterova, G. Nehlin and A-K. Borg-Karlson, *Host plant chemistry and preference in egg-laying Trioza apicalis (Homoptera, Psylloidea).* Biochem. Syst. Ecol., *25*, 477-491 (1997).

H. Krüger and B. Zeiger, *Evaluation of a fennel collection by classical extraction and solid phase microextraction headspace analysis.* In: *Proceedings of 27th International Symposium on Essential Oils, Vienna, 1996.* 160-163, Allured Publ., Carol Stream, IL (1997).

Th. Kartnig, U. Fischer and F. Bucar, *Vergleichende gaschromatographische Untersuchungen an ätherischen Wacholderölen, Fenchelölen und Rosmarinölen.* Sci. Pharm., *66*, 237-252 (1998).

H. Krüger and K. Hammer, *Chemotypes of fennel (Foeniculum vulgare* Mill.), J. Essent. Oil Res., *11*, 79-82 (1999).

O. Barazani, A. Fait, Y. Cohen, S. Diminishtein, U. Ravid, E. Putievsky, E. Lewinsohn and J. Friedman, *Chemical variation among indigenous populations of Foeniculum vulgare var. vulgare in Israel.* Planta Med., *65*, 486-489 (1999).

E. Miraldi, *Composition of the essential oils from ten Foeniculum vulgare samples of fruits of different origin.* Flav. Fragr. J., *14*, 379-382 (1999).

B. Bellomaria, G. Valentini and N. Arnold., *L'Olio essenziale di Foeniculum vulgare Mill. ssp. vulgare.* Rivista Ital. EPPOS, *27*, 43-48 (1999).

M. Braun and G. Franz, Quality criteria of bitter fennel oil in the German pharmacopoeia. Pharm. Pharmacol. Letters, *9(2)*, 48-51 (1999).

B. Simándi, A Deák, E. Rónyai, Y-X. Gao, T. Veress, E. Lemberkovics, M. Then, A. Sass-Kiss and Z. Vámos-Falusi, *Supercritical carbon dioxide extraction and fractionation of fennel oil.* J. Agric. Food Chem., *47*, 1635-1640 (1999).

N. García-Jiménez, M. Pérez-Alonso and A. Velasco-Negueruela, *Chemical composition of fennel oil, Foeniculum vulgare Miller, from Spain.* J. Essent. Oil Res., *12*, 159-162 (2000).

S. Shatar and S. Altantsetseg, Essential oil composition of some plants cultivated in Mongolian climate. J. Essent. Oil Res., 12, 745-750 (2000).

G. Ruberto, M. Tiziana Baratta, S. G. Deans and H. J. D. Dorman, Antioxidant and antimicrobial activity of Foeniculum vulgare and Crithmum maritimum essential oils. Planta Med., 66, 687-693 (2000).

D. Ehlers, J. Färber, A. Martin, K-W. Quirin and D. Gerard, *Analysis of fennel oils, a comparison between the oils and a CO2 extract.* Deut. Lebensmit. Rundsch., *96*, 330-335 (2000).

R. Piccaglia and M. Marotti, Characterization of some Italian types of wild fennel (Foeniculum vulgare Mill.) J. Agric. Food Chem., 49, 239-244 (2001).

M-H. Wu, L-Y. Nie, Y. Liu, L. Zhang and L-P. Wei, *Study on chemical components of the essential oil of Foeniculum vulgare from different areas by GC/MS.* Yaowu Fenxi Zazhi, *21*, 415-418 (2001).

K-H. Kumeczka and V. Formacek, *Essential oils analysis by capillary gas chromatography and carbon-13 NMR spectroscopy.* 2nd Edn., 117-137, J. Wiley & Sons, NY (2002). ■