Progress in Essential Oils

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Ginger Oil and Extracts

Takeoka et al. (1990) determined that (-)-camphene was the predominant enantiomer in ginger oil. They also determined that the enantiomeric ratio of α-copaene was: (+)-α-copaene (81 percent): (-)-α-copaene (19 percent).

It was reported by König et al. (1994) that (+)-ar-curcumene and (-)-β-bisabolol were the predominant enantiomers in ginger oil.

Ginger oil produced from rhizomes grown in Madagascar was examined by Möllenbeck et al. (1997). The composition of this oil was found to be as follows:

α-pinene (7.2 percent)
camphene (30.8 percent)
β-pinene (1.0 percent)
sabinene (0.2 percent)
myrcene (3.3 percent)
1,8-cineole (4.9 percent)
β-phellandrene (5.9 percent)
γ-terpinene (12.3 percent)
p-cymene (0.9 percent)
citronellal (t)
2-nonanol (t)
linalool (0.5 percent)
borneol (1.8 percent)
neral (4.1 percent)
zingiberene (2.0 percent)
geranial (9.8 percent)
ar-curcumene (2.8 percent)
β-sesquiphellandrene (4.6 percent)
nerolidol* (0.6 percent)
zingiberenol* (1.0 percent)

*correct isomer not identified; trace (<0.1 percent)

This oil analyzed by Möllenbeck et al. was a most unusual ginger oil as the monoterpenoid compounds were in excess of the normally encountered major sesquiterpenoid compounds.

Martins et al. (2001) analyzed oils produced from ginger rhizomes cultivated in two locations in Sao Tomé. The composition of these two oils is presented in T-1.

Sekiwa et al. (2001) examined the existence of geraniol precursors in ginger root that on distillation would release geraniol or its aldehyde that had been biosynthesized from it. They found that geraniol-β-D-glucopyranoside, 6-O-α-L-arabinopyranosyl-β-D-glucopyranoside, 6-O-β-D-apiofuranosyl-β-D-glucopyranoside and 6-O-β-D-xylopyranosyl-β-D-glucopyranoside, which were all present in ginger root, were precursors of geraniol which could be oxidized to geranial by the root prior to its distillation.

Li et al. (2001) compared the composition of oils produced from both fresh and dried Chinese ginger. As can be seen from the results presented in T-2 the oil compositions were very similar. He et al. (2001) analyzed the volatiles produced by extracting ginger with methanol, ethyl acetate and hexane using GC/MS. The results of this study can be seen in T-3.

The oil of ginger produced from rhizomes cultivated in northeastern India was the subject of analysis by Sharma et al. (2002). The components found in this oil were as follows:

2-heptanol (0.6 percent)
camphene (1.2 percent)
6-methyl-5-hepten-2-one (2.2 percent)
1,8-cineole (11.8 percent)
limonene (0.5 percent)
cis-linalool oxide-furanoid (0.1 percent)
linalool (2.5 percent)
camphor (0.1 percent)
camphene hydrate (0.3 percent)
borneol (2.7 percent)
α-terpineol (1.7 percent)
nerol (0.1 percent)
neral (11.6 percent)
geraniol (3.8 percent)
geranial (14.5 percent)
linalool oxide-pyranoid* (0.5 percent)
isobornyl acetate (0.6 percent)

Percentage composition of two samples of ginger oil of Sao Tomé origin **T-1**

Compound	Sample 1	Sample 2
tricyclene	-	0.2
α-thujene	0.2	-
α-pinene	1.5	2.4
camphene	3.4	9.8
6-methyl-5-hepten-2-one	0.3	0.4
sabinene	-	0.2
β-pinene	0.5	0.3
myrcene	0.7	1.4
α-phellandrene	0.8	0.2
δ-3-carene	-	t
α-terpinene	-	t
p-cymene	-	t
β-phellandrene	1.7	2.8
1,8-cineole	5.0	9.7
limonene	1.0	1.3
trans-sabinene hydrate	-	0.1
terpinolene	0.4	0.7
2-nonanone	0.1	-
linalool	1.8	1.4
camphor	0.3	0.3
citronellal	-	0.5
menthone	0.3	-
isoborneol	0.1	-
borneol	3.8	4.0
terpinen-4-ol	-	0.6
myrtenal	0.4	0.2
myrtenol	-	0.1
neral	9.1	9.0
geraniol	1.6	2.2
geranial	13.4	16.0
bornyl acetate	-	0.3
2-undecanone	0.1	-
citronellyl acetate	-	0.1
neryl acetate	-	1.0
α-copaene	0.3	0.1
β-elemene	-	0.2
β-caryophyllene	-	0.1
β-farnesene*	0.6	-
α-himachalene	0.2	-
ar-curcumene	3.4	1.5
germacrene D	0.9	-
zingiberene	15.1	8.3
(E,E)-α-farnesene	4.6	2.3
ledene	1.7	-
β-bisabolene	4.1	1.3
β-sesquiphellandrene	7.3	3.1
elemol	0.9	-
(E)-α-bisabolene	0.7	-
(E)-nerolidol	1.4	-
guaiol	0.6	-
sesquisabinene hydrate*	0.5	-
cubenol	0.4	-
β-turmerol	0.3	-
10-epi-γ-eudesmol	0.4	-
β-eudesmol	2.0	0.6
(E,E)-farnesol	1.4	-

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

2-undecanone (0.1 percent)
geranyl formate (0.4 percent)
citronellyl acetate (0.5 percent)
geranic acid (5.5 percent)
geranyl acetate (3.2 percent)
ar-curcumene (15.6 percent)
selina-4(14),11-diene (1.0 percent)
(Z)-γ-bisabolene† (1.2 percent)
β-bisabolene (4.4 percent)
elemol (4.4 percent)
(E)-nerolidol (1.0 percent)
caryophyllene oxide (0.4 percent)
cis-sesquisabinene hydrate (0.8 percent)
trans-sesquisabinene hydrate (0.5 percent)
β-eudesmol (0.6 percent)
α-bisabolol oxide* (2.7 percent)

*correct isomer not identified; †this was noted by the authors as *cis*-γ-2-cardine (?)

Trace amounts (<0.1 percent) of terpinen-4-ol, p-cymen-8-ol, allo-aromadendrene and oplopanone were also reported to be found in this same sample of ginger oil. It should be pointed out that the absence of zingiberene, the ginger-specific sesquiterpene hydrocarbon, and β-sesquiphellandrene, a commonly encountered constituent, is surprising to say the least.

Ginger is grown in Cuba for its use in traditional medicines. As cultivar, geographical origin, maturity of rhizome at harvest, agro-climatic conditions experienced during its growth cycle and oil isolation process all have an influencing effect on the oil composition of ginger. Pino et al. (2004) produced an oil in the laboratory by hydrodistillation from comminuted dried rhizomes that were obtained from a single cultivar grown on a commercial plantation near Havana. This oil was found to possess the following composition:

hexanal (0.2 percent)
α-pinene (0.2 percent)
camphene (0.6 percent)
6-methyl-5-hepten-2-one (0.2 percent)
myrcene (0.1 percent)
octanal (0.1 percent)
β-phellandrene (0.1 percent)
limonene (0.5 percent)
1,8-cineole (0.4 percent)
rosefuran (0.2 percent)
isoborneol (0.8 percent)
borneol (0.2 percent)
α-terpineol (0.5 percent)
decanal (0.2 percent)
nerol (0.1 percent)
cis-carveol (0.3 percent)
linalyl acetate (0.2 percent)
cyclosativene (0.1 percent)
α-copaene (0.3 percent)
β-elemene (0.4 percent)
italicene (0.2 percent)

β-caryophyllene (0.1 percent)
trans-α-bergamotene (0.1 percent)
α-guaiene (0.1 percent)
allo-aromadendrene (1.1 percent)
γ-muurolene (0.7 percent)
germacrene D (0.9 percent)
ar-curcumene (22.1 percent)
β-selinene (1.7 percent)
zingiberene (11.7 percent)
α-muurolene (0.3 percent)
germacrene A (0.2 percent)
β-bisabolene (11.2 percent)
γ-cadinene (1.1 percent)
β-sesquiphellandrene (10.5 percent)
cadina-1,4-diene (2.5 percent)
(E)-γ-bisabolene (0.2 percent)
germacrene B (0.4 percent)
β-calacorene (0.1 percent)
(E)-nerolidol (1.6 percent)

Comparative percentage composition of the oils produced from fresh and dried Chinese ginger rhizomes **T-2**

Compound	Fresh ginger oil	Dried ginger oil
hexanal	0.02	0.15
2-heptanone	0.03	0.01
2-heptanol	-	0.08
tricyclene	0.30	0.23
α-pinene	4.70	3.72
camphene	15.16	13.50
sabinene	0.13	0.11
β-pinene	0.49	0.11
myrcene	1.50	2.39
α-phellandrene	0.24	0.32
δ-3-carene	0.02	0.02
p-cymene	0.14	0.14
limonene + β-phellandrene	11.20	17.99
1,8-cineole	4.44	17.99
γ-terpinene	0.04	0.04
terpinolene	0.29	0.53
linalool	-	0.22
camphor	0.12	0.13
borneol	-	3.10
terpinen-4-ol	-	0.39
α-terpineol	-	1.78
citronellol	-	0.30
neral	3.66	2.97
geranial	5.76	4.74
bornyl acetate	0.20	0.36
2-undecanone	0.36	0.41
δ-elemene	-	0.13
citronellyl acetate	0.60	0.63
α-copaene	0.19	0.36
neryl acetate	-	0.17
β-elemene	0.11	0.17
(E)-β-farnesene	0.13	0.49
allo-aromadendrene	-	0.10
ar-curcumene	5.41	4.64
zingiberene	8.26	9.46
γ-muurolene	8.26	9.46
β-bisabolene	3.63	2.95
7-epi-α-selinene	1.18	0.94
β-sesquiphellandrene	5.01	4.51
elemol	0.30	-
nerolidol*	0.23	0.19
T-cadinol	0.60	0.33
β-eudesmol	-	2.02
(E,E)-farnesol	0.25	-
dibutyl phthalate†	0.04	0.03

*correct isomer not identified; †plasticizer contaminant

Trace amounts (< 0.1 percent) of 2-hexanone, 2-heptanone, 2-heptanol, tricyclene, benzaldehyde, sabinene, β-pinene, 1-octen-3-ol, 6-methyl-5-hepten-2-ol, δ-3-carene, α-terpinene, p-cymene, (Z)-β-ocimene, 2-ethyl-5-methylfuran, (E)-β-ocimene, bergamal (2,6-dimethyl-5-heptenal), γ-terpinene, *cis*-linalool oxide (furanoid), terpinolene, 2-nonanone, nonanal, β-thujone, dehydrosabina ketone, terpinen-1-ol, 3-nonen-2-one, camphor, *cis*-β-terpineol, citronellal, p-methylacetophenone, myrtenol, (E)-2-decenal, methyl nerate, isobornyl acetate, 2-undecanone, carvacrol, δ-elemene, α-cubebene, citronellyl acetate, α-ylangene, longicyclene, β-bourbonene, dodecanal, β-gurjunene, γ-elemene, aromadendrene, α-humulene, *cis*-calamenene and *trans*-calamenene were also found in this same oil. It is interesting to note the lack of a lemon-like aroma in this oil by the fact that neither neral or geranial was found in this oil.

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Percentage composition of various extracts of ginger

T-3

Compound	Methanol extract	Ethyl acetate extract	Hexane extract
acetic acid	1.43	1.49	-
cyclohexane‡	-	1.19	1.7
ethyl propionate	-	2.62	-
hexanal	1.77	0.96	0.58
6-methyl-5-hepten-2-one	0.34	-	-
heptane‡	-	-	0.50
cyclohexanone	-	0.46	16.82
α-pinene	-	0.55	25.32
camphene	-	1.45	-
myrcene	0.66	0.76	0.73
borneol	3.02	3.24	2.85
linalool	0.81	-	0.26
2-hexenol*†	-	-	0.23
α-terpineol	1.88	1.23	0.90
geranial	-	2.63	2.64
geraniol	0.36	7.06	5.52
(E)-anethole	-	2.12	0.34
2-undecanone	-	0.38	0.23
citronellyl acetate	0.61	0.45	1.14
eugenol	0.66	5.13	1.56
diethyl adipate†	1.02	0.73	-
geranyl acetate	4.03	2.85	1.71
α-copaene	0.29	-	0.20
β-elemene	0.86	0.66	0.46
zingiberone†	-	-	0.23
β-caryophyllene	0.28	1.24	0.18
γ-bisabolene*†	0.42	-	0.22
ar-curcumene	3.68	2.73	1.62
γ-elemene	2.02	1.37	0.83
zingiberene	21.24	15.07	9.95
α-farnesene*	12.01	9.97	5.85
β-bisobolene	5.29	3.89	2.56
germacrene*	-	-	0.17
β-farnesene*	9.27	7.13	4.27
zingiberenol	2.12	0.46	0.22
(Z)-nerolidol	-	1.36	0.45
elemol	0.34	0.43	0.22
zingiberone	4.51	2.18	1.00
β-eudesmol	0.97	0.44	0.18
methyl hexadecanoate	0.35	0.35	-
hexadecanoic acid	0.94	1.64	0.30
(E)-nerolidol†	0.30	-	-
5-tetradecyne†	0.52	1.87	0.38
farnesol*	0.49	0.45	0.17
paradol*	0.81	0.80	0.38

*correct isomer not identified; †incorrect identification based on GC elution order; ‡solvent impurities or rhizome contaminants

J.A. Pino, R. Marbot, A. Rosado and A. Batista, *Chemical composition of the essential oil of Zingiber officinale Roscoe from Cuba*. J. Essent. Oil Res., **16**, 186-188 (2004).

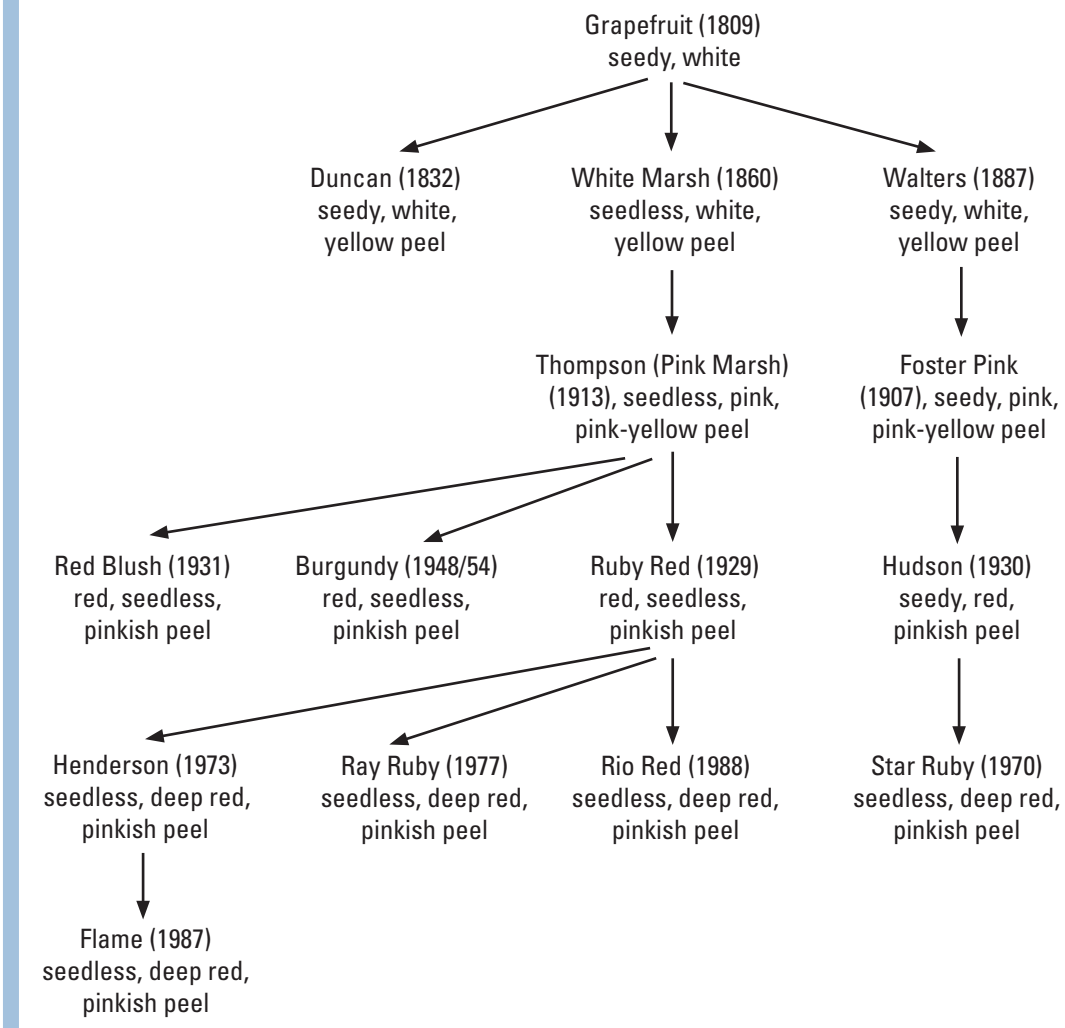
Grapefruit Oil

Florida is the major producer (ca. 60 percent) of grapefruit oil in the world. The year 2004 has been a particularly difficult year for the grapefruit plantations because of the widespread inclement weather experienced throughout the season. As a result, grapefruit oil has become scarce and high priced because supply is not sufficient for demand. Other areas that are producing the oil such as the west coast of the US, Israel, Mexico, Argentina, Cuba and South Africa are having to fill the gap.

Over the years studies on grapefruit oil have referred to the cultivars such as Duncan, Marshseedles, Foster Pink, Red Blush, etc. As a result, it is of interest to note the origin of these cultivars and their year of introduction (Saunt, 1990 and Jackson and Davies, 1999) (see F-1).

Kaiser (1993) compared the headspace and hexane wash of an entire grapefruit with a hexane extract of grapefruit peel. He found that the limonene and nootkatone contents of the headspace and hexane wash of the fruit were 2.0 percent and 50.0 percent, respectively, while the peel extract contained limonene (> 90 percent) and nootkatone (0.3 percent). The other constituents identified but not quantified in the headspace of grapefruit were (E)-β-ocimene, hexanol, β-elemene, valencene, 10-epi-α-selinene, caryophyllene oxide, (E)-nerolidol, intermedeol and 1,10-dihydronootkatone. The hexane wash of the entire fruit contained β-caryophyllene, hexyl hexanoate, valencene, 10-epi-α-selinene, octadecone, eicosane, docosane, 1,10-dihydronootkatone and (E,E)-farnesol in addition to limonene and nootkatone. Finally, Kaiser reported that the peel extract contained α-pinene, sabinene, myrcene, (E)-β-ocimene, octanal, nonanal,

Cultivars of grapefruit grown in Florida and their year of introduction **F-1**



Comparative percentage composition of Cuban grapefruit oil and some folded oils **T-4**

Compound	Grapefruit oil			
	Cold-pressed	Two-fold	Five-fold	Ten-fold
α-pinene	1.7	t	-	-
β-pinene	0.1	t	-	-
myrcene	6.9	3.3	0.8	0.3
limonene	84.8	81.6	71.3	64.0
nonanal + linalool	0.5	1.2	2.4	2.5
cis-limonene oxide	0.1	0.2	0.3	0.2
trans-limonene oxide	0.1	0.1	0.1	0.1
citronellal	0.2	0.4	0.8	0.8
α-terpineol	0.2	0.5	1.0	1.2
decanal	1.4	3.7	6.6	7.2
neral	0.2	0.8	1.6	1.8
geranial	0.4	0.9	1.8	2.2
neryl acetate	0.1	0.4	0.6	0.8
α-copaene	0.4	0.8	1.9	2.4
β-cubebene	0.5	1.0	2.2	3.4
β-caryophyllene	1.1	2.7	5.3	6.1
α-humulene	0.2	0.4	0.7	0.9
germacrene D	0.3	0.6	0.8	1.6
bicyclogermacrene	0.1	0.3	0.3	0.7
δ-cadinene	0.4	0.7	1.3	2.5
elemol	0.2	0.2	0.3	0.7
(E)-nerolidol	t	t	t	0.1
germacrene D-4-ol	t	t	t	0.1
nootkatone	t	t	0.1	0.1

t = trace (< 0.1 percent)

citronellal, octyl acetate, decanal, β-cubebene, linalool, β-caryophyllene, citronellyl acetate, α-terpineol, geranial, δ-cadinene, geranyl acetate, (E)-nerolidol, elemol, (E,E)-farnesal and (E,E)-farnesol as well as limonene and nootkatone.

The composition of folded oils of grapefruit of Cuban origin was determined by Pino and Sanchez (2000). The results of this comparative analysis can be seen in T-4.

Ogawa et al. (2000) determined that the peel and juice sac of *C. paradisi* contained 0.432 mg/g and 0.040 mg/g of auraptene, respectively.

Three cold pressed oils of grapefruit of Japanese origin were analyzed by Sawamwa (2000). The oil compositional range for these three oils was as follows:

α-pinene (0.48-0.58 percent)
β-pinene (0.06-0.08 percent)
sabinene (1.30-1.54 percent)
myrcene (1.76-1.82 percent)
limonene (93.61-94.41 percent)
(Z)-β-ocimene (0.01-0.02 percent)
(E)-β-ocimene (0.34-0.47 percent)
p-cymene (0-0.01 percent)

Comparative percentage composition of grapefruit oil of different origin with that of a hybrid grapefruit oil **T-5**

Compound	Grapefruit				Sweetie
	White (Cuba)	White (Israel)	White (Florida)	Pink (Florida)	(Israel)
α-pinene	0.51	0.55	0.48	0.53	0.58
sabinene	0.34	0.43	0.37	0.28	0.91
β-pinene	0.03	0.04	0.03	0.02	0.09
octanal	0.51	0.34	0.50	0.43	0.62
myrcene	1.87	1.88	1.92	1.90	2.00
limonene + β-phellandrene	94.5	94.4	93.4	94.3	94.0
octanol	0.05	0.03	0.04	0.03	0.02
nonanal	0.07	0.06	0.10	0.08	0.06
linalool	0.10	0.09	0.07	0.08	0.09
citronellal	0.06	0.07	0.10	0.07	0.06
α-terpineol	0.08	0.04	0.03	0.04	0.07
decanal	0.39	0.30	0.53	0.38	0.31
octyl acetate	0.04	0.03	0.07	0.06	0.01
neral	0.05	0.04	0.04	0.03	0.08
geranial	0.10	0.07	0.08	0.07	0.15
α-cubebene + geranyl acetate	0.04	0.05	0.05	0.05	0.02
α-copaene	0.10	0.09	0.14	0.10	0.09
β-cubebene + β-elemene	0.11	0.09	0.15	0.11	0.09
β-caryophyllene	0.28	0.28	0.32	0.29	0.13
α-humulene	0.04	0.04	0.05	0.04	0.03
germacrene D	0.08	0.06	0.10	0.08	0.10
bicyclogermacrene	0.03	0.02	0.04	0.03	0.02
germacrene A	0.02	0.03	0.03	0.03	0.03
δ-cadinene	0.11	0.09	0.15	0.11	0.09
germacrene C	t	t	-	-	0.04
germacrene B	-	-	-	-	0.02
nootkatone	t	0.28	0.37	0.30	t

t = trace (< 0.01 percent)

terpinolene (t-0.01 percent)
octanal (0.03-0.44 percent)
nonanal (0.01-0.03 percent)
2-octen-4-ol (0-0.01 percent)
trans-limonene oxide (0-0.06 percent)
trans-sabinene hydrate (0.01-0.03 percent)
octyl acetate (0-0.04 percent)
citronellal (0.03-0.08 percent)
α-copaene (0-0.07 percent)
decanal (0.14-0.21 percent)
β-cubebene (0.05-0.07 percent)
linalool (0.07-0.16 percent)
octanol (t-0.03 percent)
β-elemene (0.01-0.02 percent)
β-caryophyllene (0.27-0.32 percent)
α-humulene (t-0.03 percent)
citronellyl acetate (0-0.01 percent)
(E)-β-farnesene (0.01-0.06 percent)
neral (0.02-0.07 percent)
decyl acetate (0.01 percent)

Comparative major component composition of two different types of grapefruit oil **T-6**

Compound	Red grapefruit oil	White grapefruit oil
α-pinene	0.68	-
sabinene	-	0.66
myrcene	1.84	1.80
octanal	3.58	2.22
limonene	90.53	93.36
octyl formate	0.78	0.95
linalool oxide*	0.87	-
linalool	1.07	1.00
α-terpineol	0.66	-

*correct isomer not identified

α-terpineol (0.03-0.07 percent)
germacrene D (0.04-0.05 percent)
dodecanal (0.01-0.02 percent)
2,7-dimethyl-2,6-octadienol (t-0.01 percent)
α-muurolene (0-0.01 percent)
bicyclogermacrene (0-t)
geranial (0.04-0.08 percent)
cis-carvyl acetate (0-0.04 percent)
bicyclopentan-2-one (0-0.01 percent)
δ-cadinene (0.03-0.08 percent)
geranyl acetate (0.05-0.15 percent)
citronellol (0-0.01 percent)
perillaldehyde (0-0.01 percent)
nerol (0-t)
carvone (0-0.04 percent)
trans-carveol (0-0.01 percent)
α-muurolol (0-0.01 percent)
(E)-nerolidol (0-0.01 percent)
elemol (0.01-0.02 percent)
hexadecanol (0-0.01 percent)
β-sinensal (0-0.02 percent)
nootkatone (0.01-0.04 percent)

Trace amounts (< 0.01 percent) of camphene, α-phellandrene, β-phellandrene, γ-terpinene, *cis*-limonene oxide, nonyl acetate, γ-cadinene, terpinen-4-ol, undecanal, bicyclogermacrene and nerol were also found in one or more of the oils analyzed.

Feger et al. (2001) examined a number of commercial samples of grapefruit oil and compared them to an oil of a grapefruit hybrid known as "sweetie" or "oroblanco." This hybrid was produced from across between *C. paradisi* and *C. grandis* (L.) Osbeck. The results of the comparative study can be seen in T-5.

Feger et al. also characterized some additional constituents of the grapefruit hybrid (Sweetie) oil. A list of these components are as follows:

α-thujene (0.01 percent)
camphene (t)
α-phellandrene (0.03 percent)
p-cymene (t)
(E)-β-ocimene (0.01 percent)
γ-terpinene (t)
trans-sabinene hydrate (0.02 percent)
cis-linalool oxide† (t)
terpinolene (0.01 percent)
trans-linalool oxide† (t)
trans-p-mentha-2,8-dien-1-ol (t)
cis-limonene oxide + *cis*-p-mentha-2,8-dien-1-ol (0.01 percent)
trans-limonene oxide (t)
octanoic acid (t)
nonanol (t)
terpinen-4-ol (t)
trans-carveol (t)
citronellol (t)
nerol (t)
cis-carveol (0.01 percent)
carvone (t)
geraniol (t)
decanol + perillaldehyde (0.01 percent)
p-mentha-1(2),8-dien-10-ol (t)
undecanal (0.01 percent)
citronellyl acetate (t)
α-terpinyl acetate (t)
neryl acetate (0.01 percent)
δ-elemene (t)
p-mentha-1(2),8-dien-10-yl acetate (0.01 percent)
decyl acetate (0.01 percent)
dodecanal (0.04 percent)
γ-elemene (t)

β-copaene (0.02 percent)
α-guaiene (t)
(E)-β-farnesene (0.01 percent)
γ-muurolene (t)
α-muurolene (0.01 percent)
α-bulnesene (t)
cubebol (0.01 percent)
elemol (0.02 percent)
(E)-nerolidol (0.01 percent)
tetradecanal (t)
β-sinensal (0.01 percent)

[†]furanoid form; t = trace (< 0.01 percent)

Lin and Rouseff (2001) used a time-intensity GC-olfactometry procedure to determine that there were 38 aroma-active compounds in a Floridian cold-pressed grapefruit oil. The compounds in question were myrcene, limonene, 1,8-cineole, octanal, nonanal, (Z)-4-nonenal, methional, citronellal, (E)-2-nonenal (although authors mistakenly put (Z)-2-decenal in their report), decanal, (Z)-2-nonenal, linalool, octanol, mercapto-4-methyl-2-pentanol, terpinen-4-ol, (E)-2-decenal, neral, (E,E)-2,4-nonadienal, dodecanal, geranial, citronellol, nerol, (E,E)-decadienal, geraniol, *trans*-4,5-epoxy-(E)-2-nonenal, a β-ionone isomer (probably the (E)-form), *trans*-4,5-epoxy-(E)-2-decenal, 4-hydroxy-2,5-dimethyl-3(2H)-furanone (also known as Furaneol), 2(or 5)-ethyl-4-hydroxy-5(or 2)-methyl-3(2H)-furanone, eugenol, 4-vinylguaicol, β-sinensal, (3S,3aS,7aR)-3a,4,5,7a-tetrahydro-3,6-dimethylbenzofuran-2(3H)-one, (wine lactone), undecanoic acid, nootkatone and two unknown compounds. The authors pointed out that the identifications of *trans*-4,5-epoxy-2-nonenal, 2(or 5)-ethyl-4-hydroxy-5(or 2)-methyl-3(2H)-furanone, wine lactone and undecanoic acid were tentative. Lin and Rouseff concluded that the most important aroma-impact components of the oil were octanal, dodecanal, geranial, β-sinensal, linalool, geraniol, nootkatone, 1,8-cineole, *trans*-4,5-epoxy-(E)-2-decenal, 4-hydroxy-2,5-dimethyl-3(2H)-furanone and the unsaturated aldehydes such as (Z)-4-nonenal, (Z)-2-nonenal, (E)-2-nonenal, (Z)-2-decenal, (E)-2-decenal, (E,E)-2,4-nonadienal, (E,E)-2,4-decadienal. It is unfortunate that the authors did not present any quantitative data so that the importance of their impact could be estimated by dividing their concentration by their odor threshold.

The volatile constituents found in the peel of fresh grapefruit (Star Ruby cultivar) were the subject of analysis by Garcel et al. (2002). The components identified were as follows:

α-pinene (84)[a]
α-thujene (1)
camphene (< 1)
hexanal (< 1)
β-pinene (5)
sabinene (66)
myrcene (275)
limonene (14880)
β-phellandrene (19)
1,8-cineole (38)
(E)-2-hexenal (< 1)
(Z)-β-ocimene (1)
γ-terpinene (1)
(E)-β-ocimene (29)
terpinolene (1)
octanol (53)
nonanal (5)
citronellal (7)
decanal (25)
linalool (22)
cis-α-bergamotene (3)
β-caryophyllene (40)
α-humulene (6)
(E)-β-farnesene (6)
neral (7)
α-terpineol (12)
germacrene D (9)
neryl acetate (< 1)
β-bisabolene (4)
geranial (11)
δ-cadinene (17)
geranyl acetate (15)
citronellol (3)
geraniol (4)
β-sinensal (6)
nootkatone (29)

[a] = μg/g (fresh weight)

The hydrodistilled peel oils of red and white grapefruit grown in Venezuela were analyzed by Gonzalez de (2002) for major components. The results of this study can be seen in T-6.

Twenty-six samples of grapefruit oil were studied by Attenuated Total Reflectance Fourier-Transform Infrared Spectroscopy (ATR/FT-IR) and Near Infrared-Fourier Transform Raman Spectroscopy (NIR/FT-RS) by Schulz et al. (2002). They showed that through the application of Principal Component Analysis (PCA) to the spectral data, grapefruit oil could be clustered away from any other citrus oil. Through the use of cross-validation statistics a Partial Least Square (PLS) algorithma high quality prediction of the oil composition was reported. The authors noted that both ATR/FT-IR and NIR/FT-RS have the potential to replace existing analytical procedures because they could be incorporated on-line during isolation and concentration processes such as distillation or extraction.

Veriotti et al. (2002) examined the use of fast GC

coupled with a time-of-flight mass spectrometer to analyze a commercial oil of grapefruit. The oil was found to contain the following constituents:

α-pinene (1.37 percent)
β-pinene (1.27 percent)
myrcene (3.57 percent)
limonene (89.31 percent)
δ-2-carene† (0.16 percent)
octanal (0.23 percent)
linalool (0.37 percent)
verbenene† (t)
3-casen-2-ol† (t)
nonanal (t)
perillyl alcohol (0.23 percent)
limonene oxide* (0.14 percent)
α-terpineol (0.23 percent)
dihydrocarveol (t)
nerol (t)
carveol* (t)
octyl acetate (t)
decanal (0.18 percent)
neral (t)
carvone (t)
geranial (0.51 percent)
β-caryophyllene (0.73 percent)
geranyl acetate† (0.15 percent)
ocimene† (t)
α-humulene (t)
germacrene D (t)
cadinene* (t)
cadinene* (0.2 percent)
calamenene* (t)
himachalene*† (t)
nootkatone (0.14 percent)

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

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Chirality of Grapefruit

Mosandl et al. (1990) used multidimensional GC heart-cutting from a Carbowax 20 pre-column and a heptakis-(2,3,6-tri-O-methyl)-β-cyclodextrin chiral GC column to determine the enantiomeric distribution of α-pinene, β-pinene and limonene in two samples of grapefruit oil. The distribution found was as follows:

(1R,5R)-(+)-α-pinene (99-100 percent): (1S,5S)-(-)-α-pinene (0-1 percent)
(1R,5R)-(+)-β-pinene (63-66 percent): (1S,5S)-(-)-β-pinene (34-37 percent)
(4R)-(+)-limonene (ca. 100 percent): (4S)-(-)-limonene (trace)

Kreis et al. (1991) used the same separational system as Mosandl (1990) to characterize the enantiomeric distribution of the same three monoterpene hydrocarbons in lab-prepared grapefruit oil from one of the red grapefruit cultivars and from a grapefruit hybrid (Sweetie) oil. The enantiomeric distributions found for both the grapefruit oil and Sweetie oil are combined because of the similarity between them.

(1R,5R)-(+)-α-pinene (ca. 100 percent): (1S,5S)-(-)-α-pinene (0-trace)
(1R,5R)-(+)-β-pinene (38-41 percent): (1S,5R)-(-)-β-pinene (59-62 percent)
(4R)-(+)-limonene (ca. 100 percent): (4S)-(-)-limonene (0-trace)

It is possible that Kreis et al. had an error in their paper as the enantiomeric distribution of β-pinene shown above is the opposite to that presented in the Mosandl report and as they are mostly the same authors.

The enantiomeric distribution of four selected compounds in cold-pressed grapefruit oil was determined with six replications by Coleman et al. (1998) using chiral GC. The results of this study were found to be as follows:

(1R,5R)-(+)-α-pinene (93.40-94.35 percent): (1S,5S)-(-)-α-pinene (5.65-6.60 percent)
(1R,5R)-(+)-β-pinene (80.24-81.04 percent): (1S,5R)-(-)-β-pinene (18.96-19.76 percent)
(4R)-(+)-limonene (98.98-99.03 percent): (4S)-(-)-limonene (0.97-1.02 percent)
(3S)-(+)-linalool (31.47-32.62 percent): (3R)-(-)-linalool (67.38-68.53 percent)

Hara et al. (1999) used chiral GC to characterize the enantiomeric distribution of three monoterpene hydrocarbons and three oxygenated terpenoid constituents of two samples of grapefruit oil. A summary of their results can be seen as follows:

(1R,5R)-(+)-α-pinene (99.7 percent): (1S,5S)-(-)-α-pinene (0.3 percent)
(1R,5R)-(+)-β-pinene (62.0-76.8 percent): (1S,5R)-(-)-β-pinene (23.2-38.0 percent)
(4R)-(+)-limonene (99.0-99.2 percent): (4S)-(-)-limonene (0.8-1.0 percent)
(3S)-(+)-linalool (74.5-76.6 percent): (3R)-(-)-linalool (23.4-25.5 percent)
(4R)-(+)-α-terpineol (96.7-98.8 percent): (4R)-(-)-α-terpineol (1.2-3.3 percent)
(3R)-(+)-citronellal (78.6-83.4 percent): (3S)-(-)-citronellal (16.6-21.4 percent)

Cold-pressed oils of the Red Blush and Marsh grapefruit cultivars grown in Japan were subjected to chiral GC by Mitiku et al. (2001). The enantiomeric distribution of the four major monoterpene hydrocarbons were found to be as follows:

(4R)-(+)-limonene (99.46 percent): (4S)-(-)-limonene (0.54 percent)
(1R,5R)-(+)-α-pinene (99.15-99.45 percent): (1S,5S)-(-)-α-pinene (0.55-0.85 percent)
(1R,5R)-(+)-sabinene (98.37-98.39 percent): (1S,5S)-(-)-sabinene (1.61-1.63 percent)
(1R,5R)-(+)-β-pinene (63.79-72.44 percent): (1S,5R)-(-)-β-pinene (27.56-36.21 percent)

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