Progress in Essential Oils

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Tea Tree Oil

Tea tree oil has been produced commercially since the late 1920s. Until the 1980s, the industry in Australia produced 5-15 metric tonnes per annum (Davis 1999). By the beginning of the 21st century, this level of production had increased to ca. 300 metric tonnes. As a result, the composition, existence of chemotypes and genuineness of the oil have become subjects of considerable study.

According to the International Standard for tea tree oil (Anon 1996), the compositional requirements for this oil of *Melaleuca alternifolia* Cheel are as follows:

α-pinene (1.0-6.0 percent)
sabinene (t-3.5 percent)
α-terpinene (5.0-13.0 percent)
limonene (0.5-4.0 percent)
1,8-cineole (0-15.0 percent)
γ-terpinene (10.0-28.0 percent)
p-cymene (0.5-12.0 percent)
terpinolene (1.5-5.0 percent)
terpinen-4-ol (> 30.0 percent)
α-terpineol (1.5-8.0 percent)
aromadendrene (t-7.0 percent)
δ-cadinene (t-8.0 percent)
globulol (t-3.0 percent)
viridiflorol (t-1.5 percent)

t = trace (< 0.5 percent)

Homer et al. (2001) examined the natural variation of tea tree oil produced from 615 individual trees. Analyses of the oils revealed the existence of six chemotypes: terpinen-4-ol-rich, 1,8-cineole-rich and terpinolene-rich, while the other three were all 1,8-cineole-rich but differed in the terpinolene or terpinen-4-ol levels.

The content of six selected constituents of eight commercial samples of tea tree oil was found by Mori et al. (2002) to be:

α-terpinene (4.71-11.30 percent)
limonene (0.52-1.57 percent)
1,8-cineole (2.76-4.70 percent)
γ-terpinene (5.71-23.24 percent)
p-cymene (2.29-6.10 percent)
terpinen-4-ol (38.07-46.00 percent)

Hayes and Markovic (2002) reported that the major constituents of Australian tea tree oil were:

α-pinene (1.8 percent)
α-terpinene (8.6 percent)
1,8-cineole (4.6 percent)
γ-terpinene (18.2 percent)
p-cymene (3.0 percent)
terpinolene (3.0 percent)
terpinen-4-ol (42.8 percent)
α-terpineol (3.5 percent)

Southwell and Russell (2002) analyzed the oils produced from cotyledon leaves and mature leaves of the main three chemotypes (terpinen-4-ol-type, 1,8-cineole-type, terpinolene-type). The compositions of these oils can be seen in T-1.

The existence of six chemotypes of tea tree oil was disputed by Shelton et al. (2002). They found that the mixed chemotypes that were rich in 1,8-cineole with varying levels of terpinolene and terpinen-4-ol could have arisen from cross-pollination (hybridization) of the 1,8-cineole-type with either the terpinen-4-ol-type or the terpinolene-type, as intermediate forms were found in regions where cross-pollination could have taken place.

Zabaras et al. (2002) compared the compositions of the oils obtained from 15 samples of mature leaves and 16 samples of young leaves obtained from 2-year-old regrowth trees. These results are shown in T-2.

Percentage composition of cotyledon (C) leaf oils and mature (M) leaf oils of the terpinen-4-ol, 1,8-cineole and terpinolene chemotypes of *Melaleuca alternifolia* **T-1**

Compound	Terpinen-4-ol-type		1,8-Cineole-type		Terpinolene-type	
	C-oil	M-oil	C-oil	M-oil	C-oil	M-oil
α-thujene	0.7	1.0	0.4	0.1	t	1.0
α-pinene	7.4	2.6	15.5	3.4	t	1.3
sabinene	0.2	0.3	t	0.4	t	-
β-pinene	12.0	0.7	23.3	0.6	0.8	0.3
myrcene	t	0.9	1.9	2.1	0.9	1.4
α-phellandrene	1.1	0.5	2.2	0.2	t	3.2
α-terpinene	0.9	10.5	-	0.3	t	0.8
p-cymene	0.1	1.5	-	-	t	-
limonene	0.8	0.9	5.9	8.6	1.5	2.6
β-phellandrene	0.5	1.0	-	0.2	0.5	0.8
1,8-cineole	0.5	2.0	37.0	66.1	12.5	13.5
γ-terpinene	2.2	21.5	2.4	0.9	2.0	2.8
trans-sabinene hydrate	0.2	t	-	-	-	-
terpinolene	27.3	3.6	10.9	1.0	25.4	55.3
linalool	0.3	0.1	-	0.1	-	-
cis-sabinene hydrate	1.3	t	-	-	-	-
terpinen-4-ol	1.0	37.4	1.1	2.0	0.4	1.2
trans-piperitol	0.3	t	-	-	-	-
α-terpineol	0.4	2.6	4.7	7.6	1.2	2.3
cis-piperitol	0.2	t	-	-	-	-
β-caryophyllene	0.9	0.6	0.6	0.2	1.1	0.6
aromadendrene	1.1	1.8	0.8	1.1	0.9	1.8
allo-aromadendrene	1.0	0.7	1.2	0.4	1.2	0.6
ledene	3.0	1.3	1.9	1.1	1.6	1.1
bicyclogermacrene	4.3	0.8	0.8	0.1	0.6	0.2
δ-cadinene	0.6	1.5	t	0.6	t	1.3
globulol	1.0	0.5	1.3	0.2	0.7	0.6
viridiflorol	0.5	0.2	0.6	0.2	0.6	0.2

t = trace (< 0.1 percent)

Furthermore, the authors found that the rupture of oil glands on the leaves caused by mechanical damage caused an initial oil loss; however, most of this loss was recovered after 48 h.

Russell and Southwell (2002) showed that the higher concentrations of α- and β-pinene and terpinolene and lower concentrations of sabinene, *cis*-sabinene hydrate and terpinen-4-ol that were found in young seedling oils were changed to that of a more acceptable oil composition after about six weeks' growth. This constituent concentration variation reveals that data extrapolation of seedling oils to determine mature leaf oil data can lead to incorrect interpretation of the potential oil quality of the seedling. Throughout the past 20-plus years, tea tree has been grown on plantations for commercial oil production (Lee et al. 2002). These plantations are grown from seeds collected from trees found in their natural habitat in Australia. A survey of the plantations reveals that there is a wide range in plant morphology, oil yield and composition. As a result of examining 40 separate populations distributed in either warm, moist coastal lowland or in cold, dry highland catchments, they found that although there were the expected tree size differences (smaller trees in highland catchment), the trees from the highland catchment populations had greater chemotype diversity than those of the lowland catchment. This information should prove useful to commercial tea tree growers and help them in the selection of seed sources for their plantations.

Kubeczka and Formacek (2002) subjected a commercial oil of tea tree to analysis by GC and ^{13}C-NMR. Through this analysis they determined that the following constituents were found in the oil:

α-pinene (2.79 percent)
α-thujene (0.92 percent)
β-pinene (0.76 percent)
sabinene (0.38 percent)
myrcene (0.85 percent)

Comparative percentage composition of tea tree oils produced from young leaves and mature leaves **T-2**

Compound	Young leaf oils	Mature leaf oils
α-thujene	0.50-0.70	0.36-1.10
α-pinene	1.41-1.82	2.00-3.18
sabinene	3.33-7.42	-
β-pinene	0.61-0.73	0.64-1.13
myrcene	0.61-0.94	0.79-1.95
α-terpinene	1.10-2.50	3.95-7.80
mixture	2.01-8.72	5.48-9.00
γ-terpinene	1.91-4.62	8.60-20.60
trans-sabinene hydrate	5.24-6.72	-
terpinolene	0.42-0.83	1.10-2.90
cis-sabinene hydrate	30.41-46.32	-
trans-p-menth-2-en-1-ol	0.21-0.36	0.10-0.75
cis-p-menth-2-en-1-ol	0.23-0.39	0.10-0.78
terpinen-4-ol	2.51-5.74	27.72-43.91
α-terpineol	0.61-1.73	2.01-6.46
trans-piperitol	0.32-0.54	0.50-1.90
sesquiterpenes	21.62-34.43	9.17-20.71

mixture = p-cymene, limonene, β-phellandrene and 1,8-cineole

α-phellandrene (0.38 percent)
α-terpinene (8.93 percent)
limonene (1.21 percent)
β-phellandrene (0.71 percent)
1,8-cineole (4.48 percent)
γ-terpinene (19.91 percent)
p-cymene (3.85 percent)
terpinolene (3.35 percent)
α-cubebene (0.05 percent)
trans-sabinene hydrate (0.11 percent)
α-ylangene (0.06 percent)
α-copaene (0.14 percent)
α-gurjunene (0.37 percent)
linalool (0.07 percent)
trans-p-menth-2-en-1-ol (0.25 percent)
β-caryophyllene (0.40 percent)
terpinen-4-ol (40.02 percent)
aromadendrene (0.96 percent)
cis-p-menth-2-en-1-ol (0.23 percent)
allo-aromadendrene (0.47 percent)
α-elemene (0.26 percent)
α-humulene (0.09 percent)
ledene or viridiflorene (0.70 percent)
α-terpineol (2.91 percent)
α-muurolene (0.21 percent)
bicyclogermacrene (0.38 percent)
δ-cadinene (1.37 percent)
cadina-1,4-diene (0.17 percent)
calamenene* (0.16 percent)
p-cymen-8-ol (0.08 percent)
cubenol (0.17 percent)
epi-cubenol (0.16 percent)
globulol (0.25 percent)
viridiflorol (0.11 percent)
guai-5-en-11-ol (0.09 percent)
spathulenol (0.08 percent)

*correct isomer not identified

Russell and Southwell (2003) reported that the 1,8-cineole-type accumulated 1,8-cineole and associated p-menthanes, such as limonene, terpinen-4-ol and α-terpineol, gradually as the number of leaf sets increased in seedlings. In contrast, a higher-than-expected concentration of α- and β-pinene and terpinolene occurred only in early leaf formation in seedlings. It is of interest to note that there were two stages of terpinolene accumulation in the seedlings of the terpinolene-type.

Shellie et al. (2003) analyzed six samples of tea tree oil obtained from different sources in Australia. A summary of their results can be seen as follows:

α-thujene (0.85-1.13 percent)
α-pinene (2.46-2.83 percent)
camphene (0.02 percent)
sabinene (0.03-0.62 percent)
β-pinene (0.71-0.80 percent)
myrcene (0.78-1.02 percent)
α-phellandrene (0.32-0.52 percent)
α-terpinene (8.53-10.57 percent)
o-cymene (0.03-0.05 percent)
p-cymene (2.47-3.15 percent)
limonene (1.56-2.09 percent)
1,8-cineole (2.49-3.22 percent)
(E)-β-ocimene (0-0.02 percent)
γ-terpinene (21.10-22.53 percent)
trans-sabinene hydrate (0-0.09 percent)
terpinolene (3.13-3.57 percent)
p-cymenene (0.05-0.08 percent)
cis-sabinene hydrate (0.01-0.18 percent)
linalool (0.05-0.07 percent)
cis-p-menth-2-en-1-ol (0.09-0.36 percent)
trans-sabinol (0.02-0.03 percent)
trans-p-menth-2-en-1-ol (0.06-0.23 percent)
citronellal (0-0.03 percent)
δ-terpineol (0-0.02 percent)
terpinen-4-ol (34.92-43.96 percent)
p-cymen-8-ol (0.04-0.07 percent)
α-terpineol (2.40-2.81 percent)
trans-piperitol (0.03-0.08 percent)
cis-sabinene hydrate acetate (0.03-0.11 percent)
α-fenchyl acetate (0-0.03 percent)
trans-myrtanal (0-0.03 percent)
cis-verbenyl acetate (0-0.06 percent)
trans-verbenyl acetate (0-0.04 percent)
cis-piperityl acetate (0.02-0.07 percent)
α-cubebene (0.04-0.06 percent)
isoledene (0.06-0.12 percent)
α-copaene (0.08-0.20 percent)
β-patchoulene (0.05-0.12 percent)
daucene (0.02-0.04 percent)
β-cubebene (0.02 percent)
α-gurjunene (0.31-0.68 percent)
β-cedrene (0.02-0.05 percent)
β-caryophyllene (0.30-0.68 percent)
β-gurjunene (0.06-0.11 percent)
γ-elemene (0.01-0.03 percent)

cedrane† (0.06-0.11 percent)
aromadendrene (0.10-2.03 percent)
α-himachalene (0.12-0.23 percent)
α-humulene (0.07-0.14 percent)
allo-aromadendrene (0.44-0.81 percent)
β-cadinene (0.23-0.59 percent)
germacrene D (0.04-0.09 percent)
valencene (0.08-0.14 percent)
viridiflorene (0.67-1.61 percent)
bicyclogermacrene (0.32-0.59 percent)
α-muurolene (0.10-0.23 percent)
γ-cadinene (0.02-0.04 percent)
δ-cadinene (0.82-1.96 percent)
citronellyl butyrate (0.17-0.39 percent)
cadina-1,4-diene (0.12-0.29 percent)
trans-longipinanol (0.06-0.14 percent)
spathulenol (0.06-0.17 percent)
globulol (0.18-0.60 percent)
cubeban-11-ol (0.09-0.27 percent)
viridiflorol (0.06-0.21 percent)
epi-cedrol (0.07-0.22 percent)
10-epi-γ-eudesmol (0.07-0.23 percent)
epi-cubenol (0.09-0.26 percent)
T-cadinol (0.03-0.06 percent)
cubenol (0.05-0.14 percent)
α-muurolol (0.02-0.06 percent)
3-thujopsanone (0.02-0.03 percent)

†doubtful natural occurrence

As part of a study on the antioxidant activity of tea tree oil, Kim et al. (2004) determined that the main constituents of the oil were:

α-thujene (0.8 ± 0.09 percent)
α-pinene (2.1 ± 0.23 percent)
β-pinene (0.5 ± 0.05 percent)
α-phellandrene (0.4 ± 0.02 percent)
α-terpinene (9.6 ± 0.77 percent)
limonene (0.8 ± 0.05 percent)
β-phellandrene (0.8 ± 0.03 percent)
γ-terpinene (20.6 ± 0.43 percent)
terpinolene (3.3 ± 0.14 percent)
terpinen-4-ol (43.2 ± 0.14 percent)

Using the 2,2-diphenyl-1-picrylhydrazyl assay, the authors determined that 10 µL/mL of tea tree oil in methanol had ca. 80 percent free radical scavenging activity that was equivalent to the antioxidant activity of BHT of 30 mMoles.

Finally, it is of interest to note that China now has entered the tea tree oil production business, as they have planted 200-300 ha in Guangxi Province (He 2005).

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Tea Tree Chiral Constituents

Reichling et al. (2001) examined the enantiomeric distribution of three components of tea tree oil. The ratios of these three components were reported to be as follows:

(1R,5R)-(+)-α-pinene (90-92 percent):(1S,5S)-(-)-α-pinene (8-10 percent)
(4R)-(-)-terpinen-4-ol (52-66 percent):(4S)-(+)-terpinen-4-ol (34-48 percent)
(4R)-(+)-α-terpineol (55-77 percent):(4S)-(-)-α-terpineol (23-45 percent)

Shellie et al. (2001) used two-dimensional gas chromatography using a

Enantiomeric distribution of selected constituents of tea tree oil **T-3**

Compound	Mature sample[a] oil (GC x GC)		Flush sample[b] oil (GC x GC)		Flush sample[b] oil (GC)	
	%(+)	%(-)	%(+)	%(-)	%(+)	%(-)
α-thujene	76.8	23.2	79.9	20.1	83.8	16.3
α-pinene	78.8	21.2	60.6	39.4	53.9	46.1
sabinene	> 90.0	nd	69.6	30.4	nq	nq
α-phellandrene	61.7	38.3	53.0	47.0	nd	nd
limonene	62.5	37.5	82.7	17.3	75.5	24.5
trans-sabinene hydrate	74.3	25.7	78.7	21.3	83.4	16.6
cis-sabinene hydrate	82.8	17.2	95.8	4.2	95.9	4.1
linalool	nq	nq	55.7	44.3	55.5	45.5
terpinen-4-ol	68.9	31.1	73.6	26.4	73.7	26.3
α-terpineol	72.6	27.4	76.6	23.4	77.6	22.4

[a]mature commercial oil; [b]high-pH distilled oil of young leaves; nd = constituent below detection limit; nq = not quantifiable

chiral column coupled with a nonchiral column to determine the enantiomeric distribution and compared the results with those obtained from a single-chiral GC analysis. The results of these analyses are presented in T-3.

Kreck et al. (2002) examined the use of the stir bar sorptive extraction (SBSE, known commercially as Twister), a technique that has a higher absorption level to solid-phase microextraction, on the volatiles emitted from tea tree oil using chiral GC. The results obtained from the oil were as follows:

(1R,5R)-(+)-α-pinene (86-91 percent):(1S,5S)-(-)-α-pinene (9-14 percent)
(1R,5R)-(+)-sabinene (60-63 percent):(1S,5S)-(-)-sabinene (37-40 percent)
(1R,5R)-(+)-β-pinene (58-65 percent):(1S,5S)-(-)-β-pinene (35-42 percent)
(4R)-(+)-α-phellandrene (37-40 percent):(4S)-(-)-α-phellandrene (53-60 percent)
(4R)-(+)-limonene (58-62 percent):(4S)-(-)-limonene (38-42 percent)
(3S)-(+)-linalool (63-70 percent):(3R)-(-)-linalool (30-37 percent)
(1S,4S)-(+)-terpinen-4-ol (65-70 percent):(1R,4R)-(-)-terpinen-4-ol (30-35 percent)
(1R,4R)-(+)-α-terpineol (69-78 percent):(1S,4S)-(-)-α-terpineol (22-31 percent)

For comparison purposes, the authors used the same SBSE technique to determine the enantiomeric distribution of the same compounds from living plants, as can be seen as follows:

(+)-α-pinene (90-94 percent):(-)-α-pinene (6-10 percent)
(+)-sabinene (63-70 percent):(-)-sabinene (30-37 percent)
(+)-β-pinene (32-42 percent):(-)-β-pinene (58-68 percent)
(+)-α-phellandrene (32-41 percent):(-)-α-phellandrene (59-68 percent)
(+)-limonene (61-69 percent):(-)-limonene (31-39 percent)
(+)-linalool (91-95 percent):(-)-linalool (5-9 percent)
(+)-terpinen-4-ol (21-31 percent):(-)-terpinen-4-ol (69-79 percent)
(+)-α-terpineol (81-86 percent):(-)-α-terpineol (14-19 percent)

Using a single enantioselective stationary-phase column, Shellie et al. (2004) examined the enantiomeric distribution of some selected constituents of six samples of tea tree oil. The distribution data is shown as follows:

(1R,5R)-(+)-sabinene (42-62 percent):(1S,5S)-(-)-sabinene (38-58 percent)
(1R,5R)-(+)-β-pinene (64-67 percent):(1S,5S)-(-)-β-pinene (33-36 percent)
(4R)-(+)-α-phellandrene (39-41 percent):(4S)-(-)-α-phellandrene (59-61 percent)
(3S)-(+)-linalool (52-68 percent):(3R)-(-)-linalool (32-48 percent)
(1S,4S)-(+)-terpinen-4-ol (68-69 percent):(1R,4R)-(-)-terpinen-4-ol (31-32 percent)
(1R,4R)-(+)-α-terpineol (74-75 percent):(1S,4S)-(-)-α-terpineol (25-26 percent)

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Angelica Root Oil

Using chiral GC as the method of analysis, Casabianca (1996) determined that the enantiomeric ratio of α-copaene in angelica root oil (ex *Angelica archangelica* L.) was: (+)-α-copaene (> 99 percent):(-)-α-copaene (< 1 percent).

An oil of angelica root of Polish origin was found by Gora et al. (1997) to contain the following major constituents:

α-pinene (25.0 percent)
α-phellandrene (5.7 percent)
limonene (7.3 percent)
p-cymene (8.3 percent)

Doneanu and Anitescu (1998) produced a volatile extract of *A. archangelica* from grated fresh roots obtained from plants cultivated in Romania. The extract, which was produced by supercritical fluid CO_2, was analyzed by GC/MS and found to contain the following constituents:

α-thujene (0.43 percent)
α-pinene (16.66 percent)
camphene (1.09 percent)
verbenene (0.57 percent)
sabinene (0.62 percent)
β-pinene (1.12 percent)
myrcene (3.91 percent)
δ-2-carene (0.13 percent)
α-phellandrene (11.27 percent)
δ-3-carene (8.69 percent)
α-terpinene (0.31 percent)
p-cymene (5.56 percent)
limonene (13.12 percent)
β-phellandrene (8.92 percent)
(Z)-β-ocimene (2.05 percent)
(E)-β-ocimene (5.43 percent)
γ-terpinene (0.64 percent)
terpinolene (0.78 percent)
p-cymenene (0.78 percent)
trans-verbenol (0.22 percent)
butyl-1,4-cyclopentadiene (0.19 percent)
α-phellandren-8-ol (0.20 percent)
(E,Z)-1,3,5-undecatriene (0.10 percent)
terpinen-4-ol (0.14 percent)
cuminyl alcohol (0.12 percent)
p-cymen-8-ol (0.10 percent)
sabina ketone (0.18 percent)
α-terpineol (0.22 percent)
myrtenal (0.41 percent)
sabinol* (0.23 percent)
carvotanacetone (0.19 percent)
phellandral (0.27 percent)
bornyl acetate (0.98 percent)
trans-verbenyl acetate (0.16 percent)
carvacrol (0.34 percent)
trans-piperityl acetate (0.14 percent)
α-terpinyl acetate (1.23 percent)
longicyclene (0.11 percent)
α-copaene (1.16 percent)
β-elemene (0.21 percent)
β-cedrene (0.11 percent)
β-caryophyllene (0.14 percent)
β-farnesene* (0.16 percent)
α-humulene (1.20 percent)
germacrene D (1.13 percent)
zingiberene (0.16 percent)
α-muurolene (0.59 percent)
β-bisabolene (1.13 percent)
δ-cadinene (0.31 percent)
α-copaen-11-ol (0.45 percent)
elemol (0.17 percent)
germacrene B (0.10 percent)
longiborneol (0.14 percent)
13-tridecanolide (0.82 percent)

Comparative percentage composition of the root oils produced from *Angelica archangelica* of Lithuanian origin **T-4**

Compound	A	B	C	D
α-thujene	0.1	0.2	0.3	0.2
α-pinene	17.5	20.2	13.7	11.2
camphene	1.2	0.8	0.9	0.9
sabinene	6.5	3.2	1.7	1.7
β-pinene	0.9	3.0	0.4	0.4
trans-m-mentha-2,8-diene	1.3	-	-	-
myrcene	2.9	1.9	3.0	2.4
α-phellandrene	2.5	8.6	7.4	5.4
δ-3-carene	16.1	13.9	11.4	10.6
α-terpinene	1.9	0.2	0.1	0.1
p-cymene	3.3	2.0	8.4	6.8
limonene	8.5	-	-	-
β-phellandrene	1.4	14.7	16.2	15.1
(E)-β-ocimene	0.4	0.1	0.6	0.4
γ-terpinene	2.4	1.0	0.7	0.7
terpinolene	2.1	1.6	1.3	1.1
p-cymenene	0.7	-	-	-
cis-p-menth-2-en-1-ol	0.3	-	-	-
trans-p-menth-2-en-1-ol	0.3	-	-	-
cis-verbenol	0.3	0.4	0.3	0.1
trans-verbenol	0.3	0.5	0.4	0.3
trans-p-mentha-1,5-dien-8-ol	0.1	0.2	0.4	0.2
menthol	0.1	0.2	0.1	0.2
terpinen-4-ol	1.2	0.9	0.4	0.3
p-cymen-8-ol	0.2	0.3	0.1	1.0
α-terpineol	0.2	0.2	0.2	0.4
cis-piperitol	0.1	-	0.1	1.0
myrtenal	0.2	0.1	0.1	0.6
myrtenol	0.1	0.1	0.1	0.5
trans-chrysanthenyl acetate	0.4	0.1	0.1	0.1
myrtenyl acetate	0.2	-	-	-
bornyl acetate	2.7	3.1	2.8	1.8
cuminyl alcohol	0.1	0.1	0.5	1.0
trans-sabinyl acetate	0.2	0.3	-	-
isoamyl benzoate	0.2	0.2	0.4	0.2
trans-carvyl acetate	0.1	t	0.1	0.1
δ-elemene	0.2	0.2	0.1	0.2
cis-carvyl acetate	-	-	0.2	t
α-copaene	0.3	0.5	0.3	0.7
β-cubebene	-	0.4	-	-
β-elemene	0.2	0.4	0.4	0.6
isocaryophyllene	0.2	0.2	0.1	0.4
β-cedrene	0.1	0.4	0.6	0.2
β-caryophyllene	0.1	0.2	0.5	1.2
γ-elemene	0.6	0.9	1.6	0.9
α-humulene	0.6	1.1	1.3	1.2
(E)-β-farnesene	0.2	0.4	0.1	0.3
γ-muurolene	0.2	0.2	0.5	0.2
germacrene D	0.2	0.6	0.6	0.4
β-selinene	t	0.1	0.3	0.1
bicyclogermacrene	0.1	0.4	0.2	0.1
zingiberene	0.1	0.3	0.7	0.3
α-muurolene	0.3	0.5	0.6	0.3
cuparene	0.2	0.1	0.3	0.1
β-bisabolene	0.3	0.7	1.7	2.3
γ-cadinene	0.2	t	0.4	0.1
δ-cadinene	0.3	0.4	0.6	0.3
cadina-1,4-diene	0.1	0.3	0.4	0.2
α-copaen-11-ol	1.6	0.4	0.8	0.5
elemol	0.4	0.8	0.9	0.2
germacrene B	0.1	0.2	0.2	0.2
α-copaen-8-ol	0.6	0.3	0.3	0.4
spathulenol	0.2	0.1	0.2	0.3
caryophyllene oxide	0.2	0.2	0.1	0.2
13-tridecanolide	1.7	1.5	2.0	2.9
humulene epoxide II	0.2	0.3	-	-
γ-eudesmol	0.1	0.2	0.1	0.1
α-muurolol	0.1	0.5	0.2	0.4
β-eudesmol	0.8	0.5	1.5	1.6
α-eudesmol	0.2	0.2	0.5	0.4
12-methyl-tridecanolide	0.2	0.2	0.4	0.5
7-epi-γ-eudesmol	0.2	0.1	0.5	0.4
bisabolone	0.3	t	0.2	0.4
15-pentadecanolide	2.7	3.2	2.1	2.2
16-hexadecanolide	0.1	0.1	0.1	0.1
17-heptadecanolide	0.3	0.4	0.3	0.4
osthole[a]	3.6	1.9	1.7	4.7

t = trace (< 0.1 percent); [a]also known as 7-methoxy-8-isopentenylcoumarin

β-eudesmol (0.17 percent)
12-methyl-13-tridecanolide (0.33 percent)
15-pentadecanolide (0.49 percent)
osthole (0.23 percent)

*correct isomer not identified

In addition, trace amounts (0.09 percent or less) of isobutanal, 2-methyl-3-buten-2-ol, 2-methylfuran, isovaleraldehyde, 2-methyl-2-butenol, hexanal, isovaleric acid, 2-vinyl-5-methylfuran, 2-methylbutyric acid, 2-pentenoic acid, 2-heptanone, tricyclene, 2-methyl-5-isopropylfuran, 2,4-thujadiene, α-fenchene, hexanoic acid, o-cymene, m-cymene, benzyl formate, a dimethylstyrene isomer, 6-camphenone, linalool, perillene, p-mentha-1,3,8-triene, (Z,Z)-allo-ocimene, amyl benzoate, thujyl alcohol, verbenone, a carveol isomer, a chrysanthenyl acetate isomer, (Z)-3-hexenyl isovalerate, α-phellandrene epoxide, cuminaldehyde, carvone, piperitone, thymol, *cis*-pinocarvyl acetate, *trans*-carvyl

acetate, α-cubebene, eucarvone, *cis*-carvyl acetate, tetradecane, sativene, octyl isovalerate, thujopsene, γ-muurolene, β-selinene, spathulenol, caryophyllene oxide, hexadecane, α-copaen-8-ol, cedrol, dehydro-aromadendrane, γ-eudesmol, α-muurolol, 3-butylidene phthalide, dimyrcene and 17-heptadecanolide also were found in this extract.

The fresh roots of *A. archangelica* that were grown in Canada were dried, comminuted and steam distilled to produce an oil in 0.17 percent that was subjected to analysis by a combination of GC and GC/MS by Lopes et al. (2004). The constituents identified in this oil were as follows:

α-thujene (0.40 percent)
α-pinene (15.70 percent)
camphene (0.44 percent)
thuja-2,4(10)-diene (0.10 percent)
sabinene (0.68 percent)
β-pinene (1.07 percent)
myrcene (2.81 percent)
δ-2-carene (0.12 percent)
α-phellandrene (19.11 percent)
δ-3-carene (5.71 percent)
α-terpinene (0.11 percent)
p-cymene (5.03 percent)
limonene (5.91 percent)
β-phellandrene (26.61 percent)
(Z)-β-ocimene (0.88 percent)
(E)-β-ocimene (2.28 percent)
γ-terpinene (0.26 percent)
isoterpinene (0.31 percent)
terpinolene (0.51 percent)
trans-sabinene hydrate (0.06 percent)
cis-p-menth-2-en-1-ol (0.10 percent)
trans-p-menth-2-en-1-ol (0.07 percent)
trans-verbenol (0.16 percent)
terpinen-4-ol (0.09 percent)
cryptone (0.16 percent)
bornyl acetate (0.14 percent)
α-copaene (0.91 percent)
β-caryophyllene (0.20 percent)
β-copaene (0.18 percent)
α-humulene (1.13 percent)
γ-muurolene (0.64 percent)
α-muurolene (0.37 percent)
β-bisabolene (0.20 percent)
δ-cadinene (0.25 percent)
germacrene B (0.35 percent)
humulene epoxide II (0.12 percent)
13-tridecanolactone (0.65 percent)
12-methyl-13-tridecanolactone (0.06 percent)
15-pentadecanolactone (0.53 percent)
17-heptadecanolactone (0.06 percent)

In addition, trace amounts (< 0.01 percent) of hexanal, heptanal, *cis*-verbenol, borneol, α-terpineol, *cis*-piperitol and *trans*-piperitol also were found in this oil. The authors also collected five fractions throughout equal time periods during the duration of the steam-distillation process. Analyses of these fractions led to the further identification of *cis*-sabinene hydrate, 14-tetradecanolactone, 16-hexadecanolactone and 14-methyl-15-pentadecanolactone. This latter compound, which also is known as muscolide, was identified for the first time in angelica root oil.

Nivinskiene et al. (2005) analyzed oils produced from angelica roots that were collected in Lithuania from wild-growing plants from four different regions. The oils were produced from regions A, B and C throughout four different growing seasons, while the oil from region D was a single oil produced from one collection only. A summary of the results of this study can be seen in T-4.

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Pimento Berry and Leaf Oil

The composition of a steam-distilled oil of Mexican *Pimenta dioica* fruit was compared with a water-distilled oil and a supercritical fluid CO_2 extract of the same batch of pimento. The results of this study, conducted by Garcia-Fajardo et al. (1997), can be found in T-5.

Pino et al. (1997) examined an oil, a hexane extract and a supercritical fluid CO_2 extract of pimento leaves of Cuban origin. The comparative compositions of the two extracts are reported in T-6. In contrast, the leaf oil was found to contain the following constituents:

α-pinene (0.56 percent)
myrcene (0.19 percent)
α-phellandrene (1.12 percent)
p-cymene (1.87 percent)
1,8-cineole (14.50 percent)
limonene (0.10 percent)
γ-terpinene (0.56 percent)
terpinolene (1.38 percent)
menthol (0.56 percent)
methyl chavicol (0.09 percent)
carvone (0.10 percent)

Percentage composition of two oils and a supercritical fluid CO_2 extract of pimento fruit (berries) **T-5**

Compound	Steam-distilled oil	Water-distilled oil	Supercritical extract
α-pinene	t	0.1	t
sabinene	0.3	0.3	0.2
β-pinene	t	0.2	t
myrcene	17.7	16.5	6.0
δ-3-carene	t	t	-
α-terpinene	t	0.1	t
p-cymene	0.2	t	t
limonene	0.7	t	t
(Z)-β-ocimene	t	1.2	0.9
γ-teprinene	1.1	0.2	t
terpinolene	t	0.6	0.4
β-caryophyllene	6.2	2.7	5.2
α-humulene	1.1	0.2	0.2
γ-cadinene	0.6	0.1	0.2
β-selinene	t	t	t
α-selinene	0.4	t	t
δ-cadinene	t	t	t
1,8-cineole	1.9	4.1	1.3
linalool	0.4	t	t
terpinen-4-ol	0.3	0.5	0.3
methyl salicylate	t	t	-
α-terpineol	0.7	0.7	0.4
eugenol	17.3	8.3	14.9
methyl eugenol	48.3	62.7	67.9

t = trace (< 0.1 percent)

Comparative percentage composition of a hexane extract and a supercritical fluid CO_2 extract of pimento leaves of Cuban origin **T-6**

Compound	Hexane extract	CO_2 extract
menthol	1.47	-
methyl chavicol	-	0.31
carvone	1.04	-
thymol	2.72	1.82
carvacrol	2.21	1.08
eugenol	91.68	93.87
β-caryophyllene	-	1.79
α-humulene	-	0.35
α-amorphene	-	0.05
α-muurolene	-	0.05
calamenene* + γ-cadinene	-	0.05
caryophyllene oxide	-	0.07
T-cadinol	0.58	0.17
α-cadinol	0.29	0.37

*correct isomer not identified

Comparative percentage composition of a supercritical fluid CO_2 extract and oil of pimento leaves **T-7**

Compound	Extract	Oil
myrcene	0.1	0.1
limonene	0.1	0.2
1,8-cineole	1.0	0.8
(E)-β-ocimene	0.1	0.1
methyl salicylate	-	0.2
geraniol	-	0.2
eugenol	77.9	45.2
α-copaene	0.8	0.6
β-bourbonene	0.2	0.3
1,7-di-epi-α-cedrene	0.2	0.3
longifolene	< 0.1	-
β-caryophyllene	5.1	8.9
β-gurjunene	0.2	0.4
α-humulene	2.3	5.4
allo-aromadendrene	0.5	1.0
β-cadinene†	0.1	0.2
γ-muurolene	0.5	1.1
germacrene D	0.4	1.9
β-selinene	0.2	0.4
cis-β-guaiene	0.1	0.3
valencene	0.1	0.3
α-selinene	0.1	0.5
α-muurolene	0.5	1.2
γ-cadinene	0.4	0.9
δ-cadinene	1.7	3.8
trans-calamenene	0.3	0.7
cadina-1,4-diene	-	0.2
α-cadinene	0.1	0.2
α-calacorene	-	0.2
ledol	-	0.3
spathulenol	-	0.3
caryophyllene oxide	0.5	1.4
globulol	-	0.6
cis-β-elemenone	-	0.4
widdrol	-	0.6
humulene epoxide II	0.2	1.6
1,10-di-epi-cubenol	0.1	0.7
γ-eudesmol	-	2.0
T-muurolol	-	3.2
α-muurolol	1.1	1.5
α-cadinol	1.0	5.9
cadalene	-	0.3
(Z,E)-farnesol	-	0.6
nonadecane	-	0.5
squalene	4.1	0.3
triacontane	-	0.5
dotriacontane	-	2.6

†incorrect identification based on GC elution order

thymol (1.00 percent)
carvacrol (1.00 percent)
eugenol (28.04 percent)
β-caryophyllene (1.00 percent)
α-humulene (10.12 percent)
allo-aromadendrene (2.13 percent)
α-amorphene (2.77 percent)
α-muurolene (1.76 percent)
calamenene* + γ-cadinene (11.12 percent)
δ-cadinene (5.49 percent)
cadina-1,4-diene (0.49 percent)
α-calacorene (1.23 percent)
caryophyllene oxide (2.69 percent)
α-eudesmol (0.52 percent)
β-eudesmol (0.82 percent)
T-cadinol (6.64 percent)
α-cadinol (4.94 percent)

*correct isomer not identified

Marongiu et al. (2005) compared the analyses of pimento leaf oil and a supercritical CO_2 extract of the same batch of leaves of *Pimenta dioica*. The results of this comparative study are presented in T-7.

Marongiu et al. also determined that the major waxes found on the pimento leaves were:

octacosane (11.5 percent)
nonacosane (2.6 percent)
triacontane (52.8 percent)
hentriacontane (3.3 percent)
dotriacontane (29.8 percent)

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