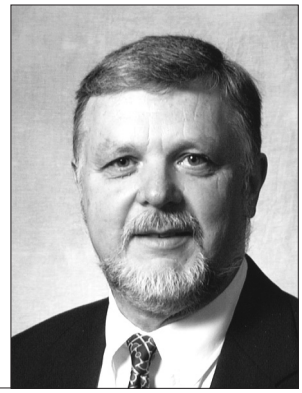

Progress in Essential Oils

By Brian M. Lawrence, R.J. Reynolds Tobacco Company

Pepper Oil

In 1993, Zhu et al. compared the composition of white and black pepper oil produced from the dried fruit of *Piper nigrum* grown in Hainan (China). A summary of the analyses can be seen in Table I.

This same year, Gopalakrishnan et al. (1993) examined the composition of four newly selected cultivars of black pepper that are currently being grown in Kerala (India). Using both GC and GC/MS analyses the oil compositions were characterized as shown in Table II.

Although linalool is a minor constituent of pepper oil, Casabianca and Graff (1996) determined that its enantiomeric distribution in pepper oil produced in Madagascar was as follows:

(3R)-(-)-linalool (81-87%): (3S)-(+)-linalool (13-19%)

Also in 1996, Casabianca examined the enantiomeric distribution of two monoterpene hydrocarbons (δ-3-carene and α-thujene) in black pepper oil using chiral GC. The ratios were found to be as follows:

(+)-δ-3-carene (1%) : (-)-δ-3-carene (99%)
(+)-α-thujene (3%) : (-)-α-thujene (97%)

Möllenbeck et al. (1997) analyzed an oil of black pepper produced from dried fruit grown in Madagascar. Using capillary GC (FID) and GC/MS, the combination of this oil was determined to be as follows:

α-pinene (25.4%)
camphene (0.8%)
β-pinene (15.7%)
δ-3-carene (10.8%)
limonene (21.0%)
p-cymene (1.0%)
δ-elemene (1.5%)
linalool (0.6%)h
(Z)-ocimenol (0.9%)
p-cymen-8-ol (t)
methyl eugenol (0.3%)
eugenol (0.5%)

t=trace (<0.1%)

The authors found that the enantiomeric distributions of limonene and linalool were as follows:

(4R)-(+)-limonene (62%) : (4S)-(-)-limonene (38%)
(3R)-(-)-linalool (91%) : (3S)-(+)-linalool (9%)

Korany and Amtmann (1997) examined the oils of Ampro (Brazilian), Lampong (Indonesian), Sungai Budi (Indonesian), Sarawak (Malaysian) and Saigon (Vietnamese) black pepper and Muntok (Indonesian) and Sarawak (Malaysian) white pepper. Although, unfortunately, the authors did not quantitate their results, they listed the components identified as follows:

α-thujuene
α-pinene
α-fenchene
camphene
sabinene
β-pinene
myrcene
allo-ocimene*†
α-cubebene
α-chamigrene†
10-epi-zonarene†
α-copaene
eremophilene†
β-gurjunene
α-gurjunene
β-caryophyllene

Table I. Percentage composition of Chinese black and white pepper oils

Compound	Black Pepper Oil	White Pepper Oil
α-thujene	0.10	-
α-pinene	5.33	3.98
camphene	0.13	-
β-pinene	9.63	9.31
myrcene	2.44	2.72
α-phellandrene	3.71	4.55
δ-3-carene	19.04	25.25
m-cymene	1.07	1.05
limonene	17.44	22.60
γ-terpinene	-	0.26
δ-3-carene†	1.03	0.98
linalool	0.34	0.20
terpinen-4-ol	0.10	-
α-terpineol	0.10	-
δ-elemene	2.65	2.09
α-copaene	1.87	0.79
β-caryophyllene	28.36	23.45
α-humulene	1.79	0.97
δ-cadinene	-	0.24
eremophil0ene	0.35	-
β-cadinene	0.74	-

† incorrect identity based on elution order

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Table II. Comparative percentage composition of the oils of four black pepper cultivars

Compound	1	2	3	4
α-thujene	0.73	1.26	1.59	0.91
α-pinene	5.28	6.18	5.07	5.32
camphene	0.14	0.18	0.14	0.13
sabinene	8.50	13.54	17.16	1.94
β-pinene	11.08	10.88	9.16	6.40
myrcene	2.23	2.30	2.20	8.40
α-phellandrene	0.68	0.20	-	2.32
δ-3-carene	2.82	0.18	-	1.03
α-terpinene	-	-	0.39	1.13
p-cymene	-	0.18	0.07	9.70
(Z)-β-ocimene + β-phellandrene	-	0.15	0.23	0.37
limonene	21.06	21.26	22.71	16.74
(E)-β-ocimene	0.18	2.84	0.30	0.17
γ-terpinene	0.01	0.49	-	0.03
trans-sabinene hydrate	0.14	-	0.30	0.19
terpinolene	0.10	0.20	0.22	0.08
trans-linalool oxide†	0.03	0.18	-	0.08
linalool	0.22	0.22	0.46	0.28
cis-p-menth-2-en-1-ol + *cis*-p-mentha-2,8-dien-1-ol	0.04	0.04	0.05	0.02
trans-p-menth-2-en-1-ol	0.01	0.01	0.01	0.01
citronellal	0.02	0.03	0.03	0.01
p-menth-8-en-1-ol	0.03	t	t	t
borneol	t	t	t	t
terpinen-4-ol	0.19	0.32	0.52	0.18
α-terpineol	0.10	0.17	0.12	0.07
dihydrocarveol	0.01	-	0.02	0.02
p-menth-8-en-2-ol	-	0.01	0.02	0.02
trans-carveol	0.01	0.01	-	0.02
cis-carveol + carvone	0.01	0.03	0.03	0.03
piperitone	0.04	t	0.03	t
carvone oxide*	0.01	0.01	-	0.01
myrtenol	0.20	0.04	0.11	0.04
α-terpinyl acetate	0.86	1.22	1.33	1.05
neryl acetate	0.20	0.07	0.05	0.13
geranyl acetate	0.12	0.01	0.09	0.11
α-cubebene + δ-elemene	3.25	0.26	0.16	2.56
α-copaene	0.82	0.49	0.44	0.71
β-elemene	0.09	0.09	0.06	0.05
β-caryophyllene	21.59	27.70	23.29	21.19
trans-α-bergamotene	0.31	-	-	0.28
α-humulene	0.21	0.20	0.11	0.29
(E)-β-farnesene	0.08	0.22	0.03	0.13
α-amorphene	1.51	1.53	1.54	1.28

Table II. (cont.) Comparative percentage composition of the oils of four black pepper cultivars

Compound	1	2	3	4
α-guaiene	0.11	0.07	-	0.10
clovene‡	0.14	0.07	0.07	0.13
germacrene D	0.04	0.03	0.04	0.26
ar-curcumene	0.26	0.12	0.04	0.29
β-selinene	0.64	0.87	1.37	0.63
α-selinene	0.07	0.12	0.48	0.14
γ-muurolene	0.73	0.93	0.16	0.58
(E,E)-α-farnesene	0.72	-	0.47	0.72
b-bisabolene + α-bisabolene*	4.25	2.15	3.10	0.49
δ-guaiene	0.82	0.17	0.09	1.85
cuparene	1.38	0.09	0.14	0.04
δ-cadinene	0.12	-	0.07	0.13
(Z)-nerolidol	0.20	0.05	0.11	0.05
elemol	0.11	0.06	0.07	0.08
(E)-nerolidol	0.12	0.04	0.07	0.03
caryophyllene alcohol	0.07	0.02	0.04	0.02
caryophyllene oxide	0.90	0.35	0.38	0.25
cedrol‡	0.07	-	0.05	0.05
α-cadinol*	1.51	0.29	0.12	1.27
α-cadinol*	0.26	0.12	0.15	0.25
β-bisabolol	0.20	0.09	0.17	0.14

Black pepper cultivars:
1. Panniyur 1
2. Panniyur 2
3. Panniyur 3
4. Culture-239

* correct isomer not identified
† furanoid form
‡ tentative identification
t = trace <0.01%

α-phellandrene
δ-3-carene
α-terpinene
p-cymene
o-cymene
limonene
β-thujene‡‡
1,8-cineole
allo-ocimene†°
pinadiene†
γ-terpinene
trans-sabinene hydrate
1,1-dimethyl-2-(3-methyl -1,3-butadienyl)-cyclopropane‡‡‡
isoterpinolene‡‡‡
terpinolene
linalool
cis-sabinene hydrate
camphor
p-mentha-1(7),2-dien-8-ol
α-guaiene
α-selinene†
α-humulene
valencene†
γ-gurjunene
β-cubebene†
cadina-4(15),6-diene‡‡
β-selinene
γ-selinene‡
octahydronaphthalene‡‡‡
δ-cadinene
hexahydronaphthalene‡‡‡
aromadendrene†
nerolidol°
longifolene†
4,8,8-trimethylspiro[2,6]nona-4,6-diene‡‡ spathulenol
1,5-dimethyl-6-methylene spiro[2,4]heptane
levomenol
terpinen-4-ol
α-terpineol
α-phellandrene epoxide
δ-elemene
α-muurolol
(E)-3-eicosene
16-octadecenal°
1-ethenyloxyhexadecane‡‡‡
eicosane

°correct isomer not identified
† incorrect identity based on elution order
‡‡ not a naturally occurring compound
‡‡‡ incorrect identification

The following year, Martins et al. (1998) analyzed the dried fruit oil of *P. nigrum* collected from the Republic of Sao Tomé e Principe, which is located 180 miles off the coast of Gabon (West Africa). They found that the oil had the following composition:

α-thujene (1.4%)
α-pinene (5.7%)
camphene (0.1%)
α-copaene (1.2%)
β-elemene (0.8%)
α-cedrene (0.3%)

β-pinene (10.7%)
sabinene (16.5%)
myrcene (2.0%)
α-phellandrene (0.7%)
α-terpinene (0.2%)
δ-3-carene (1.7%)
p-cymene (0.2%)
limonene (18.8%)
β-phellandrene (2.9%)
(E)-β-ocimene (0.5%)
γ-terpinene (0.4%)
trans-sabinene hydrate (0.3%)
terpinolene (0.4%)
linalool (1.1%)
cis-sabinene hydrate (0.1%)
terpinen-4-ol (1.7%)
δ-terpineol (0.5%)
δ-elemene (1.9%)
β-caryophyllene (15.1%)
α-gurjunene (0.2%)
α-humulene (1.1%)
α-muurolene (0.5%)
β-selinene (0.7%)
zingiberene (0.2%)
furanodiene (2.1%)
α-selinene (0.6%)
β-bisabolene (1.1%)
β-curcumene (0.1%)
δ-cadinene (0.7%)
elemol (0.3%)
germacrene B (1.4%)
caryophyllene oxide (0.9%)
(E)-nerolidol (0.3%)
T-cadinol (0.3%)
T-muurolol (0.2%)
α-eudesmol (1.2%)

In 1999, Jagella and Grosch used dilution and concentration techniques such as Aroma Evaluation Dilution Analysis and Aroma Evaluation Concentration Analysis (AEDA and AECA) and GC/olfactometry of headspace samples (GCOH) combined with enantioselective procedures to determine the important aroma components in black and white pepper. The compounds identified by the authors were as follows:

isovaleraldehyde
methyl 2-methylbutyrate
methyl isovalerate
methional
α-pinene
sabinene
β-pinene
1-octen-3-one
myrcene
α-phellandrene
p-cymene
limonene
1,8-cineole
2,5-dimethyl-3-methoxypyrazine
2-isopropyl-3-methoxypyrazine
linalool
2-phenethanol
2,3-diethyl-5-methylpyrazine
1-(E,Z)-3,5-undecatriene
piperonal (heliotropin)
wine lactone
ethyl cinnamate
β-ionone
germacrene B
butyric acid
2-methylbutyric acid
isovaleric acid
valeric acid
guaiacol
sotolone
decanoic acid
vanillin

Furthermore, Jagella and Grosch used chiral GC to determine the enantiomeric distribution of five monoterpene hydrocarbons and one monoterpene alcohol found in the pepper oils. Their results are summarized as follows:

(1R,5R)-(+)-α-pinene (19-21%) : (1S,5S)-(-)-α-pinene (79-81%)
(1R,5R)-(+)-sabinene (6%) : (1S,5S)-(-)-sabinene (94%)
(1R,5R)-(+)-β-pinene (7-8%) : (1S,5S)-(-)-β-pinene (92-93%)
(4R)-(+)-α-phellandrene (86-93%) : (4S)-(-)-α-phellandrene (7-14%)
(4R)-(+)-limonene (37-45%) : (4S-(-)-limonene (55-63%)
(3R)-(-)-linalool (52-76%) : (3S)-(+)-linalool (24-48%)

In a follow-up paper, the same authors determined that the key odorants for black pepper were as follows:

isobutanal (0.26)[a]
2-methylbutanal (0.50)
isovaleraldehyde (1.05)
(-)-α-pinene (520)
(+)-α-pinene (122)
(-)-β-pinene (990)
myrcene (218)
(+)-α-phellandrene (69.5)
(-)-limonene (1000)
(+)-limonene (820)
1,8-cineole (5.6)
(-)-linalool (30)
(+)-linalool (27.7)
butyric acid (6.73)
isovaleric acid (10.75)

[a] = mg of an aroma model of black pepper aroma

The authors also determined that 2,3-diethyl-5-methylpyrazine and 2-isopropyl-3-methoxypyrazine caused the musty/moldy off-flavor occasionally associated with black pepper.

Using the same analytical methodology as they used with black pepper, Jagella and Grosch determined that the key odorants of white pepper were as follows:

isobutanal (3.25)[a]
2-methylbutanal (0.55)
isovaleraldehyde (1.57)
(-)-α-pinene (588)
(-)-β-pinene (1065)
(-)-limonene (1115)
(+)-limonene (745)
1,8-cineole (24.2)
(-)-linalool (40.7)
(+)-linalool (14.3)
butyric acid (39.3)
isovaleric acid (2.18)
piperonal (57)
eugenol (0.48)
skatole (1.30)

[a] = mg of an aroma model of white pepper aroma

The fecal off-flavor occasionally associated with white pepper was caused by skatole, which was enhanced by p-cresol.

Also in 1999, Nussbaumer et al. examined the headspace composition of ground black pepper, the monoterpene fraction of black pepper oil, green pepper oil and a supercritical fluid extract of Muntok pepper using GC/MS. They found for the first time an unusual constituent which they characterized as being m-mentha-3(8),6-diene (syn. isosylveterpinolene). The identity of this compound, which was found in all of the above pepper isolates (see Table III), was confirmed by its synthesis.

In 2000, Menon et al. continued their work on exploring the variance in oil composition of black pepper cultivars grown in India. Although these cultivars that are not identifiable once imported as a spice, an oleoresin or an essential oil, nevertheless, the identified variance should help explain why one sample or shipment of pepper oil may differ from another sample or shipment. A summary of the results of GC and GC/MS analyses of the oils of four popular black pepper cultivars can be seen in Table IV.

Tewtrakul et al. (2000) produced a hydrodistilled oil of black pepper from material of Malaysian origin and analyzed it by a combination of GC and GC/MS. This oil was found to possess the following composition:

α-pinene (0.3%)
sabinene (2.4%)
myrcene (9.1%)
δ-3-carene (10.9%)
limonene (8.7%)
δ-elemene (2.5%)
α-copaene (3.8%)
β-elemene (1.6%)
β-caryophyllene (39.7%)
α-humulene (2.8%)
β-selinene (1.1%)
α-selinene (1.1%)
δ-cadinene (3.9%)
caryophyllene oxide (4.1%)

Table III. Selected component composition (%) in different pepper isolates				
Compound	Black Pepper Oils	Headspace Ground Pepper	Green Pepper Oil	SCF* Extract Pepper
δ-3-carene	7.49-12.64	9.25	11.79	22.94
limonene	14.75-18.76	13.44	22.88	15.78
p-cymene	0.43-0.53	0.58	1.82	1.37
m-mentha-3(8),6-diene	0.12-0.16	0.24	0.17	0.27
terpinolene	0.44-0.46	0.65	1.25	0.64

*SCF = supercritical fluid CO_2

Table IV. Comparative percentage composition of the oils of four common black pepper cultivars				
Compound	1	2	3	4
α-thujene	0-0.1	0-0.4	0.1-0.8	0.4-2.2
α-pinene	5.0-5.4	3.5-10.8	2.4-12.9	2.4-6.9
camphene	0.1-0.2	0.1-0.4	0.1-0.3	0-0.6
sabinene	0-0.6	1.8-8.0	3.8-4.1	5.5-20.9
β-pinene	14.1-15.2	4.4-11.7	2.0-7.3	6.1-11.1
myrcene	0-0.9	0-2.6	0.4-6.3	0-2.4
α-phellandrene	2.8-3.3	0.4-9.8	0.5-2.2	0.1-0.3
δ-3-carene	17.8-21.0	0.9-4.5	2.5-12.6	0.1-0.4
p-cymene	0.6-0.9	0-0.9	0.4-0.7	0-0.2
limonene	19.6-20.1	10.7-19.1	9.4-16.4	10.3-20.4
(E)-β-ocimene	0-0.2	0.1-0.2	0-0.3	0.2-0.4
γ-terpinene	0-0.2	0-0.1	0.1-0.4	0.1-0.3
terpinolene	0-0.2	0-0.1	0.1	0.1-0.2
trans-linalool oxide†	0.5-1.0	0.2-0.4	0.3-0.7	0.1-0.2
linalool	0-0.5	0.7-1.3	0.4-0.6	0.1-0.3
trans-p-menth-2-en-1-ol	-	0.1	-	-
citronellal	0-0.1	0-0.1	0-0.8	-
p-menth-8-en-1-ol	0-0.2	0.1	-	-
borneol	-	0-0.1	-	-
terpinen-4-ol	0-0.1	-	-	-
α-terpineol	0-0.3	0.2-0.3	0.2	0.1-0.2
dihydrocarveol	0-0.1	-	-	-
p-menth-8-en-2-ol	0-0.1	-	0-0.1	-
trans-carveol	0-0.1	-	-	-
piperitone	0.1	0-0.1	-	0.1
carvone oxide*	0-0.1	-	-	-
myrtenol	0-0.2	0.1	-	-
α-terpinyl acetate	0.2-0.3	0.1-0.2	0.3	0.4-0.5
neryl acetate	0.1	0-0.2	0.1-0.2	0-0.2
geranyl acetate	0.1-0.3	0-0.1	-	-
α-cubebene	1.5-2.2	0.8-1.3	1.3-3.8	0.1-0.6
α-copaene	-	0-0.1	0.7-0.9	0.6-1.1
β-elemene	0-0.1	0-0.1	-	0-1.0

Table IV. (cont.) Comparative percentage composition of the oils of four common black pepper cultivars

Compound	1	2	3	4
β-caryophyllene	19.8-25.6	25.9-47.5	23.5-45.3	24.4-46.9
trans-a-bergamotene	-	0-1.1	0-0.2	0-0.1
α-humulene	0-0.4	0-0.4	0-0.1	-
(E)-β-farnesene	0-0.1	-	1.3-2.2	-
α-amorphene	1.7-1.8	1.5-3.0	1.3-2.2	1.1-2.4
α-guaiene	-	0-0.1	-	-
ar-curcumene				
β-selinene	0.1	0.2-0.3	0.1-0.2	0.2-0.5
α-selinene	0.1	0.1-0.3	0.2-0.9	1.7-4.2
γ-murrolene	3.6-4.4	1.5-2.6	0.2-0.9	0.4-2.6
α-bisabolene*	2.5-2.9	2.2-3.8	-	0-0.4
δ-guaiene	-	0-0.4	0-1.7	0.1-0.4
cuparene	0.1-0.2	0.1-0.2	0-0.6	0.1-0.4
δ-cadinene	0-0.2	0.1	0-0.1	0.1-0.3
elemol	0.8-0.9	0-0.2	-	-
(E)-nerolidol	0-0.2	0-0.1	0-0.1	0.3-1.0
caryophyllenol*	0.1-0.2	0.5-0.8	-	0-0.1
caryophyllene oxide	0.4-0.5	1.7-4.0	0.8-3.7	0.9-3.9
cedrol	0.1	0.1-0.2	0-0.2	0.1-0.4
T-cadinol	0.1	0.2-0.4	0.1-0.4	0.4
α-cadinol	0.1	0-0.4	0-0.3	0.1-0.8

Black pepper cultivars:
1.Karimunda
2.Kalluvally
3.Thommankodi
4.Arakulam munda

* correct isomer not identified
† furanoid form

Also in 2000, Dorman et al. screened a number of oils and synthetic antioxidants for their *in vitro* antioxidant activity. Within this screening program, the authors examined a lab-distilled black pepper oil. Analysis of this oil revealed that it had the following composition:

α-thujene (0.44%)
α-pinene (6.33%)
camphene (0.38%)
sabinene (0.15%)
7-octen-4-ol† (0.17%)
α-phellandrene (2.74%)
δ-3-carene (8.53%)
α-terpinene (0.35%)
p-cymene (1.63%)
β-terpineol°† (0.34%)
terpinen-4-ol (0.24%)
α-terpineol (4.74%)
γ-terpineol† (1.48%)
neral (0.32%)
geraniol (0.54%)
(E)-anethole (0.39%)
eugenol (5.56%)
α-cubebene (0.23%)
α-copaene (2.26%)
β-elemene (0.37%)
β-caryophyllene (24.20%)
aromadendrene (0.47%)
α-humulene (2.16%)
δ-cadinene (0.35%)
caryophyllene oxide (0.84%)

° correct isomer not identified
† identity requires corroboration

Menon et al. (2001) compared the compositions of the distilled oil with the free and the bound volatiles of Indian black pepper. To obtain the free and bound volatiles, the authors initially blended fresh green pepper in distilled water, clarified by centrifugation, after which the water soluble sugars, amino acids and proteins were removed by passing the supernatant liquid through an ion exchange column. The free volatiles were removed from the eluted water mixture using pentane/diethyl ether after which the free volatiles were concentrated by solvent removal. The bound glycosides were eluted from the ion exchange column with methanol. Using vacuum distillation, the methanol was removed and the bound volatiles (glycosidic extract) was dissolved in a phosphate-citrate buffer (pH:5.0), and the mixture was treated with β-glucosidase and incubated at 37∞C. After enzymic hydrolysis, the bound volatiles were extracted with diethyl ether and then concentrated by solvent removal. The results of the analyses of a typical distilled oil, the free and bound volatiles can be seen in Table V.

It is of interest to note that the leaf oil of *P. nigrum* was found by Sumathykutty et al (1999) to contain the following constituents:

3-methyl-2-pentanol (0.01%)
(Z)-β-farnesene (0.16%)

Table V. Percentage composition of an oil, the free and bound volatiles of black pepper

Compound	Oil	Free Volatiles	Bound Volatiles	Compound	Oil	Free Volatiles	Bound Volatiles
isoamyl alcohol	-	0.1	0.4	citronellal	t	0.3	-
amyl alcohol	-	0.5	-	*cis*-β-terpineol	-	0.4	-
3-hexenol*	-	0.5	5.3	menthone	0.5	1.1	-
3-buten-2-ol	-	0.3	25.8	*trans*-β-terpineol	-	0.4	0.2
(E)-2-hexenal	-	-	0.9	δ-terpineol	-	-	4.7
hexanol	-	0.5	1.3	terpinen-4-ol	8.9	0.7	1.0
1-hepten-3-ol	-	-	1.4	menthol	-	-	0.2
nonane	-	t	-	α-terpineol	0.5	25.6	0.6
α-thujene	1.6	0.2	-	dihydrocarveol	0.5	0.9	-
α-pinene	12.1	0.7	-	neodihydrocarveol	-	0.4	1.2
benzaldehyde	-	1.3	1.3	dihydrolimonen-10-al	-	0.9	0.1
camphene	0.3	6.0	-	nerol	-	0.2	0.1
1-octen-3-ol	-	-	1.4	neral	-	0.1	0.3
sabinene	13.7	3.0	-	geraniol	-	0.1	0.3
β-pinene	14.2	2.0	-	geranial	-	t	0.2
myrcene	-	-	1.4	piperitone	-	t	0.2
2-octanol	-	-	1.9	*trans*-carvone oxide	-	0.1	0.1
α-phellandrene	-	t	-	cumin alcohol	-	t	0.6
δ-3-carene	0.2	0.4	-	thymol	-	-	0.1
1,4-cineole	-	-	0.4	(E)-cinnamyl alcohol	-	t	0.2
1,8-cineole	-	-	0.5	δ-terpinyl acetate	-	t	-
limonene	18.8	4.4	-	α-terpinyl acetate	0.6	0.1	-
(E)-3-octenal	-	-	3.0	eugenol	-	-	2.0
(E)-2-octenal	-	-	t	(Z)-isosafrole	-	-	0.1
ethyl-2-hexenol*	0.3	6.3	-	2-methylcinnamyl alcohol	-	-	0.4
γ-terpinene	0.3	4.4	-	α-cubebene	0.1	t	-
terpinolene	-	4.4	-	α-copaene	1.1	t	-
3-nonenol*	0.13	0.6	-	β-bourbonene	-	t	-
cis-linalool oxide†	0.13	0.6	-	α-farnesene*	-	0.2	-
guaiacol	-	-	0.3	β-caryophyllene	6.7	0.1	-
trans-linalool oxide†	0.2	18.6	-	β-copaene	1.5	0.1	-
α-thujone	-	-	1.7	α-humulene	1.9	0.1	-
linalool	0.3	2.8	-	α-guaiene	0.1	t	-
β-thujone	-	1.7	-	α-selinene	0.2	0.2	-
cis-p-menth-2-en-1-ol	-	0.3	-	(Z)-α-bisabolene	3.7	6.4	-
myrcenol	-	2.0	-	α-bulnesene	0.6	t	-
cis-p-mentha-2,8-dien-1-ol	-	0.3	-	γ-cadinene	2.6	t	-
cis-p-menth-2-en-7-ol	-	0.4	4.0	(Z)-nerolidol	3.1	t	0.2
trans-p-menth-2-en-1-ol	0.3	0.3	-	elemol	0.5	-	0.3
trans-limonene oxide	-	0.9	-	(E)-nerolidol	7.1	-	0.2
				caryophyllenol*	-	t	0.2

Table V. (cont.) Percentage composition of an oil, the free and bound volatiles of black pepper

Compound	Oil	Free Volatiles	Bound Volatiles
caryophyllene oxide	0.3	t	0.1
humulene epoxide I	-	t	0.1
humulene epoxide II	-	t	0.1
cedrol	0.1	0.1	0.1
α-muurolol	-	t	0.2
α-cadinol	0.2	t	0.1
β-eudesmol	-	-	0.2
α-eudesmol	0.6	t	0.3
cadina-1,4-dien-3-ol	0.6	t	0.3
β-bisabolol	0.4	t	0.1
(Z,Z)-farnesol	0.3	1.0	0.2
(Z,E)-farnesol	3.1	t	0.3
(E,Z)-farnesol	-	-	0.2
(E,E)-farnesol	-	-	0.1
vomifoliol	-	-	0.4

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

1-hexen-3-ol (0.01%)
2-hexanol (0.04%)
2-heptanol (0.01%)
α-thujene (0.01%)
α-pinene (0.03%)
sabinene (0.02%)
β-pinene (0.07%)
limonene (0.11%)
(E)-β-ocimene (0.04%)
linalool oxide*† (0.07%)
terpinolene (0.03%)
linalool (0.38%)
β-terpineol* (0.06%)
terpinen-4-ol (0.02%)
α-terpineol (0.28%)
nerol (0.07%)
geraniol (0.09%)
carvone oxide* (0.10%)
bornyl acetate (0.21%)
carvacrol (0.02%)
piperitenone (0.02%)
α-terpinyl acetate (0.06%)
δ-elemene (0.07%)
geranyl acetate (0.02%)
α-cubebene (0.22%)
methyl eugenol (0.09%)
α-copaene (0.02%)
β-elemene (0.07%)
β-bourbonene (0.14%)
β-cubebene (1.68%)
β-caryophyllene (0.14%)
α-cedrene (0.06%)
β-copaene (0.59%)
β-cedrene (0.50%)
(E)-β-farnesene (0.29%)
α-humulene (0.69%)
γ-muurolene (1.63%)
allo-aromadendrene (0.32%)
germacrene D (0.27%)
β-selinene (0.47%)
(E,E)-α-farnesene (1.55%)
α-muurolene (0.12%)
β-bisabolene (0.13%)
calamenene* (0.73%)
δ-cadinene (0.17%)
cadina-1,4-diene (1.35%)
elemol (11.52%)
(E)-nerolidol (1.92%)
caryophyllenol* (4.85%)
caryophyllene oxide (0.23%)
cedrene epoxide (0.35%)
cedrol (0.36%)
β-eudesmol (3.31%)
α-cadinol (0.75%)
cadina-1,4-dien-3-ol (3.20%)
β-bisabolol (3.32%)
(Z,E)-farnesol (4.59%)
(E,Z)-farnesol (3.53%)
(E,E)-farnesol (0.10%)

* correct isomer not identified
† furanoid form

Similarly, it is also of interest to note that the root oil of *P. nigrum* was the subject of analysis by Ao et al. (1998). Using GC/MS as their method of analysis, the authors characterized the following compounds in pepper root oil:

α-pinene (0.90%)
camphene (0.14%)
β-pinene (1.35%)
myrcene (0.19%)
α-phellandrene (0.49%)
δ-3-carene (6.00%)
p-cymene (0.37%)
limonene (2.97%)
γ-terpinene (0.07%)
terpinolene (0.20%)
α-terpineol (0.22%)
bornyl acetate (0.05%)
2-undecanol (0.08%)
α-copaene (0.09%)
β-elemene (0.59%)
isocaryophyllene (6.76%)
β-caryophyllene (51.20%)
α-humulene (3.67%)
caryophyllene alcohol (0.29%)
caryophyllene oxide (0.47%)
α-muurolol (0.08%)

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Caraway Herb, Seed and Root Oils

In 1992, Jean et al. compared the sesquiterpene hydrocarbon content of vegetative caraway herb oil and caraway herb extract produced by microwave extraction using hexane, carbon tetrachloride or toluene. The sesquiterpene hydrocarbon contents of the oil and extract were germacrene D (69.06% and 43.36%), bicyclogermacrene (3.90% and <0.10%) and β-caryophyllene (2.91% and 2.14%), respectively.

In 1997, Valterova et al. determined the relative amounts of monoterpene hydrocarbons from concentrated extracts of small plants (seedlings with one to three leaves and roots) of *C. carvi* using GC/MS. The following hydrocarbons were identified:

α-pinene (8.6%)
β-pinene (t)
sabinene (0.2%)
δ-3-carene (0.2%)
myrcene (0.2%)
α-terpinene (18.9%)
limonene (59.7%)
β-phellandrene (2.8%)
(Z)-β-ocimene (0.3%)
γ-terpinene (0.8%)
(E)-β-ocimene (1.8%)
p-cymene (1.6%)
terpinolene (2.0%)
allo-ocimene* (2.8%)

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

The enantiomeric distribution of α-pinene and limonene were determined to be as follows:

(1R,5R)-(+)-α-pinene (29%) : (1S,5S)-(-)-α-pinene (71%)
(4R)-(+)-limonene (98%) : (4S)-(-)-limonene (2%)

As part of a screening program of highland and lowland plant species that are found in pastures where cows graze, Mariaca et al. (1997) determined that pre-flowing caraway plants contained:

sabinene
limonene
(Z)-β-ocimene
(E)-β-ocimene
γ-terpinene
p-cymene
α-cubebene
β-elemene
β-caryophyllene
α-humulene

Unfortunately, these authors did not present any quantitative data. It was also a surprise to this reviewer that germacrene D was not identified.

Reichling et al. (1999) subjected a commercial sample of caraway oil to analysis using both GC and GC/MS. The oil was found to contain the following major components:

α-pinene (0.28%)
β-pinene (0.10%)
α-phellandrene (1.11%)
limonene (45.60%)
linalool (0.10%)
carvone (52.22%)

An oil of caraway produced from whole plants grown in Mongolia was found by Shatar and Altantsetseg (2000) to contain:

α-pinene (2.0%)
camphene (0.1%)
β-pinene (0.1%)
α-phellandrene (0.5%)
limonene (3.2%)
p-cymene (0.7%)
α-cubebene (0.1%)
α-copaene (0.5%)
β-bourbonene (0.7%)
linalool (0.4%)
β-elemene (5.3%)
β-caryophyllene (6.8%)
dihydrocarvone* (0.2%)
methyl chavicol (0.2%)
α-humulene (0.9%)
germacrene D (15.9%)
carvone (5.1%)
δ-cadinene (2.3%)
β-damascenone* (0.2%)
(E)-anethole (5.4%)
calamenene* (2.7%)
geraniol (0.2%)
ethyl 3-phenylpropionate (0.1%)
jasmone* (0.1%)
caryophyllene oxide (2.7%)
methyl eugenol (0.9%)
spathulenol (1.8%)
eugenol (0.3%)
T-cadinol (0.8%)
T-muurolol (1.3%)
2-methoxy-4-vinylphenol (1.3%)
α-cadinol (1.9%)
phytol (1.3%)
tetradecanoic acid (0.6%)
hexadecanoic acid (2.6%)

*correct isomer not identified

Using chiral GC, Braun et al. (2000) determined that the enantiomeric ratio of the two major components of caraway oils were as follows:

(4R)-(+)-limonene (>99.9%) : (4S)-(-)-limonene (<0.1%)
(4S)-(+)-carvone (99.9%) : (4R)-(-)-carvone (0.1%)

According to the authors, these two components should total 95% of the oil with the next major compound being myrcene (0.2-1.0%). The other minor constituents in caraway oil were listed as:

α-pinene
α-phellandrene
p-cymene
linalool
β-caryophyllene
cis-dihydrocarvone
trans-dihydrocarvone
cis-carveol
trans-carveol

Table VI. Comparative percentage composition of a volatile concentrate and an oil of caraway

Compound	Volatile Concentrate	Oil
2,4-hexadienal*	t	-
α-pinene	t	t
β-pinene	0.1	0.1
myrcene	0.6	0.4
limonene	45.3	36.7
γ-terpinene	0.2	0.2
linalool	0.1	0.1
β-thujone	0.1	0.1
cis-limonene oxide	t	t
trans-limonene oxide	0.2	0.1
geijerene	t	-
dihydrocarveol	t	t
cis-dihydrocarvone	0.1	0.2
trans-dihydrocarvone	0.2	0.2
trans-carveol	0.1	0.1
cis-carveol	0.1	0.2
carvone	51.4	60.5
perillaldehyde	1.1	1.1
β-caryophyllene	0.2	0.2
germacrene D	t	t

t = trace (<0.1%)

Table VII. Percentage composition of the main components of the seedling and adult plant root oils of *Carum carvi*

Compound	Seedling Root Oil	Adult Plant Root Oil
monoterpene hydrocarbons	3.2	1.3
octanal	2.3	16.5
nonanal	0.3	10.5
(Z)-4-decenal	0.4	1.4
unidentified aliphatic aldehyde	0.6	21.4
(E)-2-decenal	0.4	16.5
β-caryophyllene	0.9	-
germacrene D	6.4	12.6
germacrene B	68.4	13.1
other sesquiterpene hydrocarbons	4.8	1.2
unidentified sesquiterpene	1.4	0.7

The authors pointed out that carvenone, carvacrol or perillyl alcohol are artifacts formed either during distillation or oil storage.

Cabizza et al. (2001) compared the supercritical fluid extract of caraway seed with that of its oil. The authors optimized the extraction conditions so that they could produce a volatile concentrate of caraway seed free from higher molecular weight undesirable compounds. A comparison between the compositions of volatile concentrate and the oil produced by hydrodistillation (water distillation) is shown in Table VI.

Finally it is of interest to note that Stahl-Biskup and Wichtmann (1991) compared the major components of the root oils of seedlings and adult plants of caraway. The results of this study are shown in summary form in Table VII.

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Cinnamon Leaf Oil

In 1991, Cheng and Yu analyzed the leaf oil of *Cinnamomum zeylanicum* Blume produced from leaves harvested in Xishuangbanna (China). They found that there were two chemotypes: a benzyl benzoate-type and a eugenol-type. The composition of the eugenol-type was found to be as follows:

α-thujene (0.24%)
α-pinene (1.02%)
camphene (0.24%)
β-pinene (0.28%)
myrcene (0.17%)
α-phellandrene (2.50%)
δ-3-carene† (0.20%)
p-cymene (1.98%)
limonene (0.36%)
terpinolene (0.17%)
linalool (0.40%)
terpinen-4-ol (0.04%)
α-terpineol (0.19%)
(E)-cinnamaldehyde (0.43%)
eugenol (81.26%)
β-caryophyllene (1.80%)
(E)-cinnamyl acetate (0.34%)
γ-elemene (0.17%)

β-phellandrene (0.33%)
(E)-β-ocimene (0.04%)
δ-3-carene† (0.03%)
viridiflorol (0.67%)
benzyl benzoate (5.46%)

†compounds listed twice by authors

Vernin et al. (1994) used GC and GC/MS to analyze the headspace of *C. zeylanicum* leaves. The components identified in this headspace were:

p-cymene (21.35%)
α-copaene (3.46%)
benzaldehyde (3.07%)
linalool (10.50%)
salicylaldehyde (0.55%)
borneol + α-terpineol (1.36%)
(E)-cinnamaldehyde (1.44%)
eugenol (16.70%)

Ehlers et al. subjected three samples of cinnamon leaf oil to HPLC analysis (1995). The compounds characterized in these oils were as follows:

(E)-cinnamic acid (0-t)
(E)-cinnamaldehyde (0.9-1.1%)
eugenol (71.0-77.3%)
(E)-cinnamyl acetate (1.5-2.7%)
safrole (0.9-1.1%)

In 1996, Prakasa Rao determined that an oil produced in 1.8% yield from normal cinnamon leaves grown in India contained:

linalool (1.07%)
β-caryophyllene (1.96%)
benzyl benzoate (0.20%)
eugenol (84.5%)

In contrast, an oil produced in 1.2% yield from cinnamon leaves found to be deficient in potassium and phosphorus contained:

linalool (1.62%)
β-caryophyllene (1.05%)
benzyl benzoate (3.76%)
eugenol (80.6%)

Kiketsu et al. (1997) analyzed the leaf oils from single trees of*C. zeylanicum* grown in Parana (Brazil). Using GC and GC/MS as their method of analyses, the authors found that some of the leaf oils were typical being rich in eugenol whereas others had both high safrole and eugenol contents as shown in Table VIII.

A year later, Jirovetz et al. (1998) compared the composition of cinnamon leaf oils produced from *C. zeylanicum* leaves obtained from Cameroon with that of two commercial leaf oils of Seychelles origin. The analyses, which were performed using GC and GC/MS, can be seen summarized in Table IX.

More recently, Jirovetz et al. (2001) analyzed a cinnamon leaf oil produced from leaves harvested from *C. zeylanicum* growing in Calicut (India). The composition of this oil was determined by a combination of GC and GC/MS and it was found to contain:

Table VIII. Comparative percentage composition of two leaf oil types of Cinnamon grown in Brazil

Compound	Type 1	Type 2
α-pinene	0.12-0.15	t-0.2
camphene	t	t
β-pinene	t	t
α-phellandrene	t	t-0.69
α-terpinene	t	t
limonene	t-0.20	t-0.11
1,8-cineole + b-phellandrene	t-0.38	0.22-0.46
p-cymene	t-0.26	t-0.26
terpinolene	t	t
α-ylangene	t-0.21	t
benzaldehyde	0.36-0.50	t
linalool	0.51-1.33	1.44-1.67
β-caryophyllene	t	t
terpinen-4-ol	1.03-1.25	1.68-4.28
α-humulene	t	0.26-0.70
α-terpineol	t	t
safrole	t-0.56	29.57-39.52
caryophyllene oxide	0.28-0.42	t
(E)-cinnamal-dehyde	0.59-0.98	0.65-1.03
eugenol	94.14-95.09	55.08-58.66
benzyl benzoate	0.57-0.92	t-0.98

t = trace (<0.01%)

(E)-2-hexenol (0.1%)
(Z)-3-hexenol (0.1%)
1-hexen-3-ol (0.1%)
hexanol (0.1%)
α-pinene (t)
(Z)-3-hexenyl acetate (0.1%)
(E)-2-hexenyl acetate (0.1%)
p-cymene (t)
β-phellandrene (t)
(E)-β-ocimene (t)
1,8-cineole (0.1%)
limonene (0.2%)
cis-linalool oxide† (0.2%)
terpinolene (0.1%)
trans-linalool oxide † (0.1%)
linalool (85.7%)
nonanol (0.3%)
borneol (0.1%)
terpinen-4-ol (0.3%)
α-terpineol (1.1%)
dihydrocarveol (t)
linalyl acetate (0.1%)
(E)-cinnamaldehyde (1.7%)
safrole (t)
(E)-cinnamyl alcohol (0.1%)
eugenol (3.1%)
(E)-cinnamyl acetate (0.9%)
β-caryophyllene (2.4%)
α-humulene (0.2%)
eugenyl acetate (0.1%)
caryophyllene oxide (0.1%)
spathulenol (0.2%)
benzyl benzoate (0.3%)

† furanoid form
t = trace (<0.1%)

This was the first time that a cinnamon leaf oil has been found in which linalool not eugenol was the major compo-

Table IX. Comparative percentage composition of Cinnamon leaf oil (Cameroon origin) and two commercial oils (Seychelles origin)

Compound	Cameroon Leaf Oil	Seychelles Leaf Oils
eugenol	85.2	64.3-72.4
(E)-cinnamaldehyde	4.9	0.5-11.1
linalool	2.8	0.3-2.7
β-caryophyllene	1.8	2.4-3.8
α-phellandrene	0.9	0.1-1.8
caryophyllene oxide	0.5	0.2-0.5
α-pinene	0.5	0.1-0.6
p-cymene	0.4	0.1-2.3
1,8-cineole	0.3	0.2-1.1
limonene	0.3	0.1-0.5
camphene	0.2	0.5-0.6
β-pinene	0.2	0.1-0.7
β-phellandrene	0.1	0.1-0.2
α-thujene	0.1	0-0.3
γ-terpinene	0.1	0.2-0.4
(E)-β-ocimene	0.1	0.1-0.6
terpinolene	0.1	0.1-0.3
myrcene	0.1	0.1-0.6
terpinen-4-ol	0.1	0-1.2
borneol	0.1	0.1-0.3
cis-linalool oxide*	0.1	0-0.4
(E)-cinnamyl acetate	0.1	0.2-2.2
δ-3-carene	0.1	0-0.2
α-terpinene	0.1	0-0.7
eugenyl acetate	0.1	0.1-1.4
α-terpineol	0.1	0.1-0.9
safrole	t	0.1-0.2
benzyl benzoate	t	0.1-0.3
(E)-cinnamyl alcohol	t	0-0.2
α-humulene	t	0.1-0.5
γ-cadinene	t	0-0.3
(Z)-β-ocimene	t	0-t

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

nent. Obviously, this could not be intermixed with any of the eugenol-rich leaves used to produce the commercial oil, because in the case of India and Sri Lanka *C. zeylanicum* is grown on plantations. Also, unless some unusual mutation occurs, the cinnamon that grows wild throughout the Seychelles and Madagascar (the other sources of cinnamon leaf oil) originated from introductions of cinnamon trees possessing a typical chemistry.

Cinnamon leaf oil produced from leaves harvested from cinnamon shrubs growing in the Andaman Islands off the west coast of S. India was recently analyzed by Raina et al. (2001).

The composition of the oil was determined to be as follows:

2-heptanol (0.01%)
2-heptanone (0.02%)
α-thujene (0.10%)
α-pinene (0.45%)
camphene (0.05%)
sabinene (0.02%)
β-pinene (0.08%)
myrcene (0.09%)
α-phellandrene (1.19%)
δ-3-carene (0.06%)
α-terpinene (0.53%)
p-cymene (0.50%)
limonene + 1,8-cineole (0.02%)
(E)-β-ocimene (0.04%)
γ-terpinene (0.03%)
cis-linalool oxide† (0.04%)
terpinolene (0.04%)
trans-linalool oxide† (0.10%)
linalool (8.50%)
2-phenethyl alcohol (0.10%)
citronellal (0.07%)
borneol (0.02%)
terpinen-4-ol (0.09%)
(Z)-methyl cinnamate (0.18%)
methyl chavicol (0.06%)
(Z)-cinnamaldehyde (0.05%)
nerol (0.02%)
piperitone (3.31%)
safrole (0.06%)
eugenol (76.60%)
(Z)-cinnamyl acetate (2.59%)
β-caryophyllene (0.93%)
(E)-β-farnesene (0.18%)
eugenyl acetate (2.74%)
α-selinene (0.10%)
δ-cadinene (0.06%)
(E)-nerolidol (0.02%)
spathulenol (0.10%)
caryophyllene oxide (0.22%)
humulene epoxide I (0.05%)
T-cadinol (0.03%)
α-cadinol (0.06%)
α-hexylcinnamaldehyde (0.33%)
geranyl benzoate (0.05%)
2-phenethyl decanoate (0.03%)
2-phenethyl anthranilate (0.02%)

† furanoid form

Recently, Mallavarapu and Ramesh (2000) analyzed an oil produced in the laboratory exclusively from the fruits of *C. zeylanicum*. The analysis, which was a combination of GC and GC/MS, revealed that the oil contained the following components:

(E)-2-hexenal (t)
tricyclene (t)
α-pinene (11.2%)
camphene (0.6%)
β-pinene (9.2%)
myrcene (1.6%)
α-phellandrene (0.7%)
α-terpinene (0.2%)
p-cymene (0.1%)
limonene (2.8%)
1,8-cineole (0.1%)
(Z)-β-ocimene (0.1%)
(E)-β-ocimene (0.2%)
γ-terpinene (0.1%)
terpinolene (0.5%)
linalool (0.2%)
α-fenchyl alcohol (0.5%)
isoborneol (t)
borneol (0.5%)
terpinen-4-ol (0.1%)
α-terpineol (0.5%)
nerol (t)
geraniol (t)
isobornyl acetate (0.1%)
(Z)-cinnamyl acetate (0.1%)
α-copaene (2.1%)
β-elemene (0.4%)
(E)-cinnamyl acetate (0.4%)
β-caryophyllene (11.0%)
(E)-β-farnesene (0.8%)
α-humulene (2.2%)
γ-muurolene (0.2%)
germacrene D (0.2%)
α-muurolene (6.1%)
δ-cadinene (7.1%)
δ-cadinene (13.6%)
cis-calamenene (2.2%)
α-cadinene (1.2%)
elemol (1.9%)
(E)-nerolidol (0.1%)
isocaryophyllene oxide (0.2%)
spathulenol (0.8%)
caryophyllene oxide (0.4%)
globulol (0.4%)
humulene epoxide I (0.5%)
humulene epoxide II (0.6%)
1-epi-cubenol (0.1%)
T-cadinol (0.2%)
cubenol (0.9%)
α-muurolol (9.8%)
selin-11-en-4a-ol (0.1%)
α-cadinol (3.1%)
4-hydroxy-3,4-dihydrocalacorene* (0.2%)
4-hydroxy-3,4-dihydrocalacorene* (0.1%)

*correct isomer not identified
t = <0.1%

Also in 2000, Jayaprakasha et al. analyzed an oil of *C. zeylanicum* produced solely from the flowers using GC and GC/MS. This oil was characterized as containing the following constituents:

(Z)-3-hexenol (0.10%)
benzaldehyde (0.35%)
hydrocinnamaldehyde (0.18%)
borneol (0.17%)
α-terpineol (0.15%)
(E)-cinnamaldehyde
δ-cadinene (2.97%)
nerolidol* (0.95%)
caryophyllene oxide (7.29%)
globulol (3.80%)
tetradecanal (5.05%)
α-cadinol (6.35%)
(E)-cinnamyl alcohol (0.49%)
3-phenylpropyl acetate (1.99%)
α-copaene (3.03%)
trans-α-bergamotene (7.97%)
(E)-cinnamyl acetate (41.98%)
α-humulene (2.40%)
germacrene D (1.31%)
cadalene (1.39%)
epi-α-bisabolol (0.73%)
heptadecane (2.14%)
benzyl benzoate (3.19%)
pentadecanol (0.71%)
2-hexadecanone (0.71%)
2-phenethyl hexanoate (0.44%)

*correct isomer not identified

It is of interest to note that across the *Cinnamomum zeylanicum* tree, the chemical composition of that oil is quite varied, e.g.,
root oil: camphor-rich
inner bark oil: (E)-cinnamaldehyde-rich
leaf oil: eugenol-rich
flower oil: (E)-cinnamyl acetate-rich
fruit oil: sesquiterpene-rich.

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Patchouli Oil

In 1980, Mookherjee et al. reported on the odorous compounds in patchouli oil. They found that the major compounds in the oil were:

β-elemene (1.0%)
β-caryophyllene (20.0%)
α-guaiene (15.0%)
α-bulnesene (25.0%)
α-guaiene oxide (1.0%)
α-bulnesene oxide (4.0%)
caryophyllene oxide (2.0%)
norpatchoulenol (0.5%)
patchouli alcohol (30.0%)
pogostol (1.0%)

Eleven years later, Ishihara et al. (1991) noted that patchouli oil contained the following sesquiterpene hydrocarbons:

α-copaene (3.0%)
β-patchoulene (4.0%)
α-gurjunene (4.0%)
β-caryophyllene (7.0%)
α-guaiene (21.0%)
γ-patchoulene (1.0%)
α-humulene (1.0%)
α-patchoulene (12.0%)
seychellene (11.0%)
α-bulnesene (24.0%)
δ-cadinene (1.0%)

In 1993, Li et al. examined the composition of the highly volatile components found in the headspace of *P. cablin* leaves using direct vaporization-headspace cryofocusing GC/MS analysis. The components that were identified by this procedure were:

cyclobutanol
methoxycyclobutane
methyl acetate
2-butenol*
3-methyl-2-butanone
3-hydroxybutanal
3-methyl-3-buten-2-one

*correct isomer not identified

It should be noted that cyclobutanol and methoxycyclobutane are extremely unusual naturally occurring compounds. As a result, this analysis needs corroboration before the natural occurrence of all of these compounds is accepted.

In 1996, Prakasa Rao determined that the phosphorus and potassium content of patchouli leaves had a profound effect on the oil composition. A summary of their scant

Table X. Comparative major component percentage composition of patchouli oil produced from normal leaves and leaves deficient in P and K

Compound	Normal Leaf Oil	P/K Deficient Leaf Oil
seychellene	5.7	4.1
α- + δ-patchoulene	5.9	3.7
α-guaiene	10.9	6.7
α-bulnesene	14.6	9.5
patchouli alcohol	16.8	58.3
oil content (%)	3.85	3.30

Table XI. Comparative percentage composition of patchouli oil produced in different geographical regions

Compound	Chinese Oil	Indian Oil	Indonesian Oil
guaia-11-ol	-	4.00	6.29
δ-selinene	1.83	-	-
cadinene*	-	0.26	1.04
β-patchoulene	-	16.19	15.59
3-thujopsene	-	1.58	1.07
β-caryophyllene	-	2.80	2.17
α-guaiene	-	5.87	7.16
guaiene*	-	23.61	22.25
α-patchoulene	2.78	1.01	1.55
selina-3,7(11)-diene	t	1.00	2.90
patchoulene*	4.99	-	-
α-bulnesene	21.99	7.31	11.10
α-elemene	1.43	-	-
patchouli alcohol	41.00	22.77	20.00
aristolone	1.17	t	-

t = <0.01%
*correct isomer not identified

results can be seen in Table X. It should be noted that the authors did not perform any statistical analysis on their results, nor did they describe the sample size of leaves and the randomness of their selection. As a result, this study must be seen as being very preliminary in its conclusions.

Also in 1996, Yang et al. examined the antibacterial and antifungal activities of patchouli oil produced in China, India and Indonesia. Of these oils, the Chinese oil was found to possess better antimicrobial properties than the other two oils. In addition, the authors compared the oils

Table XII. Comparative percentage composition of the root and rhizome oils of *Pogostemon cablin*

Compound	Root Oil	Rhizome Oil
benzene	0.028	0.118
cyclohexane	0.105	0.337
2,3-dimethylpentane	-	0.019
cis-1,3-dimethylcyclopentane	0.011	-
1,2-dimethylcyclopentane	0.006	0.020
3-methylcyclohexane	-	0.035
trans-1,3-dimethylcyclopentane	-	0.009
heptane	0.187	0.698
isoamyl alcohol	0.005	-
toluene	0.019	0.048
hexanal	0.057	0.073
2-furfuraldehyde	0.010	-
5-methyl-2-hexanone	0.026	0.039
ethylbenzene	0.007	0.021
hexanol	0.012	-
m-xylene	0.037	0.138
p-xylene	-	0.039
1-methyl-2-pentylcyclopropane	0.009	-
benzaldehyde	0.022	0.035
α-pinene	0.138	0.081
1,(E)-5-octadien-3-ol	-	0.017
7-octen-4-ol	0.007	0.048
β-pinene	0.266	0.144
2-pentylfuran	0.195	0.176
phenylacetaldehyde	0.014	-
limonene	0.026	0.024
(E)-2-octenal	0.020	0.032
6-methyl-3,5-heptadien-2-one	0.006	-
3,5-octadien-2-one	-	0.019
terpinolene	0.007	-
nonanal	0.012	-
linalool	-	0.031
1-ethylbutybenzene	-	0.095
linalyl propionate	-	0.037
1-methylpentylbenzene	-	0.112
1-methyl-2-hydroxybenzoic acid	-	0.121
(E,E)-2,4-decadienal	0.153	0.082
nonyl acetate	0.084	0.090
eugenol	0.306	0.017
β-patchoulene	0.143	0.241
β-elemene	-	0.052
longifolene	-	0.048
β-caryophyllene	0.120	0.419
α-guaiene	0.251	0.514
seychellene	0.178	0.308

Table XII. (cont.) Comparative percentage composition of the root and rhizome oils of *Pogostemon cablin*

Compound	Root Oil	Rhizome Oil
β-selinene	-	0.081
α-patchoulene	0.360	0.201
δ-guaiene	0.545	0.182
calamenene*	-	0.038
nerolidol*	2.883	5.167
α-copaene†	0.313	-
patchouli alcohol	1.981	5.148
pogostone	81.713	63.445
(Z,E)-farnesol	0.767	1.630
(E,E)-farnesol	0.367	1.399
1-butyloctylbenzene	-	0.072
1-propylnonylbenzene	-	0.029
1-ethyldecylbenzene	-	0.042
1-methylundecylbenzene	-	0.135
3,7,11-trimethyl-2,6,10-dodeca-trienyl acetate	1.090	-
geranyl acetate	-	3.93
1-butylnonylbenzene	-	0.073
di-isobutyl phthalate‡	-	0.066
1-methyldodecylbenzene	-	0.045
hexadecanoic acid	2.213	5.146
dibutyl phthalate‡	-	0.036
heptadecanoic acid	0.035	0.197
linoleic acid	0.107	1.955
8-heptadecenoic acid	0.052	0.286
octadecanoic acid*	0.033	0.245
methyl linoleate	0.191	0.485

* correct isomer not identified
† incorrect identity based on elution order
‡ artifact

chromatographically and the results of these weak analyses can be seen in Table XI.

The following year, Rakotonirainy et al. (1997) determined that the main sesquiterpene hydrocarbons of patchouli oil were:

α-guaiene (21.5%)
seychellene (9.6%)
α-patchoulene (9.1%)
α-bulnesene (34.6%)

In 2000, Buré et al. differentiated four sesquiterpene hydrocarbon isomers in patchouli oil, which were initially separated by GC. They used dimethyl ether as the selective ionization reagent in GC-chemical ionization mass spectrometry to characterize the presence of the following four sesquiterpenes:

aromadendrene
allo-aromadendrene
dehydroaromadendrane
ledene

In 2000, Luo et al. analyzed the composition of the root and rhizome oils of *P. cablin* grown in Gaoyao County, Guangdong using GC/MS. Although these oils are not normally encountered in commerce, their composition is of interest because of the differences between the constituents found in patchouli leaf oil and those found in the rhizome and root oils of patchouli. A summary of the components found in these oils can be seen in Table XII.

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