



Progress in Essential Oils

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Juniperberry Oil

In 1983, Popesco used TLC and IR to examine the composition of juniperberry oil of Romanian origin. The following components were tentatively identified by the above-described inaccurate laboratory technique of TLC separation and characterization:

α -pinene
 camphene
 β -pinene
 myrcene
 δ -3-carene
 α -phellandrene
 α -terpinene
 limonene
 1,8-cineole
 β -phellandrene
 linalool
 camphor
 tanacetol alcohol†
 β -caryophyllene
 borneol
 α -terpinyl acetate
 geranyl acetate
 geraniol

† also known as thujyl alcohol

According to Mambetsadytov et al. (1990), the main components of Russian juniperberry oil were:

α -pinene (18.7%)
 camphene (1.4%)
 sabinene (14.6%)
 α -phellandrene (2.1%)
 limonene (1.2%)
 terpinolene (1.3%)
 borneol (1.2%)
 cedrol (0.7%)

Furthermore, they found that the monoterpene content was lowest during the summer months.

The enantiomeric distribution of terpinen-4-ol found in 8.1% amount in a commercial sample of juniperberry oil was determined by Ravid et al. (1992) to be:

(4S)-(+)-terpinen-4-ol (47%) :
 (4R)-(-)-terpinen-4-ol (53%)

In 1995, Hiltunen and Laakso examined the variation in the amounts and enantiomeric distribution in monoterpene

Table I. Percentage comparison of juniperberry oils

Compound	1W	1C	3W	3C	6W	6C
α -thujene	1.28	0.91	2.31	0.82	3.10	0.40
α -pinene	27.01	27.78	33.93	22.45	46.55	9.78
camphene	0.57	0.19	0.64	0.18	0.70	0.08
sabinene	6.49	10.50	7.08	8.65	3.79	4.64
β -pinene	2.19	1.83	3.02	1.65	3.46	0.91
myrcene	6.82	10.40	9.94	8.82	11.35	5.65
α -terpinene	1.77	0.14	2.50	0.27	2.93	0.27
p-cymene	1.42	0.42	1.83	0.36	1.95	0.29
limonene + 1,8-cineole	1.75	1.43	2.89	1.38	3.51	1.07
γ -terpinene	2.80	0.31	4.22	0.56	4.81	0.53
linalool	1.81	0.48	1.86	0.52	0.08	0.52
<i>trans</i> -sabinene hydrate	1.25	0.36	0.70	0.21	-	0.10
borneol	2.25	0.15	0.65	0.17	-	0.12
terpinen-4-ol	17.00	1.46	22.87	1.58	12.77	2.10
α -terpineol	1.55	0.12	2.19	0.13	1.54	0.11
β -cubebene	-	0.72	-	0.73	-	1.02
β -caryophyllene	-	6.70	-	7.22	-	10.32
α -humulene	-	4.37	-	5.03	0.43	7.18
germacrene D	-	12.76	-	12.92	0.32	14.31
γ -cadinene	-	1.27	-	1.51	0.45	1.96

1W, 3W, 6W = whole berries distilled for 1, 3 and 6 hours, respectively
 1C, 3C, 6C = comminuted berries distilled for 1, 3 and 6 hours, respectively

hydrocarbons in juniperberry oils (30 samples). They found that the variation was as follows:

(-)- α -pinene (6.5-85.1%)	(+)- δ -3-carene (0.2-14.7%)
(+)- α -pinene (0.6-86.8%)	(-)- β -pinene (0.1-5.9%)
myrcene (1.5-35.1%)	(-)-limonene (0.1-0.8%)
(-)-camphene (0.2-0.5%)	(+)-limonene (0.2-20.9%)
(+)-sabinene (0.3-16.7%)	(+)- β -phellandrene (0.2-1.5%)
(+)- β -pinene (0.1-3.1%)	terpinolene (0.1-1.2%)

Also in 1995, Chatzopoulou and Katsiotis examined the compositional differences between whole and comminuted juniperberries that were distilled for 1, 3 and 6 hours. As can be seen in Table I, the oil composition is directly related to the state of the juniperberries and the distillation time.

The following year, Asztemborska et al. (1996) used chiral GC analyses to examine the enantiomeric form of some monoterpene hydrocarbons in juniperberry oil produced from fruit collected in different regions of Poland. They found that oils produced from fruit collected in the northern part of Poland possessed both enantiomeric forms of α -pinene (the major oil constituent), although the (+)-enantiomer predominated. In contrast, an oil produced from fruit collected in southern Poland the (-)-enantiomer predominated. β -pinene was found to exist as the (-)-enantiomer for all oils studied. The enantiomeric distribution of limonene varied somewhat although the (+)-enantiomer predominated, whereas the enantiomeric distribution of camphene showed the (+)-enantiomer predominant in some oils and the (-)-enantiomer predominating in others. Finally, although (+)- β -phellandrene was the predominant enantiomer, it ranged in composition from trace to almost 20% for the Polish oils studied.

In 1997, Ochocka et al. examined the monoterpene hydrocarbon content of juniperberry oils produced from plants harvested in North and Central Poland. They found that the monoterpenes varied as follows:

α -pinene (45.1-80.4%)	α -terpinene (0-1.3%)
camphene (0.2-0.7%)	limonene (1.2-9.8%)
β -pinene (1.6-5.3%)	β -phellandrene (0-0.7%)
sabinene (0-15.8%)	γ -terpinene (0-2.5%)
δ -3-carene (0-0.5%)	p-cymene (0-0.6%)
myrcene (9.9-46.3%)	terpinolene (0-1.9%)

An oil of juniperberries produced in Croatia was analyzed by Kustrak et al. (1997) by GC and GC/MS. Unfortunately, the authors only identified the constituents but did not report any quantitative data. The components that were identified were as follows:

tricylene	terpinolene
α -thujene	p-mentha-1,3,8-triene
α -pinene	cyclosativene
α -fenchene	α -copaene
camphene	β -bourbonene
thuja-2,4(10)-diene	cyperene
verbenene	γ -elemene
β -pinene	β -caryophyllene
myrcene	epi- α -santalene
δ -2-carene	germacrene D
α -phellandrene	β -selinene
δ -3-carene	cis- β -guaiane
α -terpinene	viridiflorene
p-cymene	germacrene D
limonene	γ -cadinene
β -phellandrene	trans-calamenene
(Z)- β -ocimene	α -cadinene
(E)- β -ocimene	germacrene B
γ -terpinene	cis-sabinene hydrate

Table II. Percentage composition of juniperberry oil produced in different seasons

Compound	Spring greenberry oil	Autumn greenberry oil	Autumn blackberry oil
α -pinene	39.51-42.51	27.22-62.08	38.88-57.06
camphene	0.19-0.24	0.18-0.32	0.20-0.31
β -pinene	1.89-2.52	2.08-3.47	2.00-3.41
sabinene	0.35-14.60	5.06-10.86	0.79-16.47
δ -3-carene	-	0-0.03	0.02-0.03
myrcene	14.21-20.23	5.41-14.67	9.14-19.90
α -phellandrene	0-0.09	0-0.04	0.02-0.40
α -terpinene	0-0.03	0.06-0.14	0.03-0.25
limonene	1.31-12.53	1.44-30.96	1.73-7.18
1,8-cineole	0.34-0.59	0.38-0.63	0.37-0.59
γ -terpinene	0.03-0.06	0-0.34	0.11-0.62
p-cymene	0-0.50	0-0.03	0.02-0.22
terpinolene	0.33-0.62	0.80-1.05	0.49-0.91
3-octanol	0.20-0.96	0.19-0.64	0.24-0.54
α -p-dimethylstyrene	0.02-0.13	0.02-0.18	0.04-0.15
decanal	0-0.02	0.04-0.13	0-0.11
linalool	0.28-0.34	0.23-0.31	0.22-0.26
terpinen-4-ol	0-0.16	0-0.04	0.05-0.15
bornyl acetate	0.64-0.69	0.25-1.51	0.97-1.08
β -caryophyllene	2.02-6.61	0.79-2.16	1.81-3.43
furfuryl alcohol	0.17-0.33	0.07-0.62	0.15-0.34
α -terpineol	0.50-2.64	0.64-1.24	0.85-0.98
carvone	0.14-0.35	0.15-0.27	0.19-0.33
geranyl acetate	-	0-0.26	0-0.02
citronellol	6.75-15.57	6.76-7.12	5.06-12.75
nerol	0.17-0.36	0.11-0.21	0.24-0.41
myrtenol	0.28-0.73	0.24-0.98	0.60-0.70
cedrol	0.60-1.84	0.56-1.20	0.99-1.24
geraniol	0.52-0.91	0.14-1.15	0-0.67
eugenol	0.76-2.33	0.45-1.97	0.96-1.30
thymol	-	0-0.21	0.03-0.27
borneol	1.61-4.51	0.86-1.43	1.30-2.54
carvacrol	0.16-0.29	0.05-0.24	0.03-0.20

trans-sabinene hydrate	α -terpineol
cis-p-menth-2-en-1-ol	cis-piperitol
trans-p-menth-2-en-1-ol	trans-piperitol
borneol	trans-chrysanthenyl acetate
terpinen-4-ol	methyl citronellate
p-cymen-8-ol	bornyl acetate

Koukos and Papadopoulou (1997) compared the composition of juniperberry oil produced from green berries in the spring and autumn and black (ripe) berry oil produced in the autumn in Greece. The results of study are shown in Table II.

Table III. Variation in main components (%) in lab-distilled and commercial juniperberry oils

Compound	Lab-distilled oils (16) ^a	Commercial oils (15) ^a
α -pinene	18.1-51.3	26.5-70.5
β -pinene	1.1-2.9	0.7-12.6
myrcene	3.2-21.2	0.3-29.9
limonene	2.4-6.4	2.7-22.1
terpinolene	0.3-2.4	trace-13.6
α -terpineol	0.3-1.7	trace-4.9
bornyl acetate	0.2-0.4	trace-2.0
β -caryophyllene	0.7-4.0	trace-8.2
germacrene D	1.4-8.0	trace-9.5
δ -cadinene	0.7-3.6	trace-4.1

^a number of samples

Using GC/MS as their method of analysis Menut et al. (1997) examined the composition of a commercial sample of juniperberry oil. It was found to possess the following composition:

α -thujene (0.8%)	β -elemene (0.8%)
α -pinene (62.2%)	β -caryophyllene (1.8%)
camphene (0.4%)	γ -elemene (0.3%)
sabinene (6.6%)	(Z)- β -farnesene (0.3%)
β -pinene (2.8%)	α -humulene (1.2%)
myrcene (8.1%)	γ -muurolene (0.3%)
α -phellandrene (0.2%)	germacrene D (1.4%)
p-cymene (0.1%)	epi-cubebol (0.2%)
limonene (2.7%)	α -muurolene (0.5%)
γ -terpinene (0.1%)	γ -cadinene (0.3%)
terpinolene (0.3%)	cis-calamenene (0.1%)
α -pinene oxide (0.4%)	δ -cadinene (0.5%)
pinocarveol† (0.2%)	germacrene B (0.7%)
p-cymen-8-ol (0.1%)	spathulenol (0.2%)
terpinen-4-ol (0.6%)	caryophyllene oxide (0.2%)
α -terpineol (0.2%)	humulene oxide* (0.1%)
bornyl acetate (0.3%)	α -cadinol (0.2%)
α -copaene (0.3%)	

* correct isomer not identified

† presumed trans-form because of elution order

In 1999, Kartnig et al. examined the major component composition and enantiomeric distribution of six of the chiral constituents of lab-distilled and commercial juniperberry oils. The results of this study can be found in Tables III. and IV.

- H. Popesco, *The chemical composition of some essential oils from plants of Romanian provenance*. Clujul Medical, 56(2), 168-170 (1983).
- M. B. Mambetsadykov, Z. S. Dzhamagulova and Kh. M. Sushanio, *Chemical composition and pharmacological properties of common juniper essential oil*. Khim-Farm. Zh., 24(9), 59-60 (1990).
- H. Ravid, E. Putievsky, I. Katzir and R. Ikan, *Determination of the enantiomeric composition of terpinen-4-ol in essential oils using a permethylated β -cyclodextrin coated chiral capillary column*. Flav. Fragr. J., 7, 49-52 (1992).
- R. Hiltunen and I. Laakso, *Gas chromatographic analysis and biogenetic relationships of monoterpene enantiomers in Scots Pine and juniper needle oils*. Flav. Fragr. J., 10, 203-210 (1995).
- P. S. Chatzopoulou and S. T. Katsiotis, *Procedures influencing the yield and quantity of the essential oil from Juniperus communis L. berries*. Pharm. Acta Helv., 70, 247-253 (1995).
- M. Asztemborska, D. Zook, R. Ochocka and G. Perez, *Enantiomeric ratio of selected lower terpenoids in plant material of Juniperus communis L.* Rivista Ital. EPPOS, (Numero Speciale), 512-521 (1996).
- J. R. Ochocka, M. Asztemborska, D. R. Zook, D. Sybilska, G. Perez and L. Ossicini, *Enantiomers of monoterpene hydrocarbons in essential oils from Juniperus communis*. Phytochemistry, 44, 869-873 (1997).
- D. Kustrak, A. Baerheim Svendsen and J. Karlsen, *Composition of the essential oil of berries of Juniperus communis L. of Croatian origin*. In: *Proceedings of 27th International Symposium on Essential Oils, Vienna, 1996*. Edits., Ch. Franz., A. Mathé and G. Buchbauer, p. 192-194, Allured Publ., Carol Stream, IL (1997).
- P. K. Koukos and K. I. Papadopoulou, *Essential oil of Juniperus communis L. grown in Northern Greece: Variation of fruit oil yield and composition*. J. Essent. Oil Res., 9, 35-39 (1997).
- C. Menut, G. Lamaty and J-M. Bessiere, *Etude comparative des huiles essentielles de baies de Juniperus oxycedrus et Juniperus communis*. Rivista Ital. EPPOS, (Numero Speciale), 279-283 (1997).
- Th. Kartnig, E. Fischer and F. Bucar, *Gas chromatographische Untersuchungen und Ätheroleum Juniperi unterbesonderer Berücksichtigung de Trennung enantiomerer Komponenten*. Sci. Pharm., 67, 77-82 (1999).

Table IV. Enantiomeric distribution of six chiral components in lab-distilled and commercial juniperberry oils

Compound	Enantiomeric distribution	
	Lab-distilled oils (16) ^a	Commercial oils (15) ^a
(-)- α -pinene : (+)- α -pinene	71.6 : 28.4	68.3 : 31.7
(-)-sabinene : (+)-sabinene	0 : 100.0	0 : 100.0
(-)- β -pinene : (+)- β -pinene	97.1 : 2.9	95.0 : 5.0
(-)-limonene : (+)-limonene	13.7 : 86.3	34.9 : 65.1
(-)-terpinen-4-ol : (+)-terpinen-4-ol	80.5 : 19.5	31.0 : 69.0
(-)- β -caryophyllene : (+)- β -caryophyllene	100 : 0	100 : 0

^a number of samples

Juniper Leaf, Branch and Wood Oils

In 1989, Bats et al. analyzed a commercial juniper oil produced by continuous steam distillation of the crushed branches, needles and some wood of *J. communis* that was harvested in southwestern France. Oil analysis (see Table V.) revealed that the wood oil was as expected richer in sesquiterpenoid compounds than the branch oil.

Two years later, Adams (1991) analyzed an oil produced from *J. communis* var. *depressa* of U.S. origin using GC (retention indices) and GC/MS (component identification) and found that it contained the following constituents:

2-hexenal* (trace)	verbenone (0.9%)
tricyclene (trace)	<i>trans</i> -carveol (0.6%)
α -pinene (14.1%)	citronellol (4.0%)
camphene (0.2%)	methyl thymol (0.1%)
thuja-2,4-(10)-diene (trace)	carvone (0.3%)
sabinene (0.2%)	<i>cis</i> -myrtanol (0.1%)
β -pinene (2.1%)	carvenone (0.3%)
myrcene (4.4%)	geraniol (0.4%)
δ -2-carene (trace)	<i>trans</i> -myrtanol (0.9%)
α -phellandrene (trace)	methyl citronellate (1.3%)
δ -3-carene (0.2%)	bornyl acetate (5.2%)
α -terpinene (trace)	citronellyl acetate (0.5%)
p-cymene (trace)	neryl acetate (0.2%)
limonene (1.1%)	geranyl acetate (1.9%)
β -phellandrene (1.1%)	β -elemene (0.2%)
amyl isovalerate (trace)	β -caryophyllene (0.2%)
γ -terpinene (trace)	geranyl acetone (0.2%)
<i>trans</i> -sabinene hydrate (trace)	α -humulene (0.2%)
fenchone (trace)	(Z)- β -farnesene (0.3%)
terpinolene (1.4%)	germacrene D (0.9%)
linalool (2.0%)	ar-curcumene (0.2%)
nonanal (trace)	zingiberene (0.6%)
isoamyl isovalerate (0.4%)	α -muurolene (0.1%)
α -fenchol (0.2%)	β -bisabolene (0.6%)
<i>cis</i> -p-menth-2-en-1-ol (trace)	γ -cadinene (0.2%)
α -campholenal (2.3%)	δ -cadinene (0.8%)
<i>trans</i> -pinocarveol (1.2%)	γ -elemene† (0.3%)
<i>trans</i> -p-menth-2-en-1-ol (trace)	(E)-nerolidol (3.8%)
<i>cis</i> -verbenol (0.6%)	germacrene D-4-ol (1.2%)
<i>trans</i> -verbenol (3.4%)	spathulenol (1.2%)
camphene hydrate (1.1%)	caryophyllene oxide (0.2%)
citronellal (0.5%)	β -oplopenone (0.2%)
isopinocamphe (0.4%)	T-cadinol (0.2%)
pinocarvone (0.4%)	T-muurolol (0.2%)
borneol (1.8%)	α -muurolol (0.1%)
p-mentha-1,5-dien-8-ol (0.4%)	α -cadinol (0.8%)
terpinen-4-ol (2.5%)	epi- α -bisabolol (3.2%)
p-cymen-8-ol (0.3%)	(Z,Z)-farnesol (0.4%)
α -terpineol (3.9%)	(E,E)-farnesol (1.6%)
myrtenal (2.2%)	(E,Z)-farnesol (0.4%)
pinocamphe (0.6%)	manool (0.3%)

† incorrect identification based on elution order

Adams also produced a needle oil from *J. communis* var. *saxabilis* of Swiss origin and analyzed it by GC/MS. A summary of the components found in this oil can be seen as follows:

(E)-2-hexenal (1.2%)	terpinen-4-ol (7.3%)
tricyclene (trace)	p-cymen-8-ol (trace)
α -thujene (4.1%)	α -terpineol (0.4%)
α -pinene (14.1%)	methyl thymol (0.1%)
α -fenchene (0.1%)	bornyl acetate (0.2%)
camphene (0.2%)	α -terpinyl acetate (0.5%)
verbenene (0.1%)	citronellyl acetate (0.1%)
sabinene (32.8%)	<i>trans</i> -myrtanyl acetate (trace)
β -pinene (1.9%)	β -elemene (trace)
myrcene (5.0%)	β -caryophyllene (trace)
δ -2-carene (0.4%)	α -humulene (trace)
α -phellandrene (0.5%)	germacrene D (0.4%)
δ -3-carene (0.5%)	(E)-methyl isoeugenol (0.2%)
α -terpinene (1.9%)	α -muurolene (0.2%)
p-cymene (0.3%)	germacrene A (0.2%)
limonene (6.7%)	γ -cadinene (0.4%)
β -phellandrene (0.6%)	δ -cadinene (0.8%)
(E)- β -ocimene (0.1%)	α -cadinene (trace)
γ -terpinene (3.4%)	germacrene B (0.3%)
<i>cis</i> -sabinene hydrate (1.8%)	germacrene D-4-ol (1.8%)
terpinolene (3.0%)	1-epi-cubenol (trace)
<i>trans</i> -sabinene hydrate (1.3%)	T-cadinol (0.5%)
linalool (trace)	α -muurolol (0.1%)
isoamyl isovalerate (trace)	α -cadinol (1.3%)
β -thujone (0.6%)	manoyl oxide (0.2%)
<i>trans</i> -p-menth-2-en-1-ol (0.3%)	abietatriene (0.2%)
<i>cis</i> -sabinol (trace)	abietadiene (trace)
borneol (trace)	

In 1993, Schilcher et al. reported that the composition of three lab-distilled oils in *Juniperus communis* needles varied as follows:

α -thujene (0-0.60%)	p-cymene (trace-0.65%)
α -pinene (0.62-0.69%)	limonene (3.00-4.50%)
camphene (trace-0.54%)	terpinen-4-ol (0.51-0.82%)
sabinene (3.84-11.11%)	bornyl acetate (22.88-37.44%)
myrcene (2.99-5.25%)	

Also in 1993, Chatzopoulou and Katsiotis analyzed an oil produced from *J. communis* needles obtained from plants growing on Mount Olympus at an altitude of 1300m. Using both GC and GC/MS as their methods of analysis, a representative oil was found to contain:

tricyclene (0.12%)	<i>trans</i> -sabinene hydrate (0.16%)
α -thujene (1.68%)	fenchone (0.03%)
α -pinene (41.25%)	3-octanol (0.02%)
α -fenchene (0.09%)	terpinolene (1.16%)
camphene (0.27%)	linalool (0.11%)
sabinene (17.38%)	<i>cis</i> -sabinene hydrate (0.05%)
β -pinene (2.05%)	1-octen-3-ol (0.08%)
myrcene (2.66%)	β -thujone (0.13%)
δ -2-carene (0.66%)	<i>trans</i> -p-menth-2-en-1-ol (0.25%)
α -phellandrene (0.18%)	<i>cis</i> -p-menth-2-en-1-ol (0.22%)
δ -3-carene (0.69%)	camphor (0.29%)
α -terpinene (1.22%)	citronellal (0.33%)
p-cymene (0.92%)	pinocarvone (0.06%)
β -phellandrene (0.35%)	<i>trans</i> -carveol (0.03%)
limonene (4.23%)	borneol (0.06%)
1,8-cineole (1.21%)	terpinen-4-ol (2.78%)
(E)- β -ocimene (0.18%)	α -terpineol (0.51%)
γ -terpinene (2.09%)	citronellol (0.19%)

Table V. Percentage composition of the branch and wood oils of *Juniperus communis*

Compound	Juniper branch oil	Juniper wood oil
α -thujene	1.3	-
α -pinene	18.7	5.3
camphene	0.2	trace
sabinene	5.0	0.1
β -pinene	1.2	0.4
myrcene	1.8	0.2
α -phellandrene	0.3	-
δ -3-carene	0.6	0.3
α -terpinene	1.1	-
p-cymene	0.9	trace
limonene	2.0	0.3
(E)- β -ocimene	trace	-
γ -terpinene	1.8	-
α -p-dimethylstyrene	0.2	-
terpinolene	1.0	-
terpinen-4-ol	2.0	trace
α -terpineol	0.2	-
bornyl acetate	0.2	-
α -terpinyl acetate	0.1	-
α -cubebene	0.5	0.2
α -copaene	0.3	0.3
isolongifolene	0.5	0.6
α -cedrene + unknown	2.7	4.6
β -cedrene + β -caryophyllene	.30	3.9
thujopsene	25.0	42.4
α -humulene	1.0	1.0
germacrene D	0.7	0.4
cuparene	5.2	6.4
δ -cadinene	2.6	2.1
caryophyllene oxide	0.2	0.2
cedrol	2.6	10.9
α -bisabolol	0.2	0.4

linalyl acetate (0.08%)
 bornyl acetate (0.36%)
 citronellyl acetate (0.51%)
 α -copaene (0.32%)
 β -cubebene (0.03%)
 β -elemene (0.13%)
 β -caryophyllene (1.69%)
 α -humulene (1.56%)
 γ -muurolene (0.26%)
 germacrene D (1.83%)

α -muurolene (0.21%)
 γ -cadinene (0.71%)
 δ -cadinene (0.91%)
 calacorene* (0.06%)
 α -cadinene (0.08%)
 caryophyllene oxide (0.77%)
 humulene oxide* (0.65%)
 T-cadinol (0.76%)
 α -cadinol (0.72%)

* correct isomer not identified

Two years later, Caramiello et al. (1995) studied the composition of *J. communis* needle oils produced from plants growing spontaneously in northern Italy. The compounds identified in these oils were as follows:

α -pinene (8.4-22.0%)	(Z)- β -ocimene (0.4-0.6%)
α -fenchene (2.8-4.0%)	p-cymene (0.4-2.6%)
camphene (0-0.2%)	terpinolene (1.7-2.6%)
β -pinene (0.6-2.2%)	β -thujone (0.6-1.3%)
sabinene (32.0-47.5%)	bornyl acetate (0.1-1.4%)
δ -3-carene (0-0.3%)	β -caryophyllene (0-1.2%)
myrcene (3.0-3.9%)	terpinen-4-ol (5.6-11.1%)
α -terpinene (1.3-2.4%)	α -terpineol (0.4-2.5%)
limonene (2.5-2.9%)	germacrene D (0.4-2.6%)
1,8-cineole (0.3-1.7%)	δ -cadinene (0.2-1.7%)
β -phellandrene (0.3-2.9%)	β -eudesmol (0.5-2.0%)
γ -terpinene (2.3-4.1%)	

The amounts and enantiomeric distribution of monoterpene hydrocarbons in the low sabinene chemotype and high sabinene chemotype of *J. communis* were examined by Hiltunen and Laakso (1995). Their results can be seen summarized in Table VI.

Rezzi et al. (1997) used GC and ^{13}C -NMR to determine that two samples each of Corsican and Portuguese lab-distilled needle oils of *J. communis* ssp. *alpina* Suter were qualitatively and quantitatively different as shown in Table VII.

A needle oil of *J. communis* var. *saxatilis* was examined by Karlsen et al. (1997) using GC, GC/MS and chiral GC analyses. Although the authors stated that the needle oil of this Norwegian juniper contained more than 60% (-)-sabinene, they did not quantitate any other of the following constituents:

tricyclene	α -copaene
α -thujene	β -bourbonene
(+)- α -pinene	β -elemene
(-)- α -pinene	cyperene
(-)- α -fenchene	β -caryophyllene
(+)-camphene	α -guaiane
(-)-camphene	α -humulene
(+)- β -pinene	isogermacrene D
(-)- β -pinene	cis-murola-4(14),5-diene
(-)-sabinene	γ -murolene
δ -2-carene	germacrene D
δ -3-carene	β -bisabolene
myrcene	β -selinene
(+)- α -phellandrene	α -murolene
(-)- α -phellandrene	α -bulnesene
α -terpinene	γ -cadinene
(+)-limonene	7-epi- α -selinene
(-)-limonene	δ -cadinene
β -phellandrene	cadina-1,4-diene
γ -terpinene	α -cadinene
(E)- β -ocimene	selina-3,7(11)-diene
p-cymene	germacrene B
terpinolene	trans-sabinene hydrate
α -cubebene	linalool
isodene	cis-sabinene hydrate

Table VI. Variation in the percentage composition of the chiral and non-chiral monoterpene hydrocarbons in the low and high sabinene chemotype leaf oils of *Juniperus communis*

Compound	Low sabinene chemotype (20) ^a	High sabinene chemotype (10)
α -thujene	-	0.8-3.7
(-)- α -pinene	14.9-42.2	10.2-52.6
(+)- α -pinene	40.0-71.4	3.5-33.9
myrcene	1.7-4.5	2.7-5.5
(+)-sabinene	0.6-1.3	10.1-47.9
(+)- β -pinene	0.9-4.9	1.0-2.3
(+)- δ -3-carene	4.4-12.7	3.5-11.5
(-)- β -pinene	1.2-3.1	1.9-3.5
(-)-limonene	0.1-1.2	0.2-2.9
(+)-limonene	0.2-1.6	0.8-8.0
(+)- β -phellandrene	0.3-11.0	0.6-11.1
γ -terpinene	-	0.2-1.6
terpinolene	0.2-1.1	0.6-3.5

Table VII. Comparative percentage composition of Corsican and Portuguese *Juniperus communis* ssp. *alpina* needle oils

Compound	Corsican oils	Portuguese oils
α -thujene	-	1.6
α -pinene	2.9-4.7	19.7-23.5
δ -2-carene†	0.4-0.9	-
β -pinene	-	1.1-1.2
sabinene	-	11.4-13.6
myrcene	3.4-3.7	3.5-3.6
α -phellandrene	4.0-5.6	-
limonene	39.7-41.8	21.9-30.9
β -phellandrene	14.8-19.3	6.2-3.5
p-cymene	0.9-1.1	5.0-9.0
terpinolene	0-1.1	-
linalool	-	0-0.5
terpinen-4-ol	-	5.7-16.6
citronellyl acetate	0.9-1.6	-
α -terpinyl acetate	8.0-9.9	-
α -terpineol	2.7-6.5	0-1.6
δ -cadinene	0.6-0.8	-

† incorrect identification based on elution order

cis-p-menth-2-en-1-ol	trans-pulegol
trans-p-menth-2-en-1-ol	trans-piperitol
bornyl acetate	cis-piperitol
methyl thymol	α -terpineol
terpinen-4-ol	perilla ketone

Also in 1997, Ochocka et al. examined the variability in monoterpene hydrocarbons in oils produced from 10 samples of juniper needles harvested from shrubs located in northern and central Poland. The range of hydrocarbons found can be seen as follows:

α -pinene (27.8-89.7%)	α -terpinene (0-6.3%)
camphene (0.2-0.9%)	limonene (1.1-15.8%)
β -pinene (1.2-2.9%)	β -phellandrene (0.5-19.1%)
sabinene (0.3-42.5%)	γ -terpinene (0-11.8%)
δ -3-carene (0-3.3%)	p-cymene (0-1.6%)
myrcene (3.0-6.6%)	terpinolene (0-4.4%)

The authors also found that (-)- β -pinene and (+)-sabinene were the only enantiomers of the two hydrocarbons present in the oils.

The major components of the needle oils of *J. communis* var. *communis* of Bulgarian origin were determined by Stoyanova (1997) to be as follows:

α -pinene (10.98-30.78%)	limonene (4.55-13.92%)
β -pinene (4.12-33.20%)	terpinen-4-ol (0.57-1.05%)
δ -3-carene (0.13-0.93%)	bornyl acetate (1.13-2.56%)

For comparison purposes, Stoyanova also determined that the main components to oils of *J. communis* var. *nana* (also of Bulgarian origin) were as follows:

α -pinene (28.28-42.11%)	limonene (8.12-10.05%)
β -pinene (1.05-5.84%)	terpinen-4-ol (1.19-1.85%)
δ -3-carene (2.05-2.30%)	bornyl acetate (2.11-3.04%)

The same year, Milhau et al. (1997) analyzed a hydrodistilled oil of twigs and needles of *J. communis* using GC/MS. This oil was found to contain the following components:

α -thujene (0.2%)	terpinolene (0.5%)
α -pinene (44.3%)	terpinen-4-ol (3.1%)
camphene (1.3%)	α -terpineol (1.5%)
β -pinene (11.1%)	myrtenol (0.4%)
myrcene (9.6%)	bornyl acetate (0.5%)
α -phellandrene (0.4%)	β -caryophyllene (1.2%)
δ -3-carene (0.6%)	α -humulene (0.6%)
α -terpinene (1.3%)	germacrene D (0.6%)
p-cymene (1.2%)	γ -cadinene (1.4%)
limonene (18.0%)	δ -cadinene (0.4%)
γ -terpinene (0.4%)	benzyl benzoate (0.3%)

In 1998, Wibe et al. found that the headspace obtained from the branches of Norwegian *J. communis* contained the following relative amounts of the enantiomeric forms of seven monoterpene hydrocarbons:

(+)- α -pinene (18.0%)	(-)-sabinene (0.1%)
(-)- α -pinene (18.1%)	(+)- δ -3-carene (4.7%)
(+)-camphene (0.1%)	(-)- δ -3-carene (0%)
(-)-camphene (0.2%)	(+)-limonene (5.7%)
(+)- β -pinene (0.5%)	(-)-limonene (0.5%)
(-)- β -pinene (1.3%)	(+)- β -phellandrene (0.3%)
(+)-sabinene (47.4%)	(-)- β -phellandrene (2.8%)

In 2000, Adams used a combination of GC and GC/MS to examine the composition of a lab-distilled leaf oil produced from *J. communis* var. *communis* of Swedish origin. The components identified in this oil were as follows:

(E)-2-hexenal (0.7%)	borneol (0.2%)
tricyclene (0.3%)	terpinen-4-ol (0.2%)
α -thujene (0.1%)	naphthalene (trace)
α -pinene (56.8%)	p-cymen-8-ol (trace)
α -fenchene (0.4%)	α -terpineol (0.2%)
camphene (0.6%)	citronellol (trace)
sabinene (0.7%)	bornyl acetate (0.9%)
β -pinene (4.4%)	β -elemene (0.2%)
myrcene (5.2%)	β -caryophyllene (0.7%)
δ -2-carene (0.2%)	α -humulene (0.5%)
α -phellandrene (2.1%)	germacrene D (0.7%)
δ -3-carene (4.7%)	α -muurolene (0.2%)
p-cymene (0.3%)	germacrene A (0.1%)
limonene (6.9%)	γ -cadinene (0.2%)
β -phellandrene (6.9%)	δ -cadinene (0.5%)
(Z)- β -ocimene (0.2%)	germacrene B (0.3%)
amyl isobutyrate (0.2%)	germacrene D-4-ol (0.8%)
γ -terpinene (trace)	T-cadinol (trace)
terpinolene (1.1%)	T-muurolol (0.4%)
isoamyl isovalerate (0.1%)	α -cadinol (0.5%)
3-methyl-2-butenyl isovalerate* (0.1%)	(E)- α -atlantone (0.3%)

*correct isomer not identified

- J-P. Bats, J-J. Moulines, G. Bourgeois, C. Vacchiano, D. Coutiere and J-F. Arnaudo, *Chemical Composition of an Industrial essential oil from Juniper branches (Juniperus communis L.)*. In: *Proceedings 11th International Congress for Essential Oils, Fragrances and Flavours. Vol. 4. Chemistry Analysis and Structure*. Edits. S. C. Bhattacharyya, N. Sen and K. L. Sethi, pp. 37-41, Oxford & IBH Publ. Co., New Delhi (1989).
- R. P. Adams, *Analysis of Juniper and other forest tree oil*. In: *Modern Methods of Plant Analysis New Series, Vol. 12, Essential oils and waxes*. Edits. H. F. Linskens and J. F. Jackson, p. 131-157, Springer Verlag, New York (1991).
- H. Schilcher, D. Emmrich and C. Koehler, *Gas chromatographischer Vergleich von ätherische Wacholderölen und deren toxikologische Bewertung*. Pharm. Ztg., Wiss., 138(3/4), 85-91 (1993).
- P. S. Chatzopoulou and S. T. Katsiotis, *Chemical investigation of the leaf oil of Juniperus communis L.* J. Essent. Oil Res., 5, 603-607 (1993).
- R. Caramiello, A. Bocca, G. Buffa and M. Maffei, *Chemotaxonomy of Juniperus communis, J. sibirica and J. intermedia*. J. Essent. Oil Res., 7, 133-145 (1995).
- R. Hiltunen and I. Laakso, *Gas chromatographic analysis and biogenetic relationships of monoterpene enantiomers in Scots Pine and juniper needle oils*. Flav. Fragr., J., 10, 203-210 (1995).
- S. Rezzi, C. Cavaleiro, A. Bighelli, L. Salgueiro, A. Proença da Cuna and J. Casanova, *Analyses d'huiles essentielles de Juniperus communis ssp. alpina de Corse et du Portugal par RMN du carbone-13*. Rivista Ital. EPPOS, (Numero Speciale), 697-702 (1997).
- J. Karlsen, G. Fladseth, J. Remme, A. Baerheim Svendsen, V. Holm and R. Hiltunen, *Enantiomeric composition of the monoterpene hydrocarbons occurring in the needles of Juniperus communis L. var. saxatilis Pall. (Norwegian mountain juniper)*. In: *Proceedings of 27th International Symposium on Essential Oils, Vienna 1996*. Edits., Ch. Franz, A. Mathé and G. Buchbauer, p. 189-192, Allured Publ., Carol Stream, IL (1997).

- J. R. Ochocka, M. Asztemborska, D. R. Zook, D. Sybilska, G. Perez and L. Ossicini, *Enantiomers of monoterpene hydrocarbons in essential oils from Juniperus communis*. Phytochemistry, 44, 869-873 (1997).
- M. Stoyanova, *Comparative study on the needle essential oils of Juniperus communis and J. communis var. nana Willd. in Bulgaria*. In: *Proceedings of 27th International Symposium on Essential Oils, Vienna 1996*. Edits., Ch. Franz, A. Mathé and G. Buchbauer, pp. 194-195, Allured Publ., Carol Stream, IL (1997).
- G. Milhau, A. Valentin, F. Benoit, M. Mallié, J-M. Bastide, Y. Pélissier and J-M. Bessière, *In vitro antimalarial activity of eight essential oils*. J. Essent. Oil Res., 9, 329-333 (1997).
- A. Wibe, A-K. Borg-Karlson, M. Persson, T. Norin and H. Mustaparta, *Enantiomeric composition of monoterpene hydrocarbons in some conifers and receptor neuron discrimination of α -pinene and limonene enantiomers in the pine weevil Hylobius abietis*. J. Chem. Ecol., 24, 273-287 (1998).
- R. P. Adams, *Systematics of Juniperus based on leaf essential oils and random amplified polymorphic DNAs (RAPDs)*. Biochem. Syst. Ecol., 28, 515-528 (2000).

Eucalyptus citriodora Oil

In 1994, Chaudhry et al. used GC (for quantitative data) and GC/MS (for component identification) to analyze an oil of *Eucalyptus citriodora* Hook. (syn. *Corymbia citriodora* (Hook.) J., D. Hillet, L.A.S. Johnson) produced using a Likens-Nickerson simultaneous distillation and extraction apparatus from leaves and terminal branches harvested in Pakistan. The constituents identified in the oil were as follows:

3-methylbutanal (trace)	citronellol (12.0%)
α -pinene (0.5%)	citronellyl formate (1.3%)
β -pinene (0.4%)	lavandulol (0.4%)
limonene (trace)	geranial (trace)
dihydroterpineol† (trace)	citronellyl acetate (1.9%)
2,6-dimethyl-5-heptenal (trace)	β -caryophyllene (1.6%)
terpinen-4-yl acetate† (trace)	α -humulene (trace)
citronellal (79.0%)	γ -cadinene (0.4%)
isopulegol (2.7%)	elixene‡ (trace)
α -terpineol (trace)	patchoulene† (trace)

† compound misidentified based on elution order

‡ misnaming of germacrene B (based on elution order). This confusion in nomenclature was caused by the Chemical Abstracts CAS numbering and lack of discrimination between γ -elemene, bicyclogermacrene, germacrene B and elixene.

Also in 1994, Dethier et al. examined the composition of the oils of *Eucalyptus* species of Burundian origin using GC and GC/MS. They found that an oil of *E. citriodora* contained the following constituents:

α -pinene (0.6%)	borneol (0.1%)
β -pinene (1.7%)	terpinen-4-ol (0.1%)
p-cymene (0.1%)	α -terpineol (0.4%)
1,8-cineole (4.9%)	citronellol (20.4%)
limonene (0.5%)	citronellyl acetate (10.3%)
γ -terpinene (1.2%)	β -caryophyllene (3.5%)
terpinolene (0.3%)	α -humulene (0.2%)
linalool (0.3%)	bicyclogermacrene (1.0%)
citronellal (46.9%)	spathulenol (0.1%)
isopulegol (6.2%)	caryophyllene oxide (0.1%)
iso(iso)pulegol (0.7%)	

Two years later, Sohounhloué et al. (1996) compared the composition of the leaf oils of three *Eucalyptus* species including *E. citriodora* by GC and GC/MS. Using retention indices and MS for component identification and GC-FID for quantitative data without the use of an internal standard, the oil contained the following components:

α -pinene (0.10%)	citronellol (13.05%)
β -pinene (0.42%)	citronellyl acetate (2.05%)
1,8-cineole (0.52%)	β -caryophyllene (0.51%)
isopulegol (10.33%)	(E,E)-farnesol (0.90%)
citronellal (65.45%)	

The following year, Asefa and Dagne (1997) used GC and GC/MS to determine that an oil of *E. citriodora* of Ethiopian origin contained:

α -pinene (0.2%)	citronellal (79.3%)
β -pinene (0.2%)	citronellol (8.3%)
decane (0.2%)	citronellyl acetate (2.3%)
myrcene (trace)	β -caryophyllene (0.2%)
linalool (0.2%)	eugenol (0.1%)
isopulegol (5.5%)	

An oil of Rwandan *E. citriodora* was analyzed by Chalchat et al. (1997) using GC and GC/MS. It was found to possess the following composition:

α -pinene (1.32%)	α -humulene (0.04%)
α -thujene (0.21%)	γ -amorphene (0.02%)
isobutyl isobutyrate (0.16%)	γ -muurolene (0.12%)
β -pinene (1.40%)	α -terpineol (0.08%)
sabinene (2.33%)	α -terpinyl acetate (0.45%)
α -phellandrene (trace)	α -muurolene (1.23%)
myrcene (0.58%)	geraniol (0.75%)
α -terpinene (0.05%)	γ_2 -cadinene (trace)
limonene (5.66%)	δ -cadinene (0.65%)
1,8-cineole (55.44%)	cadina-1,4-diene (3.04%)
γ -terpinene (0.17%)	α -cadinene (0.13%)
(E)- β -ocimene (0.02%)	citronellol (8.88%)
p-cymene (1.39%)	calamenene (0.41%)
terpinolene (0.45%)	p-cymen-8-ol (0.36%)
cis-rose oxide (0.19%)	geraniol (0.34%)
trans-rose oxide (0.05%)	cis-p-menth-1(7),8-dien-2-ol (0.03%)
α -p-dimethylstyrene (0.07%)	α -calacorene (0.06%)
α -cubebene (0.04%)	caryophyllene oxide (0.15%)
citronellal (7.19%)	germacrene D-4-ol (0.15%)
1-octen-3-ol (0.18%)	cubenol (0.08%)
α -gurjunene (0.06%)	epi-cubenol (0.12%)
β -cubebene (0.26%)	spathulenol (0.06%)
neoisopulegol (0.24%)	α -muurolol (0.34%)
isopulegol (0.62%)	T-muurolol (0.30%)
carvenone (0.06%)	α -cadinol (0.55%)
β -caryophyllene (0.48%)	
terpinen-4-ol (0.49%)	

* correct isomer not identified

It should be pointed out that this oil is very atypical. Either it is an example of a chemotypic form of *E. citriodora* or the original plant material was misidentified.

Chalchat et al. (1997) also compared the composition of two oils of *E. citriodora* produced in Calvi and Kétou

in Benin. The oils, which were found to be very similar, contained the following components:

α -pinene (0.07-0.32%)	isopulegol (4.90-7.64%)
β -pinene (0.30-0.43%)	β -caryophyllene (0.56-0.92%)
myrcene (0.12%)	citronellyl acetate (0.90-1.99%)
limonene (0.07-0.08%)	citronellol (7.65-7.70%)
1,8-cineole (0.27-0.47%)	trans-p-menth-2-en-8-ol (trace-0.15%)
citronellal (72.24-79.72%)	cis-p-menth-2-en-8-ol (trace)
pulegol* (1.50-2.45%)	
linalool (0.94-1.90%)	

* correct isomer not identified

Also in 1997, Kaul et al. analyzed a fresh oil of *E. citriodora* of South Indian origin and compared its composition to that of an aged oil. As can be seen from the results presented in Table VIII, the citronellal content of the aged oil is reduced due to oxidation of citronellal to isopulegol.

A sample of Bangladeshi *E. citriodora* oil was found by Mondello et al. (1998) to contain:

tricyclene (trace)	terpinen-4-ol (0.11%)
α -pinene (0.06%)	α -terpineol (0.01%)
sabinene (0.02%)	nerol (0.06%)
β -pinene (0.30%)	citronellol (5.94%)
myrcene (0.11%)	neral (0.03%)
p-cymene (0.02%)	geraniol (0.02%)
limonene (0.35%)	geraniol (0.05%)
2,6-dimethyl-5-heptenal (0.30%)	δ -terpineol (0.18%)
γ -terpinene (0.05%)	citronellyl acetate (0.38%)
p-mentha-3,8-diene (0.05%)	β -elemene (0.04%)
terpinolene (0.02%)	(Z)-jasmone (0.07%)
linalool (0.10%)	β -caryophyllene (0.80%)
cis-rose oxide (0.05%)	α -humulene (0.05%)
trans-rose oxide (0.08%)	germacrene D (0.04%)
neoisopulegol (7.28%)	spathulenol (0.01%)
citronellal (76.98%)	caryophyllene oxide (0.14%)
iso(iso)pulegol (4.13%)	β -asarone (0.02%)
neiso(iso)pulegol (0.36%)	

Also in 1999, Moudachirou et al. determined that *E. citriodora* oil produced in different locations in Benin revealed the following compositional variability:

α -pinene (trace-0.2%)	isopulegol (1.9-15.0%)
β -pinene (0.1-0.6%)	β -caryophyllene (0.2-1.7%)
myrcene (trace-0.2%)	citronellyl acetate (trace-4.2%)
limonene (trace-0.1%)	citronellol (2.5-12.8%)
1,8-cineole (trace-0.7%)	trans-p-menth-2-en-8-ol (trace-0.3%)
citronellal (55.1-89.9%)	cis-p-menth-2-en-8-ol (trace)
pulegol* (0.8-4.7%)	
linalool (trace-2.8%)	

*correct isomer not identified

Recently, Dagne et al. (2000) analyzed an oil of *E. citriodora* produced in Ethiopia. The constituents they identified in the oil were:

α -pinene (0.8%)	citronellal (73.3%)
β -pinene (0.7%)	citronellol (11.9%)
1,8-cineole (1.3%)	geraniol (0.4%)
isopulegol (8.9%)	β -caryophyllene (1.7%)

Table VIII. Percentage composition of fresh and aged oil of <i>Eucalyptus citriodora</i>		
Compound	Fresh oil	Aged oil
α -thujene	0.05	-
α -pinene	0.40	0.19
sabinene	0.08	-
β -pinene	0.84	0.15
myrcene	0.27	0.25
α -phellandrene	0.06	-
α -terpinene	0.03	0.20
p-cymene	0.03	0.17
limonene + 1,8-cineole	0.54	0.55
(Z)- β -ocimene	0.45	0.29
(E)- β -ocimene	0.07	0.18
γ -terpinene	0.34	0.31
<i>cis</i> -linalool oxide†	0.41	0.69
<i>trans</i> -linalool oxide†	0.05	0.09
terpinolene	0.12	0.10
linalool	0.43	0.73
citronellal	79.77	50.42
isopulegol* + borneol	4.71	16.16
terpinen-4-ol	0.23	0.57
α -terpineol	0.03	0.17
citronellol	5.43	17.32
geraniol	0.57	2.00
citronellyl acetate	0.72	1.08
geranyl acetate	0.11	0.42
β -caryophyllene	1.79	5.47
aromadendrene	0.03	-
α -humulene	0.08	0.26
β -bisabolene	0.11	0.23
γ -cadinene	0.05	0.08
elemol	0.04	-
isocaryophyllene oxide	-	0.10
caryophyllene oxide	0.04	0.06
* major component		
† furanoid form		

Also in 2000, Betts compared the headspace of the fresh leaves of *E. citriodora* and compared them with a steam-distilled oil. The results of this study can be seen in Table IX.

F. M. Chaudhry, S. Akbar, R. Amad, A. Waheed and M. Rashid, *Chemical constituents of the essential oil of Eucalyptus citriodora Hook. (Myrtaceae) grown in Pakistan*. Sci. Int. (Lahore), 6, 373-375 (1994).

M. Dethier, A. Nduwimana, Y. Cordier, C. Menut and G. Lamaty, *Aromatic plants of tropical Central Africa. XVI. Studies on essential oils of Eucalyptus species grown in Burundi*. J. Essent. Oil Res., 6, 469-473 (1994).

- D. K. Sohounhloue, J. Dangou, B. Gnomhossou, E. X. Garneau, H. Gagnon and F-I. Jean, *Leaf oils of three Eucalyptus species from Benin: E. torelliana* F. Muell., *E. citriodora* Hook. and *E. tereticornis* Smith. J. Essent. Oil Res., 8, 111-113 (1996).
- A. Asefa and E. Dagne, *Essential oils of three Eucalyptus species acclimatized in Ethiopia*. Bull. Chem. Soc. Ethiopia, 11(1), 47-50 (1997).
- J-C. Chalchat, A. Muhayimana, J. B. Habimana and J. L. Chabard, *Aromatic plants of Rwanda II. Chemical composition of essential oils of ten Eucalyptus species growing in Ruhunde Aboretum, Butare, Rwanda*. J. Essent. Oil Res., 9, 159-165 (1997).
- J-C. Chalchat, M. Moudachirou, J. D. Gbenou, J. L. Chabard and C. Lartigue, *Essential oils of Eucalyptus citriodora and Eucalyptus camaldulensis from Benin; chemical composition, optimization*. Rivista Ital. EPPOS (Numero Speciale), 642-649 (1997).
- P. N. Kaul, A. K. Bhattacharya, B. R. Rajeswara Rao, G. R. Mallavarapu and S. Ramesh, *Atherosches Ölaus Eucalyptus citriodora. Zusammensetzung des in Indien erzeugten Produkts*. Parfum. Kosmet., 78(10), 38-40 (1997).
- L. Mondello, A. Verzera, I. Bonaccorsi, J. U. Chowdhury, M. Yusef and J. Begum, *Studies in the essential oil bearing plants of Bangladesh. Part V. Composition of the leaf oils of Eucalyptus citriodora Hook. and E. alba Reinw ex Blume*. J. Essent. Oil Res., 10, 185-188 (1998).
- M. Moudachirou, J. D. Gbenou, J-C. Chalchat, J. L. Chabard and C. Lartigue, *Chemical composition of essential oils of Eucalyptus from Bénin: Eucalyptus citriodora and E. camaldulensis. Influence of location, harvest time, storage of plants and time of steam distillation*. J. Essent. Oil Res., 11, 109-119 (1999).

E. Dagne, D. Bisrat, M. Alemayehu and T. Worku, *Essential oils of twelve Eucalyptus species from Ethiopia*. J. Essent. Oil Res., 12, 467-470 (2000).

T. J. Betts, *Solid phase microextraction of volatile constituents from individual fresh Eucalyptus leaves of three species*. Planta Med., 66, 193-195 (2000).

Cubeb Oil

An oil produced from *Piper cubeba* L. berries has been an item of commerce for over 100 years. The oil is used for its dry woody, spicy, peppery tones in fragrances and, to a lesser extent, for its spiciness in flavors.

A survey of the literature reveals that Razdan and Bhattacharyya (1954, 1955) characterized a cadinene and α -copaene in an oil of *P. cubeba* berries of Indian origin.

In 1962, Ikeda et al. examined the monoterpene hydrocarbon (9.5%) composition of cubeb oil. Using retention time data on a packed column as the method of identification, the authors characterized the presence of the following compounds:

α -pinene (12.1%)	limonene (0.9%)
α -thujene (13.2%)	β -phellandrene (12.7%)
β -pinene (2.3%)	γ -terpinene (1.5%)
sabinene (47.1%)	ocimene* (0.1%)
α -phellandrene (1.9%)	p-cymene + terpinolene (2.6%)
α -terpinene (1.1%)	
myrcene (4.5%)	

*correct isomer not identified

Five years later, Wenninger et al. (1967) isolated a number of sesquiterpene hydrocarbons from a variety of essential oils so that they could obtain high resolution infra spectra of them. As part of this study, they determined that the major sesquiterpene hydrocarbons in cubeb oil were:

α -cubebene	α -humulene
β -cubebene	δ -cadinene
β -elemene	calamenene*
β -caryophyllene	

*correct isomer not identified.

In 1974, Terhune et al. isolated two sesquiterpene hydrocarbons namely bicyclosesquiphellandrene (1 β , 7 α , 10 β -cadin-4(14),5diene) and 1-epi-bicyclosesquiphellandrene (1 α , 7 α , 10 β -cadin-4(14), 5-diene) in an oil of *P. cubeba*.

Using a combination of GC/MS and retention indices, Ramaswami et al. (1988) reported that major sesquiterpene hydrocarbons found in cubeb oil were as follows:

δ -elemene	α -muurolene
α -cubebene	germacrene D
α -copaene	cadin-1,4-diene
β -cubebene	δ -cadinene
allo-aromadendrene	calamenene*

*correct isomer not identified

Chiral GC analysis was used by Takeoka et al. (1990) to determine that α -copaene existed as pure (-)- α -copaene in cubeb oil. Two years later, König et al. (1992) used a heptakis-(6-O-methyl-2,3-pentyl)-O- β -cyclodextrin chiral GC column to prove that the enantiomeric form of (E)-nerolidol found in cubeb oil was exclusively (-)-(E)-nerolidol.

A year earlier, Viollon et al. (1991) analyzed an oil of cubeb of Sri Lankan origin using capillary gas chromatography. Although the authors only used retention times and compound co-injection as their method of compound identification, they only characterized constituents that had been irrefutably previously identified. The composition of this Sri Lankan cubeb oil was found to be:

α -pinene (0.3%)	allo-aromadendrene (5.0%)
sabinene (0.7%)	α -terpineol (2.3%)
1,8-cineole (0.3%)	γ -humulene (4.2%)
α -cubebene (5.1%)	β -bisabolene (2.0%)
α -copaene (8.1%)	α -muurolene (1.7%)
β -cubebene (0.2%)	calamenene* (1.0%)
β -elemene (1.0%)	cubebol (30.9%)
β -caryophyllene (3.4%)	nerolidol* (3.6%)

*correct isomer not identified

Four years later, Shankaracharya et al. (1995) used GC/MS to analyze an oil of cubeb produced in the laboratory from commercial samples of *P. cubeba* berries. The oil was found to contain the following constituents:

α -pinene (5.44%)	myrcene (1.15%)
sabinene (28.09%)	α -phellandrene (0.58%)

Table IX. Comparative percentage composition of the headspace and oil composition of *Eucalyptus citriodora*

Compound	Headspace	Oil
α -pinene	0-0.12	0.14
β -pinene	0.40-0.79	0.36
myrcene	0-0.18	-
limonene	0.11-2.20	-
terpinolene	0.31-0.49	-
linalool	0-0.14	0.66
isopulegol	0.80-1.41	3.41
citronellal	72.94-80.51	80.10
iso(ISO)pulegol	0-0.85	8.51
citronellol	3.49-5.44	4.18
citronellyl acetate	0.99-3.81	0.02
β -caryophyllene	9.17-11.76	0.39
α -humulene	0.08-0.50	-
bicyclogermacrene	1.45-1.68	-

Table X. Comparative major component percentage composition of the oils of two cubeb samples produced by different isolation methods

	Cubeb A		Cubeb B	
	Steam distilled oil	Hydro distilled oil	Steam distilled oil	Hydro distilled oil
α -pinene	2.0	0.9	1.2	1.0
sabinene	29.6	23.1	3.8	4.9
limonene	2.6	1.9	2.2	2.0
γ -terpinene	0.7	0.7	0.6	0.1
cis-sabinene hydrate	1.2	1.0	0.5	0.1
linalool	1.0	0.8	0.8	0.8
terpinen-4-ol	2.1	2.2	0.3	0.2
α -cubebene	3.7	2.6	5.0	4.0
α -copaene	7.8	5.8	9.8	7.6
β -cubebene	7.1	6.0	3.9	8.9
β -caryophyllene	6.1	6.7	9.5	8.0
allo-aromadendrene	5.8	6.1	9.2	11.0
γ -muurolene	6.9	7.0	11.5	10.9
germacrene D	5.8	7.4	9.1	11.1
cubebol	6.2	7.8	16.4	11.1
nerolidol*	2.4	3.1	3.0	3.5
globulol	1.5	2.6	2.7	3.5
cubenol	1.1	1.2	2.9	1.8

*correct isomer not identified

(Z)-b-ocimene† (0.81%)	camphor (0.04%)	α-copaene (4.01%)	α-murolene (0.62%)
β-phellandrene† (0.76%)	terpinen-4-ol (2.69%)	β-cubebene (4.39%)	α-farnesene* (trace)
p-cymene (0.59%)	α-terpineol (0.30%)	β-caryophyllene (1.69%)	δ-cadinene (trace)
limonene (4.41%)	myrtenol (trace)	α-humulene (0.45%)	cubebol (15.18%)
(E)-b-ocimene (0.07%)	cuminaldehyde (0.01%)	allo-aromadendrene (1.67%)	calamenene* (trace)
γ-terpinene (1.14%)	carvone (trace)	γ-murolene (4.20%)	elemol (0.32%)
cis-sabinene hydrate (2.73%)	safrole (0.08%)	γ-curcumene (trace)	elemicin (trace)
terpinolene (0.31%)	δ-elemene (0.10%)	germacrene D (2.89%)	ledol (0.20%)
trans-sabinene hydrate (trace)	α-cubebene (1.65%)	methyl isoeugenol* (trace)	nerolidol*a (1.45%)
linalool (3.22%)	α-ylangene (0.07%)	myristicin (trace)	germacrene D-4-ol (0.77%)
			spathulenol (trace)
			globulol (1.76%)
			dillapiol (0.16%)
			bisabolol*† (0.37%)
			cubenol (0.56%)
			isoelemicin*a (0.39%)
			guaial† (0.06%)
			(E)-asarone (1.39%)
			farnesol* (trace)

*correct isomer not identified

†incorrect identification based on elution order

a (E)-isomer based on elution order

The authors also compared the main component compositions of oils produced from two different lots of cubeb berries that were produced by steam distillation and hydrodistillation. The results of the experiment can be seen in Table X. It is interesting to note that the two oils differ quite drastically; one being rich in sabinene while the other being more sesquiterpene-rich. Also, it was not possible to draw any meaningful conclusions on the influence of the isolation technique on oil composition other than perhaps that cubebol when present as a major constituent appears to thermally degrade to β-cubebene.

This author (Lawrence) has examined the composition of some oils of *P. cubeba* using a range of modern analytical techniques. The constituents identified in these oils were as follows:

α-thujene (trace-0.1%)
 α-pinene (1.3-2.2%)
 β-pinene (trace-0.2%)
 sabinene (2.1-4.6%)
 myrcene (trace-0.1%)
 α-phellandrene (trace-0.1%)
 α-terpinene (trace-0.1%)
 limonene (0.1-0.2%)
 1,8-cineole (0.6-0.8%)
 β-phellandrene (trace)

γ -terpinene (trace-0.1%)	γ -humulene (4.4-4.9%)
(E)- β -ocimene (trace)	phellandral (trace)
p-cymene (trace-0.1%)	β -bisabolene (1.5-1.6%)
terpinolene (trace)	zonarene (trace-0.1%)
(Z,Z)-allo-ocimene (trace)	α -muurolene (1.1-1.2%)
2-nonanone (trace)	cis-piperitol (trace-0.1%)
trans-sabinene hydrate (trace)	δ -cadinene (8.5-9.5%)
α -p-dimethylstyrene (trace-0.1%)	γ -cadinene (0.1-0.3%)
α -cubebene (7.1-8.5%)	cadina-1,4-diene (trace-0.1%)
δ -elemene (0.2-0.3%)	cuminaldehyde (0.1-0.2%)
bicycloelemene (trace)	cis-calamenene (3.5-3.8%)
α -copaene (10.4-14.3%)	p-cymen-8-ol (0.1-0.3%)
camphor (trace)	safrole (trace)
α -gurjunene (trace)	epi-cubebol (trace-0.1%)
cis-sabinene hydrate (trace-0.3%)	palustrol (trace-0.1%)
2-undecanone (trace)	cubebol (8.9-10.0%)
β -cubebene (7.1-11.1%)	caryophyllene oxide (trace-0.1%)
cis-p-menth-2-en-1-ol (trace)	ledol (trace)
linalool (trace-0.1%)	(E)-nerolidol (2.1-3.5%)
β -elemene (1.0-1.2%)	cubenol (0.8-1.5%)
β -caryophyllene (2.4-3.7%)	epi-cubenol (1.5-3.5%)
trans-p-menth-2-en-1-ol (trace)	globulol (trace)
γ -elemene (trace)	(E)-methyl isoeugenol (trace)
allo-aromadendrene (3.0-4.2%)	T-muurolol (trace)
borneol (0.2-0.3%)	α -cadinol (0.5-1.0%)
isoborneol (trace)	pilgerol (trace)
carvotanacetone (0.7-1.2%)	dillapiole (trace-0.1%)
γ -muurolene (trace-0.1%)	myristicin (trace-0.1%)
α -terpineol (1.9-2.2%)	(E)-asarone (0.9-3.7%)
ledene (trace)	apiole (0.1-0.2%)
germacrene D (0.1-0.2%)	

More recently, a commercial sample of cubeb oil was analyzed by GC/MS (Lawrence) and found to contain the following major constituents:

α -pinene (7.8%)	β -cubebene (5.3%)
sabinene (29.5%)	β -elemene (2.1%)
myrcene (1.4%)	β -caryophyllene (1.1%)
α -phellandrene (1.6%)	allo-aromadendrene (2.2%)
α -terpinene (1.3%)	α -terpineol (2.8%)
limonene (2.8%)	γ -humulene (1.9%)
1,8-cineole (2.5%)	δ -cadinene (1.1%)
p-cymene (1.1%)	cis-calamenene (2.2%)
α -cubebene (5.7%)	cubebol (5.7%)
α -copaene (5.6%)	(E)-nerolidol (1.8%)

R. K. Razdan and S. C. Bhattacharyya, *Sesquiterpenes from Piper cubeba Linn. Part I*. Perfum. Essent. Oil. Rec., 45, 181-183 (1954).

R. K. Razdan and S. C. Bhattacharyya, *Sesquiterpenes from Piper cubeba Linn. Part II*. Perfum. Essent. Oil Rec., 46, 8-13 (1955).

R. M. Ikeda, W. L. Stanley, S. H. Vannier and E. M. Spitler, *The monoterpene hydrocarbon composition of some essential oils*. J. Food Sci., 27, 455-458 (1962).

J. A. Wenninger, R. L. Yates and M. Dolinsky, *High-resolution infrared spectra in some naturally occurring sesquiterpene hydrocarbons*. J. Assoc. Offic. Anal. Chem., 50, 1313-1335 (1967).

S. J. Terhune, J. W. Hogg and B. M. Lawrence, *Essential oils and their constituents XI. Bicyclosesquiphellandrene and 1-epibicyclosesquiphellandrene. Two new dienes based on the cadalene skeleton*. Phytochemistry, 13, 1183-1185 (1974).

S. K. Ramaswami, P. Briscese, R. J. Gargiullo and T. von Geldern, *Sesquiterpene hydrocarbons: from mass confusion to orderly line up*. In: *Flavors and Fragrances: A World Perspective*. Edits., B. M. Lawrence, B. D. Mookerjee and B. J. Willis, Elsevier Science Publ. B.V., Amsterdam, pp. 951-980 (1988).

G. Takeoka, R. A. Flath, T. R. Mon, R. G. Buttery, R. Teranishi, M. Güntert, R. Lautamo and J. Szejtli, *Further applications of per methylated β -cyclodextrin capillary gas chromatographic columns*. J. High Resol. Chromatogr., 13, 202-206 (1990).

C. Viollon, J. Simeray, D. Leger and J. P. Chaumont, *Étude d'une huile essentielles de Piper cubeba L. fils originaire de Ceylan*. Plant. Med. Phytother., 25, 118-122 (1991).

W. A. König, B. Gehrcke, D. Icheln, P. Evers, J. Dönnecke and W. Wang, *New, selectively substituted cyclodextrins as stationary phases for the analysis of chiral constituents of essential oils*. J. High Resol. Chromatogr., 15, 367-372 (1992).

N. B. Shankaracharya, L. Jaganmohan Rao, S. Nagalakshmi and J. Puranaik, *Studies on the chemical composition of cubeb (Piper cubeba Linn.)*. PAFAI J., 17(1), 33-39 (1995).

B. M. Lawrence, unpublished information. ■