Progress in Essential Oils

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Pennyroyal Oil

The composition of an oil of *Mentha pulegium* L. (also known as pennyroyal oil), produced from plants collected in the vicinity of Vlasotince (Serbia) was the subject of analysis by Chalchat et al. (2000). The components characterized in the oil were as follows:

α-pinene (0.3%)
camphene (t)
β-pinene (0.4%)
limonene (1.0%)
1,8-cineole (1.3%)
3-octanone (0.7%)
p-cymene (0.3%)
3-methylcyclohexanone (t)
3-octyl acetate (1.0%)
3-octanol (1.8%)
menthone (30.9%)
isomenthone (5.5%)
camphor (1.0%)
(Z)-3-hexenyl isovalerate (0.2%)
neomenthyl acetate (4.3%)
neomenthol (13.8%)
pulegone (14.1%)
α-humulene (0.4%)
menthol (0.1%)
piperitone (3.4%)
carvone (0.2%)
caryophyllene oxide (9.0%)

t = trace (< 0.1%)

Kokkini et al. (2004) examined the main oxygenated components of oils of *M. pulegium* produced from plants (38 populations) collected from three different climatic zones in Greece. The results of this study are shown in **T-1**. As can be seen from these results, some of the oils were rich in piperitone, menthone, isomenthone and piperitenone, and isopiperitenone to a lesser extent.

Martins et al. (2004) determined that an oil from *M. pulegium* grown in Brazil in an experimental garden was found to possess the following composition:

α-pinene (0.44%)
sabinene (t)
β-pinene (0.34%)
3-octanol (0.82%)
limonene (0.31%)
1,8-cineole (t)
menthone (16.13%)
isomenthone (19.91%)
menthol (0.49%)
isomenthol (1.88%)
pulegone (54.74%)
piperitone (2.03%)
trans-carvyl acetate (2.92%) [†]
β-caryophyllene (t)

t = trace (< 0.3%)
[†] unusual constituent, identity requires corroboration

Al-Amier et al. (2005) analyzed an oil produced from the MPH-7 clone of *M. pulegium* grown in Egypt. The components characterized in this oil were found to be as follows:

α-pinene (0.08%)
β-pinene (0.07%)
α-terpinene (0.03%)
1,8-cineole (0.82%)
linalyl acetate [†] (0.08%)
menthyl acetate (0.12%)
pulegone (52.72%)

[†] not a normally found constituent of *M. pulegium* oil.

As can be seen, the authors only identified less than 54% of the oil. Therefore the data is of little value at best.

A steam distilled oil of *M. pulegium* produced from plants collected

T-1 Comparative main oxygenated components of oils produced from plants collected in three different Greek climatic zones

Compound	Northern zone oil	Mid-zone oil	Southern zone oil
menthone	0.3–10.2	0.4–12.1	0.2–53.4
menthofuran	0–0.1	0–t	0–t
isomenthone	0.1–36.0	2.6–38.3	0.1–45.1
neomenthol	0–1.9	0–0.8	0–12.4
neoisomenthol	0–2.6	0–0.5	0–12.4
neoisomenthyl acetate	0–2.0	-	1–1.0
isomenthol	0–2.6	0–1.9	0–7.7
pulegone	t–82.4	34.8–74.4	0.1–90.7
cis-isopulegone	0–0.7	0–0.2	0–0.2
trans-isopulegone	0–0.9	0–0.6	0–1.0
piperitone	0.2–83.6	0–3.4	0–97.2
isopiperitenone	0.1–23.5	0.4–9.3	0–16.5
piperitenone	1.2–19.9	1.6–39.8	t–21.8

t = trace (< 0.1%)

in the vicinity of Batak in the Rhodope mountains (Bulgaria) was analyzed by Stoyanova et al. (2005). The composition of this oil was as follows:

α-thujene (0.6%)
sabinene (0.1%)
β-pinene (0.8%)
3-octanol (2.4%)
limonene (1.2%)
menthone (5.8%)
isomenthone (11.3%)
cis-isopulegone (1.2%)
menthol + neoisomenthol (1.3%)
isomenthol (0.4%)
pulegone (45.4%)
piperitone (5.1%)
isopiperitenone (0.5%)
menthyl acetate (0.2%)
piperitenone (21.7%)

Trace amounts (< 0.1%) of camphene, α-phellandrene, 1,8-cineole and neomenthol were also found in this oil.

Oils produced from wild Indian *M. pulegium* collected from Sanasar (Jammu region) and Patan (Kashmir valley) were analyzed by Agnihotri et al. (2005). Although the oil from Patan possessed the highest amount of pulegone, both oils were of the pulegone-type as shown below:

sabinene (t–0.1%)
β-pinene (t–0.3%)
γ-terpinene (0.9–1.2%)
β-ocimene* (0–0.7%)
3-octanol (0–0.2%)
linalool (0.1–0.6%)
neoisopulegol (0–0.7%)
isopulegol (0–0.4%)
menthone (8.3–8.7%)
pulegol* (t–0.3%)
isomenthone (3.8–4.0%)
neomenthol (0.7–1.3%)
piperitol* (0–0.9%)
pulegone (65.9–83.1%)
piperitone (1.3–3.2%)
pulegyl acetate* (0.1–1.2%)
menthyl acetate (0.1%)
piperitenone (t–0.8%)
β-caryophyllene (0.1–0.9%)
germacrene D (0–1.4%)
caryophyllene oxide (0.3–1.9%)

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

The oils of 14 Tunisian natural populations of *M. pulegium* were characterized by Ben Fadhel et al. (2006). They found that the oils could be grouped into three chemotypes:

Chemotype 1: (pulegone-type). The most commonly encountered chemotype; oils rich in pulegone with varying proportions of menthone and isomenthone.

Chemotype 2: (pulegone-menthol-type). Oils containing a high proportion of menthol and different amounts of pulgone.

Chemotype 3: (carvone/pulegone-type). This type is rare.

El-Ghorab et al. (2006) analyzed an oil produced from *M. pulegium* plants grown in Tersa (Egypt) using GC/MS. This oil was found to possess the following composition:

isovaleraldehyde (0.30%)
α-pinene (0.10%)
β-phellandrene† (0.23%)
myrcene (0.34%)
3-octanol (0.16%)
limonene (1.31%)
1,8-cineole (0.29%)
ocimene* (0.35%)
phenylacetaldehyde (0.25%)
3-methyl-2-cyclohexen-1-one† (0.12%)
sabinene hydrate* (0.32%)
trans-linalool oxide (furanoid) (0.45%)
isoamyl acetate (0.23%)
amyl valerate (0.07%)
2-phenethyl alcohol (2.35%)
2-octyl acetate (0.25%)
trans-limonene oxide (0.12%)
trans-p-menth-2-en-1-ol (0.13%)
citronellal (0.12%)
karahanaenone (0.11%)
pinocamphone (< 0.01%)
isopinocamphone (0.42%)
neodihydrocarveol (0.46%)
trans-carveol (0.83%)
pulegone (43.46%)
piperitone (12.20%)
geraniol (0.39%)
o-guaicol acetate† (0.39%)
ambersage‡ (0.10%)
thymyl acetate (1.62%)
2-hydroxypiperitone (2.73%)
carvacryl acetate (2.57%)
1-hydroxy-p-menth-3-one* (1.03%)
γ-elemene (3.64%)
p-menthene-1,3-diol*† (0.42%)
β-humulene (0.21%)

9-epi-β-caryophyllene (0.23%)
γ-gurjunene (1.24%)
p-menthane-1,2,3-triol[†] (6.51%)
γ-muurolene (1.23%)
β-selinene (1.78%)
isomenthyl acetate[†] (0.23%)
cis-β-guaiene (3.03%)
bicyclogermacrene (1.22%)
α-muurolene (0.17%)
trans-β-guaiene (0.65%)
(E, E)-α-farnesene (0.37%)
germacrene D-4-ol (0.35%)
caryophyllene oxide (0.44%)
khusinol (0.07%)
hexadecanoic acid (1.32%)
phytol (0.91%)
heptacosane (2.19%)

[°] correct isomer not identified
[†] incorrect identification based on GC elution order
[‡] component identity unknown

Oils produced using micro-simultaneous distillation and extraction from dried whole pennyroyal (*M. pulegium*) leaves from three different Spanish markets were analyzed by Diaz-Maroto et al. (2007). The comparative composition of the three oils studied was as follows:

hexanal (0–0.08%)
3-methylcyclopentanone (0.06–0.13%)
2,5-diethyltetrahydrofuran[°] (0.03–0.07%)
3-methylcyclohexanone (4.52–6.29%)
α-pinene (0.82–1.10%)
camphene (0.03–0.05%)
1-cyclohexylethanone (0.23–0.35%)
β-pinene (0.45–0.58%)
3-octanol (0.21–0.59%)
α-phellandrene (0.04–0.06%)
p-cymene (0.03–0.09%)
limonene + 1,8-cineole (1.28–1.79%)
p-cymenene (0.39–0.63%)
terpinolene (0.04–0.09%)
nonanal + linalool (0.08–0.12%)
3-octyl acetate (0.14–0.18%)
camphor (0.05%)
neoisopulegol (0.04%)
isopulegol (3.40–5.81%)
menthone (0.14–0.25%)
menthofuran (0.12–0.25%)
isopulegone[°] (1.74–1.91%)
menthol (0.14–0.18%)
terpinen-4-ol (0.23–0.27%)
piperitone oxide[°] (14.9–16.9%)
piperitol[°] (1.05–1.66%)
pulegone (41.1–42.3%)
piperitone (5.37–5.96%)
isopiperitenone (0.98–1.23%)
thymol (t–0.30%)
menthyl acetate (2.23–2.53%)
carvacrol (t)
piperitenone (4.56–6.05%)
β-damascenone[°] (0.03–0.05%)
β-caryophyllene (0.02–0.06%)
α-humulene (0.03–0.11%)
methyl isopulegone[†] (2.36–3.20%)
methyl pulegone[†] (0.32–0.39%)
caryophyllene oxide (0.49–0.94%)

[°] correct isomer not identified
t = trace (< 0.10%)

[†] unusual constituent, never has been found before naturally occurring.

Mkaddem et al. (2007) analyzed the variability of oils produced from 14 accessions from different geographical regions in Tunisia, each representing different climatic zones. The oil compositions varied as follows:

α-pinene (t–1.0%)
camphene (t–0.4%)
β-pinene (t–1.0%)
myrcene (t–1.0%)
α-terpinene (t–0.9%)
limonene (t–5.0%)
β-ocimene[°] + γ-terpinene (t–1.2%)
p-cymene (t–1.2%)
(Z)-3-hexenol (t–1.0%)
terpinolene (t–1.3%)
1,8-cineole (t–2.4%)
menthone (t–2.0%)
menthofuran (0.7–10.0%)
isomenthone (2.9–34.2%)
linalool (t–1.5%)
linalyl acetate (t–3.6%)
menthyl acetate (0.4%–4.9%)
neomenthol (0.2–4.3%)
terpinen-4-ol (t–2.2%)
menthol (0.1–21.2%)
isomenthol (t–2.9%)
pulegone (17.5–70.2%)
α-terpineol (t–1.7%)
borneol (t–1.6%)
verbenone (t–3.3%)
carvone (t–55.7%)
geranyl acetate (t–2.1%)
myrtenol (t–1.6%)
nerol (t–1.5%)
geraniol (t–1.6%)
methyl eugenol (t–3.1%)
eugenol (t–1.8%)
caryophyllene oxide (t–1.7%)

t = trace
[°] correct isomer not identified

Cook et al. (2007) analyzed oils produced from the inflorescences, leaves and stems of three populations from *M. pulegium* collected from the island of Zakynthos (Greece). A summary of the results of this study can be seen in **T-2**.

T-2 Comparative percentage composition of the main oxygenated constituents of oils produced from the inflorescences, leaves and stems of three regions in Zakynthos (Greece)

Compound	Inflorescence oils	Leaf oils	Stem oils
menthone	0.1–0.2	0.4–0.9	1.1–2.8
menthofuran	0.1	0.1–0.3	0–0.9
isomenthone	4.3–7.9	18.2–28.6	8.5–16.8
neoisomenthyl acetate	-	0–0.1	0–2.3
trans-isopulegone	0.6–0.8	0.6–0.9	0.5–1.0
menthol	-	-	0.6–1.4
neoisomenthol	0–0.1	0.2–1.2	0.2–0.7
pulegone	52.9–75.8	52.0–57.4	32.8–52.5
isomenthol	-	0–0.1	0–0.6
piperitone	0.5–2.2	1.7–5.2	1.7–3.8
isopiperitenone	0.3–0.7	0.2–0.4	0–0.6
piperitenone	12.0–35.0	5.1–15.0	10.3–26.0

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Chirality

The enantiomeric distribution of certain constituents of *M. pulegium* oil were confirmed by Lorenzo et al. (2002) to be as follows:

(1R, 3R, 4S)-(-)-menthol (100%) : (1S,3S,4R)-(+)-menthol (0%)

(1R,3S,4R)-(+)-isomenthol (100%) : (1S, 3R, 4S)-(-)-isomenthol (0%)

(1R)-(+)-pulegone (100%) : (1S)-(-)-pulegone (0%)

(1R,4S)-(-)-menthone (100%) : (1S,4R)-(+)-menthone (0%)

(1R,4R)-(+)-isomenthone (100%) : (1S,4S)-(-)-isomenthone (0%)

Brokl et al. (2006) used SPME coupled with GC/MS, to examine the enantiomeric distribution of selected volatiles produced from 0.1 g of six samples of *M. pulegium* powder that were heated to 60°C in an enclosed vial. The enantiomeric distributions that were determined using a chiral GC column are listed next.

Comparative percentage composition of the fruit and leaf of *Piper cubeba* **T-3**

Compound	Berry oil	Leaf oil
α-thujene	2.5	0.7
α-pinene	1.8	3.2
camphene	t	0.3
sabinene	9.1	3.8
β-pinene	0.2	3.8
myrcene	0.2	0.5
α-phellandrene	0.4	0.2
α-terpinene	t	0.1
p-cymene	0.1	0.4
limonene	2.3	3.4
1,8-cineole	0.3	-
β-phellandrene	t	0.1
(E)-β-ocimene	0.1	0.3
γ-terpinene	0.1	0.2
cis-sabinene hydrate	0.4	0.3
trans-sabinene hydrate	2.5	8.2
linalool	0.2	1.2
trans-β-terpineol	t	0.2
terpinen-4-ol	0.1	-
α-terpineol	0.1	0.7
2-undecanone	t	0.7
2-methylundecanal	t	0.1
γ-elemene †	0.1	-
α-cubebene	1.5	0.8
cyclosativene	0.2	-
α-copaene	3.8	0.9
β-elemene	9.4	1.4
β-cubebene	t	0.2
β-caryophyllene	2.5	5.0
trans-α-bergamotene	0.2	-
α-humulene	0.9	1.5
allo-aromadendrene	-	0.2
trans-cadina- 1(6),4-diene	0.2	0.3
γ-muurolene	1.7	0.3
(E)-β-farnesene	0.2	0.1

Compound	Berry oil	Leaf oil
germacrene D	0.1	-
cis-muurola-4(14),5-diene	0.3	0.3
epi-cubebol	4.6	4.2
α-muurolene	0.6	1.2
β-himachalene	0.2	0.1
(Z)-α-bisabolene	0.3	0.1
γ-cadinene	0.1	16.6
cubebol	5.6	4.8
δ-cadinene	t	0.1
cis-calamenene	-	0.3
(E)-γ-bisabolene	1.2	0.5
trans-cadina-1(2),4-diene	t	0.4
trans-calamenene	-	0.1
α-calacorene	t	0.1
cis-muurol-5-en-4β-ol	t	0.1
(E)-nerolidol	0.1	1.5
germacrene B	0.1	-
ledol	0.2	-
β-calacorene	0.1	0.4
spathulenol	0.1	0.1
1-hydroxy-1,7-dimethyl-4-isopropyl-2,7-cyclodecadiene	0.2	1.0
epi-globulol	0.5	0.4
globulol	0.1	-
viridiflorol	t	0.1
guaiol	2.8	0.1
epi-cubenol	0.3	0.7
T-cadinol	0.3	2.7
T-muurolol	0.3	0.5
α-muurolol	0.1	0.2
α-cadinol	0.2	1.9
selin-11-en-4α-ol	t	0.1
α-bisabolol	0.1	0.2

† should be δ-elemene

(1R-5R)-(+)-α-pinene (6.7%) : (1S,5S)-(-)-α-pinene (93.3%)

(1R,5R)-(-)-β-pinene (4.1%) : (1S, 5S)-(+)-β-pinene (95.9%)

(1R,4S)-(-)-menthone (100%) : (1S,4R)-(+)-menthone (0%)

(1R)-(+)-pulegone (100%) : (1S)-(-)-pulegone (0%)

(1R,3S,4S)-(+)-neomenthol (94.0%) : (1S,3R,4R)-(-)-neomenthol (6.0%)

(1S,3S,4R)-(-)-menthol (100%) : (1R,3R,4S)-(+)- menthol (0%)

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Cubeb Oil

Cubeb oil, which is obtained from the steam distillation of dried *Piper cubeba* L. berries, is produced only in Indonesia or in the Western world from cubeb fruit of Indonesian origin.

Since 2001 (Lawrence), little work has been reported on the composition of this somewhat uncommon oil. Earlier it was reported by König et al. (1994) that the enantiomeric distribution of δ-cadinene in cubeb oil was as follows:

(+)-δ-cadinene (95%) : (-)-δ-cadinene (5%)

They also reported that (1R,4S)-(-)-*trans*-calamenene was the predominant enantiomer in the oil.

Flath et al. (1994) determined that the average level of α-copaene in cubeb oil was 0.3% and its enantiomeric distribution was as follows:

(-)-α-copaene (99.7%) : (+)-α-copaene (0.3%)

Although α-terpineol was only found at a level of 0.4% in a commercial sample of cubeb oil, Ravid et al. (1995) determined that its enantiomeric distribution was as follows:

(4R)-(+)-α-terpineol (58%) : (4S)-(-)-α-terpineol (42%).

Ripe berries and leaves of *P. cubeba* collected from Jatiroto, Temanggung, central Java, Indonesia, were shipped to the Netherlands. Oils were separately produced from both organs by hydrodistillation by Bos et al. (2007). Analyses of the oils using both GC-FID and GC/MS can be seen in **T-3**. In addition, trace amounts (< 0.1%) of tricyclene, 5-methyl-3-heptanone, benzaldehyde, 6-methyl-5-hepten-2-one, decane, 2-octanol, δ-3-carene, 2-ethyl-4-pentenal, terpinolene, m-cymene, 2-nonanone, undecane, camphor, *cis*-verbenol, isoborneol, sabina-ketone, (E)-2-nonenal, borneol, umbellulone, cryptone, methyl salicylate, *cis*-piperitol, nerol, methyl thymol, geraniol, (E,E)-2,4-decadienal, *cis*-α-bergamotene, *cis*-muurola-3,5-diene, α-cadinene, γ-gurjunene epoxide, elemol, isoaromadendrene epoxide, 1,10-di-epi-cubenol, β-eudesmol, β-bisabolol, (E,E)-farnesol and (Z,E)-farnesol were also identified as components of the berry oil. However, it should be noted that the authors only characterized 60% of the oil. In contrast, the authors characterized 77.9% of the leaf oil, which was also found to contain trace amounts (< 0.1%) of tricyclene, terpinolene, m-cymene and β-bourbonene as components.

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