Progress in Essential Oils

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Mediterranean Pine Oil

Mediterranean, or Aleppo pine, which is known taxonomically as *Pinus halepensis* Miller, is the dominant tree of the forest ecosystems throughout the dry and semi-arid areas of the Mediterranean Basin (Marstre et al., 2003). It can be found in southeast Spain, on the arid calcareous cliffs in Italy, Portugal and France. Oils produced from the needles and leaves of *P. halepensis* are occasionally found as commercial oils.

Zafria and Garcia-Peregrin (1976) examined the composition of the oils produced from the needles and twigs of *P. halepensis* of Spanish origin. The average main constituents of the needle and twig oils can be seen in **T-1**.

Ekundayo (1988) reviewed the compositions of pine oils and reported that the oil of *P. halepensis* contained:

α-thujene (6.1%)
α-pinene (32.1%)
sabinene (35.9%)
β-pinene (3.1%)
δ-3-carene (4.1%)
terpinolene (18.5%)

Using GC retention times as their method of component identification, Vidrich et al. (1988) compared the composition of the needle and wood oils of *P. halepensis*. A summary of their results is shown in **T-2**.

Tazerouti et al. (1993) used GC/MS only to analyze two samples of *P. halepensis* needle oils produced from needles collected from two different regions of Algeria. The composition of these oils is summarized in **T-3**. In addition, trace (<0.05%) amounts of pentane, diethyl ether, acetone, ethyl acetate, ethanol, p-cymene, α-cubebene, α-pinene oxide, α-copaene, (Z)-3-hexenyl isovalerate, γ-muurolene, δ-selinene, bicycloelemene, *cis*-piperitol,

T-1. Average percentage composition of the main constituents of the needle and twig oils of *Pinus halepensis* of Spanish origin

Compound	Needle oil	Twig oil
α-thujene	6.1	-
α-pinene	32.1	27.2
β-pinene	3.1	0.5
sabinene	35.9	65.0
δ-3-carene	4.3	7.2
limonene	t	2.6
terpinolene	18.5	-

T-2. Comparative percentage composition of the needle and wood oils of *Pinus halepensis*

Compound	Needle oil	Wood oil
α-pinene	8.5	19.8
camphene	0.1	0.4
β-pinene	1.1	0.8
sabinene	6.1	-
δ-3-carene	0.9	t
myrcene	12.5	44.9
α-phellandrene	0.8	-
α-terpinene	0.8	0.4
limonene	1.0	0.4
1,8-cineole	1.7	0.2
γ-terpinene	0.2	0.1
p-cymene	11.4	0.5
3-octanol	0.1	t
decanal	0.8	0.5
linalool	0.4	0.1
α-cedrene	0.1	0.2
β-caryophyllene	26.3	20.4
methyl chavicol	5.1	4.1
borneol	-	0.3
geranyl acetate	0.9	0.6
citronellol	1.3	0.3
myrtenol + nerol	0.1	0.1
citronellol	0.4	t
eugenol	0.6	0.4
carvacrol	1.7	0.7
oil yield	1.5	0.6

t=trace (<0.05%)

geraniol, ethyl dodecanoate, nerol, 2-phenethyl isobutyrate, a nerolidol isomer, cubenol, elemol, 2-phenethyl hexanoate, 2-phenethyl tiglate, α-muurolol, β-eudesmol, manoyl oxide, a kaurenol isomer and diethyl phthalate were also characterized as contaminants or constituents of one or both of the needle oils.

Needle-bearing twigs of *P. halepensis* that were collected from the provenance of Attiki (Central Greece) were cut int small pieces and steam distilled for 2 hr to yield an oil that was analyzed by Roussis et al. (2001) using GC-FID and GC/MS. The composition of this oil was determined to be as follows:

T-3. Percentage composition of the needle oils of *Pinus halepensis* from two regions of Algeria

Compound	Needle oil 1	Needle oil 2
tricyclene	1.6	t
α-pinene	6.7	17.6
camphene	0.2	0.3
β-pinene	2.0	1.6
sabinene	7.0	2.6
δ-3-carene	1.9	0.1
α-terpinene	0.7	t
limonene	0.8	0.1
β-phellandrene	1.0	0.7
(Z)-β-ocimene	0.1	0.1
γ-terpinene	1.2	t
(E)-β-ocimene	2.1	t
p-cymene	0.3	3.1
terpinolene	0.2	t
(Z)-3-hexenol	t	0.1
α-ylangene	0.2	0.2
δ-elemene	-	0.2
camphor	t	0.1
linalool	0.4	2.0
bornyl acetate	t	0.2
β-elemene	t	0.2
β-caryophyllene	7.1	2.7
cis-caran-2-ol†	t	0.5
α-elemene	t	0.6
α-humulene	2.8	1.4
α-terpineol	0.3	1.5
germacrene D	0.2	t
α-muurolene	0.3	0.2
δ-cadinene	0.9	0.5
geranyl acetate	t	0.3
2-phenethyl acetate	-	0.1
calamenene*	t	0.2
p-cymen-8-ol	t	0.1
α-terpinyl butyrate	t	1.5
2-phenethyl butyrate	1.1	1.9
2-phenethyl 2-methylbutyrate	1.0	10.3
2-phenethyl isovalerate	7.4	8.4
humulene epoxide II	0.2	0.2
cadinenol*	t	0.4
guaiol	0.2	0.2
methyl isoeugenol*	0.2	t
T-cadinol	-	0.2
methyl isoeugenol*	0.3	t
α-cadinol	0.2	0.1

†incorrect identification; t=trace (<0.05%); *correct isomer not identified

α-pinene (15.8%)
camphene (1.3%)
β-pinene (4.4%)
myrcene (1.9%)
α-phellandrene (0.1%)
δ-3-carene (15.0%)
α-terpinene (0.4%)
limonene (10.2%)
(Z)-β-ocimene (1.0%)
γ-terpinene (0.3%)
terpinolene (2.8%)
linalool (0.2%)
terpinen-4-ol (0.1%)
α-terpineol (0.1%)
α-fenchyl acetate (0.2%)
neryl acetate (0.3%)
α-gurjunene (0.5%)
β-caryophyllene (18.1%)
α-humulene (3.2%)
β-gurjunene (0.3%)
germacrene D (0.4%)
aristolene[†](0.4%)
α-muurolene (0.3%)
δ-cadinene (0.4%)
elemol (0.2%)
guaiol (0.5%)
cembrene (7.5%)
(13E)-labdene-8,15-diol (0.3%)

[†]aristolene is the synonym of β-gurjunene, so the identification is incorrect

Trace amounts (<0.05%) of methyl thymol, δ-elemene, citronellyl acetate, geranyl acetate, globulol and α-eudesmol were also characterized in this oil.

Hmamouchi et al. (2001) used GCI-FID and GC/MS to examine a lab-distilled (0.16%) oil of the needles of *P. halepensis* that were collected from an arboretum at Oued Cherrat (Rabat, Morocco). The constituents characterized in the needle oil were:

α-thujene (0.4%)
α-pinene (2.33%)
camphene (0.5%)
β-pinene (3.1%)
sabinene (3.7%)
myrcene (16.3%)
α-phellandrene (1.6%)
α-terpinene (1.3%)
limonene (1.3%)
1,8-cineole (1.3%)
γ-terpinene (2.4%)
p-cymene (0.7%)
terpinolene (10.1%)
α-copaene (0.5%)
terpinen-4-ol (3.8%)
β-caryophyllene (14.2%)
α-humulene (3.2%)
α-terpineol (0.6%)
α-muurolene (0.5%)
geranyl acetate (5.3%)
δ-cadinene (1.0%)
caryophyllene oxide (1.2%)
2-phenethyl acetate (2.5%)
cadinol[*] (1.1%)

[*]correct isomer not identified

Macchioni et al. (2003) compared the compositions of the needles, branches and cones of *P. halepensis* of Italian origin. The analyses, which were conducted using GC-FID and GC/MS can be seen summarized in **T-4**.

The needles of *P. halepensis* were collected from Sidi Feradj (SF), Djelfa (DJ) and Saida (SD) provenances in Algeria by Dob et al. (2007). Oils produced by hydrodistillation of the air-dried needles were produced in 0.5% (SF), 0.8% (DJ) and 0.9 (SD) yields were examined by GC-FID and GC/MS. The oils, which were richer in sesquiterpene compounds than monoterpene compounds possessed the following compositional range:

tricyclene (t–0.2%)
α-pinene (0.7–6.4%)
sabinene (0.1–0.8%)
β-pinene (1.0–5.6%)
myrcene (0.2–0.5%)
α-phellandrene (t–0.1%)
hexyl acetate (t–0.1%)
δ-3-carene (0–0.4%)
α-terpinene (t–0.5%)
limonene (0.1%)
(E)-β-ocimene (0.1–1.3%)
γ-terpinene (t–0.3$)
terpinolene (0.1–2/4%)
α-pinene oxide (0.1–3.0%)
linalool (0–0.1%)
camphor (0.1–0.3%)
borneol (t–1.2%)
terpinen-4-ol (t–0.6%)
p-cymen-8-ol (0.1–0.6%)
α-terpineol (t–0.1%)
α-terpinyl acetate (0.1%)
α-cubebene (0.1–1.1%)
citronellyl acetate (0.1–1.4%)
α-ylangene (t–0.1%)
β-caryophyllene (19.8–25.8%)
α-guaiene (0.1–0.2%)
aromadendrene (4.2–8.5%)
α-humulene (0.6–10.5%)
allo-aromadendrene (t–0.2%)
γ-muurolene (0.2–0.8%)
germacrene D (0.1–2.2%)
bicyclogermacrene (1.0–1.3%)
β-bisabolene (0.1–0.8%)
δ-cadinene (0.1–0.6%)
β-sesquiphellandrene (0.1–1.2%)
(Z)-nerolidol (0.1–2.2%)
elemol (0.1–1.1%)
α-muurolol (t–0.1%)
γ-eudesmol (t–0.1%)
manoyl oxide (1.7–4.3%)

t=trace (<o.02%)

Tekih et al. (2014) examined the composition and antibacterial activity of oil produced from the needles, twigs and buds of *P. halepensis* growing in Northwestern Algeria. Analysis of the oil using GC-FID and GC/MS of the bulked hydrodistilled oils that were produced from aerial parts collected from 10 different locations. The oils were found to range in composition as follows:

α-thujene (0.4–1.0%)
α-pinene (12.2–24.5%)
camphene (0.1–0.3%)
sabinene (1.5–6.3%)
β-pinene (1.7–2.2%)
myrcene (15.2–32.0%)
α-phellandrene (0–0.2%)
δ-3-carene (0.6–5.5%)
α-terpinene (0.1–1.8%)
p-cymene (0.2–1.8%)
β-phellandrene (0.7–1.4%)
limonene (0.6–1.4%)
(Z)-β-ocimene (0–1.4%)
(E)-β-ocimene (0.5–3.4%)
γ-terpinene (0.2–2.6%)
terpinolene (1.8–13.8%)
linalool (0.1–0.8%)
perillene (t–0.1%)
cis-p-menth-2-en-1-ol (0.1–0.3%)
trans-p-menth-2-en-1-ol (t–0.2%)
terpinen-4-ol (1.0–8.2%)
α-terpineol (t–0.7%)
bornyl acetate (t–0.3%)
citronellyl acetate (t–0.1%)
neryl acetate (0.1–0.2%)
geranyl acetate (t–0.5%)
α-copaene (0.1–0.3%)
β-caryophyllene (7.0–17.1%)
α-humulene (1.3–3.4%)
2-phenethyl isovalerate (4.8–10.9%)
germacrene D (0.1–0.2%)
α-muurolene (t–0.6%)
δ-cadinene (t–0.5%)
(E)-α-bisabolene (0.1–0.3%)
2-phenethyl tiglate (0–0.2%)
2-phenethyl angelate (t–3.3%)
caryophyllene oxide (0.2–2.2%)
guaiol (0.1–0.5%)
humulene epoxide[a] (t–0.1%)
epi-cubenol (0.1–0.2%)
T-cadinol (t–0.1%)
T-muurolol (0.1–0.3%)
α-cadinol (t–0.3%)
bulnesol (0–0.1%)
cembrene (0.1–1.6%)
m-camphorene (0–0.4%)
cembrene A (0–0.3%)

T-4. Comparative percentage composition of the cone, needle and branch oils of Italian *Pinus halepensis*

Compound	Cone oil	Needle oil	Branch oil
tricyclene	0.5	-	0.1
α-thujene	-	0.1	-
α-pinene	53.6	18.1	27.9
camphene	1.5	0.3	0.3
thuja-2,4(10)-diene	1.3	-	-
sabinene	-	9.4	0.1
β-pinene	1.9	2.0	0.7
myrcene	13.7	27.9	42.1
δ-3-carene	1.1	1.7	2.1
α-terpinene	-	0.5	0.1
p-cymene	0.5	-	0.1
limonene	0.7	1.1	0.4
β-phellandrene	0.3	1.0	0.4
(E)-β-ocimene	-	0.4	-
γ-terpinene	-	0.8	0.1
cis-sabinene hydrate	-	0.1	-
terpinolene	0.4	9.9	0.4
perillene	0.3	-	-
linalool	-	0.3	-
α-campholenal	1.0	-	-
trans-pinocarveol	1.5	-	0.1
cis-verbenol	1.2	-	-
camphor	0.4	-	0.1
pinocamphone	0.3	-	-
pinocarvone	0.7	-	-
umbellulone	-	0.1	-
p-mentha-1,5-dien-8-ol	1.2	-	-
borneol	-	-	0.2
terpinen-4-ol	0.2	1.1	0.1
α-terpineol	-	0.2	0.2
myrtenal	1.2	-	-
verbenone	0.8	-	-
trans-carveol	0.2	-	-
isobornyl acetate	0.9	-	-
α-cubebene	-	0.1	-
cyclosativene	-	-	0.5
α-copaene	0.3	0.4	1.0
geranyl acetate	-	0.3	-
β-caryophyllene	6.7	16.4	14.3
(E)-β-farnesene	-	0.2	-
α-humulene	1.1	2.9	2.4
9-epi-β-caryophyllene	-	0.1	-
γ-muurolene	-	-	0.2
germacrene D	-	0.1	1.0
2-phenethyl isovalerate	-	1.2	-
epi-cubebol	-	0.2	-
α-muurolene	0.4	0.4	2.7
γ-cadinene	0.2	0.3	-
δ-cadinene	0.3	0.3	0.5
caryophyllene oxide	2.3	0.1	0.4
guaiol	-	0.3	-
humulene epoxide II	0.3	-	-
α-eudesmol	0.2	0.1	-
neocembrene	-	0.1	-
sandaracopimaridiene	0.3	-	-
abietatriene	0.2	-	-
abietadiene	0.2	-	-

p-camphorene (0–1.1%)
geranyl linalool (0–3.0%)

t=trace (<0.05%); [a]isomer II

It is also interesting to realize that two camphorene isomers are identical to myrcene dimers often found in myrcene-rich oils.

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