Progress in Essential Oils

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Armoise oil, *Artemisia herba-alba* oil: Part 1[a]

Armoise oil is produced from the thujone chemotype of *Artemisia herba-alba* Asso. This member of the Asteraceae family, which is also known as *Sheeh* in Arabic, or desert wormwood in English, is an aromatic dwarf shrub or seimishrub. The distribution of *A. herba-alba* is from the dry areas of Andalucia, Levante and Aragon (Spain), extending into southern France. It is much more abundant in the Middle East and North Africa, especially Algeria, Egypt, Israel, Jordan, Morocco and Tunisia.

Like many members of the Asteraceae family, chemotypic forms of the essential oils of *A. herba-alba* are known to exist (Lawrence 1981, 1982, 1994, 2003 and 2009).

Ravid et al. (1993) reported that (-)-camphor was the major enantiomer found in *A. herba-alba* oil.

Five separate *A. herba-alba* plants (ca. 2009 from each) that were collected in the Southern Negev were immediately subjected to hydrodistillation. Analysis of the oils by Fleisher et al. (2002) using GC-FID and GC/MS revealed that the oils possessed different compositions. For example, there were oils that were rich in (a) α- and β-thujone, (b) β-thujone only, (c) camphor, (d) chrysanthenol and (e) chrysanthenyl acetate. The compositions of the monoterpene ketone-rich oils can be seen in **T-1**. Trace amounts (<0.1%) of artemisia triene and α-copaene were found in all three chemotypes. Limonene, amyl isovalerate, 6-methyl-5-hepten-2-one, 3-octanol, 1-octen-3-ol, pinocarvone and *cis*-carveol were also found in the camphor-rich chemotype, amyl isovalerate and bornyl acetate were also found in the chemotype that was rich in α- and β-thujone, while only acetic

[a]Part 2 of this article will appear in the April edition of this magazine.

T-1. Percentage composition of oils of *Artemisia herba-alba* that were rich in monoterpene ketones

Compound	1	2	3
tricyclene	0.1	t	0.2
α-pinene	t	–	0.2
camphene	0.1	0.2	4.6
β-pinene	0.2	t	0.2
sabinene	0.3	–	0.5
myrcene	0.1	–	0.2
α-phellandrene	0.3	–	0.3
α-terpinene	t	–	0.1
1,8-cineole	26.6	10.8	26.0
γ-terpinene	0.4	0.1	0.4
p-cymene	3.1	0.4	3.2
terpinolene	0.1	–	0.1
2-methylbutyl 2-methylbutyrate	t	0.1	–
yomogi alcohol	0.5	–	0.3
santolina alcohol	0.4	–	0.1
α-thujone	0.9	40.9	0.1
β-thujone	44.0	34.9	4.4
artemisia alcohol	0.7	–	–
camphor	t	4.2	42.1
terpinen-4-ol	2.3	0.2	1.5
myrtenal	0.4	0.3	0.6
trans-pinocarveol	1.0	0.5	t
lyratyl acetate	2.3	0.2	2.7
myrtenyl acetate	0.2	t	0.9
borneol	0.3	0.8	0.9
piperitone	0.1	0.1	0.1
carvone	0.2	0.1	0.3
cuminaldehyde	0.1	0.1	–
trans-piperitol	0.1	t	–
lyratol	3.2	0.2	0.5
myrtenol	0.6	0.1	0.3
p-mentha-1,5-dien-7-ol	0.1	–	t
p-cymen-8-ol	0.3	t	0.3
(Z)-jasmone	–	0.1	0.1
cuminyl alcohol	0.3	0.1	0.4
thymol	0.1	–	0.1
carvacrol	0.3	–	0.4
4-isopropylphenol	–	0.2	t
methyl jasmonate	0.1	–	–
hexadecanoic acid	–	0.2	–
linoleic acid	–	0.2	–

t = trace (<0.1%); 1. β-thujone-rich chemotype; 2. α- and β-thujone-rich chemotype; 3. camphor-rich chemotype

T-2. Percentage composition of the *Artemisia herba-alba* oils rich in either chrysanthenol or chrysanthenyl acetate

Compound	1	2
α-pinene	0.1	t
1,8-cineole	1.8	0.2
p-cymene	0.1	0.1
2-methylbutyl 2-methylbutyrate	0.1	0.1
1,2,3-trimethylbenzene	0.1	t
β-thujone	0.1	t
acetic acid	0.1	t
α-copaene	0.5	t
chrysanthenone	0.1	t
linalool	0.1	0.1
cis-chrysanthenyl acetate	8.9	69.0
β-caryophyllene	0.4	0.3
terpinen-4-ol	0.6	0.5
myrtenal	0.1	t
cis-chrysanthenyl propionate	6.6	0.9
cis-chrysanthenyl isobutyrate	1.7	0.2
trans-pinocarveol	2.1	0.2
α-terpineol	t	0.1
verbenone	t	0.1
cis-chrysanthenyl isovalerate	0.1	t
cis-chrysanthenol	30.0	6.8
myrtenal	0.1	0.1
(Z)-jasmone	0.7	0.1
spathulenol	0.1	0.1
eugenol	0.1	t
methyl jasmonate	0.3	0.6

t = trace (<0.1%); 1. chrysanthenol-rich chemotype; 2. chrysanthenyl acetate-rich chemotype

acid was characterized as a unique trace constituent of the β-thujone chemotype.

The results of the analyses of the chrysanthenol and chrysanthenyl acetate chemotypes can be seen in **T-2**. In addition, trace amounts (<0.1%) of 1,2,4-trimethylbenzene, caryophyllene oxide, β-oplopenone and α-cadinol were found in both chemotype oils; trace amounts of carvone and carvacrol were found in the chrysanthenol-rich chemotype, and trace amounts of tricyclene, camphene, β-pinene, 1,4-cineole, myrcene, α-phellandrene, limonene, amyl isovalerate, α-thujone, neral, germacrene D, *cis*-calamenene and methyl eugenol were characterized as trace constituents of the chrysanthenyl acetate-rich chenotype.

In Morocco there are two problem fungi [*Phytothera citrophthora* (Smith) Leonian and *Botrytis cinerea* Pers.] that cause post-harvest devastation on fresh citrus fruits and many other fresh fruits and vegetables. Cheloli et al. (2004) screened a number of Moroccan essential oils against these pathogens. One of the oils screened was an oil of *A herba-alba*. The main constituents of this oil were determined to be:

camphene (8.5%)
1,8-cineole (6.4%)
α-thujone (33.2%)
β-thujone (9.0%)
camphor (46.0%)

Artemisia herba-alba plants collected from Tataouine (Tunisia) were stripped of leaves and these were subjected to hydrodistillation for 3 hr by Neffati et al. (2008). The oil, which was produced in 1.85% yield, was analyzed by GC-FID and GC/MS. It was determined to possess the following composition:

α-thujene (0.1%)
α-pinene (0.1%)
camphene (1.1%)
sabinene (0.2%)
β-pinene (0.1%)
myrcene (0.1%)
α-phellandrene (0.1%)
α-terpinene (1.3%)
limonene (11.0%)
isoamyl 2 methylbutyrate (19.5%)
(Z)-β-ocimene (0.3%)
γ-terpinene (0.1%)
pinocarvone (38.3%)
carvone (0.4%)
α-copaene (12.2%)
geranyl aceate (0.9%)
β-caryophyllene (0.2%)
β-gurjunene (1.4%)
aromadendrene (0.4%)
(Z)-β-farnesene (0.5%)
germacrene D (0.1%)
geranyl propionate (0.2%)
β-selinene (0.4%)
bicyclogermacrene (0.1%)
α-muurolene (0.1%)
γ-cadinene (0.1%)
δ-cadinene (0.1%)
(E)-nerolidol (0.6%)
spathulenol (0.5%)
1-epi-cubenol (0.6%)
T-cadinol (0.1%)
T-muurolol (0.1%)
β-eudesmol (0.2%)

Boutemak et al. (2009) examined the steam distillation process for *A. herba-alba* that was harvested from the sub-Saharan highlands in southern Algeria. In the process the parameters of distillation time, biomass and steam (water) flow rate were examined in the laboratory. The results of this study revealed that the optimum conditions and parameters for steam distillation were biomass (30 g), distillation time (60 min) and steam flow rate (1.65 mL/min). The composition of the oil as determined by GC/MS only by Boutemak et al. was found to be as follows:

tricyclene (0.3%)
α-thujene (0.1%)
α-pinene (1.1%)
camphene (3.1%)
verbenene (0.2%)
sabinene (0.9%)
β-pinene (0.2%)
myrcene (0.7%)
α-terpinene (0.6%)
p-cymene (0.6%)
limonene (0.1%)
β-phellandrene (0.1%)
1,8-cineole (5.3%)
γ-terpinene (0.1%)
trans-sabinene hydrate (0.3%)
filifolone (6.6%)
α-thujone (5.8%)

β-thujone (5.9%)
chrysanthenone (40.9%)
camphor (19.4%)
pinocarvone (0.7%)
borneol (0.2%)
terpinen-4-ol (0.5%)
p-mentha-1,8-dien-3-one (0.4%)
verbenone(0.4%)
4- (1,1-dimethylethyl)-1,2-benzenediol†(0.9%)
filifolide A (2.3%)
(Z)-jasmone (1.7%)
germacrene D (0.5%)
caryophyllene oxide (0.1%)

†incorrect identification

Artemisia herba-alba harvested during its flowering stage from an experimental garden in Medenine, which is an arid region of southern Tunisia, was examined for the influence of drying time and method on the main constituents of the oil by Mighri et al. (2009a). Using a combination of GC-FID, retention indices and ^{13}C-NMR, the authors characterized 16 constituents of the oil. They also determined that the oil content varied from 1.84–2.53%, depending on the number of air-drying days. The constituents identified in the fresh herb oil were as follows:

camphene (0.4%)
α-terpinene (2.1%)
p-cymene (0.7%)
1,8-cineole (8.5%)
γ-terpinene (1.4%)
α-thujone (22.7%)
β-thujone (21.7%)
chrysanthenone (7.8%)
camphor (8.6%)
borneol (0.8%)
terpinen-4-o1 (4.3%)
cis-chrysanthenyl acetate (1.6%)
bornyl acetate (0.5%)
trans-sabinyl acetate (6.8%)
germacrene D (1.0%)
spathulenol (0.8%)

Milghri et al. (2009b) examined the effects of harvest frequency, ontogenetic development stage and biomass yield on oil composition and potential hectare yield. They found that the highest biomass and essential oil yield was obtained at the flowering stage. At that time, a yield of 26.2 kg/ha was projected from these results. Over the course of the experiment, the authors found that the main constituents varied as follows:

camphene (0.2–2.1%)
p-cymene (t–3.3%)
1,8-cineole (6.0–22.9%)
α-thujone (12.2–25.9%)
β-thujone (19.5–33.8%)
chrysanthenone (0.5–8.6%)
camphor (4.5–11.1%)
terpinen-4-ol (1.9–5.0%)
trans-sabinyl acetate (1.3–6.8%)

t=trace (<0.1%)

Transplanted seedlings of *A. herba-alba* that originated from the Kirchaou area of Southern Tunisia were grown in an experimental garden in Medenine. Mighri et al. (2009c) compared the oil yield and composition of *A. herba-alba* harvested over three years at three levels of cutting (2.5%, 50% and 75% plant amounts) from cultivated plants at the vegetative and flowering stages, and wild plants at their flowering stage. A summary of the results of this study are shown in **T-3**. Mohsen and Ali (2009) collected 18 plants from different localities in the sub-arid to Saharan domains of Tunisia. Oils were produced from the leaves and stems of each of the collections by hydrodistillation in yields ranging from 0.68% to 1.93%. Separate analysis of each oil using GC-FID and GC/MS revealed that they ranged in composition. The main constituents being 1,8-cineole, α- and β-thujone, chrysanthenone, camphor, borneol, chrysanthenyl acetate (probably *cis*-), sabinyl acetate (probably *cis*-), davana ethers and davanone.

The range of constituents characterized in the 18 oils was as follows:

2-hexenal* (0–0.7%)
hexaneol (0–0.3%)
geraniolene† (0–0.1%)
santolinatriene (0–0.5%)
2,5-diethenyl-2-methyltetrahydrofuran (0–0.5%)
tricyclene (0–0.3%)
α-pinene (0–0.6%)
camphene (0–2.1%)
3,5-dimethyl-2(5H)-furanone†(0.06%)
sabinene (0–1.5%)
β-pinene (0–1.2%)
1-octen-3-ol (0–1.0%)
myrcene (0–0.6%)
α-phellandrene (0–0.2%)
yomogi alcohol (0–9.5%)
δ-2-carene (0–1.2%)
α-terpinene (0–0.5%)
p-mentha-1(7),8-diene (0–0.4%)
p-cymene (0–2.8%)
1,8 –cineole (0.6–27.0%)
santolina alcohol (0–3.7%)
cis-asbusculone (0–4.6%)
γ-terpinene (0–1.9%)
artemisia ketone (0–2.7%)
cis-sabinene hydrate (0–2.1%)

T-3. Comparative percentage composition of the oils of the flowering and vegetative stage and the flowering stage of cultivated and wild *Artemisia herba-alba*

Compound	Cultivated plants		Wild plants
	VS-oil	FS-oil	FS-oil
camphene	0.6–1.6	0.9–1.4	1.2–1.6
sabinene	0.4–0.5	0.3–1.4	0.5–0.7
α-terpinene	0.6–0.9	0.6–1.3	0.8–1.8
p-cymene	1.5–5.5	1.5–2.8	0.2–1.9
1,8-cineole	6.1–12.3	6.7–9.3	9.8–11.8
γ-terpinene	1.4–2.2	0.8–1.4	0.7–0.8
α-thujone	21.2–24.2	15.5–24.4	14.4–23.1
β-thujone	16.2–27.8	20.6–33.7	19.3–28.2
chrysanthenone	0.5–1.1	0.5–3.8	0.4–0.5
camphor	3.6–10.3	4.6–6.3	6.6–10.3
trans-pinocarveol	0.1–1.7	1.0–2.6	0.1–1.1
borneol	1.1–1.8	0.7–1.8	1.3–1.7
terpinen-4-ol	2.4–4.2	2.2–3.8	2.0–2.6
cis-chrysanthenyl acetate	0.1–0.3	0.1–1.2	0.3–0.7
bornyl acetate	0.5–0.9	0.3–0.7	0.5–0.9
trans-sabinyl acetate	3.9–6.1	2.8–6.3	3.9–6.1
germacrene D	0.1–1.6	0.5–1.0	0.9–1.4
spathulenol	0.3–0.5	0.3–1.0	0.3–0.5

VS=vegetative stage; FS=flowering stage

trans-arbusculone (0–3.5%)
artemisia alcohol (0–3.0%)
terpinolene (0–0.8%)
isochrysanthenone (0–4.0%)
α-thujone (0–42.2%)
β-thujone (0–24.1%)
cis-p-menth-2-en-l-ol (0–2.2%)
chrysanthenone (0–17.4%)
trans-pinocarveol (0–2.8%)
verbenol (0–4.6%)
cis-sabinol (0–5.9%)
camphor (0–17.8%)
sabina ketone (0–0.5%)
pinocarvone (0–1.2%)
borneol (0–10.8%)
α-phellandren-8-ol† (0–1.2%)
lavandulol (0–1.4%)
terpinen-4-ol (0.9–8.7%)
α-thujenal† (0–0.7%)
p-cymen-8-ol (0–1.1%)
α-terpineol (0–1.0%)
cis-piperitol (0–1.4%)
myrtenal (0–1.3%)
myrtenol (0–1.2%)
verbenone (0–0.4%)
trans-piperitol (0–1.7%)
octyl acetate (0–1.1%)
nor-davanone (0–0.8%)
cuminaldehyde (0–1.6%)
2-methylhexyl butyrate† (0–0.2%)
carvone (0–0.7%)
piperitone (0–4.6%)
piperitone oxide° (0–1.2%)
cis-chrysanthenyl acetate (0–13.0%)
isopiperitenone (0–0.4%)
bornyl acetate (0–2.0%)
terpinen-4-yl acetate (0–0.5%)
sabinyl acetate° (0–22.5%)
myrtenyl acetate (0-0.7%)
thymol (0–0.5%)
carvacrol (0–0.6%)
α-copaene (0–0.7%)
methyl cinnamate° (0–0.8%)
jasmone° (0–2.3%)
cis-davanafuran (0–0.5%)
α-humulene (0–1.1%)
ethyl cinnamate° (0–2.5%)
germacrene D (2.0–6.7%)
β-selinene (0–1.2%)
lyratyl isovalerate (0–1.2%)
bicyclogermacrene (1.2–6.2%)
davana ether (0–6.2%)
davana ether° (0–15.9%)
davana ether° (0–7.3%)
nerolidol° (0–3.5%)
spathulenol (0–3.7%)
globulol (0–1.8%)
caryophyllene oxide (0–1.0%)
β-copaen-4α-ol (0–1.1%)
epi-globulol (0–2.1%)
davanone (0–20.1%)
rosifoliol (0–1.0%)
1,7,7-trimethylbicyclo[2.2.1]hept-2-yl 3-methyl-2-butenoate† (0–0.9%)
α-acorenol (0–2.5%)
T-cadinol (0–3.5%)
3-hydroxyisodavanone (0–5.4%)
β-eudesmol (0–1.0%)
α-cadinol (0–2.5%)
selin-ll-en-4α-ol (0–1.6%)
xanthoxylin[a†] (0–2.1%)
(E)-dihydrofarnesol (0–1.1%)
1,2-dehydro-3-hydroxy-isodavanone (0–3.6%)
2-hydroxy-β-davanone (0–0.9%)
phytol (0–0.5%)

°correct isomer not identified
†questionable identification
[a]also known as 2-hydroxy-4, 6-dimethoxyacetophenone

The 18 oils can be grouped together according to their major constituents (those found in amounts exceeding 10%). As a result, the following chemical forms were found amongst the 18 oils:

1. Oils rich in α-thujone (three oils)
2. Oils rich in 1,8-cineole and camphor (two oils)
3. Oils rich in α-thujone and β-thujone (two oils)
4. Oils rich in α-thujone and sabinyl acetate (one oil)

5. Oils rich in davana ether and davanone (one oil)
6. Oils rich in sabinyl acetate and davanone (one oil)
7. Oils rich in chrysanthenone and davana ether (one oil)
8. Oils rich in α-thujone, chrysanthenyl acetate and sabinyl acetate (one oil)
9. Oils rich in α-thujone, sabinyl acetate and davanone (one oil)
10. Oils rich in α-thujone, β-thujone and camphor (one oil)
11. Oils rich in chrysanthenone, davana ether and davanone (one oil)
12. Oils rich in 1,8-cineole, α-thujone, camphor and sabinyl acetate (one oil)
13. Oils rich in 1,8-cineole, α-thujone, β-thujone, and camphor (one oil)

Finally one oil did not have a single constituent in any amount greater than 7.5%.

B. M. Lawrence. *Armoise oil*. Perfume Flavor., **6**(1), 37–38 (1981); **7**(5), 44–46 (1982); **14**(3), 71–74 (1989); **19**(5), 94–95 (1994); **28**(2), 62–67 (2003); **34**(8), 54–58 (2009).

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