

## **Progress in Essential Oils**

Brian M. Lawrence, Consultant

## Armoise oil, *Artemisia herba-alba* oil: Part 2<sup>b</sup>

Dahmani-Hamzaoui and Baaliouamer (2010) collected *A. herba-alba* plants during their flowering stage from the Boussaada region in the northern Sahara desert region of Algeria. Oils were produced from air-dried and chopped plants using either hydrodistillation or microwave distillation. Analysis of the oils using GC-FID and retention indices only revealed that the main constituents of the oils that were similar in composition were as follows:

santalinatriene (0.8-0.9%) tricyclene (0.2%)  $\alpha$ -thujene (0.5%) camphene (4.5-4.9%) sabinene (0.4%) β-pinene (0.5-0.6%) yomogi alcohol (0.1%) 1,2,3-trimethylbenzene (0-0.1%) p-cymene (0.1%) 1,8-cineole (12.4-13.4%) santolina alcohol(0.1%) $\gamma$ -terpinene (0.4%) cis-sabinene hydrate (1.1%) artemisia alcohol (1.1%)  $\alpha$ -thujone (1.0%)  $\beta$ -thujone (1.9–2.1%) chrysanthenone (3.2-3.3%) camphor (48.1-49.3%) pinocarvone (5.5-5.6%) borneol (7.1-7.3%) terpinen-4-ol (0.8-0.9%) myrtenal (0.1%) myrtenol (0.1%) trans-piperitol (0.2%) cis-carveol (0.1-0.2%) cuminaldehyde (t-0.1%) (E)-tagetenone (0.1%) piperitone (0.1%) cis-chrysanthenyl acetate (0.9-1.0%) lyratyl acetate (0.1%) lyratyl propionate (t-0.1%)

<sup>b</sup>Part 1 of this article appeared on pages 48–52 of the March 2015 edition of this magazine; www.perfumerflavorist.com/magazine  $\begin{array}{l} \alpha\text{-copaene}\ (0.3\%)\\ (Z)\text{-jasmone}\ (0.6\%)\\ \text{isocaryophyllene}\ (0.1\%)\\ \beta\text{-chamigrene}\ (t\text{-}0.1\%)\\ \gamma\text{-muurolene}\ (2.0\text{-}2.1\%)\\ \alpha\text{-muurolene}\ (0.1\%)\\ \gamma\text{-cadinene}\ (0.1\%)\\ \gamma\text{-cadinene}\ (0.1\%)\\ \delta\text{-cadinene}\ (0.1\%)\\ (E)\text{-nerolidol}\ (t\text{-}0.1\%)\\ \text{spathulenol}\ (0.1\%)\\ \text{viridiflorol}\ (t\text{-}0.1\%)\end{array}$ 

Trace amounts (<0.05%) of  $\alpha$ -thujene, thuja-2,4(10)-diene, 1-octem-3-ol, myrcene, 1,3,5-trimethylbenzene,  $\alpha$ -phellandrene, o-isopropenyltoluene,  $\alpha$ -terpinene, limonene,  $\beta$ -phellandrene, (E)- $\beta$ -ocimene, terpinolene, *trans*-sabinene hydrate, filifolone, *trans*-pinocarveol, *trans*-verbenol, isothujyl alcohol, isoborneol,  $\delta$ -terpineol, santalinyl acetate, thuj-3-en-10-al, p-cymen-8-ol,  $\alpha$ -terpineol, *cis*-piperitol, verbenone, *trans*-piperitol, *trans*-carveol, (E)-tagetenone isobornyl acetate, bornyl acetate, cumin alcohol, sabinyl acetate isomer, filfolide,  $\alpha$ -terpinyl acetate, eugenol,  $\beta$ -elemene,  $\beta$ -cubebene, (E)-jasmone, methyl eugenol,  $\beta$ -caryophyllene, aromadendrene,  $\alpha$ -guaiene, allo-aromadendrene, ethyl (E)-cinnamate,  $\beta$ -selinene,  $\gamma$ -cadinene, cadina-1,4-diene, ledol, caryophyllene oxide, globulol,  $\beta$ -copaen-4 $\alpha$ -ol and davanone were also characterized in this oil.

Imelouane et al. (2010) analyzed a lab-distilled oil that was produced in 1.0% yield of *A. herba-alba* plants collected from an undisclosed region of Morocco using GC-FID and GC/MS. The constituents that were collectively characterized in this oil were:

## T-4. Comparative percentage composition of the four chemotypes of *Artemisia herba-alba* of Tunisian origin

Compound	Type 1	Type 2	Туре З	Type 4
$\alpha$ -pinene	1.1	0.8	1.4	2.2
camphene	1.6	1.0	1.1	1.4
sabinene	0.3	0.5	0.4	1.5
$\alpha$ -terpinene	0.8	0.9	1.0	1.2
p-cymene	1.0	0.9	1.8	1.7
1,8-cineole	5.0	4.5	12.3	18.4
γ-terpinene	0.6	0.6	0.8	2.0
α-thujone	5.5	49.3	24.1	10.7
β-thujone	58.0	15.0	24.3	14.1
chrysanthenone	2.1	1.4	1.8	1.4
camphor	5.4	3.9	7.5	10.8
<i>trans</i> -pinocarveol	1.7	1.4	2.2	3.5
borneol	1.7	1.4	2.6	2.5
bornyl acetate	0.5	0.3	0.6	1.2
trans-sabinyl acetate	3.4	7.6	3.8	7.8
(E)-jasmone	0.2	0.3	0.2	1.2
germacrene D	0.8	0.8	1.1	1.3

Type 1. β-thujone-rich; Type 2. α-thujone-rich; Type 3. α- and β-thujone-rich; Type 4. 1,8 cineole, camphor; α-thujone and β-thujone-rich

Reproduction in English or any other language of all or part of this article is strictly prohibited. © 2015 Allured Business Media.

tricyclene (0.4%) $\alpha$ -pinene (0.6%) camphene (7.2%) sabinene (1.0%) 1-octen-3-ol (0.3%)  $\alpha$ -phellandrene (0.4%)  $\alpha$ -terpinene (0.3%) p-cymene (0.5%) 1,8-cineole (7.1%)  $\gamma$ -terpinene (0.3%) terpinolene (0.3%)  $\beta$ -thujone (7.0%) chrysanthenone (0.4%) camphor (43.1%) sabina ketone (1.1%)borneol (4.9%) terpinen-4-ol (1.1%) verbenone (0.2%) cis-carveol (0.3%) carvone (0.2%)bornyl acetate (3.8%) thymol (1.0%)  $\gamma$ -elemene (0.1%) bicycloelemene (0.2%)eugenol (0.2%)  $\alpha$ -copaene (0.3%) verbenone (0.5%)  $\beta$ -cubebene (0.2%)  $\alpha$ -amorphene (0.2%) germacrene D (1.4%)  $\alpha$ -patchoulene (0.2%) germacrene B (0.6%) bicyclogermacrene (0.1%)  $\delta$ -cadinene (0.2%)

Trace amounts (<0.09%) of cuminyl alcohol, spathulenol, viridiflorol and kaurene were also characterized in the oil.

Mighri et al. (2010) examined the composition of the oils of four chemical types of *A. herba-alba* using GC-FID and GC/ MS. The plants, which were harvested from an experimental garden at the Institut des Region Arides (Medenine, Tunisia) during their flowering stage, were initially air-dried before the leaves and flowers, minus the large stems, were subjected to hydrodistillation for 4 hr. The comparative composition of the four oil types can be seen in **T-4**.

Boukrich et al. (2010) collected A. herba-alba plants from the semi-arid and arid regions of Tunisia. They collected 10 individual plants from Msaken (Sahel central Tunisia), an inferior semi-arid region (300–400 mm rainfall annually), eight individual plants from El Kef (northwestern Tunisia), a superior semi-arid region (400–600 mm rainfall annually), and eight individual plants from Samâaliat and Kirchaou (southeastern Tunisia), an inferior arid climate (100–200 mm rainfall annually). Each accession was weighted and airdried in the shade for 20 days, after which they were subjected to separate hydrodistillation for 4 hr. The oil yields were 1.55–4.12% (central Tunisia), 1.98–4.86% (southeastern Tunisia) and 1.65–2.82% (northwestern Tunisia).

Each of the oils was analyzed using GC-FID, <sup>13</sup>C-NMR, retention indices and, in a few situations, GC/MS. As one might expect the major constituents varied drastically. For example,  $\alpha$ -thujone (trace–79.9%), chrysanthenone (trace–64.8%), camphor (trace–47.9%) and *trans*-sabinyl acetate (trace–43.8%). A number of other constituents were found in amounts exceeding 10%, including 1,8-cineole (23.5%), davanone (20.7%),  $\beta$ -thujone (19.0%), pinocarvone (14.8%) and camphene (10.2%).

As armoise oil of commercial value is  $\alpha$ -thujone-rich, it is of interest to note that all but one of the central Tunisian oil and one oil sample from the Southeastern Tunisia samples possessed the following range in composition:

α-pinene (0-0.7%) camphene (0-1.1%)sabinene (0.3-6.5%) myrcene (0-3.3%) p-cymene (0.2-1.0%) 1,8-cineole (0.4-2.8%) α-thujone (48.7–79.9%) β-thujone (7.2–18.2%) chrysanthenone (0-2.9%) camphor (0-17.1%) trans-pinocarveol (0.2-1.9%) pinocarvone (0.2-3.2%) borneol (0-3.9%) terpinen-4-ol (0.2-1.0%) cis-chrysanthenyl acetate (0–1.9%) bornyl acetate (0-1.0%)trans-sabinyl acetate (0–0.9%) (Z)-jasmone (0–1.1%) germacrene D (0.6-5.1%) bicyclogermacrene (0.1-1.0%) spathulenol (0.1-1.1%)

The other oil samples contained varying amounts of the other dominant constituents. This shows that collections of *A. herba-alba* from its natural environment can result in the production of oils that are totally dissimilar to the named commercial oil of the specific botanical origin.

Artemisia herba-alba plants were collected from Mount Bir Elhfay (Sidi Bouzid, Tunisia) and subjected to hydrodistillation by Kadri et al. (2011). Using GC/MS and GC-FID as the method of analysis, the oil was found to contain the following correctly identified constituents:

 $\begin{array}{l} \alpha \text{-pinene} \ (2.8\%) \\ \text{camphene} \ (1.7\%) \\ 1,8-\text{cineole} \ (8.9\%) \\ \alpha \text{-thujone} \ (24.9\%) \\ \beta \text{-thujone} \ (24.9\%) \\ \beta \text{-thujone} \ (8.3\%) \\ \text{chrysanthenone} \ (4.7\%) \\ \text{camphor} \ (10.8\%) \\ \text{borneol} \ (3.1\%) \\ \text{chrysanthenyl} \ acetate^* \ (3.3\%) \\ \text{bornyl} \ acetate^* \ (5.3\%) \\ \alpha \text{-copaene} \ (0.9\%) \\ \beta \text{-caryophyllene} \ (0.9\%) \\ \text{germacrene} \ D \ (14.5\%) \\ \delta \text{-cadinene} \ (1.3\%) \end{array}$ 

° correct isomer not identified

Behtari et al. (2012) collected A. herba-alba plants at their vegetative and flowering stages from four different altitudes (1,100, 1,200, 1,280 and 1,380 m) in the North Rangeland of Gorgan Province (Iran). Air-dried vegetative and flowering stage plants (100 g of each) from each altitude were subjected to hydrodistillation to produce oils of 0.59-0.80% and 0.43-0.92% yields, respectively. The oil compositions from the plants collected from different altitudes were found to be very similar. As a result, the authors only subjected the oils produced from vegetative and flowering plants to analysis using both GC-FID and GC/MS. The components characterized in the two oils can be found in T-5.

An oil produced from *A. herba-alba* plants collected from Makther Seliana (Tunisia) were separated into leaves and stems. The leaves were dried and subjected to hydrodistillation for 3 hr. Analysis of the oil by Amri et al. (2013) using GC-FID and GC/MS revealed the following composition:

 1,8-cineole (0.7%)

 α-thujone (7.8%)

 β-thujone (2.2%)

 chrysanthenone (15.0%)

 trans-pinocarveol (1.3%)

 camphor (39.1%)

 trans-sabinol (1.7%)

 trans-verbenol (0.3%)

 eucarvone (0.8%)

 isoborneol (4.0%)

 viridene (0.5%)

 terpinen-4-ol (0.8%)

 dihydrocarveol (0.3%)

 myrtenol (0.4%)

## T-5. Comparative percentage composition of the vegetative and flowering plant oils of *Artemisia herba-alba* of Iranian origin

Compound	Vegetative plant oil	Flowering plant oil
sabinene	0.5	-
myrcene	4.5	-
1,8-cineole	8.0	-
artemisia ketone	13.0	21.3
<i>trans</i> -sabinene hydrate	8.5	0.8
trans-sabinene hydrate acetate	0.6	-
chrysanthenone	0.7	0.5
$\alpha$ -terpineol	-	1.3
camphor	-	1.9
p-menth-3-en-8-ol	2.9	-
isoborneol	2.8	-
borneol	1.0	-
<i>cis</i> -pinocarveol	7.5	29.6
<i>trans</i> -carveol	4.1	2.2
davanone	2.1	-
isobornyl acetate	2.1	-
tridecane	-	3.0
neoisodihydrocarvyl acetate	2.0	2.3
β-caryophyllene	2.5	1.5
aromadendrene	4.7	1.9
germacrene A	1.7	-
<i>trans</i> -calamenene	1.0	0.3
lpha-calacorene	0.4	-
caryophyllene alcohol	1.1	1.1
caryophyllene oxide	2.2	0.8
γ-eudesmol	-	0.6
$\alpha$ -eudesmol	4.6	1.2
tetradecane	-	0.8
(E,E)-farnesol	-	1.7
(E,Z)-farnesol	2.9	0.7
cedryl acetate	0.9	0.9
isopropyl tetradecanoate	0.7	-
nonadecane	2.8	9.3
eicosene*	0.3	0.5
octadecanol	0.5	2.0
heneicosane	1.7	6.0
tricosane	-	1.2
*correct isomer not identified		

verbenone (0.4%) *cis*-chrysanthenyl acetate (0.9%) *trans*-linalool oxide acetate<sup>\*</sup> (0.3%)  $\alpha$ -terpinen-7-al<sup>†</sup> (0.4%)  $\gamma$ -terpinen-7-al<sup>†</sup> (0.5%)(Z)-patchenol<sup>†</sup> (3.1%)(E)-patchenol<sup>†</sup> (9.5%)spathulenol (0.8%)ar-turmerone (0.5%)

<sup>°</sup>correct isomer not identified <sup>†</sup>questionable identification

- N. Dahmani-Hamzaoui and A. Baaliouamer, Chemical Composition of Algerian Artemisia herba-albaessential oils isolated by microwave and hyrodistillation. J. Essent. Oil Res., 22, 514–517 (2010).
- B. Imelouane, A. El Bachiri, M. Ankit, K. Khedid, J.P. Wathelet and H. Amhamdi, Essential oil composition and antimicrobial activity of Artemisia herba-alba Asso grown in Morocco. Banat. J. Biotech., 1(2), 48–55 (2010).
- H. Mighri, H. Hajlaoui, A. Akrout, H. Najjaa and M. Neffati, Antimicrobial and antioxidant activities of Artemisia herba-alba essential oil cultivated in Tunisian arid zone. Compt. Rend. Chimie, 13, 380–386 (2010).
- F. Boukrich, S. Zouari, M. Neffati, C. Abdelly, K. Liu, J. Casanova and F. Tomi, *Chemical variability* of Artemisia herba-alba Asso growing wild in semi-arid and arid land (Tunisia). J. Essent. Oil Res., **22**, 331–335 (2010).
- A. Kadri, I. Ben Chobba, Z. Zarai, A. Békir, N. Gharsallah, M. Damak and R. Gdoura, *Chemical constituents and antioxidant activity* of the essential oil from aerial parts of Artemisia herba-alba grown in Tunisian semi-arid region. Afric. J. Biotech., **10**, 2923–2929 (2011).
- B. Behtari, F. Gholami, K.A. Khalid, G.D. Tilaki and R. Bahari, *Effect of growth stages and altitude on* Artemisia herba-alba Asso essential oil growing in Iran. J. Essent. Oil Bear Plants, 15, 307–313 (2012).
- I. Amri, L. DeMartino, A. Marandio, H. Lamia, H. Mohsen, E. Scandolera, V. DeFeo and E. Mancini, *Chemical composition and biological* activities of the essential oil from Artemisia herba-albagrowing wild in Tunisia. Nat Prod. Commun., 8, 407–410 (2013).

To purchase a copy of this article or others, visit www.PerfumerFlavorist.com/magazine.