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Chemical composition of the essential oil of aerial parts of *Artemisia herba-alba* Asso. from Oum El-Bouaghi (Algeria) and chemotaxonomic survey

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Abstract
Hydrodistilled essential oil from fresh aerial parts of *Artemisia herba-alba*, collected from Oum El-Bouaghi (Eastern Algerian), was GC and GC/MS analyzed. Forty compounds were characterized representing 93.6% of the essential oil with the prevalence of chrysanthenone (16.2%), camphor (15.6%), β-thujone (14.2%), α-thujone (9.1%), 1,8-cineole (8.9%), and piperitenone (7.6%). This composition is compared to numerous reported essential oils from *Artemisia herba-alba*, worldwide distributed.

Keywords: Artemisia herba-alba Asso., Asteraceae, essential oil, chrysanthenone, camphor, α,β-thujone, 1,8-cineole, piperitenone.

Introduction
The genus *Artemisia*, belonging to the Asteraceae family, includes about 400 species, distributed in the Mediterranean region, Northern Africa, Western Asia, Southwestern Europe and in Arabian Peninsula. The Algerian flora comprises 13 species of *Artemisia* [1] of which the most reported species *A. herba-alba* Asso., commonly called in Algerian folk medicine "shih". This species revealed several biological activities such as antioxidant, insecticidal, antimicrobial, anticorrosive and relaxing [2-9]. In continuation of our works on Asteraceae essential oils [10-16], we report here the chemical composition of the hydrodistilled essential oil from fresh aerial parts of *Artemisia herba-alba* Asso., collected from Ain Babbouche - Province of Oum El Bouaghi (North Eastern Algerian), which is well known in Algerian folk medicine for its use as an antispasmodic plant. A bibliographic survey on the compositions of *Artemisia herba-alba* essential oils is given here.

I-Experimental
Plant material
Fresh flowering aerial parts of *Artemisia herba-alba* Asso. were collected in July 2012 from Ain Babbouche-Province of Oum El Bouaghi (Northern Eastern Algerian). A voucher specimen was deposited at the herbarium of University, Constantine, Algeria (LOST Aha/07/12).

Essential Oil extraction
The hydrodistillation of fresh aerial parts (100 g) of *Artemisia herba-alba* Asso. for 3 h, in a Clevenger-type apparatus according to the British Pharmacopoeia [17], yielded 1.0 % (w/w), of a good smell yellow essential oil which was stored at 4°C until analyzed.

Gas chromatography

GC analysis was performed on a Shimadzu GC17A gas chromatograph equipped with a split/splitless injector (250°C) and a flame ionization detector (250°C). Retention times for comparison with authentic compounds were measured using a cross-linked DB5-MS column (40 m × 0.18 mm, film thickness 0.18 μm). The oven temperature was programmed as isothermal at 60°C for 5 min, then raised to 275°C at 5°C/min and held at this temperature for 5 min. Helium was used as the carrier gas with a rate of 1 ml/min. Relative percentage amounts were calculated from peak area without using correction factors.

Gas Chromatography-Mass spectrometry

Gas chromatography-mass spectrometry: GC-MS was performed using a Shimadzu QP5050 mass selective detector using a cross-linked DB5-MS column (40 m × 0.18mm, film thickness 0.18 μm). The oven temperature was programmed as isothermal at 60°C for 5 min, then raised to 275°C at 5°C/min and held at this temperature for 5 min. Helium was used as the carrier gas with a rate of 1 ml/min. 0.1 μl oil was introduced directly into the MS source via a transfer line (280°C) with a split ratio of 1:50 and a linear velocity of 30.0 cm/sec. Ionization was obtained by electron impact (70 eV, source temperature 200°C, resolution 1000).

Identification of components

Essential oil components were identified based on their retention indices (determined with reference to a homologous series of normal alkanes), and by comparison of their mass spectral fragmentation patterns with those reported in literature [18, 19] and with authentic compounds for major components.

3- Results and discussion

Hydrodistillation of fresh aerial parts of *Artemisia herba-alba*, collected from Ain Babbouche - Province of Oum El Bouaghi (Eastern Algerian), furnished 1.0% of a yellowish essential oil. 40 Compounds, representing 93.6% of the essential oil, were identified. Table 1 shows the percentage composition of this essential oil characterized by the main presence of chrysanthenone (16.2%), camphor (15.6%), β-thujone (14.2%), α-thujone (9.1%), 1,8-cineole (8.9%), and piperitenone (7.6%).

Except piperitenone which is found for the first time as a main component of an *Artemisia herba-alba* essential oil, other major components of the present essential oil were also mainly present in reported essential oils of this species [3-5,7,16-31], mostly grown at the Maghreb area (Table 2).

As shown in table 3, studied essential oils from *Artemisia herba-alba*, growing in different areas in Algeria are characterized by the presence of α-thujone as a chemotype for **Ar1,** growing at Laghouat (66.7 %) and as a major component of **Ar6** (6.9 %), **Ar7** (28.1%), **Ar8** (27.7%), **Ar9** (23.5%), **Ar10** (25.6%), **Ar11** (31.5%), **Ar3** (7.9%), **Ar13** (47.1%) and **Ar14** (5.8%) (see references in table 2).

The predominance of 1.8-cineole in **Ar2** (13.4%), **Ar5** (5.8%), **Ar6** (8.6%), **Ar7** (8.2%) and **Ar8** (9.8 %) has also characterized this essential oil. It has also been demonstrated that β-thujone was a major component of **Ar1** (41.2%), **Ar4** (15.0%), **Ar7** (7.8%), **Ar10** (15.6%), **Ar11** (9.1%), **Ar12** (22.3%), **Ar13** (10.6%) and **Ar14** (5.9%). Whereas, chrysanthenone was a main component in **Ar3** (5.0%), **Ar4** (15.8%), **Ar6** (12.2%), **Ar8** (7.6%), **Ar9** (19.0%), **Ar10** (16.4%), **Ar11** (21.3%), **Ar13** (7.3%) and **Ar14** (40.9%). Furthermore, camphor reached the maximum value of 49.3% in **Ar2** and was mainly found in **Ar4** (19.4%), **Ar5** (5.6%), **Ar6** (33.1%), **Ar7** (22.8%), **Ar8** (17.3%), **Ar9** (18.7%), **Ar10** (14.2%), **Ar11** (10.4%), **Ar13** (10.3%) and **Ar14** (19.4%) (table 3).

Each one of the following major components were reported to be less abundant among essential oils from species distributed in Algeria: camphene in **Ar2** (4.9%) and **Ar6** (7.1%) and (*E*)-pinocarveol in **Ar1** (22.2%) and in **Ar4** (16.9%) from Méchria and M'sila respectively, besides to (*Z*)-chrysanthenylacetate in **Ar3** (25.1%) and **Ar11** (8.6%), and davanone (36.1%) which is the main component of **Ar5** growing in Djelfa.

Table 1. Chemical composition of *Artemisia herba-alba* Asso. essential oil.

N°	**Compound**	**RI**[a]	**%**
01	(2,3,3-Trimethyl-2-oxiranyl)methanol	927	1.0
02	α-Pinene	932	0.4
03	Camphene	946	2.8
04	Thuja-2,4(10)-diene	953	0.3
05	β-Pinene	974	0.1
06	Mesitylene	994	0.8
07	δ-2-Carene	996	0.4
08	1,2,3-Trimethylbenzene	1020	0.2
09	β-Phellandrene	1025	0.2
10	1,8-Cineole	1026	8.9
11	γ-Terpinene	1054	0.1
12	Terpinolene	1086	0.1
13	Filifolone	1087	2.0
14	α-thujone	1101	9.1
15	β-thujone	1112	14.2
16	Chrysanthenone	1124	16.2
17	*trans*-Pinocarveol	1135	1.3
18	Camphor	1141	15.6
19	Eucarvone	1146	0.3
20	Pinocarvone	1160	2.0
21	Borneol	1165	1.6
22	Terpinen-4-ol	1174	0.6
23	Myrtenol	1194	0.4
24	Safranal	1196	0.1
25	Shisofuran	1198	0.2
26	Verbenone	1204	1.6
27	*cis*-Ascaridol	1234	0.1
28	(E)-Ocimenone	1235	0.5
29	*trans*-Chrysanthenyl acetate	1235	1.8
30	Isopiperitenone	1240	0.6
31	Bornyl acetate	1284	0.4
32	Piperitenone	1340	7.6
33	Piperitenone oxide	1366	1.3
34	Germacrene D	1484	0.1
35	Spathulenol	1577	0.1
36	Globulol	1585	0.1
37	β-Copaen-4α-ol	1590	0.1
38	Viridiflorol	1592	0.2
39	α-Cedrol	1600	0.1
40	(E)-γ-Atlantone	1706	0.1
Identified Compounds			**93.6**

[a]RI: (retention index) measured relative to *n*-alkanes (C_6-C_{24}) on the non-polar DB5-MS column.

Table 2: Data of reported *Artemisia herba-alba* Asso.
You have to verify the presence of the other species exemple ref A

Code	**Locality**		**Ref**
Ar1	Méchria (West Algerian)		[3]
Ar2	Boussaada (Algeria)		[20]
Ar3	Biskra (Algeria)		[21]
Ar4	M'sila (Algeria)		[22]
Ar5	Dejelfa (Algeria)		[23]
Ar6	Benifouda (Algeria)		[24]
Ar7	Bougaa (Algeria)		[24]
Ar8	Boussaada (Algeria)		[24]
Ar9	Boutaleb (Algeria)		[24]
Ar10	Bordj Bou Arréridj (Algeria)		[25]
Ar11	Biskra (Algeria)		[25]
Ar12	Laghouat (Algeria)		[25]
Ar13	Ghardaïa (Algeria)		[25]
Ar14	Southern Algerian		[26]
Ar15	Morocco		[6]
Ar16	Oujda (Morocco)		[27]
Ar17	Errachidia (Morocco)		[27]
Ar18	Machraa (Morocco)		[28]
Ar19	Médenine (Tunisia)	Flowering (Cultivated)	[29]
Ar20		Vegetative (Cultivated)	[29]
Ar21		Flowering (Wild)	[29]
Ar22	Gafsa (Ayaycha mountain) (Tunisia)		[4]
Ar23	Tunisia		[2]
Ar24	Makther Seliana (Tunisia)		[30]
Ar25	Kirchaou Southeastern (Tunisia)		[31]
	Kairouan(Tunisia)		ref A
Ar26	Jordan		[32]
Ar27	Valencia (South of Spain)		[33]
Ar28	Aranjuez (Spain)		[34]
Ar29	Ouest Azerbaijan (Iran)		[35]

Ar**:** *Artemisia herba-alba* Asso.

According to table 4, it appears that oils from *Artemisia herba-alba* from Morocco were mainly characterized by the presence of camphor in four growth? areas of the species: **Ar15** (24.4%), **Ar16** (8.4%), **Ar17** (17.8%) and **Ar18** (31.9%) please indicate the regions. Chrysnthenone was also mainly found in **Ar15** (30.6%), **Ar17** (6.4%) and **Ar18** (25.8%) while, α,β-thujone were found to be the major components in **Ar16** from Oujda (21.2%, 46.7%) and **Ar17** (17.3%, 9.9%), respectively (see references in Table 2).

However, (Z)-Chrysanthenyl acetate (10.9%), davanone (6.6%) and 1.8-cineole (5.0%) were found in the species collected from Errachidia (**Ar17**), whereas camphene (5.5%) was the major component only in species from the Machraa region (**Ar18**).

Table 3: Percentages of major components (≥ 5%) of essential oils of *Artemisia herba-alba* Asso. species grown in different areas of Algeria.

Compounds[a]	Ar1	Ar2	Ar3	Ar4	Ar5	Ar6	Ar7	Ar8	Ar9	Ar10	Ar11	Ar12	Ar13	Ar14
Camphene		4.9				7.1								
1,8-Cineole		13.4			5.8	8.6	8.2	9.8						5.3
Filifolone														6.6
α-Thujone			7.9			6.9	28.1	27.7	23.5	25.6	31.5	66.7	47.1	5.8
β-Thujone	41.2			15			7.8			15.6	9.1	22.3	10.6	5.9
Chrysanthenone			5.0	15.8		12.2		7.6	19.0	16.4	21.3		7.3	40.9
Camphor		49.3		19.4	5,6	33.1	22.8	17.3	18.7	14.2	10.4		10.3	19.4
(E)-Pinocarveol	22.2			16.9										
Pinocarvone		5.6												
Borneol		7.3												
Verbenone			7.2											
(Z)-Chrysanthenyl acetate			25.1								8.6			
Myrtenyl acetate			7.4											
Davanal					8.8									
γ-Muurolene									7.1					
Davanone					36.1									
(2E,3Z)-6-Me-3,5-Heptadienal-2-ethylidene			8.4											

[a]: Order of elution is given from an apolar column (HP-5 MS).

Table 4. Percentages of major components (≥ 5 %) of essential oils of *Artemisia herba-alba* Asso. species of Morocco.

Components[a]	Ar15	Ar16	Ar17	Ar18
Camphene				5.5
1,8-Cineole			5.0	
α-Thujone		21.2	17.3	
β-Thujone		46.7	9.9	
Chrysanthenone	30.6		6.4	25.8
Camphor	24.4	8.4	17.8	31.9
(Z)-Chrysanthenyl acetate			10.9	
Davanone			6.6	

[a]: Order of elution is given from an apolar column (HP-5MS).

Table 5 showed that essential oils of *Artemisia herba-alba,* growing in Tunisia, were mainly characterized by the presence of □-thujone and camphor in almost all the studied oils and also found to be the major components in **Ar19** (22.0%, 5.8%), **Ar20** (21.2%, 9.9%), **Ar21** (23.1%, 10.3%), **Ar23** (24.9%, 10.8%), **Ar24** (7.8%, 39.1%) and **Ar25** (11.3%, 11.3%). β-Thujone and 1,8-cineole were mainly detected in **Ar19** (24.0%, 9.3%), **Ar20** (16.2%, 12.3%), **Ar21** (19.3%, 11.8%), **Ar23** (8.3%, 8.9%) and **Ar25** (17.4%, 17.1%). Chrysanthenone was also found to be a major component of **Ar24** (15.0%) and **Ar25** (7.2%) growing in Makther Seliana and Kirchaou, respectivly.

Ar20 and **Ar23** were characterized by the main presence of terpinen-4-ol (5.3%) and Germacrene D (14.5%) respectively. Chrysanthenone (15.0% and 7.2%) was mainly found only in **Ar24** and **Ar25**

respectively. In the other hand, the presence of terpinen-4-ol (10.6%) and carvone (9.10%) was reported to be exclusive as main components, found in **Ar22**, growing in Gafsa (Tunisia).

Table 5. Percentages of major components (≥ 5 %) of essential oils of *Artemisia herba-alba* Asso. species of Tunisia.

Components[a]	**Ar19**	**Ar20**	**Ar21**	**Ar22**	**Ar23**	**Ar24**	**Ar25**
1,8-Cineole	9.3	12.3	11.8		8.9		17.1
α-Thujone	22.0	21.2	23.1		24.9	7.8	11.3
β-Thujone	24.0	16.2	19.3		8.3		17.4
Chrysanthenone						15.0	7.2
Camphor	5.8	9.9	10.3		10.8	39.1	11.3
Terpinen-4-ol		5.3					
(E)-Piperitol				10.6			
Carvone				9.1			
(E)-Sabinyl acetate							6.2
(E)-Patchenol						9.5	
Germacrene D					14.5		

[a]: Order of elution is given from an apolar column (HP-5MS).

As shown in table 6, concerning essential oils from *Artemisia herba elba* growing in other countries, 1,8-cineole was a common major component in **Ar27** (10.2%), **Ar28** (13.3%) and **Ar29** (7.4%) while, camphor was found to be a main component in **Ar28** (15.0%) and **Ar29** (34.9%).

Table 6. Percentages of major components (% ≥ 5) of essential oils of *Artemisia herba-alba* Asso. species of other countries.

Components[a]	**Ar26**	**Ar27**	**Ar28**	**Ar29**
Myrcene		5.1		
p-Cymène		13.5		
1,8-Cineole		10.2	13.3	7.4
Santolina alcohol	13.0			
γ-Terpinene		5.5		
Artemisia ketone	12.4			
α-Thujone	24.7			
β-Thujone				35.7
Chrysanthenone		6.7		
Camphor			15.0	34.9
α-Terpineol			6.3	
(Z)-Chrysanthenyl acetate		5.6		
(E)-Sabinyl acetate	5.4			
β-Cubebene			6.0	
Davanone		18.1		
Caryophyllene acetate	5.7			

[a]: Order of elution is given from an apolar column (HP-5 MS).

Exclusively, the components santolina alcohol (13.0%), artemisia ketone (12.4%), α,β-thujone (24.7%), (E)-sabinyl acetate (5.4%) and caryophyllene acetate (5.7%) were mainly found in the species growing in Jordan (**Ar26**). The presence of α-terpineol (6.3%) and β-cubebene (6.0%) as major components in species growing in Aranjuez area (Spain) was reported. The Essential oil from the species growing in Valencia (**Ar27**), has been characterized by the main presence of myrcene (5.1%), *p*-cymène (13.5%), γ-terpinene (5.5%), chrysanthenone (6.7%), (Z)-chrysanthenyl acetate (5.6%) and davanone (18.1%) (see references in table 2).

Thus, there are similarities in the compositions of essential oils of *Artemisia herba-alba* grown at Maghreb countries (Tables 3-5). 1,8-Cineole was mainly found in most oils from Algeria (5.3%-13.4%) and Tunisia (9.8%-17.1%) together with α,β-thujone commonly distributed in oils from Algeria (5.8%-66.7%, 5.9-41.2%), Morocco (17.%-21.2%, 9.9%-46.7%) and Tunisia (17.8%-24.9%, 8.3%-24.0%, respectively) and camphor which was a major component in oils from Algeria (5.6-49.3%), Morocco (58.4%-31.9%) and Tunisia (5.8-39.1%). 1,8-Cineole (7.4%-13.3%), α,β-thujone (24.7%-35.7%) and camphor (15.0%-34.9%) were also mainly detected in essential oils from other countries (Table 6)

From this bibliographic survey, the composition of the present essential from *Artemisia herba-alba* grown at Ain-Babbouche-Provine of Oum El-Bouaghi, appears to be highly similar to **Ar6** (Benifouda, Algeria), **Ar14** (Southern Algerian), **Ar17** (Errachidia, Morocco) and **Ar25** (Kirchaou, Tunisia) with the major presence of 1,8-cineole, α,β-thujone, chrysanthenone and camphor. However, piperitenone is reported here, for the first time, as a main component of *Artemisia herba-alba* essential oil.

Moreover, the interests of *Artemisia herba-alba* oils are various, either from the biological side [2-7], or the electrochemical side [8] but they may be tested as green corrosion inhibitors because of some major components like 1,8-cineole [36].

Conclusion:

From this investigation, we have shown that the essential oil of *Artemisia herba-alba* Asso, collected at Ain Babbouche-Provine of Oum El Bouaghi (Eastern Algerian), is characterized by the main presence of chrysanthenone (16.2%), camphor (15.6%), β-thujone (14.2%), α-thujone (9.1%), 1,8-cineole (8.9%), and piperitenone (7.6%). The latter is found as a major component of *Artemisia herba-alba* Asso. essential oil, for the first time. 1,8-Cineole, α,β-thujone and camphor, were also mainly found in reported essential oils from Maghreb, Spain, Jordan and Iran. However, other major components were exclusive to each area. This difference may be due to the nature of the soil, climate, period of collecting...

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