Available online at www.joac.info

ISSN: 2278-1862

Journal of Applicable Chemistry

2013, 2 (3): 584-588

(International Peer Reviewed Journal)

Essential Oil Composition of *Marrubium vulgare L* Growing Wild in Eastern Algeria

Abderazak Abadi [1]and Aicha Hassani[2]*

1. Laboratoire de molécules bio-active et valorisation de la biomasse, École normale supérieure, BP 92, Kouba-Algiers, **ALGERIA**
2. Laboratoire de chromatographie, faculté de chimie, USTHB, Algiers, **ALGERIA**

Email: Ryadabadi@Gmail.Com

Received on 6th April and finalized on 26th April 2013.

ABSTRACT

In this study, the essential oil of the aerial parts of Marrubium vulgare L. obtained by hydro distillation was analyzed by gas chromatography coupled to mass spectrometry (GC-MS) in order to determine their chemical composition. Fifty components in the oil of M. vulgare were identified. The results revealed that the major components of the essential oil are : 4,8,12,16-Tetramethyl heptadecan-4-olid (16.97%), Germacrene D-4-ol(9.61%),α- pinéne(9.37%), Phytol(4.87%), Dehydro-sabina ketone (4.12%), Piperitone(3.27%), δ – Cadinene (3.13%), 1-Octen-3-ol(2.35%) and Benzaldehyde(2.31%) .

Keywords: *Marrubium vulgare* Lamiaceae, Essential oil composition, GC, GC/MS, α- pinene, Phytol.

INTRODUCTION

In recent years, essential oils of plants and their other products from secondary metabolism have been in high demand for the manufacturers of foods flavoring, fragrance, cosmetics, and pharmaceutical industries due to the growing interest of consumers in ingredients from natural sources. Many plants have been used for different purposes, such as food, drugs and perfumery. They have been screened for their potential uses as alternative remedies for the treatment of many infections and preservation of foods from the toxic effects of oxidants [1].

Lamiaceae is composed of more than 240 genera, most of them are highly aromatic due to the presence of external glandular structures, namely peltate and capitate trichomes that produce essential oils. According to Lawrence [2], it is possible to distinguish beteween the Lamiaceae oil-rich and oil-poor species. The latter being characterized by hydrocarbon-rich oils, such as germacrene D, β-caryophyllene, (E)-β-farnesene, δ-cadinene and α-humulene, among others.

The *Marrubium* genus is represented by about 30 species [3]. Considered oil-poor species [2], little is known about their essential oils since more importance has been given to their maceration extract, which is consisted of the known and dominant active component marrubiin [4] . *Marrubium vulgare*, commonly known as horehound or hoarhond, is native in Europe, Western Asia and North Africa, and is cultivated worldwide as a source for food flavoring and for medicinal purposes [5,6]. The name ‘’marrubium’’ refers to the bitter taste of the herb and ‘’hoar’’ to the white pubescence covering the plant [7]. Under Polish climatic conditions, *Marrubium vulgare* L. is a perennial plant. Medicinal properties of horehound have

been long known and the origin of its use goes back to ancient Egypt. The medicinal raw material is the herb of horehound (*Marrubi herba*) [8]. The herb consists of whole or crushed flowering aerial parts of *Marrubium vulgare* L. [9], and it shows multiple effects on human organism [10,11,12]. The essential oil of *Marrubium vulgare* L. has a relaxant and expectorant effect as well as avasodilator [13]. In Algeria, *Marrubium vulgare* is used in folk medicine to cure several diseases of the digestive tract, such as diarrhoea, as well as diabetes, rheumatism, cold and respiratory pains [14,15].

Pursuing our studies on the Algerian flora, this work reports the morphology and distribution of the glandular trichomes of M. vulgare growing spontaneously in Algeria and the composition of its oil during the flowering and vegetative phases.

MATERIALS AND METHODS

Plant materials (aerial parts) of *M. vulgare* L. were grown in the zone of Nigrine district of El-Ater in the wilaya of Tebessa, north east of Algeria. The whole plants were collected during the period of May to June 2009.

Distillation of essential oil: The samples were dried in the shade in natural air far from moisture and all pollutants for a fortnight in the room temperature.100 g of ground rosemary were submitted to water distillation for 4 h using a Clevenger apparatus. The distilled essential oils were dried over anhydrous sodium sulfate, filtered and stored at 4°C.

Gas chromatography: The gas chromatographic analysis was performed using a Hewlett Packard 6890 chromatograph equipped with a nonpolar column HP5MS (30x 0.25 mm) and film thickness 0.25 microns and a flame ionization detector. The procedure conditions are - Carrier gas - nitrogen

Flow rate 0.8ml min^{-1}, Injector temperature - 250 °C

Detectors temperature is 300 °C. The temperature program is from 60 to 250 at 2°C min^{-1} with two levels, 8 minutes at 60 °C and 15 min at 280°C.

The injection of 0.4µl of pure essential oil and 1µl of absolute mode(mode split 1: 20).In order to determine retentions indices (RI) a series of n-alkanes (C5–C28) mixture was analysed under the same operative conditions on HP-5 columns and the sample indices were calculated following Van den Dool and Kratz [16].

Gas chromatography and mass spectrometry (GC/MS) analysais conditions : The essential oils were analyzed on an apparatus of gas chromatography coupled to mass spectrometry brand Hewlet Packard 5973A, equipped with an apolar capillary column (HP5MS, 30m x 0.25mm, phase thickness: 0.25µm). The conditions are-

The detection mode - electronic impact, Ionization current - 70 eV

Carrier gas – helium, Flow rate -0.7ml min^{-1}

The source pressure is 10-7mbar

Interface temperature: 280 ° C, Injection: 250 ° C,

The programming of the oven: 2 ° C min^{-1} from 60 ° C to 280 ° C, with

isothermal: 8min at 60 ° C. and 15 minutes at 280 ° C. 0.1 to 0.2µl of pure essential oil and 1µl absolutely were injected in split mode 1: 20.

The identification of the essential oil constituents was based on a comparison of their retention times to *n*-alkanes, compared to published data and spectra of authentic compounds using their mass spectra compared to the Wiley version 7.0 library[17,18,19]. as well as by comparison of the fragmentation patterns of mass spectra with those reported in the literature (Adams, 2007). The chromatographic conditions were identical to those used for GC analysis.

RESULTS AND DISCUSSION

The study showed that the essential oil content in the dry herb of *Marrubium vulgare* L. was on average 0.05%[20]. Figure 1 shows the peaks of GC-MS spectrum. The search analysis in the digital library. The percentages and the retention indices of the identified components are listed in table 1 in the order of their

elution on the HP-5MS column. GC-MS analysis of *M.vulgare* essential oil led to the identification of fifty compounds, accounting for 82.42% of the total oil. The yield of essential oil obtained by hydrodistillation from aerial part of plant was 0.04%. Table1 illustrates also the nine components with a supremacy of three major compononents: 4, 8, 12, 16Tetramethyl heptadecan-4-olid (16.97%), Germacrene D-4-ol(9.61%), α-pinene(9.37%). They represnt about 36% of 56% and shows the different chemical groups with a dominance of other compounds with 41.64% of the total rate of volatile oil, followed by oxygenated sesquiterpene with a lower rate (13.17%) and, monoterpene hydrocarbon (12.61%) oxygenated monoterpene(9.46%), sesquiterpene hydrocarbon (5.58%) respectively.

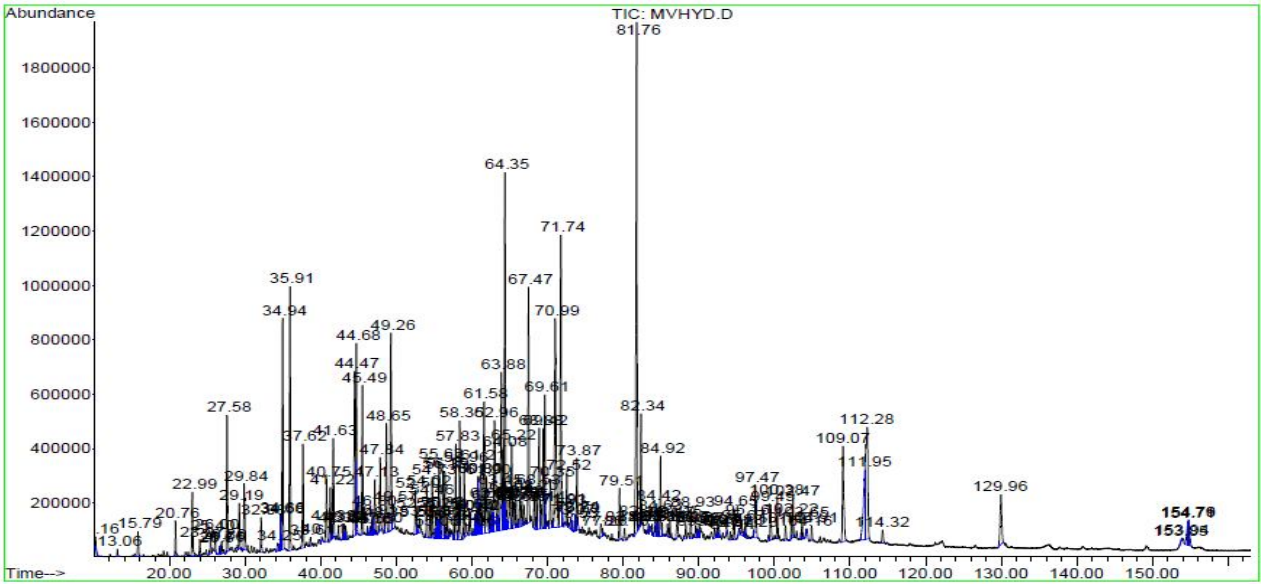

Fig-1.: GC-MS of Essential oil

APPLICATION

The essential oil of the aerial parts of Marrubium vulgare L. obtained was analyzed by gas chromatography coupled to mass spectrometry (GC-MS) in order to determine their chemical composition. Fifty components in the oil of M. vulgare were identified.

CONCLUSIONS

Essential oil of *M. vulgare* from Algeria had significant differences in the chemical composition as compared to the same essential oil from other country, which can be attributed to several factors. The results demonstrated that the major components of the essential oil are - 4,8,12,16-Tetramethyl heptadecan-4-olid (16.97%), Germacrene D-4-ol(9.61%), α- pinéne(9.37%), Phytol(4.87%), Dehydro-sabina ketone (4.12%), Piperitone(3.27%), δ– Cadinene (3.13%), 1-Octen-3-ol(2.35%) and Benzaldehyde(2.31%).

ACKNOWLEDGEMENTS

The authors gratefully acknowledge Mrs Aicha Hassani Professor at The University of ENS Kouba algiers for her help and advice and the Technical staff in the laboratory of both Laboratoire de molécules bio-active et valorisation de la biomasse, École normale supérieure Kouba-Algiers; and Laboratoire de chromatographie, faculté de chimie, USTHB, Algiers, Algeria for their support.

Table 1. Chemical composition, retention indices (IR) and percentage composition of the *M. vulgare* essential oil.

N°	IR	Compound	%	Identification
1	823	Trans -2-Hexanal	0.75	GC,GC/MS
2	903	Heptanal	0.1	GC
3	906	Santolina triene*	0.71	GC,GC/MS
4	937	**α- pinene**	**9.37**	GC,GC/MS
5	946	Camphene	0.51	GC,GC/MS
6	953	**Benzaldehyde**	**2.31**	GC
7	962	Sabinene	0.37	GC
8	983	**1-Octen-3-ol**	**2.35**	GC
9	990	Myrecene	0.47	GC,GC/MS
10	995	Octanol-3	0.64	GC
11	1000	Dichlorobenzene<1,>*	0.72	GC,GC/MS
12	1022	p-Cymene	0.63	GC,GC/MS
13	1029	1-8-cineole	0.1	GC
14	1038	cis-Ocimene	0.2	GC
15	1055	γ –Terpinene	0.85	GC,GC/MS
16	1113	ß-Thujone	0.81	GC,GC/MS
17	1117	**Dehydro-sabina ketone***	**4.12**	GC,GC/MS
18	1122	Camphor	0.83	GC,GC/MS
19	1219	Carvone	0.89	GC
20	1224	**Piperitone**	**3.27**	GC
21	1239	Neral	0.27	GC,GC/MS
22	1250	Geraniol	0.92	GC
23	1261	Anethole<E>	0.47	GC,GC/MS
24	1275	Geranial	0.78	GC
25	1282	Thymol	0.17	GC,GC/MS
26	1284	2-Undecanone	0.98	GC,GC/MS
27	1291	Cymen-7-ol<p>*	0.95	GC
28	1467	α-Humulene	0.12	GC
29	1481	Germacrene D	0.88	GC
30	1491	ß- Guaiene	0.23	GC,GC/MS
31	1501	α- Farnesene	0.23	GC,GC/MS
32	1505	γ – Cadinene	0.44	GC,GC/MS
33	1510	Trans –calamenene	0.21	GC
34	1513	**δ – Cadinene**	**3.13**	GC,GC/MS
35	1521	Trans-Cadina-1-4-diene*	0.21	GC,GC/MS
36	1529	α- calacorene	0.73	GC
37	1538	**Germacrene D-4-ol**	**9.61**	GC,GC/MS
38	1566	Spathulenol	0.87	GC
39	1574	Salvial-4(14)-en-1-one*	0.96	GC,GC/MS
40	1579	ß- oplopenone	0.63	GC,GC/MS
41	1845	trans-trans-Farnesyl acetate*	0.8	GC
42	1862	cis-cis-Farnesyl acetone*	0.98	GC,GC/MS
43	1876	Trans-cis-Farnesyl acetone*	0.77	GC,GC/MS
44	1895	Nonadecane	0.53	GC,GC/MS
45	1921	**Phytol**	**4.87**	GC,GC/MS
46	2102	n-Heneicosane*	0.8	GC,GC/MS
47	2135	Linoleic acid*	1.0	GC,GC/MS
48	2210	Sclareol*	0.81	GC,GC/MS
49	2303	Tricosane*	0.96	GC,GC/MS
50	2327	**4,8,12,16Tetramethyl heptadecan-4-olid***	**16.97**	GC,GC/MS
	Total		82.*46*	
		Grouped Compounds		
		Monoterpene hydrocarbon	12.61	
		Oxygenated monoterpene	9.46	
		Sesquiterpene hydrocarbon	5.58	
		Oxygenated sesquiterpene	13.17	
		Others Compounds	41.64	

*New Compounds

REFERENCES

[1] Barlow SM Hudson BJF (Ed.). (pp. 23). Elsevier, Amsterdam. **1990.**

[2] B.M. Lawrence, Science. Edits., R.M. Harley and T. Reynolds, pp: 399-436, Royal Botanic Gardens, Kew **1992.**

[3] M.S.Abu-Asaband RD.Cantlno, In: Advances In Lablate Science. Edits. R, M. Harley and T. Reynolds, pp: 97-112, Royal Botanic Gardens, Kew **1992.**

[4] V. Schiemper, A. Ribas, M. Nlcolau and V. Cechinel-Fliho, *Phytomedecine,* **1996**,3,211-216

[5] W. Letchamo and S. Mukhopadhyay, Vanfabîlity In chromosomes, he,b 4elo'. *J. Hortic.ScI.,* **1997**,72, 741-748.

[6] S. Sahpaz et al., *Journal of Ethnopharmacology*, **2002,** 79, 389 - 392.

[7] J.E.Slmon, A.F.Chadwickand LE.Craker, Herbs-anIndexedblbllograptry 1971-1980. p. 48, Elsevler, Amsterdam, **1984.**

[8] Wolski T., Matosiuk D., Baj T., Ziewiec A., Szanta zwyczajna , *Postępy Fitoterapii*,**2007**, 1, 39-45.

[9] Polish Pharmacopoeia VIII. PTFarm., Warszawa, **2008**, 2249-2250.

[10] Bradley P. R., British herbal compendium, vol. 1, British Herbal Medicine Association, **1992**, 218-220.

[11] El Bardai S., Wibo M., Hamaide M-Ch., Lyoussi B., Quetn-Leclerq J., Morel N.,*British Journal of Pharmacology*, **2003**, 140, 1211-1216.

[12] Kohlmünzer S., Farmakognozja, Wydawnictwo Lekarskie PZWL Warszawa, **2007**, 308.

[13] Wyk B.E., Wink M., Rośliny lecznicze świata, MedPharm Polska, **2008**, 198.

[14] Rachid Belhattab and Larbi Larous, *J . Essent. Oil Res.,* **2006,** 18, 369-373.

[15] Y. Mahmoudi, La thérapeutique par les plantes communes en Algérie. Ed. Palais du livre, Blida, **1990**.

[16] H. Van den Dool, P.D. Kratz, *J. Chromatogr.* **1963,** 11 , 463.

[17] F. Macchioni, P.L. Cioni, G. Flamini, I. Morelli, S. Maccioni, M. Ansaldi, *Flavour Frag. J.* **2003,** 18,139.

[18] V. Roussis, P. Katerina, V. Constantinos, P.V. Catherine, O. Antonio, *J. Essent. Oil Res*. **2001,** 13, 118.

[19] R.P. Adams, Identification of Essential Oils by Ion Trap Mass Spetroscopy, Allured Publishing Corporation, Carol Stream, IL, USA, **1995**.

[20] Zawiślak G., Cropping evaluation of while horehound (*Marrubium vulgare* L.) grown from sowing and seedling. *Herba Pol*., **2009**, 55(3), 63-68.