*International Letters of Chemistry, Physics and Astronomy* *Online: 2013-05-03*
*ISSN: 2299-3843, Vol. 13, pp 210-214*
*doi:10.56431/p-5t09it*
*CC BY 4.0. Published by Academic Open Access LTD, 2013*

# Chemical composition of *Marrubium vulgare L.* essential oil from Algeria

**Abderazak Abadi[1], 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

*E-mail address: ryadabadi@gmail.com

**ABSTRACT**

The chemical constituants of the essential oil from aerial parts of Marrubium vulgare, collected in Algeria, were analyzed by GC and GC/MS. The oil yield of the dried plant aerial parts, obtained by hydrodistillation, was 0.04 % (w/w). 50 compounds, accounting for 82.46 % of the oil, were identified. The major constituants were: 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

## 1. INTRODUCTION

In recent years, essential oils obtained from vegetative parts of plants and their by products are highly demanded by the manufacturers of foods flavoring, perfumes, cosmetics, and pharmaceutical industries due to the growing interest of consumers in ingredients from natural sources. 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 [1], 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 [2]. Considered oil-poor species [1], 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 [3]. *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 [4,5]. The name ‘’marrubium’’ refers to the bitter taste of the herb and ‘’hoar’’ to the white pubescence covering the plant [6]. Under Polish climatic conditions, *Marrubium vulgare* L. is aperennial plant. Medicinal properties of horehound have been long known and the origin of its use goes

This paper is an open access paper published under the terms and conditions of the Creative Commons Attribution license (CC BY)
(https://creativecommons.org/licenses/by/4.0)

back to ancient Egypt. The medicinal raw material is the herb of horehound (*Marrubi herba*) [7]. The herb consists of whole or crushed flowering aerial parts of *Marrubium vulgare* L. [8], and it shows multiple effects on human organism [9-11]. The essential oil of *Marrubium vulgare* L. has a relaxant and expectorant effect as well as avasodilator [12]. 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 [13,14].

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.

## 2. EXPERIMENTAL

### 2. 1. Plant material

*Marrubium vulgare* yielded during the spring in May 2009, in the zone of Nigrine district of El-Ater in the wilaya of Tebessa, north east of Algeria.

### 2. 2. Distillation of essential oil

*Marrubium vulgare*: samples were dried in the shade in natural air far from moisture and all pollutants for a fortnight in the room temperature. The dried aerial parts were ground prior to the operation and then 100 g of ground marrubium were submitted to water distillation for 4 hrs using a Clevenger apparatus. The distilled essential oils were dried over anhydrous sodium sulfate, filtered and stored at 4 °C.

### 2. 3. Gas chromatography

The gas chromatographic analyzes were performed using a Hewlett Packard 6890 chromatograph equipped with a nonpolar column HP5MS (30 x 0.25 mm d.i., Film thickness 0.25 microns) and a flame ionization detector. The procedures conditions were as follow: carrier gas: nitrogen, flow rate 0.8 ml/min, injector temperature: 250 °C, detectors temperature: 300 °C, temperature program: from 60 to 250 at 2 °C / min, with two levels: 8 minutes at 60 °C and 15 min at 280 °C, injection of 0.4 µl 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 [15].

### 2. 4. Gas chromatography and mass spectrometry

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, 30 m x 0.25 mm, phase thickness: 0.25 µm). The detection mode: electronic impact, ionization current: 70 eV, carrier gas: helium, flow rate: 0.7 ml/mn, the source pressure: 10-7mbar, interface temperature: 280 °C, injection: 250 °C, the programming of the oven: 2 °C / min from 60 °C to 280 °C, with isothermal: 8 min at 60 °C. and 15 minutes at 280 °C. 0.1 to 0.2 µl of pure essential oil and 1µl absolutely were injected in split mode 1: 20.

**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

### 2. 5. Component identification

Identification of components was made on the basis of their retention indices on non-polar (HP-5) and/or on polar (PEG) columns and by computerised matching of the acquired mass spectra with those stored in the spectrometer data base using Willey mass spectral library and with the literature [16-18].

## 3. RESULTS AND DISCUSSION

The study showed that the essential oil content in the dry herb of *Marrubium vulgare* L. was on average 0.05 % [19]. The results obtained through our study are recorded in Table1.

Concerning the dominant components, which rates were more than 1 % of the total composition of the oil, nine components among fifty were at least determined. These former represent 56 % of 82.42 % the total rate of the collected volatil oil. Table 1 illustrates also the nine components with a supremacy of three major compononents: 4,8,12,16-Tetramethyl heptadecan-4-olid (16.97 %), Germacrene D-4-ol (9.61 %), α- pinene (9.37 %). They represnt about 36 % of 56 %. Table 1 shows the different chemical groups with a dominance of other compounds with 41.64 % of the total rate of volatil 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.

## 4. CONCLUSION

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 were: 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 %).

**ACKNOWLEDGMENTS**

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.

## References

[1] B. M. Lawrence, *Chemlcal consttuents of Lablate oils and theirexplotation.in: Advances in Lablate Science*. Edits., R. M. Harley and T. Reynolds, pp: 399-436, Royal Botanic Gardens, Kew (1992).

[2] M. S. Abu-Asaband, R. D. Cantlno, *Pollen moiphologyln subIamlIyLamIcIdeae (Lablateae) and its pfrylogenetlc Implications*. In: Advances In Lablate Science. Edits. R. M. Harley and T. Reynolds, pp: 97-112, Royal Botanic Gardens, Kew (1992).

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

[4] W. Letchamo, S. Mukhopadhyay, *J. Hortic. Sci.* 72 (1997) 741-748.

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

[6] J. E. Slmon, A. F. Chadwickand, L. E. Craker, *Herbs-anIndexedblbllograptry,* 1971-1980. p. 48, Elsevler, Amsterdam (1984).

[7] Wolski T., Matosiuk D., Baj T., Ziewiec A., *Postępy Fitoterapii* 1 (2007) 39- 45.

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

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

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

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

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

[13] Rachid Belhattab, Larbi Larous, *J . Essent. Oil Res*. 18 (2006) 369-373.

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

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

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

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

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

[19] Grażyna Zawiślak, *Herba Pol*. 55(3) (2009) 63-68.