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Chemical Composition of Essential Oils of *Retama monosperma* (L.) Boiss. From Morocco.

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ABSTRACT

The chemical composition of the essential oils of branches and flowers of *Retama monosperma* from Morocco was investigated. In branches sixteen compounds were identified. The oil consisted mainly of alkanes (31.8%), nor-isoprenoids (25.4%) and oxygenated sesquiterpenes. Analysis of the flowers oil resulted in the identification of twenty-three constituents. The flowers oil revealed the presence of alkanes (25.8%), fatty acids (56.7%), fatty acid esters (6.7%) and nor-isoprenoids (3.1%) as the main subclasses. Hexadecanoic acid (0-30.6%), stearic acid (4-13%), heptacosane (4.6-12.9%), pentacosane (10.9-12.2%), (E)-phytol (0-11.6%), oleic acid (0-11.3%), caryophyllene oxide (0.2-10.5%), β-damascone (0.1-6.5%) and β-damascenone (0.7-5%) were dominant compounds in the analysed essential oils. The results may suggest that volatile oils of Retama monosperma from Morocco can be used in perfumery, flavouring, cosmetics and toiletries.

Keywords: *Retama monosperma* (L.) Boiss., Fabaceae, Essential oil, fatty acid, alkanes, norterpenoids.

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INTRODUCTION

The genus *Retama* (Fabaceae) consists of three plant species (*R. monosperma, R. sphaerocarpa and R. raetam*) mainly from East Mediterranean regions, North Africa and the Canary Islands [1]. *R. monosperma* (L.) Boiss. and *R. raetam* (Forssk.) Webb (local name "*Rtem*") are used in folk medicine of North and East Mediterranean regions as emetic, purgative, vermifuge, healing, vulnerary, sedative [2], anthelmintic and antiseptic agents [3].

Several studies have been published on the chemical composition of alkaloids content of *R. raetam* [4], its essential oils [5,6] and its flavonoids [7,8]. Many other articles describe its various pharmacological activities including antibacterial [7], antifungal, antiviral [8], cytotoxic [9,10], hypoglycemic [11], diuretic [12], anti-hypertensive [13] and antioxidant [6,8]. In contrast to *R. raetam*, relatively few studies have been done on *R. monosperma* (L.) Boiss. The previous chemical researches on this species have focused especially on its alkaloids [14, 15]. However, pharmacological studies show an antileukaemic effect *in vivo* [16], anti-inflammatory activities [17] and a potential anticancer activity against cervical cancer cell lines *in vitro* [18,19]. Recently, significant antifungal activity [20], anticorrosive property [21] and antioxydant capacity [22] of *Retama monosperma extracts* have been also reported. Two the best of our knowledge, no data exist in the literature concerning the essential oil from *R. monosperma* (L.) Boiss. The general aim of this study is to analyse the essential oils of branches and flowers of *R. monosperma* by gas chromatography-mass spectrometry (GC-MS).

MATERIALS AND METHODS

Plant Material

The branches and flowers of *Retama monosperma* (L.) Boiss. were collected during the full flowering period in February 2015 from El Jadida, Morocco. The plant was previously identified by Dr. M. Fennane from Scientific Institute of Rabat, Morocco. Voucher specimens (Ref.77816 RAB) have been deposited in the herbarium of Institute.

Essential oil extraction

The samples were dried and only branches were powdered. Essential oils were obtained by hydrodistillation using a Clevenger-type apparatus for 5 h. The flowers and branches yielded 0.02% and 0.03% (w/w) of pale yellowish oils respectively. The oils were dried over anhydrous Na_2SO_4 and stored in sealed vials at low temperature before analysis.

Gas Chromatography

GC analyses were performed on a Perkin-Elmer Sigma-115 gas chromatograph equipped with a FID and a data handling processor. Separation was achieved using a HP-5MS fused- silica capillary column (30 m × 0.25 mm i.d., 0.25 µm film thickness). Column temperature: 40 °C, with 5 min initial hold, and then to 260 °C at 2 °C/min, 260 °C (20 min) using He as carrier gas (1.0 mL/min); injection mode splitless (1 µL of a 1:1000 n-hexane solution). Injector and detector temperatures were 250 °C and 290 °C, respectively. Analysis was also run using a fused silica HP Innowax polyethylenglycol capillary column (50 m × 0.20 mm), 0.20 mm film thickness. In both cases, helium was used as carrier gas. Retention indices (*R*i) were determined in relation to a homologous series of n-alkanes (C8–C24) under the same conditions. Relative concentrations of the components were obtained by peak area normalization. No response factors were calculated.

GC-MS analysis

GC-MS analyses were performed using an Agilent 6850 Series II gas chromatograph linked on-line with an Agilent Mass Selective Detector MSD 5973Network. The column was a HP-5 fused-silica capillary column (30 m × 0.25 mm i.d.; 0.33 mm film thickness). Temperature conditions were the same as used for GC analysis. Interface temperature was 295 °C; mass range 29–350 *m/z*, ionization energy 70 eV, multiplier energy 2000 V, scan time 1 s. Helium was used as carrier gas at 1.0 mL/min. The components were identified based on the comparison of their relative retention times and mass spectra with those of standards, Wiley7N

library data of the GC–MS system and literature data [23]. The results were also confirmed by the 90 comparison of the elution order of the compounds with their relative retention indices on non-polar phases reported in literature [23].

RESULTS AND DISCUSSIONS

The chemical composition of *R. monosperma* essential oil obtained by GC-MS analysis is shown in Table 1.

Table1: Chemical composition of *Retama monosperma* (L.) Boiss. Essential oils

RT[a]	RI[b]	Compound	Branches (%)	Flowers (%)
13.86	908	Santolinatriene	0.9	1.9
17.05	967	Sabinene	0.2	0.3
18.01	1242	β-Cyclocitral	0.3	0.2
20.47	1291	Dihydrodulan I (trans)	-[c]	0.1
20.63	1300	Theaspirane A	2.5	0.2
21.19	1318	Theaspirane B	3.0	0.1
21.55	1320	2,6,10,10-Tetramethyl-1-oxa-spiro[4.5]dec-6-ene	0.8	0.2
23.46	1381	β-Damascenone	5.0	0.7
24.39	1419	β-Damascone	6.5	0.1
24.51	1425	4-(2,6,6-Trimethylcyclohexa-1,3-dienyl)butan-2-one	4.9	0.3
25.89	1433	4-(2,6,6-Triméthyl-1-cyclohexen-1-yl-3-buten-2-ol	-	1.2
26.60	1483	β -Ionone	2.7	0.9
29.38	1582	Caryophyllene oxide	10.5	0.2
30.23	1612	β-Himachalene oxide	-	0.7
38.17	1928	Hexadecanoic acid methyl ester	-	1.3
38.57	1949	9-Hexadecenoic acid	-	1.8
38.88	1972	Hexadecanoic acid	-	30.6
39.80	1997	Ethyl hexadecanoate	-	5.4
39.92	2132	(E)-Phytol	11.6	-
40.31	2143	Oleic acid	-	11.3
41.05	2168	Stearic acid	4.0	13.0
42.01	2500	Pentacosane	10.9	12.2
42.83	2600	Hexacosane	8.0	9.0
43.64	2700	Heptacosane	12.9	4.6
		Total identified	84.8	96.3

[a]RT: Retention time

[b]RI: Retention index measured relative to n-alkanes (C6-C24).

[c]: not detected

Branches oil

Sixteen compounds were identified, representing 84.8% of the essential oil. The essential oil consisted mainly of alkanes (31.8%), nor-isoprenoids (25.4%), oxygenated diterpene (11.6%) and oxygenated sesquiterpenes (10.5%). Alkanes were the main subclass of essential oil constituents with heptacosane (12.9%), pentacosane (10.9%) and hexacosane (8.0%). Nor-isoprenoids were the second most abundant components. Among them, β-damascone (6.5 %) predominated followed by 4-(2,6,6-Trimethylcyclohexa-1,3-dienyl)butan-2-one (4.9%), β-damascenone (5%), theaspirane B (3.0%), β-ionone (2.7%) and theaspirane A (2.5%). (*E*)-phytol (11.6%) was the only oxygenated diterpene in the branches oil. Two monoterpenes, santolinatrienne (0.9%) and sabinene (0.2%), and only one oxygenated monoterpenoid β-cyclocitral (0.3%) were identified. Stearic acid (4.6%) was the only fatty acid identified in the essential oil of branches.

Flowers oil

Analysis of the flowers essential oil resulted in the identification of twenty three constituents comprising 96.3% of the total oil. As shown in Table 1, fatty acids (56.7%) were found to be the most abundant compounds followed by n-alkanes (25.8%), fatty acid esters (6.7%) and norterpenoids (3.8%). Hexadecanoic acid (30.6%) was the major constituent of n-alkanes subclass associated with stearic acid (13%), oleic acid

(11.3%) and 9-hexadecenoic acid (1.8%). Three alkanes, pentacosane (12.2%), hexacosane (9.0%) and heptacosane (4.6%) were identified. Ethyl hexadecanoic acid (5.4%) and methyl hexadecanoic acid (1.3%) were the only fatty acid esters identified in the flowers oil. Among the norterpenoids, β-damascone (0.1 %) 4-(2,6,6-Trimethylcyclohexa-1,3-dienyl)butan-2-one (0.3%), β-damascenone (0.7%), theaspirane B (0.1%), β-ionone (0.9%), theaspirane A (0.2%), 4-(2,6,6-Triméthyl-1-cyclohexen-1-yl)-3-buten-2-ol and dihydrodulan I (0.1%) were identified. Two components comprising 0.9% were oxygenated sesquiterpeniods (caryophyllene oxide and β-himachalene oxide). Two monoterpenes, santolinatrienne (1.9%) and sabinene (0.3%), and only one oxygenated monoterpene β-cyclocitral were also identified.

The essential oils from flowers and branches of *R. monosperma* were both rich in hydrocarbons. Long-chain alkanes have been found in other essential oils [24-28]. Fatty acids and fatty acid esters have also been found in some floral oils such as *Rosa damascena* [27]. Several carotenoid degradation products (C_{13} norisoprenoids) were present in both branches and flowers oils from *Retama monosperma*. Flowers oil showed a low presence of norisoprenoids in contrast to the branches oil. The theaspiranes are notable components of tobacco [29] and have also been found in relatively abundant quantities in the essential oil of *Pterospartum tridentatum* (Fabaceae) [30]. The comparison of our results with the literature showed significant differences with essential oils obtained from the flowers of *R. raetam* of Tunisia or Libya. Nonanal and α-humulene, reported as the main components in the essential oil of *R. raetam* flowers of Tunisia [6] were not found in our sample. Also, β-linalool identified as major component in the volatile oil of flowers of *R. raetam* of Libya [5], was not present in our oil. Moreover the presence of norterpenoids has never been reported for essential oils of *R. raetam* flowers from Tunisia or Libya.

In this paper, chemical compositions of the essential oils from branches and flowers of *R. monosperma* were reported for the first time. The ionones and the damascones occur naturally in a wide variety of flowers, fruits, and leaves, and are materials of major importance in perfumery [31]. They usually occur at a very low level but their very intense odors mean that they still make a significant contribution to the odors of oils containing them. Other volatile carotenoid degradation products that occur in essential oils and contribute to their odors include the theaspiranes and edulans [31]. According to literature [32], ketones identified in the essential oils of *Rosa* namely β- damascenone, β-damascone and β-ionone contribute considerably to the distinctive scent of rose oil. Even though these compounds exist in less than 1% quantity of rose oil, they make up for slightly more than 90% of the odour content due to their low odour detection thresholds.

CONCLUSION

The pleasant aroma of *R. monosperma* during the full flowering is almost certainly due to the presence at significant levels of norterpenoids. The two oils of *R. monosperma* can be used in perfumery, flavouring, cosmetics and toiletries.

To the best of our knowledge, for the first time, we herein report the chemical composition of essential oils of *R. monosperma* from Morocco.

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