

Essential Oil Composition of *Asteriscus maritimus* (L.) Less. from Spain**

Keywords: *Asteriscus maritimus*; Compositae, Essential Oil, Seasonal Variation, α -Pinene, *p*-Cymene, α -Phellandrene, β -Phellandrene, Foenol

Abstract

The essential oil composition of different aerial parts (stems+leaves and flowers) of *Asteriscus maritimus* has been analysed by gas chromatography which was coupled with mass spectrometry. A total of 43 compounds have been identified from the different fractions studied, representing more than the 90% of the total oil for each one. Both aerial parts shared most of the main compounds although quantitative differences have been detected. The oils extracted from the stems and leaves showed α -pinene (27.5%) and *p*-cymene (10.0%) as major components. In the flower oils these compounds were also representative, α -pinene (9.0%) and *p*-cymene (7.3%), although the main ones were β -phellandrene (11.8%), foenol (10.9%) and α -phellandrene (10.0%). These compounds were representatively found in the other fraction: β -phellandrene (8.38%), α -phellandrene (7.28%) and foenol (5.6%). The monoterpene fraction was predominant in the stems and leaves oil (54.6%) while the sesquiterpene fraction was the largest one in the flowers oil (55.3%).

Introduction

The genus *Asteriscus* Miller belongs to the *Compositae* family. This genus and the other two of the same tribe (*Ighermia* Wiklund and *Pallenis* Cass.) contain a total of 15 species that grow wildly in a variety of coastal and desert habitats throughout the Mediterranean and Middle East [1,2]. Although most of the species are endemic of the Macaronesian region, in Europe there are two species described: *A. aquaticus* (L.) Less and *A. maritimus* (L.) Less. [3]. *A. maritimus* (= *Odontospermum maritimum* (L.) Sch.Bip.= *Bubonium maritimum* (L.) Hill) is a scabrid, hispid perennial species with stems rarely having more than 20cm, woody and much-branched, with petiolate leaves from oblong to oblong-spatulate. The outer involucral bracts are around 1cm, coriaceous below, with an obtuse apex, equalling or shorter than ligules. The ligules are deeply 3-toothed and the tubular florets 5-lobed [3,4].

Although *Asteriscus* is not a very large genus, few studies have been published related to it [5-18]. The study of the molecular systematic of some Macaronesian species exposed that *Asteriscus* is paraphyletic [5]. On the other hand, extracts of organic solvents from *A. imbricatus* DC. showed antifungal activity and anticorrosion inhibition [6]. However, most of the studies have been focused only on one species, *A. graveolens* (Forssk.) Less., describing their flavonoids [7], new derivatives [8,9] and essential oil activities [10-12]. The essential oil of this species was characterized by a high content of 6-oxocyclonerolidol (66.7%) and 6-hydroxycyclonerolidol (8.8%) which exhibited fungicidal properties towards *Alternaria* sp. [10]. Other report suggests that these compounds could be considered as chemical markers of this genus that characterize the stem and leaf oil, while *cis*-8-acetoxychrysanthenyl acetate, which has been isolated



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for the first time, was the major compound of the flower oil [11]. The last paper related to this species agreed with the previous ones, being 6-oxocyclonerolidol (74.9%) and 6-hydroxycyclonerolidol (11.8%) as the major components. Besides, the essential oil exhibited inhibition of mild steel corrosion [12]. We could have only found other report about essential oil composition [13]. The oils extracted from *Pallenis spinosa* (L.) Cass (= *A. spinosus* (L.) Chultz Bip) showed germacra-1-(10),5-dien-3,4-diol (18.4%), α -cadinol (14.1%), 3-acetoxygermacra-1(10),5-dien-4-ol (13.0%), *t*-cadinol (8.2%) and δ -cadinene (5.8%) as main constituents [13].

Asteriscus maritimus has also been studied during the previous years from different point of view. Under water and saline stress conditions, this species showed lower biomass, an early reduction in leaf expansion growth and a substantial degree of stomatal regulation [14]. Recently, biological studies have shown that the diversity of arbuscular mycorrhizal fungi in this species improves salt tolerance by increasing efficiency of photosystem II, stomatal conductance and glutathione content and by reducing oxidative damage [15,16]. Finally, two previous studies have shown that the insecticidal, antimicrobial and anti-acetylcholinesterase activities were revealed by the essential oils [17,18]. The essential oil of aerial parts of *A. maritimus* from Italy showed insecticidal activity. Fourteen compounds were identified out of which one myrtenyl acetate (44.2%), terphenyl (17.5%) and (*Z*)- β -farnesene (12.9%) were the principal ones [17]. The root oil of *Asteriscus maritimus* growing in Tunisia yielded Sixty six compounds which represented 96.7% of the total oil, characterized by a high proportion of oxygenated compounds (65.0%). The root oil exhibited antifungal activity against *Aspergillus flavus*, *A. niger*, *Botrytis cinerea* and *Penicillium* sp [18].

The aim of this paper is to contribute the knowledge of the chemical composition of *Asteriscus maritimus* species along with the chemical compositions of its different aerial parts and comparing our results with those previously reported.

Materials and Methods

Plant material

Aerial parts of *Asteriscus maritimus* were collected from The

Regional Park of Calblanque, Murcia (Spain) in 19-III-2005. All the materials belonged to the same population and around 15-20 specimens were collected. A voucher specimen (MACB-94543) has been lodged at the Herbarium of the Faculty of Biology, Complutense University, Madrid, Spain.

Isolation of volatile oil

The oils from the different aerial parts of *A. maritimus* were air dried and were isolated by steam distillation with cohobation for 8 h. according to the method recommended in the Spanish Pharmacopoeia. The oils were dried over anhydrous magnesium sulphate and stored at 4°C in the dark. The different distilled fractions yielded a very low amount of pale yellow oil, being 0.17% and 0.42% from stems+leaves and flowers respectively, based on dry weight.

Gas Chromatography (GC)

The analytical gas chromatography (GC) was carried out on a Varian 3300 gas chromatograph fitted with a fused methyl silicone DB-1 column (50 m x 0.25 mm, 0.25 µm film thickness). Temperature was programmed from 95°C-240°C at 4°C min⁻¹. Injection was performed at 250°C in the split mode (1:100). Nitrogen was used as the carrier gas (1.5 mL min⁻¹). Detection was performed by FID at 300°C. Injection volume for all the samples was 0.1 µL of pure oil.

Gas Chromatography–Mass Spectrometry (GC-MS)

GC-MS analyses were carried out on an Agilent Technologies 6890 gas chromatograph coupled a Hewlett-Packard 5973 quadrupole mass detector. Injections were carried out in split mode (20:1) at 250°C. Separations were performed using two columns with different stationary phase (i) a SE-30 capillary column (50 m x 0.22 mm, 0.25 mm film thickness) temperature programmed from 70°C to 220°C at 4°C min⁻¹, and (ii) a DB-Wax column (60 m x 0.32 mm, 0.25 mm) programmed from 70°C to 220°C at 3°C min⁻¹. Helium at 1 mL min⁻¹ was used as carrier gas. Mass spectra were recorded in electronic impact (EI) mode at 70 eV, scanning the 35-350 m/z range. Interface and source temperature were 280°C and 230°C, respectively. All analyses were performed in duplicate.

Qualitative and quantitative analyses

Most constituents were tentatively identified by GC by comparison of their retention indices with those of authentic standards available in the author's laboratory or with retention indices from references [19-23]. Further identification was achieved by GC-MS: the fragmentation patterns of the mass spectra were compared with those stored in the spectrometer data base using the WILEY.L built-in library. Other constituents were either synthesised or identified in oils of known composition. Semiquantitative analysis was carried out directly from peak areas in the GC profile.

Results and Discussion

According to our results and previously reported ones, *Asteriscus* does not produce high quantity of essential oils. While *P. spinosa* showed the lowest yield (0.04%) [13], the other species of the genus studied till date had similar results: *A. graveolens* showed an yield (0.06%) [12] and *A. maritimus* from Italy showed the yield of 0.06% [17]. It is worth noting that for *P. spinosa* and *A. maritimus*, the yields were calculated on fresh weight. In our study, the oil amount

was little bit higher for both studied fractions: 0.17% for stems+leaves oil and 0.42% for flowers. The yield was based on dry weight that could explain the differences between our results and those above mentioned. Besides, as far as we know it is the first time that the aerial parts of this plant are distilled separately. The flowers contained more oil than the stems and leaves. The oil increase during the flowering period could attract the pollinators of this species to facilitate its cross fecundation, as we have previously published for a relative species, *Santolonia rosmarinifolia* L. ssp. *rosmarinifolia* [24]. However, more research should be carried out on this species and other of the same genus to check whether the different fractions of the plant have different yields.

The components identified from the different aerial parts of *Asteriscus maritimus*, their retention indices and their percentage composition are summarised in Table 1 where all the compounds are arranged in order of their elution on the DB-1 column. A total of 43 compounds have been identified from the different fractions studied, representing more than the 90% of the total oil for each one. We have found qualitative differences between the studied fractions although both of them share practically all their principal and representative constituents. The oil from the stems and leaves showed α -pinene (27.5%) and *p*-cymene (10.0%) as major components, while from oil from the flower fractions showed α -pinene (9.0%) and *p*-cymene (7.3%), but out of which the main ones were β -phellandrene (11.8%), fonenol (10.9%) and α -phellandrene (10.0%). These compounds were represented in the other fraction although their percentage compositions were lower than 10%: β -phellandrene (8.3%), α -phellandrene (7.2%) and fonenol (5.6%).

With respect to the terpenoid compounds we have also found differences between the analysed parts (Table 1). While the monoterpene fraction was predominant in the stems and leaves oil (54.6%), the sesquiterpene fraction was higher in the flowers oil (54.9%). However, in both of them the monoterpene hydrocarbons were more abundant 53.7% (A.m.SL) and 38.6% (A.m.Fl) than the oxygenated monoterpenes. Contrary in the sesquiterpene fraction which the oxygenated compounds showed higher percentage composition 29.3%(A.m.SL) and 34.9%.

Previous reports suggest that the compounds 6-oxocyclonerolidol and 6-hydroxycyclonerolidol "could be considered as chemical markers of this genus" [11]. We disagree with this affirmation. These compounds have been already mentioned in only one of the studied species, *A. graveolens* [10-12]. An exhaustive studies are necessary to check that affirmation, although may be they could be significant for the cited species.

Finally, remarkable differences have been found between our results and those previously published [17]. The oil analysed by us seemed to be more complex with a total of 43 compounds identified in comparison with the 14 constituents cited. Besides, it is worth nothing that not only the main compounds were different in both studies, compounds as myrtenyl acetate (44.2%), terphenyl (17.5%) and (*Z*)- β -farnesene (12.9%), could not be detected by us although were reported as main ones. In fact, we only detected, in low amounts, 4 of the 14 constituents were described. These differences could be caused by the develop state of the samples or because of chemotypes existence. A phenological study of both populations should be done to

Table 1: Essential Oil composition of the aerial parts of *A. maritimus* from Spain.

Compound	I	A.m.SL	A.m.FI
α-pinene	934	27,5	9,0
sabinene	982	0,3	0,1
myrcene	991	0,4	0,4
α-phellandrene	1005	7,2	10,0
p-cymene	1019	10,0	7,3
β-phellandrene	1027	8,3	11,8
cis-sabinene hydrate	1060	t	t
terpinen-4-ol	1170	t	t
α-terpienol	1180	t	t
thymol methyl ether	1230	0,2	0,2
bornyl acetate	1280	0,6	t
trans-verbenyl acetate	1290	t	0,1
iso-verbenol acetate	1305	t	0,2
δ-elemene	1330	t	t
α-ylangene	1365	t	t
β-cubebene	1390	0,1	t
α-cedrene	1407	0,1	0,2
E-caryophyllene	1414	t	1,0
β-gurjunene	1430	0,8	0,7
γ-elemene	1431	t	t
cis-muurolo-4(14),5-diene	1462	0,5	1,2
allo-aromadendrene	1465	1,6	3,1
α-selinene	1480	0,5	t
epi-cubebol	1487	1,3	2,0
bicyclogermacrene	1496	1,1	3,7
sesquicineole	1507	3,0	6,3
cubebol	1510	t	t
δ-cadinene	1518	3,5	9,1
cadina-1,4-diene	1532	0,5	1,0
α-cadinene	1545	t	t
1-nor-bourbonene	1551	4,9	0,1
globulol	1582	t	0,2
viridiflorol	1592	0,1	0,2
E-dehydro-apofarnesol	1595	t	t
1-epi-cubenol	1623	0,1	0,1
fönonol*	1630	5,6	10,9
epi-α-muurolol + epi-α-cadinol	1642	1,9	5,7
α-muurolol	1647	0,5	t
α-cadinol	1652	t	6,8
epi-α-bisabolol	1690	0,7	t
cis-14-muurolol-5-en-4-one	1694	t	t
(E,Z)-farnesol + 6S,7R-bisabolene (84, 100)*	1738	3,5	t
n.i. 1	1839	0,7	t
n.i. 2	1857	0,3	t
n.i. 3	1891	t	0,4
bis (2methylpropenyl) ester 1,2-benzenedicarboxylic acid*	1894	0,3	0,2
n.i. 4	1975	6,4	1,9
n.i. 5	1982	t	0,2
Monoterpene hydrocarbons		53.7	38.6
Oxygenated monoterpenes		0.9	0.5
Sesquiterpene hydrocarbons		8.8	20.0
Oxygenated sesquiterpenes		29.3	34.9
Total		92.7	94.0

I= Kováts retention indices on DB-1 column; t=traces (%<0.1); n.i.= not identified; A.m.=*Asteriscus maritimus*; SL=stems and leaves; FI=Flowers; *=Tentatively identified; n.i. 1 I=1839 220[M*](10), 159(100), 132(80), 91(40), 105(35), 177(30), 202(15); n.i. 2 I=1857 220[M*](10), 143(100), 43(100), 93(60), 121(35), 67(25), 205(5); n.i. 3 I=1891 260[M*](3), 132(100), 159(40), 43(20), 202(15); n.i. 4 I=1975 280[M*](5), 43(100), 81(90), 71(40), 159(35), 123(20), 177(15); n.i. 5 I=1982 278[M*](5), 149(100), 41(10), 76(10), 104(10), 205(10), 223(10), 123(10), 177(5)

contrast this hypothesis. The climatic conditions of the different places where the samples were collected could not cause these differences, because *A. maritimus* grows in coasts of the Mediterranean where the climate conditions are very similar. May be the characteristics of the soil could cause these differences. We have previously reported the effect of the soil in the essential oil composition of *Eryngium campestre* L. [25], although most of the differences were quantitative but not qualitative. However, we will try to study other Spanish populations of this species to study it.

The root essential oil of this species has also been studied and they exhibited antifungal activity against *Aspergillus flavus*, *A. niger*, *Botrytis cinerea* and *Penicillium* sp and low anti-acetylcholinesterase activity [18]. This part of the plant seems to be more complex, more compounds were identified and the terpenoid fractions were also different. The root oil was characterized by high amounts of oxygenated compounds (65.0%) while in our study 30.2% and 35.4% were registered for A.m.SL and A.m.FI. The hydrocarbon compounds were predominant in our oils 62.5% (A.m.SL) and 58.6% (A.m.FI) and lower in the root oils 31.7%. However, with respect to the monoterpenes and sesquiterpenes the stems and leaves fraction was similar to the root one: 54.6% in comparison with 51.1% for monoterpenes and 38.1% in comparison with 45.9% for sesquiterpenes [18]. One more time the phenological state of this species seems to affect the chemical composition. Further researches are necessary to analysis the variability between populations and between the different parts of this species.

Conclusion

The aerial parts of *A. maritimus* yielded low amount of essential oil. Quantitative differences have been found between the A.m.SL and A.m.FI oils. The A.m.SL oil was characterized by monoterpene compounds and the A.m.FI oil by sesquiterpene ones. The chemical composition of the essential oil seems to be affected by the part of the plant used. The major components were found to be α-pinene (27.5%) and p-cymene (10.0%) for of A.m.SL oil and β-phellandrene (11.8%), fönonol (10.9%) and α-phellandrene (10.0%) for A.m.FI oil.

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