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Essential Oils Composition of Two Endemic Umbelliferae Herbs Growing Wild in Turkey

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Abstract: The present study was carried out to determine the essential oil composition of aerial parts of two endemic umbelliferae herbs (*Malabaila lasiocarpa* Boiss. and *Stenotaenia macrocarpa* Freyn & Sint. ex Freyn) collected from Bingol (Turkey), using headspace solid-phase microextraction method and gas chromatography (GC) interfaced with mass spectrometer analysis. Forty six and forty three compounds were identified for *M. lasiocarpa* and *S. macrocarpa*, respectively, representing 91.40% and 90.86% of their respective essential oils. Germacrene D (20.71%), β-elemene (12.40%), spathulenol (11.60%) and β-selinene (9.67%) were identified as the major compound of *M. lasiocarpa*. β-sesquiphellandrene (19.68%), hexyl isobutyrate (12.65%) and octanal (9.53%) were found to be the major compounds of *S. macrocarpa*. Essential oil composition of *M. lasiocarpa* has been determined for the first time and the results have been discussed in view of chemotaxonomy, natural products and potential usefulness of these plants.

Key words: *Malabaila lasiocarpa*, *Stenotaenia macrocarpa*, HS-HSPME, essential oil, chemotaxonomy.

1. Introduction

The Apiaceae (or Umbelliferae) family has a cosmopolitan spreading, but most of Apiaceae taxa are confined to Northern temperate areas, and high altitudes in the tropic regions and they are commonly distinguished by the presence of sheathing petioles and hollow stems [1]. Apiaceae (in Turkey called “Maydanozgiller”) has annual and perennial herbs, rarely shrubby, the leaves are generally alternate, usually exstipulate, the petioles are often large and sheared at the base, the inflorescence is usually a compound umbel, and the flowers are generally hermaphrodite [2]. Umbelliferae is a large family, composed of more than 3,700 species belonging to 434 genera all around the world [3]. In Turkey, Apiaceae family is represented by about 102 genus and 465 species from which 130 are endemic, with a 30% endemism rate [2, 4-6]. Plants of this family, generally known as carrot or parsley family, are mostly aromatic and economically important plants are well known with regard to their economic significance and varied profile of essential oils [7]. In addition, Apiaceae has a range of chemical compounds with apoptosis, hepatoprotective, antibacterial, vaso-relaxant and antitumor activities [8] and is rich in secondary metabolites, including essential oils [9]. Moreover, the chemical compounds detected in the Apiaceae family include: volatile oils, coumarins, acetylenes and flavonoids, while terpenes, sesquiterpenes and alkaloids are scarce [10]. The genus *Malabaila* Hoffm. belongs to Apiaceae family, and is represented by six species (*M. aurea* (Sm.) Boiss., *M. involucrata* Boiss. & Spruner, *M. lasiocarpa* Boiss., *M. pastinacifolia* Boiss. & Bal., *M. dasyantha* (K. Koch) Grossh., *M. secacul* Banks & Sol.) in Turkey flora. *Malabaila lasiocarpa* is an endemic plant and described as erect perennial [2].

The major volatile oil compounds determined in

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Malabaila species are *p*-cymene and *a*-phellandrene [11], while isobergapten, bergapten, imperatorin, pimpinellin, isopimpinellin, sphondin and umbelliferone are found in *M. graveolens* and *M. dasycarpa* fruits [12], in addition to marmesin and dihydroimperatorin. Essential oil composition of *Malabaila* is not well documented, although there have been some researches on the composition of essential oil of aerial parts of *M. secacul* (Miller) Boiss. [13] and *M. aurea* Boiss. [14]. In this study, the essential oil composition of *M. lasiocarpa* is studied for the first time. The genus *Stenotaenia* Boiss., which also belongs to Umbelliferae family, is represented in Turkey by only *S. macrocarpa*. Thus, *S. macrocarpa* is a monotypic, endemic, aromatic and important plant in Turkey Flora [2]. To our knowledge, essential oil constituents of *Stenotaenia* genus are poorly known in literature [15, 16].

In the present study, the chemical essential oil composition of *M. lasiocarpa* and *S. macrocarpa* is determined and examined to indicate the source of particular essential oils for flavour, fragrance and other potential usefulness.

2. Materials and Methods

2.1 Plant Materials

Plant samples were collected from their natural habitats. *M. lasiocarpa* was collected by Kilic, collected number: 5344, from Bingöl (Turkey), vicinity of Dikme plateau, *Quercus* forest bottoms, stony slopes, on June 2013 at an altitude of 1,650-1,700 m. *S. macrocarpa* was collected by Ömer Kılıç, collected number: 5447, from Bingöl (Turkey), vicinity of Dikme village, slopes, on July 2013 at an altitude of 1,650-1,700 m. The taxonomic description of the plant samples was made according to Davis [2]. Plant samples was dried according to standard herbarium techniques and stored in the Bingol University Herbarium. General herbarium samples of *M. lasiocarpa* and *S. macrocarpa* are shown in Figs. 1 and 2.

2.2 Extraction Procedure

Aerial parts of *M. lasiocarpa* and *S. macrocarpa* were triturated by a liquidizer. The 5 g of powder of plant samples were placed in a vial (40 mL) sealed with a septum-type cap, the vial was equipped with a valve and was carried out by a head space solid phase microextraction (HS-SPME), method using a divinyl benzene/carboxen/polydimethylsiloxane fiber. Before the analysis the fiber was conditioned in the injection port of the gas chromatography (GC) as indicated by the manufacturer. The vial was kept at 35 °C with continuous internal stirring and the sample was left to equilibratefor 30 min; then, the SPME fiber was exposed for 40 min to the headspace while maintaining the sample at 35 °C. After sampling, the SPME fiber was introduced into the GC injector, and was left for 3 min allow analysis of the thermal desorption. In order to optimize the technique, the effects of various parameters, such as sample, sample headspace volume and sample heating, temperature and extraction time were programmed on the extraction efficiency as previously reported [17].

2.3 GC Analysis

A Varian 3800 GC, exactly interfaced with a Varian 2000 ion trap mass spectrometer (MS), was used with a splitless injection mode and an injector temperature of 260 °C. The GC is equipped with 60 m long column packed with CP-Wax 52 CB 0.25 mm i.d.. The oven temperature was 45 °C held for 5 min, then increased to 80°C at a rate of 10 °C/min, and to 240 °C at a rate of 2 °C/min. Helium was the carrier gas which used at a stable pressure of 10 psi (pounds per square inch), the transfer line temperature was 250 °C, with an electron impact ionisation mode an acquisition range of 40 m/z to 200 m/z and a scan rate of 1 us^{-1}. The compounds were identified using the National Institute of Standards and Technology (NIST) library (NIST/WILEY/ EPA/NIH), mass spectral library and verified by the retention indices which were calculated as described by Dool and Kratz [18].

Fig. 1 Plant of *Malabaila lasiocarpa*.

The relative amounts were calculated on the basis of peak-area ratios.

3. Results and Discussion

The major components of *Malabaila lasiocarpa* were germacrene D (20.71%), β-elemene (12.40%), spathulenol (11.60%), β-selinene (9.67%) (Table 1). The main constituents of *Stenotaenia macrocarpa* were: β-sesquiphellandrene (19.68%), hexyl isobutyrate (12.65%) and octanal (9.53%) (Table 1).

. β-sesquiphellandrene (19.68%) was found to be the main compound of *S. macrocarpa*; whereas it was found in very low amount in the essential oil of *M. lasiocarpa* (Table 1). Similarly, β-sesquiphellandrene (25.3%) was detected as the main compound of essential oil of *Stenotaenia nudicaulis* from Iran [15], whereas this compound was not reported among the main constituents of *S. macrocarpa* from Turkey [15]. Hexyl butyrate (15.7%) was found one of the predominant compounds in the essential oil *S. nudicaulis*

Fig. 2 Plant of *Stenotaenia macrocarpa*.

Table 1 Essential oil composition of studied species (%).

Compounds	RRI*	*Malabaila lasiocarpa* (%)	*Stenotaenia macrocarpa* (%)
2-hexenal	965	0.21	0.12
Tricyclene	982	1.03	-
α-pinene	1,024	0.04	0.30
Benzaldehyde	1,028	-	0.20
Camphene	1,030	0.51	-
Verbenene	1,042	0.12	-
Sabinene	1,053	0.33	0.10
β-pinene	1,057	4.08	2.01
Rycene	1,060	1.30	0.35
Octanal	1,045	-	9.53
p-cymene	1,063	-	0.34
α-phellandrene	1,065	0.07	-
α-terpinene	1,087	0.20	0.10
Limonene	1,105	2.35	1.45
γ-terpinene	1,115	0.19	-

(Table 1 continued)

Compounds	RRI*	Malabaila lasiocarpa (%)	Stenotaenia macrocarpa (%)
1,8-cineole	1,130	-	0.30
β-ocimene	1,137	0.72	0.20
Octan-1-ol	1,140	-	2.05
Linalool	1,145	0.40	0.55
Fenchol	1,162	1.22	-
Cis-verbenol	1,170	0.15	-
Camphor	1,184	-	1.60
Hexyl isobutyrate	1,188	4.07	12.65
Cyclohexanone	1,190	0.30	-
Carvone	1,193	0.05	-
Borneol	1,200	0.27	0.70
α-terpineol	1,215	-	0.12
α-terpinolene	1,230	0.43	-
2-cyclohexen-1-one	1,254	0.63	0.24
Methyl acetate	1,257	-	0.32
Geraniol	1,275	0.66	0.10
Bornyl acetate	1,282	0.42	1.08
Thymol	1,297	1.95	1.05
Carvacrol	1,346	0.98	-
α-terpinyl acetate	1,365	-	0.45
α-copaene	1,369	1.06	0.85
β-elemene	1,377	12.40	3.02
β-bourbenene	1,380	-	2.05
Methyl eugenol	1,388	1.02	-
β-caryophyllene	1,393	3.68	4.06
α-cedrene	1,405	-	1.02
Trans-farnesene	1,413	0.24	0.65
α-farnesene	1,418	2.69	1.52
γ-cadinene	1,420	0.02	-
Germacrene D	1,432	20.71	3.90
β-selinene	1,440	9.67	2.72
Bicyclogermacrene	1,443	1.05	-
α-humulene	1,449	-	0.85
Naphtalene	1,456	0.76	-
Allo-aromadendrene	1,460	-	0.71
δ-cadinene	1,459	1.02	-
Nerolidol	1,485	-	0.55
Spathulenol	1,495	11.60	3.45
Caryophyllene oxide	1,498	0.85	1.45
β-bisabolene	1,505	-	1.60
Muurolene	1,523	0.23	-
β-sesquiphellandrene	1,532	0.03	19.68
α-cadinol	1,539	0.56	1.20
β-farnesene	1,582	1.05	-
β-eudesmol	1,635	-	3.25
β-bisabolol	1,675	-	2.30
Hexadecanoic acide	1,710	0.03	-
Ericosane	1,895	0.05	0.02
Total		91.40	90.86

RRI: relative retention index.

[15]. It was observed that this compound was not determined as major in the essential oils composition of *S. macrocarpa* neither in this study (Table 1) nor in a previous one [16]. However, hexyl isobutyrate (12.65%) and octanal (9.53%) were found to be major compounds of *S. macrocarpa* (Table 1). In the previous study on this species [16], octanal was also determined as one of the main constituent (16.7%). It is noteworthy that this compound was not reported neither in *M. lasiocarpa* (Table 1) nor in *S. nudicaulis* oils [16]. Besides, β-elemene (12.40%) and β-selinene (9.67%) were the main compounds of *M. lasiocarpa* (Table 1). Another study on *M. secacul* (Miller) Boiss. showed that β-elemene (18.5%), β-selinene (17.5%) and germacrone (16.0%) were the major components of stem oil whilst hexyl 3-methyl butyrate (26.3%), β-elemene (15.8%), hexyl 2-methyl butyrate (14.9%) and hexyl butyrate (10.6%) were the main compounds of flower oil [20]. The analysis of aerial parts of the *M. isfahanica* Alava. from Iran exhibited that a total of 13 constituents represented more than 94% of the volatile compounds. The major were limonene oxide (16.44%), β-cyclocitral (12.56%) and β-pinene (12.41%) [21]. In our study, limonene oxide and β-cyclocitral were not determined whilst limonene (2.35%) and β-pinene (4.08%) were found in low content in *M. lasiocarpa* oil (Table 1). The compound spathulenol which was determined in high concentration (11.60%) was not detected among the major components of *M. secacul* [20].

Essential oils from aromatic and medicinal plants are used in many industrial fields for perfuming and flavoring of different products [22, 23] and have been known since antiquity to have biological activity, mostly antibacterial, antifungal and antioxidant features. With growing interest in the use of plant essential oils in both food and pharmaceutical industries, the systematic examination of plant extracts for these features has become increasingly significant [24]. In addition, many of these volatile substances have diverse ecological functions. In fact, they can act as internal messengers, defensive substances against herbivores and attracting pollinating insects to their host [25]. Over the past 15 years, interest in botanical insecticides, naturally occurring insecticides derived from plant samples, has increased as a result of environmental worries and insect populations becoming resistant to conventional chemical insecticides [26]. Insecticidal activity of essential oils and plant extracts against different stored-product pests has been investigated [27-29]. Essential oils from different plant species have larvicidal, ovicidal and repellent properties against various insect species and are regarded as environmentally compatible pesticides [26]. Many researches about essential oils of plant taxa can be found in the literature [30-32]. However, the present study allow, on one hand, to know essential oil composition of *S. macrocarpa* for the first time and, on the other hand, to expand data regarding essential oil composition of *M. lasiocarpa*. Different chemotypes were reported in literature and for the same species, the main components were found to differ in relation to the plants origin [33, 34].

4. Conclusions

In conclusion, germacrene D/β-elemene/spathulenol are the most probable chemotypes of *M. lasiocarpa* whilst β-sesquiphellandrene/hexyl isobutyrate/octanal are the most probable chemotypes of *S. macrocarpa* in eastern Anatolian region of Turkey. Also, this study showed that *M. lasiocarpa* and *S. macrocarpa* have rich and diversified essential oils, thus these endemic and important plants can be used in flavors, fragrances, aromatherapy, against herbivores and insecticides. Also this study may be useful for further researches on these species or other belonging to Umbelliferae family both in Turkey and other countries of the world. In addition, the essential oils composition of the *M. lasiocarpa* and *S. macrocarpa* from Turkey show that they have contributed to the medicinal usage of this plants as a crop and their oils in the pharmaceutical, cosmetic and industrial purposes.

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