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SPME GC/MS Analysis of Three *Ornithogalum* L. species from Turkey

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Abstract: In this study, a solid phase micro extraction (SPME) method with gas chromatography-mass spectrometry (GC-MS) was used for analysis of volatile compounds in flowers and bulbs of three *Ornithogalum* species. The samples of flowers and bulbs of *Ornithogalum sigmoideum, Ornithogalum orthophyllum, Ornithogalum oligophyllum* was separately analyzed by SPME-GC-MS. A comparison of volatile compounds was made between species and the parts studied. A total of 70 compounds were identified and different volatile compounds were determined in distinct parts of the species. The major volatile organic compound of the flowers of *O. sigmoideum* and *O. ornithogalum* was furan (54.5% and 57.0% respectively). For *O. oligophyllum* the major volatile organic compound was nonanal (19.2%). Analyses revealed that SPME-GC-MS method is appropriate for the analysis of volatile compounds of *Ornithogalum* species.

Keywords: *Ornithogalum sigmoideum; Ornithogalum orthophyllum; Ornithogalum oligophyllum*; GC/MS, SPME.

1. Introduction

The genus *Ornithogalum* (Liliaceae) includes about 150 species which are distributed in temperate regions of Europe, Asia, and Africa [1] and recorded by 34 species in Turkish flora [2-4]. The bulbs of the plant which has medical and economic value are used as emetic and against abscess since the time of Dioscorides. Also *O. sigmoideum* bulbs are consumed as food and sold in local markets [5, 6]. Phytochemical studies of *Ornithogalum* species revealed that the main constituents were cholestane glycosides, cholestane bidesmosides, cardenolide glycosides, flavonoid glycosides and saponins [7-11]. Recent studies showed that some of the compounds isolated from *Ornithogalum* species demonstrated antimicrobial, antioxidant, cytostatic, antitumor activities [12-14]. The cytostatic activity of the kolestan glycosides isolated from *O. saundersiae* were examined on human leukemia cells and compounds were found to be active [12]. But, according to our literature search, there were no studies for SPME-GC/MS analysis of *O. sigmoideum, O. orthophyllum,* and *O. oligophyllum.* The objective of this study was to determine volatile compounds from parts (flowers and bulbs) of three

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Ornithogalum species using SPME-GC-MS method. Comparisons of volatile compound were made between species and the parts that studied.

2. Materials and Methods

2.1. Plant materials

Flowered plants were collected from different districts in Turkey. *O. orthophyllum* (Oor) was collected from Ordu, city center (at heights of 0-20 m) in 30.03.2013. *O. sigmoideum* (Os) was collected from Trabzon, Geçit village (at heights of 600 m) in 31.03.2013. *O. oligophyllum* (Ool) was collected from Trabzon, Akçaabat, Karadağ (at heights of 1940 m) in 12.05.2013. Voucher specimens were authenticated by Dr. Gülin Renda and have been deposited in the Herbarium of Istanbul University, Faculty of Pharmacy; ISTE. The herbarium numbers are; ISTE 101045; ISTE 101047; ISTE 101048, respectively. Flowers and bulbs were seperated and cleaned to remove any residual compost. Plant materials stored at room temperature in air-tight container. Fresh plant materials (1 g, each) were grounded and placed in a 10 mL vial sealed with a silicone-rubber septum cap.

2.2. GC-MS instrument

GC analysis was carried out using a Shimadzu 2010 Plus (USA) gas chromatograph coupled to a Shimadzu QP2010 (USA) Ultra mass selective detector. The separation was performed by means of a Restek Rxi-5MS capillary column (60 m × 0.25 mm × 0.25 μm) (USA). A manual SPME holder and one type of fiber (65 μm-blue hub plain, polydimethylsiloxane/divinyl-benzene (PDMS/DVB)) and 10 mL vials from Supelco (Bellefonte, USA) were used for the extraction procedures.

2.3. SPME and GC-MS Analysis

A polydimethylsiloxane/divinylbenzene fiber was used for the extraction of the volatile components. Before the SPME analysis, the fibers were conditioned for 5 min at 250 ^{o}C in the GC injector. ~1.00 g of the plants was transferred into a 10 mL vial. The fiber coating was placed to the head space for temperature and times (incubation and extraction times) values set according to the experiment. SPME were done at 50 ^{o}C with incubation time of 5 min, and extraction time of 10 min. Each sample was analyzed and mean reported. The fiber containing the extracted aroma compounds were then injected into the GC-MS injector (split mode). The oven program was as follows: initial temperature was 60 ^{o}C for 2 min, which was increased to 240 ^{o}C at 3 min, final temperature 250 ^{o}C was held for 4 min. Helium (99.999%) was used as carrier gas with a constant flow-rate of 1 mLmin^{-1}. Detection was carried out in electronic impact mode (EI); ionization voltage was fixed to 70 eV, Scan mode (40-450 *m/z*) was used for mass acquisition. The volatile compounds were identified by comparison of their retention indices (relative to C6-C30 alkane standards), and by comparison with the mass spectra of the two libraries (FFNSC1.2 and W9N11).

3. Results and Discussion

The results of the SPME-GC-MS analyses of the flowers and bulbs of *Ornithogalum* species are given in table 1. In total 70 compounds were identified and quantified from the species, *O. orthophyllum, O. sigmoideum,* and *O. oligophyllum*. Furan and nonanal were the major components of the flowers and furan, hexanal and ethyl palmitate were the major components of the bulbs. While 1-pentanol was first which came out from the column (RT=8.00 min), tetracosane was kept in the column fort the longest of all (RT=61.8 min).

A total of 40 (flower) and 26 (bulb) compounds were identified and quantified from *O. sigmoideum*. The main compounds of the flowers were furan (54.5%) and nonanal (17.4%). In the bulbs of the *O. sigmoideum*, furan (57.9%) and hexanal (7.6%) were the main compounds. For the *O.*

orthophyllum, a total of 22 (flower) and 36 (bulb) compounds were identified and quantified. The main compounds of flowers were furan (57.0%), nonanal (18.8%) and heptanal (11.2%). Hexanal (7.6%) and heneicosane (6.3%) were the major constituents of the bulbs of this species. A total of 18 and 4 constituents were identified and quantified in flowers and bulbs of *O. oligophyllum*, respectively. While nonanal (19.2%) and hexanal (17.3%) were the main components in the flowers, ethyl palmitate (45.0%) was the major compound of the bulbs.

Generally the numbers of volatile compounds present in the oil of *O. oligophyllum* bulbs and flowers are much less than other two species. However in the bulbs of this species remarkable abundance of the fatty acids and esters (80.2%) was observed. It can be related with the altitude, locality or climatic conditions.

In the literature some of GC-MS studies on bulbs of *Ornithogalum* species showed the presence of steroids [15,16]. GC-MS analysis of the dichloromethane extract of the bulbs of *O. cuspidatum* was investigated. With vacuum liquid chromatography of the dichloromethane extract 5 fractions were collected. Analyses of these fractions led the identification of steroidal compounds [15]. Taking into account, another extraction method may be useful to identify steroids of three *Ornithogalum* species studied. One of other GC-MS analysis of *Ornithogalum* species was about GC-MS analyses of the essential oils obtained by hydrodistillation of the dried and ground bulbs, n-hexane extract, methanol extract and the hydrolysed methanolic extract *O. procerum*. It was reported that the essential oils are mainly composed of oxygenated hydrocarbons, the n-hexane extract contains predominantly hydrocarbons, and the hydrolyzed methanolic extract comprises polysterol-type compounds [1]. In our case the analyses showed that *Ornithogalum* species flowers and bulbs were characterized by a high content of aldehydes which could be use as marker. But oxygenated monoterpenes were present in minor percentages in all samples. Also in literature one of the high content aldehydes, nonanal was considered and reported as a marker compound in *Paliurus spina-christi* honey in a HS-SPME analysis [17].

As a result the volatile organic compounds of *O. sigmoideum*, *O. orthophyllum* and *O. oligophyllum* have not been studied previously with SPME-GC-MS method. Also no previous reports about essential oil analysis of these species were found in the literature. Comparative study of the main volatiles of different parts of three *Ornithogalum* species growing in the Black Sea Region of Turkey resulted similar composition with high proportion of furan and nonanal.

Table 1. Identified volatile components from flowers and bulbs of *Ornithogalum* species.

		Flowers, (%)[a] Area			Bulbs, (%)[a] Area		
Compound	RI[b]	Os[c]	Oor[d]	Ool[e]	Os[c]	Oor[d]	Ool[e]
1-Pentanol	794	-	-	-	0.3	-	-
2,4-Dimethylhexane[f]	818	3.2	-	-	-	-	-
Hexanal	820	-	-	17.3	7.6	7.6	-
Furfural	848	-	-	0.3	-	-	-
3(*Z*)-Hexen-1-ol	867	-	1.4	-	-	-	-
2(*E*)-Hexenal	867	1.0	-	3.5	-	-	-
1-Hexanol	879	0.3	0.7	1.4	0.8	0.6	-
Styrene	907	-	-	-	-	0.1	-
Nonane	908	0.1	0.8	-	-	0.1	-
Heptanal	912	4.2	11.2	-	1.3	1.4	-
Anisole	929	-	-	-	-	4.5	-
Camphene	961	-	-	-	-	2.4	-
2(*E*)-Heptenal	962	0.1	-	2.3	0.4	-	-

Benzaldehyde	970	-	-	3.8	1.6	0.1	-
1-Heptanol	973	0.2	2.7	-	-	-	-
1-Octen-3-ol	982	-	-	2.3	-	-	-
7-Octen-4-ol[f]	982	-	0.1	-	-	-	-
Sabinene	984	-	-	-	-	2.4	-
2,3-Octadiene[f]	988	-	-	-	0.2	-	-
6-Methyl-5-hepten-2-one	993	-	-	-	0.6	-	-
2-Amylfuran	997	-	0.6	0.8	2.6	-	-
α-Phellandrene	998	-	-	-	-	4.2	-
Octanal	1008	0.8	0.7	4.5	0.5	-	-
O-methyl oxime hexanal	1027	0.6	-	-	-	-	-
Limonene	1037	-	-	-	-	4.6	-
3-Ethyl-2-methyl-1,3-hexadiene[f]	1041	-	-	-	-	1.3	-
3(E)-Octen-2-one	1043	-	-	1.4	-	-	-
Benzene acetaldehyde[f]	1052	0.5	0.3	5.1	0.8	-	2.0
2(*E*)-Octenal	1063	0.2	0.4	0.7	0.8	-	-
γ-Terpinene	1066	-	-	-	-	0.3	-
1-Octanol	1072	0.9	0.5	0.4	0.9	-	-
Furan[f]	1082	54.5	57.0	-	57.9	5.7	-
Terpinolene	1096	-	-	-	-	1.0	-
Undecane	1102	0.1	0.3	-	-	-	-
Linalool	1104	-	-	-	-	0.1	-
Nonanal	1108	17.4	18.8	19.2	3.1	4.9	17.8
2(*E*)-Nonenal	1164	0.1	-	0.6	-	-	-
1-Nonanol	1172	0.5	1.7	-	-	-	-
Naphthalene	1196	0.2	-	-	-	-	-
Decanal	1209	0.9	0.6	3.5	1.5	2.0	-
2,3-Dihydrobenzofuran[f]	1220	0.7	-	-	-	-	-
Eucarvone	1229	-	-	1.4	-	-	-
2(*E*)-Decenal	1264	0.4	0.1	-	-	-	-
2-Undecanone	1296	0.1	-	-	-	-	-
Tridecane	1299	0.3	0.2	-	-	1.1	-
Carvacrol	1305	-	0.2	-	-	-	-
Undecanal	1310	0.2	-	-	-	-	-
2(*E*),4(*E*)-Decadienal	1321	-	-	-	-	3.0	-
Tetradecane[b]	1399	0.3	0.4	-	0.3	5.4	-
Methyl-4-methoxysalicylate[f]	1450	1.9	-	-	-	5.9	-
Geranylacetone	1457	-	-	-	0.4	-	-
Phytan[f]	1461	-	0.7	-	-	2.7	-
Pentadecane	1499	0.4	0.2	-	0.6	3.0	-

Tridecanal	1513	0.1	-	-	0.7	-	-
Hexadecane	1600	0.9	-	-	-	2.2	-
Methyl jasmonate	1658	-	-	-	-	0.2	-
Methyl dihydrojasmonate	1662	0.2	-	-	1.2	-	-
Pristane[f]	1705	-	-	-	-	0.5	-
Octadecane	1799	0.1	-	-	0.2	-	-
2-Ethylhexylformate[f]	1811	0.6	-	-	2.1	4.5	-
Isopropylmyristate	1826	0.2	-	-	2.5	0.9	-
Hexahydrofarnesylacetone	1847	0.3	-	2.3	-	-	-
Hexamethylpyranoindane[f]	1868	0.3	-	-	3.6	1.1	-
Nonadecane	1899	0.1	-	-	-	1.0	-
Methyl palmitate	1928	0.4	-	-	-	1.3	-
Ethyl palmitate	1995	0.5	-	-	-	5.4	45.0
Eicosane	2000	0.5	-	-	-	-	-
Heneicosane	2100	0.7	-	-	3.6	6.3	-
Ethyl linoleate	2165	-	-	-	-	2.7	35.2
Tetracosane	2400	-	-	-	-	5.1	-
Monoterpene hydrocarbons:		-	-	-	-	14.9	-
Oxygenated monoterpenes:		-	0.2	1.4	0.4	0.1	-
Fatty acid esters:		1.5	-	-	2.1	13.9	80.2
Alkanes:		6.7	2.6	-	4.7	27.4	-
Aldehydes:		26.5	32.1	60.8	18.3	21.0	17.8
Alcohols:		1.9	7.1	4.1	2.0	0.6	-
Others:		59.4	57.6	4.5	68.6	17.7	-
Total:		96.0	99.6	70.8	96.1	95.6	98.0

[a] %Area obtained by FID peak-area normalization. [b]RI calculated from retention times relative to that of *n*-alkanes (C_6-C_{30}) on the non-polar Restek Rxi-5MS column. [c]*Os: O. sigmoideum;* [d]*Oor: O. orthophyllum;* [e]*Ool: O. Oligophyllum.* [f]Constituent identified by mass spectra matching.

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