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Chemical composition of essential oils from *Artemisia glabella* Kar. et Kir. and *Artemisia rupestris* L. obtained by different extraction methods

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Abstract

The aim of the research was to investigate the chemical composition of essential oils and volatiles from two species of *Artemisia glabella* and *Artemisia rupestris* growing in Kazakhstan. Two different techniques, the conventional hydrodistillation (HD) and modern fast micro-steam distillation-solid-phase microextraction (MSD-SPME) have been used to obtain the volatiles. Chemical profiles of the volatiles were comparatively analyzed with GC-FID/MS techniques. The yields of essential oils from *A. glabella* and *A. rupestris* obtained by a hydrodistillation were 0.2% and 0.1%, respectively. The major components of *A. rupestris* essential oil were myrcene (9.5%), β-elemene (5.4%) and capric acid (5.1%). The oil of *A. glabella* was found to be rich with 1,8-cineole (12.2%), cumin aldehyde (9.4%), α-terpineol (5.7%) and borneol (5.2%).

Keywords: *Artemisia glabella*, *Artemisia rupestris*, essential oil, GC/FID, GC/MS, MSD-SPME.

Introduction

The genus *Artemisia* L. (Compositae) is one of the most widespread in the flora of Kazakhstan. Eighty-one species of *Artemisia* L. grow on the territory of Kazakhstan, of which 16 are endemic species (Pavlov, 1966). Wormwoods are of great interest as the object of research due to their wide distribution throughout the territory of Kazakhstan. A high content of essential oils with a valuable chemical composition in *Artemisia* makes it possible to produce medicinal substances with original pharmacological properties based on them.

Artemisia glabella Kar. et Kir. is found on stony mountain and hill slopes, on dry pebbled river beds and among rocks (Pavlov, 1966). It is known that *A. glabella* contains a number of biologically active compounds including sesquiterpene lactones, arglabin, argolide, dihydroargolide, matricarin, 1β,10α-dihydroxyarglabin, and flavonoids, cirsilineol, pectolinarigenin, casticin, bonanzin (Adekenov et al., 1982, 1983, 1993, Kulmagambetova et al., 2000). According to Atazhanova et al., (1999) the main constituents of essential oil were 1,8-cineole (12.0%), linalool (8.0%), 4-terpineol (6.5%), α-terpineol (5.0%) and sabinol derivatives (5.0%). Due to the fact that essential oil from *A. glabella* has antibacterial, antifungal and antiviral activities (Seidakhmetova et al., 2002) the Epherol spray was developed on its basis, which has antimicrobial and anti-inflammatory effects and improves the mucus drainage. The drug is recommended at treatment of upper airway diseases, chronic obstructive bronchitis and pneumonia in the complex therapy that includes traditional and officinal drugs. The main biologically active ingredient of the Epherol spray is 1,8-cineole (Atazhanova, 2008).

A. rupestris grows in a steppe zone on saline and solonetzic meadows, in stony and sandy dry river beds, sometimes on non-saline steppe meadows, on stony and crushed rock slopes of the subalpine and alpine mountain belts (Pavlov, 1966). *A. rupestris* is used in Traditional Chinese herbal medicine as an antibacterial, antiviral, anti-tumor agent (Xiao, et al., 2008). It is also a source of rupestric acid which exhibits an antiviral activity. The essential oil from *A. rupestris* collected in China has previously been reported to contain 1-hexadecanol (18.1%), hexadecanoic acid (11.2%) (Bicchi, et al., 1985), α-terpinyl acetate (37.2%), spatulenol (10.7%), α-terpineol (10.1%), linalool (7.6%), 4-terpineol (3.9%) as major constituents (Liu, et al., 2013).

The main goal of the present work was to make comparative study on the volatiles chemical profiles of *A. glabella* and *A. rupestris* collected in Kazakhstan. The essential oil of *A. rupestris*. growing in Kazakhstan was never investigated until now. The conventional hydrodistillation (HD) and rapid modern Microsteam Distillation - Solid Phase Microextraction (MSD-SPME) procedures were applied for obtaining of the volatiles from the plant material. MSD-SPME is a modern and rapid volatile sampling and concentration technique introduced for the extraction of the volatiles from small amount of aromatic plant materials in a short time. This technique involved concurrent solid-phase microextraction combined with continuous hydrodistillation of the volatiles. This method offered important advantages in time (even less than a minute) and energy saving for the isolation of the volatiles. MSD-SPME combined with GC/FID and GC/MS has been proven to be simple, sensitive, rapid, solventless and non-toxic “green” technique for volatile constituents analysis at the microscale level.

Materials and Methods

Plant material

The aerial parts of *A. glabella* (leaves, calathids, flower buds) were collected during the budding phase in June, 2016 at a pilot pharm of Karaganda Pharmaceutical Plant near the Bereznyaki village of Bukhar-Zhyrau district, Karaganda region (Kazakhstan). The aerial parts of *A. rupestris* (leaves, flower buds) were harvested during the budding phase in May, 2016 in the vicinity of Karkaralinsk, along the Zhyrym River floodplain (Kazakhstan). The herbs were dried under the shade. Botanical identifications of the both species were performed by Dr.A.N. Kupriyanov. The voucher specimens (AG and AR) were deposited in the Herbarium of Laboratory of Terpenoids Chemistry in Karaganda International Research Production Holding (IRPH).

Hydrodistillation

Air-dried aerial parts of *A. glabella* and *A. rupestris* (50.0 g) were ground and hydrodistilled in a Clevenger-type apparatus (3 hours) (European Pharmacopoeia-2017). The oil yields were calculated on a dry weight basis. The oils were dried over anhydrous sodium sulfate and stored in sealed vials in refrigerator (4°C), until GC-FID/MS analyses. The oils were dissolved in *n*-hexane (10 %, v/v) to conduct chromatographic determination of the compositions.

Microsteam distillation - solid phase microextraction

The ground plant material (1.0 g) was put into the flask (25 mL) together with water (3.0 mL) and heated. The flask was fitted with a Claisen distillation head with plug and a condenser set up for refluxing rather than distillation. Heating was achieved using electric heater, and threaded plug was used for SPME fiber assembly. A manual SPME holder (57330-U, SUPELCO, Bellefonte, PA) and the PDMS-DVB (polydimethylsiloxane-divinylbenzene) 65 µm fiber “bluetype” were used for SPME procedure of volatiles. The fiber was conditioned at 250°C for 15 min before the experiment. After the SPME needle pierced the plug, the fiber was expressed through the needle and exposed to the headspace above a plant sample. MSD-SPME procedure was carried

out at the boiling temperature of water used as solvent. The time of equilibrium was a period between loading of SPME fiber into flask and starting of the extraction. Extraction time for 3.0 min was used as suitable time after equilibrium. After the extraction (trapping) of the volatiles, the loaded SPME fiber was withdrawn into the needle, and then the needle was removed from the plug and subsequently used for thermal desorption in the injection port of GC-FID and GC/MS systems.

GC-FID and GC/MS analyses

The essential oils were dissolved in *n*-hexane (10%, v/v) before the chromatographic determination of their compositions. In MSD-SPME technique, the termal desorption of the volatiles from the fiber coating was performed by heating the fiber in the injection port at 250°C for 10 min. The SPME fiber was reconditioned at 250°C for 15 min before the each extraction experiments. The fiber was subjected to a blank injection to ensure fiber integrity and the absence of any analytes after each reconditioning period.

GC/MS analysis was carried out with an Agilent 5975 GC-MSD system (Agilent, USA; SEM Ltd., Istanbul, Turkey). HP-Innowax FSC column (60 m × 0.25 mm, 0.25 µm film thickness, Agilent, USA) was used with a He carrier gas at 0.8 mL/min. GC oven temperature was kept at 60°C for 10 min and programmed to 220°C at a rate of 4°C/min, kept constant for 10 min at 220°C, and then programmed to increase at a rate of 1°C/min to 240°C. The oil was analyzed with a split ratio of 40:1 while the SPME experiments were in splitless mode. The injector temperature was 250°C. Mass spectra were taken at 70 eV and the mass range was from *m*/*z* 35 to 450. The GC-FID analysis was carried out with capillary GC using an Agilent 6890N GC system (SEM Ltd., Istanbul, Turkey). Flame ionization detector (FID) temperature was set at 300°C in order to obtain the same elution order with GC/MS. Simultaneous injection was performed using the same column and appropriate operational conditions.

Identification and quantification of compounds

Compounds were identified by comparison of the chromatographic peaks retention times with those of authentic compounds analyzed under the same conditions, and by comparison of the retention indices with literature data. Comparisons of MS fragmentation patterns with those of standards and mass spectrum database search were performed using the Wiley GC-MS Library (Wiley, New York, NY, USA), MassFinder software 4.0 (Dr. Hochmuth Scientific Consulting, Hamburg), Adams Library, and NIST Library. Confirmation was also achieved by using the in-house "Başer Library of Essential Oil Constituents" database, obtained from chromatographic runs of pure compounds performed with the same equipment and conditions. A C_8–C_{40} *n*-alkane standard solution (Fluka, Buchs, Switzerland) was used to spike the samples for the determination of relative retention indices (RRI). Percent composition was obtained for each constituent on the basis of GC-FID analysis of the volatiles.

Results and Discussion

This is the first report on the composition of the volatiles obtained by HD and MSD-SPME techniques from *A. glabella* and *A. rupestris* growing in Kazakhstan. GC/FID and GC/MS analysis performed simultaneously on the isolated volatiles using HD and MSD-SPME from each Artemisia species showed that they have similar compositions with varying percentages of some components depending on the technique applied. This technique provided rapid recovery (3 min) of volatiles with the same composition as that obtained by hydrodistillation (in Clevenger apparatus) from 1.0 g of plant material. MSD-SPME was therefore well suitable for the extraction of aroma compounds from minute amounts (1.0 g) of aromatic plants. Furthermore, the isolated product can be directly used for GC/FID and GC/MS analysis without further preparation. MSD-SPME

is useful for the analytical determination of volatiles and not for the preparation of essential oils.The aim of the given research is to update data on the chemical composition of essential oils and volatiles from two species of *Artemisia* L. found in Kazakhstan (*A. glabella* and *A. rupestris*) produced by means of the conventional (hydrodistillation) and modern fast MSD-SPME extraction techniques. The yields of essential oils from *A. glabella* and *A. rupestris* obtained by a hydrodistillation were 0.2% and 0.1%, respectively. The comparative chemical composition analysis of *A. glabella* and *A. rupestris* is presented in Table 1 with their RRI values and a relative percentage.

The essential oil from *A. rupestris* obtained by means of a hydrodistillation represented a yellow color liquid with a pungent smell. Based on the gas chromatographic analysis, 69 components have been identified which makes 78.10% of the total oil amount (Table 1). The main part of essential oil contains sesquiterpenes (49.5%) and monoterpenes (13.9%), hydrocarbons (8.3%) and acids (6.4%). The major components of *A. rupestris* essential oil were myrcene (9.5%), β-elemene (5.4%), capric acid (5.1%), γ-costol (3.9%), selin-11-en-4α-ol (3.1%), spathulenol (3.8%), cedrol (3.3%), β-selinene (3.3%), valencene (3.7%).

Sixty-two volatile constituents received from *A. rupestris* by MSD-SPME have been determined. The main compounds were found to be as valencene (9.2%), α-selinene (5.7%), myrcene (5.5%), β-selinene (5.4%), (*Z*)-β-farnesene (4.9%) and β-elemene (3.6%).

The essential oil from *A. glabella* produced by means of a hydrodistillation represents the green mobile liquid with a pleasant and persistent scent. Gas chromatographic analysis revealed 75 components which represent 81.7% of the total oil amount. The main components were the following: 1,8-cineole (12.2%), cumin aldehyde (9.4%), α-terpineol (5.7%), borneol (5.2%), camphor (3.6%) and cumin alcohol (3.7%). Sixty-four volatile components of *A. glabella* have been identified by means of GC-FID/MS analysis from the volatiles obtained by MSD-SPME technique. The major components were cumin aldehyde (16.0%), 1,8-cineole (12.8%), cumin alcohol (6.9%), borneol (5.4%), camphor (5.2%) and α-terpineol (4.8%).

The research results showed that *A. glabella* essential oil mainly contains monoterpenes (65.8%) with a prevalence of the oxygenated ones (59.7%), and a low content of sesquiterpenes (12.1%), 6.5% of which are oxygenated. The volatile components with monoterpenes content of 75.3%, the majority of which are the oxygenated monoterpenes (71.6%), have been revealed during the MSD-SPME experiments.

The results from both species gave similar compound distributions except for their quantities.

Table 1. The chemical composition of essential oils and volatiles from *A. glabella* Kar. et Kir. and *A. rupestris* L. obtained by different methods

No	RRI	Components	*A. rupestris*		*A. glabella*		ID
			HD %	MSD-SPME %	HD %	MSD-SPME %	
1	1032	α-Pinene	0.3	-	2.0	1.0	a,b,c
2	1035	α-Thujene	-	-	0.1	-	a,b,c
3	1076	Camphene	-	-	0.4	0.2	a,b,c
4	1118	β-Pinene	-	-	0.3	0.1	a,b,c
5	1132	Sabinene	-	-	0.1	0.1	a,b,c
6	1138	Thuja-2,4(10)-diene	-	-	0.1	0.1	a,b,c
7	1174	Myrcene	9.5	5.5	-	-	a,b,c
8	1176	α-Phellandrene	-	-	0.3	0.2	a,b,c

No	RRI	Components	*A. rupestris*		*A. glabella*		ID
			HD %	MSD-SPME %	HD %	MSD-SPME %	
9	1188	α-Terpinene	-	-	0.3	0.1	a,b,c
10	1195	Dehydro-1,8-cineole	-	-	0.1	-	a,b,c
11	1213	1,8-Cineole	0.3	1.1	12.2	12.8	a,b,c
12	1218	β-Phellandrene	-	-	-	0.1	a,b,c
13	1255	γ-Terpinene	-	-	0.6	0.2	a,b,c
14	1280	*p*-Cymene	-	-	1.5	1.1	a,b,c
15	1290	Terpinolene	-	-	0.1	0.1	a,b,c
16	1299	2-Methylbutyl isovalerate	0.2	0.2	-	-	a,b,c
17	1303	Pentyl 3-methylbutanoate (= *Amyl isovalerate*)	-	0.1	-	-	a,b,c
18	1420	Presilphiperfol-7-ene	0.2	0.6	-	-	b,c
19	1348	6-Methyl-5-hepten-2-one	-	0.1	-	-	a,b,c
20	1350	1-Tridecene	-	0.1	-	-	a,b,c
21	1400	Nonanal	-	0.1	-	-	a,b,c
22	1437	α-Thujone	0.1	-	-	-	a,b,c
23	1444	7-α-(H)-Silphiperfol-5-ene	-	0.2	-	-	b,c
24	1506	Silphiperfol-6-ene	0.3	0.1	-	-	b,c
25	1450	*trans*-Linalool oxide (*Furanoid*)	-	-	0.1	0.1	a,b,c
26	1474	*trans*-Sabinene hydrate	-	-	0.3	0.3	a,b,c
27	1475	Acetic acid	-	0.8	-	-	a,b,c
28	1478	*cis*-Linalool oxide (*Furanoid*)	-	-	0.1	0.1	a,b,c
29	1490	Siphin-1-ene	-	0.3	-	-	b,c
30	1497	α-Copaene	-	-	0.3	0.1	a,b,c
31	1529	Dill ether	-	-	2.7	0.1	a,b,c
32	1532	Camphor	0.2	0.5	3.6	5.2	a,b,c
33	1553	Linalool	0.2	0.9	0.4	4.3	a,b,c
34	1556	*cis*-Sabinene hydrate	-	-	0.2	0.4	a,b,c
35	1565	Linalyl acetate	-	1.1	-	-	a,b,c
36	1568	1-Methyl-4-acetyl-cyclohex-1-ene	-	0.2	-	-	a,b,c
37	1571	*trans*-*p*-Menth-2-en-1-ol	-	-	0.1	0.2	a,b,c
38	1577	α-Cedrene	0.5	1.0	-	-	a,b,c
39	1582	*cis*-Chrysanthenyl acetate	-	2,3	0.1	0.1	a,b,c
40	1586	Pinocarvone	-	-	0.1	-	a,b,c
41	1590	Bornyl acetate	0.1	-	0.8	0.8	a,b,c
42	1600	β-Elemene	5.4	3.6	0.1	-	a,b,c
43	1611	Terpinen-4-ol	-	-	1.9	1.5	a,b,c
44	1612	β-Caryophyllene	0.3	0.5	0.5	0.3	a,b,c
45	1613	β-Cedrene	0.4	0.9	-	-	a,b,c
46	1617	Lavandulyl acetate	-	-	0.4	-	a,b,c
47	1620	3,9-Epoxy-*p*-menth-1-ene	-	-	-	0.2	a,b,c

No	RRI	Components	*A. rupestris*		*A. glabella*		ID
			HD %	MSD-SPME %	HD %	MSD-SPME %	
48	1628	Aromadendrene	0.2	0.7	-	-	a,b,c
49	1638	*cis-p*-Menth-2-en-1-ol	-	-	0.2	-	a,b,c
50	1645	6-Acetoxy-3,7-dimethyleneoctene*	-	0.9	-	-	c
51	1651	Bornyl isobutyrate	-	-	0.2	0.2	a,b,c
52	1655	Isobornyl propionate	-	-	0.3	0.3	a,b,c
53	1663	*cis*-Verbenol	-	-	0.2	-	a,b,c
54	1664	*trans*-Pinocarveol	-	-	0.3	-	a,b,c
55	1668	(*Z*)-β-Farnesene	2.3	4.9	-	-	a,b,c
56	1682	δ-Terpineol	-	-	-	0.3	a,b,c
57	1683	*trans*-Verbenol	-	-	0.9	0.7	a,b,c
58	1686	Lavandulol	-	-	1.8	1.4	a,b,c
59	1688	Selina-4,11-diene (=*4,11-Eudesmadiene*)	0.6	0.7	0.3	-	a,b,c
60	1694	Drima-7,9(11)-diene	-	-	0.7	0.4	b,c
61	1704	γ-Muurolene	0.4	-	-	0.4	a,b,c
62	1706	α-Terpineol	0.4	1.3	5.7	4.8	a,b,c
63	1709	α-Terpinyl acetate	0.2	-	-	-	a,b,c
64	1719	Borneol	0.3	0.6	5.2	5.4	a,b,c
65	1725	Verbenone	-	-	-	0.3	a,b,c
66	1726	Germacrene D	-	-	1.4	-	a,b,c
67	1740	Valencene	3.7	9.2	-	-	a,b,c
68	1741	β-Bisabolene	-	-	1.2	0.5	a,b,c
69	1742	β-Selinene	3.3	5.4	-	-	a,b,c
70	1744	α-Selinene	2.9	5.7	-	-	a,b,c
71	1744	Phellandral	-	-	0.5	-	a,b,c
72	1755	Bicyclogermacrene	0,3	-	-	-	a,b,c
73	1764	*cis*-Chrysanthenol	-	0.3	1.9	1.1	a,b,c
74	1765	Geranyl acetone	-	0.6	-	-	a,b,c
75	1766	Decanol	-	-	-	t	a,b,c
76	1773	δ-Cadinene	0.3	-	0.3	-	a,b,c
77	1776	γ-Cadinene	0.2	-	0.1	-	a,b,c
78	1783	β-Sesquiphellandrene	-	-	0.1	-	a,b,c
79	1785	7-*epi*-α-Selinene	0.2	-	-	-	a,b,c
80	1786	Neryl propionate	-	-	-	0.3	a,b,c
81	1788	*ar*-Curcumene	-	-	0.1	-	a,b,c
82	1802	Cuminaldehyde	0.4	0.5	9.4	16.0	a,b,c
83	1804	Myrtenol	-	-	0.3	0.6	a,b,c
84	1806	Methyl salicylate	-	0.4	-	-	a,b,c
85	1823	*p*-Mentha-1(7),5-dien-2-ol	-	-	0.1	0.2	a,b,c
86	1828	9-Decen-1-ol	-	-	-	0.2	a,b,c

No	RRI	Components	*A. rupestris*		*A. glabella*		ID
			HD %	MSD-SPME %	HD %	MSD-SPME %	
87	1830	Nootkatene	-	0.9	-	-	a,b,c
88	1831	Citronellyl butyrate	-	0.5	-	-	a,b,c
89	1834	Citronellyl isovalerate	1.2	-	-	-	a,b,c
90	1840	*trans*-p-Menth-2-en-7-ol	-	-	-	0.9	a,b,c
91	1857	Geraniol	-	-	0.3	0.3	a,b,c
92	1868	(*E*)-Geranyl acetone	0.1	-	-	-	a,b,c
93	1870	Hexanoic acid	-	-	-	0.2	a,b,c
94	1871	Neryl isovalerate	-	-	-	0.3	a,b,c
95	1900	Nonadecane	0.3	0.4	-	-	a,b,c
96	1912	*cis*-Dihydrocarveol	-	-	0.9	0.2	a,b,c
97	1921	α-Phellandrene epoxide	-	-	0.4	-	a,b,c
98	1933	Neryl valerate	-	-	-	0.1	a,b,c
99	1940	4-Isopropyl salicylaldehyde	-	-	0.7	0.2	a,b,c
100	1958	(*E*)-β-Ionone	-	0.3	-	-	a,b,c
101	1990	Cameroonan-7-α-ol	0.4	-	-	-	b,c
102	1973	1-Dodecanol	-	-	0.4	-	a,b,c
103	1992	Neophytadiene	-	0.2	-	-	a,b,c
104	2000	Eicosane	t	-	-	-	a,b,c
105	2008	Caryophyllene oxide	1.2	-	1.1	1.7	a,b,c
106	2030	Methyl eugenol	-	2,0	-	-	a,b,c
107	2037	Salvial-4(14)-en-1-one	1.2	-	-	0.2	a,b,c
108	2050	(*E*)-Nerolidol	0.4	0.4	2.0	1.3	a,b,c
109	2055	(8R,8αS)-8,8α-Dimethyl-3,4,6,7,8,8α-hexahydronaphthalen]-2(1H)-one*	-	1.7	-	-	c
110	2084	Octanoic acid	0.5	0.6	-	-	a,b,c
111	2100	Heneicosane	0.9	0.3	-	-	a,b,c
112	2110	Salviadienol	-	-	-	0.4	a,b,c
113	2113	Cumin alcohol	-	2.9	3.7	6.9	a,b,c
114	2131	Hexahydrofarnesyl acetone	0.7	-	0.5	-	a,b,c
115	2135	Hexadecanal	t	-	-	-	a,b,c
116	2143	Cedrol	3.3	-	-	-	a,b,c
117	2144	Rosifoliol	-	-	t	t	a,b,c
118	2146	Spathulenol	3.8	3.3	2.4	3.0	a,b,c
119	2149	α-Cedrol	-	2.0	-	-	a,b,c
120	2153	Neointermedeol	1.0	-	-	-	a,b,c
121	2179	1-Tetradecanol	-	-	0.3	-	a,b,c
122	2183	(*E*)-Sesquilavandulol	-	-	1.0	0.5	a,b,c
123	2185	1,3,5-Trimethoxybenzene	-	0.3	-	-	a,b,c
124	2186	Eugenol	-	0.3	0.6	-	a,b,c
125	2188	13-nor-Valenc-1(10)-en-11-one	-	1.3	-	-	c

No	RRI	Components	*A. rupestris*		*A. glabella*		ID
			HD %	MSD-SPME %	HD %	MSD-SPME %	
126	2192	Nonanoic acid	-	0.8	0.4	0.5	a,b,c
127	2225	Geranyl-α-terpinene*	-	0.6	0.5	-	a,b,c
128	2239	Carvacrol	-	-	-	0.8	a,b,c
129	2241	*p*-Isopropyl phenol	-	1.8	-	-	a,b,c
130	2245	4-Isopropyl phenol	-	-	3.0	4.1	a,b,c
131	2247	*trans*-α-Bergamotol	0.3	-	0.1	-	a,b,c
132	2255	α-Cadinol	0.2	-	-	-	a,b,c
133	2257	β-Eudesmol	-	-	0.2	-	a,b,c
134	2304	Torilenol (= *1-Hydroxy-6,8-cyclo-4(14)-eudesmene*)	0.4	0.3	0.2	-	a,b,c
135	2264	Intermedeol (=*11-Eudesmol-4*)	0.8	-	-	-	a,b,c
136	2273	Selin-11-en-4α-ol	3.1	1.8	-	-	a,b,c
137	2289	Alismol (=*Guaia-6,10(14)-diene-4-β-ol*)	2.3	-	-	-	a,b,c
138	2298	Decanoic acid	5.1	3.1	-	-	a,b,c
139	2300	Tricosane	1.1	-	-	-	a,b,c
140	2306	9-Geranyl-*p*-cymene	0.8	0.5	0.3	-	a,b,c
141	2316	(*Z*)-9-Tricosene	2.6	-	-	-	a,b,c
142	2324	Caryophylla-2(12),6(13)-dien-5α-ol (=*Caryophylladienol II*)	-	-	-	0.2	a,b,c
143	2325	13-nor-7,8-Epoxy-eremophil-1(10)-en-11-one	-	-	0.2	-	a,b,c
144	2355	(Z)-Nuciferyl acetate	-	0.8	-	-	a,b,c
145	2368	Eudesma-4(15),7-diene-1-β-ol	0.5	0.3	0.4	0.4	a,b,c
146	2389	*Caryophyllenol I* (=*Caryophylla-2(12),6-dien-5α-ol*)	-	-	-	0.2	a,b,c
147	2396	Caryophyllenol-II (=*Caryophylla-2(12),6-dien-5-β-ol*)	-	0.4	-	-	a,b,c
148	2466	Costol isomer	2.5	-	-	-	c
149	2500	Pentacosane	1.1	-	-	-	a,b,c
150	2510	9-Pentacosene	0.3	-	-	-	a,b,c
151	2515	Coumarin	-	1.0	-	-	b,c
152	2533	γ-Costol	3.9	-	-	-	a,b,c
153	2604	α-Costol	-	-	0.2	-	a,b,c
154	2606	β-Costol	1.2	-	-	-	a,b,c
155	2607	1-Octadecanol	t	-	-	-	a,b,c
156	2607	14-Hydroxy-δ-cadinene	t	-	-	-	a,b,c
157	2610	Benzophenone	t	-	-	-	a,b,c
158	2617	Tridecanoic acid	t	-	-	-	a,b,c
159	2622	Phytol	0.9	-	-	-	a,b,c
160	2655	Benzyl benzoate	0.4	-	-	-	a,b,c
161	2670	Tetradecanoic acid	0.8	-	-	-	a,b,c

No	RRI	Components	*A. rupestris*		*A. glabella*		ID
			HD %	MSD-SPME %	HD %	MSD-SPME %	
		(= *Myristic acid*)					
162	2700	Heptacosane	0.5	-	-	-	a,b,c
		Total	**78.1**	**80.2**	**81.7**	**85.3**	

RRI: Relative Retention Indices calculated against *n*-alkanes (C_8-C_{40}) on HP-Innowax column; **%** calculated from FID data;
a: Identification based on retention index of genuine compounds on the HP-Innowax column; **b**: Identification on the basis of computer matching of the mass spectra from Başer Library; **c**: Tentative identified on the basis of computer matching of the mass spectra from Adams, Mass Finder, Wiley and NIST libraries; **t**: Trace (< 0.1 %).

Comparison of the obtained results with the literature data (Xiao, et al., 2008; Bicchi, et al., 1985) showed the considerable differences in the chemical composition of *A. rupestris* essential oil extracted by various hydrodistillation methods. This difference in chemical composition of *A. rupestris* essential oil could be due to the growth locations of the wormwood. However, there was no significant difference observed in the composition of essential oil from *A. glabella* extracted by various methods.

Thus, the plant volatile compounds from *A. glabella* and *A. rupestris* have been extracted for the first time using the MSD-SPME technique. This method is the fast, cost-effective and economical in terms of raw materials; it also reduces the extraction time, while, allowing us to extract the maximum amount of volatiles.

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