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Eurasian Journal of Analytical Chemistry, 2018, 13(4), em37
ISSN:1306-3057
Research Paper https://doi.org/10.29333/ejac/92533

GC/MS Analysis of the Volatile Constituents from Arum Cyreniacum Flowers

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Received 1 April 2018 ▪ Accepted 30 April 2018

ABSTRACT

Arum cyreniacum (family Araceae) is a Libyan plant have many medicinal uses. The volatile constituents of the flowers of the plant were extracted separately with two different solvents (n-hexane and chloroform). The two volatiles were analyzed using GC/MS. It was found that the volatile constituents of the flowers extracted with n-hexane consists of 32 compounds in which, the oxygenated monoterpenes is the most abundant class (51.43%) with 1,8-cineole as a major compound (43.32%), while the chloroform extract substantiated the presence of esters hydrocarbons and sterols as main groups (44.95%, 30.38% and 16.05% respectively).

Keywords: *Arum cyreniacum*, Araceae, volatile constituents, GC/MS

INTRODUCTION

The genus *Arum* is an important genus in the family *Araceae*. This genus is composed of 28 species, largely distributed in Europe, North Africa, Middle East and Central Asia. This genus is represented in Libya by only one endemic species known as *Arum* cyreniacum [6, 7].

By reviewing the literature about the chemical constituents and biological activity of *Arum* genus, it was found that, the plants of this genus have many biological activity as treatment of rheumatic pain, diaphoretic, diuretic, expectorant, strongly purgative and vermifuge, affect on the cells of the immune system, antioxidant activity, anti-cancer activity (against hepato carcinoma, breast carcinoma cells and lymphoplasticleukemia) and have antimicrobial activity [11, 12, 13]. The phytochemicals like volatile oil, terpenes, flavonoids, lectins and alkaloids were studied in Arum genus. Kite et al. [8-10] studied the odours of many *Arum* species and they identified 36 compounds, in which butanoïc acid esters, 1-decene, terpenes (citronellene and its derivatives), *p*-cresol, methyl salicylate, indole and 2-heptanone are common compounds. Some species appear clearly different like *A. creticum* or *A. palaestinum*, whose rotten fruit odour is due to benzyl alcohol and ethyl acetate. *Arum rupicola* var. *rupicola* is also different because of a mixture of various sesquiterpenes even if *p*-cresol is abundant [14].

Skatole (3-methyl indole) methyl amine and ammonia have been detected in the condensates produced from cuts of *A. italicum* and *A. dioscoridisi*. Fifty-six compounds were identified from the odour of *A. maculatum*. The major components being: 2-heptanone, indole, *p*.cresol, Also, several ketones and esters were detected and the majority of the compounds were terpenoids [8]. By reviewing the available literature, it was found nothing about the chemical constituents of the volatiles from the flowers of *Arum cyrenicum* so the aim of this study is the isolation and identification of volatile constituents from the *Arum cyrenicum* flowers using solvent extraction.

MATERIALS AND METHODS

Plant material: *Arum cyrinaicum* was collected from Aljabal AlAkhder region - Libya during the flowering stage. The plant was kindly identified and authenticated by Dr. Naser Elshekhi, lecturer of taxonomy at Botany Dept,

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Table 1. GC/MS data of the volatiles of n-hexane extract *of A. cyrenaicum* flowers

No.	Compounds	R_t(min)	Rel.%	Mass spectral data		
				M^+	B.P.	Fragments (%)
1	α-Pinene	10.44	8.27	136	93	27(14),77(14).92(14)
2	1,8-cineole	12.54	43.32	154	43	41(26),55(23),81(38)
3	ᵞ-Terpinene	13.58	2.06	136	93	43(23),77(32),121(26)
4	Linalool	15.20	1.85	154	71	41(85),55(64),93(55)
5	*Cis*-sabinol	16.51	1.97	152	92	41(47),81(58),109(29)
6	Umbellunone	17.30	0.50	150	108	79(28),91(51),135(25)
7	Isoborneol	17.51	0.55	154	95	41(38),43(23),110(20)
8	(-)-4-Terpineol	17.91	2.70	154	71	43(41),55(23),93(47),111(55)
9	1-methyl -histidine,	18.18	1.83	169	95	42(20),54(11),96(88)
10	p-cymenol	18.48	1.69	150	43	39(11),91(17),135(26)
11	Myrtenol	18.55	0.56	152	79	41(26),91(41),108(26)
12	(6-Hydroxymethyl-2,3-dimethyl phenyl)methanol	20.17	0.27	166	148	77(17),91(38),105(41)
13	Linalyl acetate	20.67	5.99	196	93	43(52),69(23),80(38),121(41)
14	1-Methoxy-4,4a,5,6,7,8-hexa hydro-2(3H)-naphthalenone	21.27	0.47	180	41	27(73),39(91),79(85),109(67)
15	Cyclohexene.4-(1,1-dimethyl ethyl	23.20	0.45	138	57	41(38),67(35),81(26),67(35)
16	α-Terbinenyl acetate	23.76	2.42	196	121	59(20),93(82),136(61)
17	4-tButylcyclohexyl acetate	24.36	0.88	198	57	43(35),67(35),82(0)
18	*trans*-caryophyllene	25.94	0.29	204	93	53(35),69(67),79(85),91(97)
19	α- Muurolene	27.22	1.57	204	161	55(26),79(55),91(64),105(67)
20	α-curcumene	28.32	0.33	204	119	41(55),69(29),93(52)
21	Phenol,2,6-bis(1,1-dimethylethyl 4-methyl	28.83	0.34	220	205	57(23),145(0.08),220(26)
22	Epiglobulol	30.23	1.02	222	43	41(67),55(41),69(52),82(58)
23	(-)-Spathulenol	30.82	12.12	220	43	41(70),55(29),69(35),91(41)
24	Globulol	30.97	3.00	222	43	41(76),109(55),204(44)
25	Veridiflorol	31.17	0.52	222	109	43(96),161(72),204(22)
26	Ledol	31.47	0.52	222	43	41(73),109(44),204(21)
27	á-Nootkatol	32.50	0.60	222	119	91(52),161(48),202(16)
28	Longipinocarvone	35.09	0.78	220	41	55(61),79(52),91(47),134(76)
29	Methyl palmitate	39.90	0.31	270	74	43(17),87(85),143(20)
30	Methyl oleate	43.93	0.28	296	55	69(78),83(56),264(27)
31	Tricosane	48.10	0.34	324	57	71(64),85(44),99(14)
32	Heptacosane	52.06	0.73	380	43	57(94),71(54),85(37)
33	Unidentified compounds		1.47			

R_t = Retention time, M = Molecular ion peak, B.P. = Base peak.

Faculty of Science, Binghazi University. A voucher speciemin was deposited at the herbarium of faculty of science, Sirt University. The flowers of the plant were separated from the aerial parts, air dried and grinded to a fine powder for extraction.

Extraction of volatiles using two different solvents: Two batches of about 50 g each of powdered dry flowers, one of it was macerated in 250 ml n-hexane and the other was macerated in chloroform for 24 hr. two times. The solvents were evaporated in vacuo at about 30 °C, the pale yellow extract and dark extract (0.5 g and 1.1 g respectively) were subjected to GC/MC analysis using the following conditions:

Gas chromatography: Instrument: TRASC GC, Splitless Mode. Column: BD-5 capillary column (30 m, 0.25 mm internal diameter, 0.25 µm film). Temperature program: Injector 50°C, Initial Temp. 38°C, Rate, 2°C/min. to 200°C, Final Temp. 200°C for 5 min. Flow gas: Helium at 10 ml/min.

Mass spectroscopy: Instrument: TRACE DSQ. Full scan 50-450, positive ion, Ion source 200°C, mass transpher line 200 °C. Library: NIST. The mass spectra were measured in EI scan Mode at (70 e. v.) from 50-450 mass unit and are summarized in **Table 1** and **2**.

Table 2. GC/MS data of the volatile of *A. cyrenaicum* flowers extracted with chloroform

No.	Compounds	R_t(min)	Rel.%	Mass spectral data		
				M^+	B.P.	Fragments (%)
1	Octadecane	24.27	0.94	254	57	43(96),71(92), 254(14)
2	murrangatin isovalerate	28.86	7.95	360	205	57(46),121(23),221(8)
3	Docosane	34.54	2.06	310	43	57(93), 71(82),85(26)
4	6,10,14-trimethyl- 2-Pentadecanone	35.70	4.66	268	58	43(55),109(44),250(15)
5	**Methyl** isohexadecanoate	39.90	3.18	270	74	41(36),87(88),220(18)
6	Ethyl palmitate	41.50	13.60	284	88	69(28),101(51),157(12)
7	Isopropyl Palmitate	42.20	7.12	298	43	60(54),102(83),256(34)
8	Pentacosane	43.84	2.50	352	43	57(91),71(63),85(47)
9	Ethyl linoleate	45.28	3.80	308	67	41(72),81(83),95(68)
10	eicosyl Oleate	45.41	1.59	562	57	69(91),97(78),264(56)
11	Isopropyl linoleate	45.91	3.87	322	67	81(86),95(71),279(36)
12	Myristyl oleate	46.01	2.88	478	55	67(97),91(78),269(41)
13	eicosyl Octadecanoate	46.60	0.96	564	285	57(92), 97(83),286(11)
14	3-acetoxy-7,8-Epoxylanostan-11-ol	48.13	8.36	502	44	57(93),244(71),304(15)
15	Nonacosane	50.14	1.61	408	41	71(88),85(66),99(55)
16	Tetratriacontane	52.08	14.72	478	57	71(91),85(75),99(64)
17	Dioctyl phthalate	53.13	2.39	390	149	57(65),167(54),279(34)
18	17-Pentatriacontene	55.46	2.76	490	43	69(95),83(82),97(77)
19	Tetratetracontane	55.75	7.85	618	57	69(86),83(75),97(24)
20	Ethyl iso-allocholate	59.18	4.00	436	43	55(85),107(59),400(12)
21	Anodendroside G, monoacetate	62.13	1.18	602	71	86(93),207(56),515(86)
22	17-Phenyltritriacontane	62.52	0.69	540	91	43(67),105(81),315(28)
23	19.68 Ergost-5-en-3-ol	64.75	1.69	400	43	55(79), 95(56), 382(34)

R_t = Retention time, M = Molecular ion peak, B.P. = Base peak.

RESULTS AND DISCUSSION

The data in **Table 1** proved that, the volatile constituents of the flowers extracted with n-hexane consists of 35 compounds (32 of them were identified and representing about 98.53% while the other three compounds were unidentified which constituted 1.47%) belonging to many classes as follow: the oxygenated monoterpenes is the most abundant class (51.43%) with 1,8-cineole as a major compound (43.32%), the second class is oxygenated sesquiterpenes (18.54%) in which Spathulenol is the highest one (12.12%) followed by the esters group where it constitute about 11.86% with the principle compound viz. Linalyl acetate. The nonoxygenated monoterpenes, aromatics and nitrogenous components were found to form 10.33%, 2.30% and 1.83% respectively.

While the data in **Table 2** representing the chemical composition of volatile constituents of flowers extracted with chloroform substantiated the presence of esters hydrocarbons and sterols as main groups (44.95%, 30.38% and 14.05% respectively) with ethyl palmitate (13.60%), tetratriacontane (n-C34, 14.72%) and 3-acetoxy-7,8-Epoxylanostan-11-ol (8.36%).

If we compare the chemical constituents of volatile in both solvents, it is concluded that, the oxygenated monoterpenes and oxygenated sesquiterpenes are main in case of hexane while these compounds are not present in case of chloroform. Also, the steroidal compounds are absent in case of n-hexane extraction while in case of chloroform extraction is consider as a main group where it represented about 14.05%. It is noted that, these data were disagree with that reported by Kite et al.in 1995 where they analyzed the odour of *A. maculatum* by non-invasive headspace and they identified the major components as: 2-heptanone, indole (each comprising 8-23% of the volatiles among the inflorescences studied) and bicyclogermacrene (10-14%), *p*.crsol was also a notable odouors. Component (0.2-6%) as were several ketones and ester, but simple aliphatic amines were not detected; the majority of the compounds were terpenoids [9]. Also, Diaz & Kite, in 2002, were found that, the odor composition of *A. italicum* differs from A. maculatum. The main compounds were: 1 – decene, methyl butyrate, and ß – citronellene [11]. These differences may be due to the method of extraction of the volatile constituents, where the headspace is more efficient for the aroma compound while the solvent extraction may resulted in less volatile components. **In conclusion** this is the first report about the study of the chemical constituents of volatiles extracted from the flowers of *Arum cyreniacum*.

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