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Chemical Composition of the Essential Oils from the Flower, Leaf and Stem of *Aquilegia olympica* Grown in Turkey

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Essential oil was extracted from the flower, leaf and stem of *Aquilegia olympica* by hydrodistillation and analyzed by GC-FID and GC-MS. A total of 64, 40 and 52 compounds were identified, constituting over 88.4, 87.3 and 95.3 % of oil composition of the flower, leaf and stem of *A. olympica*, respectively. Oxygenated monoterpes were shown to be the main group of terpenoid constituents in the ratio of 9.9, 33.6 and 32.1 %, respectively. But, the major components of the oils of *A. olympica* were linalool (6.5, 10.7 and 23.1 %) and palmitic acid (20.1, 26.3 and 10.5 %, respectively).

Key Words: *Aquilegia olympica* Boiss., Essential oil, GC-FID, GC-MS.

INTRODUCTION

Aquilegia L. (Ranunculaceae) represented with only one species in Turkey. It is a perennial herb with erect woody stocks. Many taxa of *Aquilegia* are used as ornamental plants because of its very attractive flowers in a varied colour range. The flowers of *Aquilegia olympica* Boiss. are spurred, bell-shaped and white-blue colour. This alpine species was firstly described from Turkey and mainly known from Caucasus[1]. Stems of *A. olympica* has been used as a folk medicine (in Trabzon, Turkey) to cure constipation. As well, it has diuretic and diaphoretic effects[2].

Previous phytochemical studies on the aerial parts (leaf, flower and root) of species of the *Aquilegia* L. genus (*A. vulgaris* L., *A. alpina* L., *A. canadensis* L., *A. caerulea* James, *A. flabellata* Sieb. et Zucc., *A. hybrida* Scott-Elliot, *A. olympica* Boiss., *A. pyreneica* D.C., *A. vitoleili* L., *A. atrata* W.D.J. Koch) have shown the isolation and identification of a number of phenolic, flavonoids and alkaloid compounds[3-6]. The literature search revealed no reports are available on the essential oil composition from the flower, leaf and stem parts of the *A. olympica*. The crude

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essential oils were investigated by GC-FID and GC-MS technique[7-17]. The identification of the substances was performed by comparison of retention indexes on HB-5 column (determined relatively to the retention times of a series of *n*-alkanes), authentic compounds and mass spectra with literature (Nist and Wiley)[7-17]. In the present work, we report the constituents of the essential oils of the flower, leave and stem from *A. olympica*.

EXPERIMENTAL

Aquilegia olympica Boiss. was collected in Çaykara-Arpaözü Village, Trabzon, Turkey (at heights of *ca.* 2100 m) in the northeastern part of Turkey on June 10, 2008. The plant was authenticated by Prof. S. Terzioglu1. Voucher specimen was deposited in the Herbarium of the Faculty of Forestry, KATO (KATO: 11672), Karadeniz Technical University, Turkey.

Isolation of the essential oils: The fresh plant materials were separated into flower, leaf and stem parts and they were freezed with liquid nitrogen and then grounded into small pieces. The essential oils from fresh aerial parts (*ca.* 110 g, each) of *A. olympica* were isolated by hydrodistillation in a Clevenger-type apparatus[8,9] with cooling bath (-15 ºC) system (4 h) (yields: 0.12, 0.08 and 0.10 % (v/w), respectively). The obtained oils were extracted with HPLC grade *n*-hexane (0.5 mL) and dried over anhydrous sodium sulphate and stored at 4-6 ºC in a sealed brown vial.

Gas chromatography (GC): The capillary GC-FID analysis was performed using an Agilent-5973 Network System, equipped with a FID (supplied with air and hydrogen of high purity) and a split inlet. The chromatographic column used for the analysis was HP-5 capillary column (30 m × 0.32 mm i.d., film thickness 0.25 µm). Helium was used as carrier gas, at a flow rate of 1 mL/min. The injections were performed in splitless mode at 230 °C. One µL essential oil solution in hexane (HPLC grade) was injected and analyzed with the column held initially at 60 °C for 2 min and then increased to 240 °C with a 3 °C/min heating ramp. The identity of each compound was supported by comparing their retention indices (RI) with published values[7-17]. The sample was analyzed twice and the percentage composition of oil was computed from the GC peak areas without using correction factors.

Gas chromatography-mass spectrometry (GC/MS): GC-MS analysis was performed using an Agilent-5973 Network System. A mass spectrometer with an ion trap detector in full scan mode under electron impact ionization (70 eV) was used. The chromatographic column used for the analysis was HP-5 capillary column (30 m × 0.32 mm i.d., film thickness 0.25 µm). Helium was used as carrier gas, at a flow rate of 1 mL/min. The injections were performed in splitless mode at 230 °C. One µL essential oil solution in hexane (HPLC grade) was injected and analyzed with the column held initially at 60 °C for 2 min and then increased to 240 °C with a 3 °C/min heating ramp.

Identification of constituents: Retention indices of all the components were determined by Kovats method using *n*-alkanes (C_6-C_{32}) as standards. The constituents of the oils were identified by comparison of their mass spectra with those of mass spectral libraries (NIST and Wiley 7NL), authentic compounds (α-pinene, limonene, γ-terpinene, linalool, α-terpineol, geraniol, tridecane, tetrdecane, hexadecane, heptadecane, docosane, tricosane, tetracosane and pentacosane) and with data published in the literature[7-17].

RESULTS AND DISCUSSION

The GC-FID and GC-MS analysis of the essential oils from the flower, leaf and stem of *A. olympica* are presented in Table-1. Altogether, 83 essential compounds were identified by GC and GC-MS with HP-5 column. The flower oil was revealed the presence of 64 components, representing 88.4 % of the total oil. The major compounds of the flower oil were palmitic acid (20.1 %), *n*-octanol (16.3 %), linalool (6.5 %), ethyl octadecanoate (4.8 %), humulene epoxide II (2.3 %). Fifty two components accounting for 95.3 % of constituents of the stem oil were identified and the major compounds were palmitic acid (26.3 %), ethyl octadecanoate (15.2 %), linalool (10.7 %), *n*-octanol (5.4 %) and pentadecanal (2.7 %). On the other hands, 40 compounds were identified in the leaf, representing 87.3 % of the total oil. The major constituents of the leaf oil were linalool (23.1 %), 2-acetylmethyl-3-carene (11.1 %), palmitic acid (10.5 %), α-terpineol (6.6 %) and geranyl formate (4.6 %). The essential oil of the leaf was constituted by fewer compounds with respect to the flower and stem (40 *versus* 64 and 52). Oxygenated monoterpenes (9.9, 33.6 and 14.8 %, respectively) were the major constituent identified in terpenoids of oils.

The chemical class distributions of the essential oils of the constituents are summarized in Table-2. The compounds were separated into six classes, which were terpenoids (monoterpene hydrocarbons, oxygenated monoterpenes, sesquiterpene hydrocarbons, oxygenated sesquiterpene, diterpene hydrocarbons, oxygenated diterpene, terpene related compounds), aldehydes, carboxylic acids, esters, hydrocarbons and others (Table-2). The oxygenated monoterpenes and carboxylic acids were the major constituents in all three part of the plant in the ratio of 9.9, 33.6, 14.8 and 21.5, 14.0, 31.5 %, respectively. The numbers of the identified terpenoids in the flower, leaf and stem of *A. olympica* were 39, 20 and 27 compounds in the ratio of 29.7, 62.9 and 24.3 %, respectively. Twenty eight components were common to all tree part of plant with the total ratio of 67.4, 74.3 and 85.9 %, respectively. It could be concluded that the compositions of the volatile oils extracted from the flower, leaf and stem were different as expected. All parts of the oils were rich in non-terpenoid components mostly aldehydes, carboxylic acids, esters, hydrocarbons and others in the total ratio of 58.7, 24.4 and 71.0 %, respectively.

TABLE-1
IDENTIFIED COMPONENTS IN THE ESSENTIAL OILS OF *A. olympica*[a,b]

Compounds	Area (%)			RI	
	Flower	Leaf	Stem	Exp.	Lit.
Monoterpenes					
α-Pinene[c]	0.2		0.3	936	939
Limonene[c]	0.2		1.1	1027	1029
γ-Terpinenec[c]			0.3	1058	1060
Allo-ocimene	0.1			1134	1132
Monoterpenoids					
Linalool[c]	6.5	23.1	10.7	1096	1097
cis-Rose oxide			0.1	1108	1108
trans-Rose oxide	0.1		0.1	1125	1126
cis-Limonene oxide	0.1		0.1	1140	1137
trans-Pinocamphone	0.5	1.2	1.6	1162	1163
Terpinen-4-ol		0.2	0.6	1178	1177
α-Terpineol[c]	1.9	6.6	1.3	1191	1189
Safranal		0.1		1201	1197
Geraniol[c]	0.1	2.4	0.2	1255	1253
3-Bornanone			0.1	1286	MS
(*E*)-β-Damascenone	0.2			1388	1385
2,5-Bornanedione	0.5			1581	MS
Sesquiterpenes					
α-Copaene	0.2			1379	1377
(*E*)-β-Caryophyllene	0.1	4.6		1417	1419
β-Longipinene	0.1			1402	1401
cis-Thujopsene	0.8			1429	1431
(*E*)-α-Bergamotene	0.3			1435	1435
α-Humulene	0.3			1452	1455
(*E*)-β-Farnesene	0.8			1460	1457
α-Acoradiene		0.1		1464	1466
γ-Muurolene	1.3		0.2	1479	1480
Ar-Curcumene	0.4			1483	1481
α-Muurolene	0.9	0.1	0.1	1498	1500
δ-Amorphene		0.2		1512	1512
(*Z*)-α-Bisabolene	2.2			1509	1507
δ-cadinene	1.1		0.3	1524	1523
(*E*)-γ-Bisabolene	0.2	0.1	0.2	1532	1531
(*E*)-Nerolidol	0.8			1565	1563
Sesquiterpenoids					
(*E*)-Sesquilavandulol	0.5			1633	1633
Cedr-8(15)-en-10-ol	0.5			1649	1652
α-Bisabolol	0.6			1687	1686
(*Z*,*E*)-Farnesol	0.1			1701	1701
(*Z*)-Nuciferol	0.9			1724	1726
α-Oxobisabolone	0.4			1747	1748
Diterpenes					
Abieta-8,12-diene	1.0		1.1	2025	2023
Abietatriene	0.7	1.3	0.5	2053	2057

Diterpenoid					
Agathadiol			0.2	2356	MS
Terpene related compounds					
Isogeijerene C		0.1	1.5	1247	1250
α-Ionene		0.3	0.2	1257	1255
Neryl formate	0.5			1283	1282
Dihydroedulan I		2.8	0.2	1290	1292
Geranyl formate	0.1	4.6	2.6	1296	1298
Solanone		2.7	0.1	1371	1374
2-Acetylmethyl-3-carene	1.6	11.1	0.2	1396	MS
(*E*)-β-Ionone	0.2	0.8	0.1	1489	1489
Humulene epoxide II	2.3			1608	1608
Hexahydro farnesyl acetone	0.4	0.5	0.3	1845	1847
Others					
Benzaldehyde	0.1	0.3	0.4	961	960
2-Pentylfuran	0.8	0.1	1.4	991	993
Octanal	0.7		0.2	999	999
Benzeneacetaldehyde	0.6	1.3	1.7	1042	1042
n-Octanol	16.3	0.4	5.4	1071	1068
2*E*, 6*Z*-Nonadienal	0.2			1155	1156
Decanal	0.1		0.1	1204	1202
Tridecane[c]	0.1			1302	1300
3'-Methoxy acetophenone	0.6			1301	1298
2*E*, 4*E*-Decadienal			0.1	1314	1317
4'-Methoxy acetophenone			0.4	1352	1350
Tetradecane[c]	0.1	0.1	0.3	1400	1400
Dodecanoic acid		0.3		1580	1580
Hexadecane[c]			0.2	1600	1600
Tetradecanal		0.5		1612	1613
Heptadecane[c]	1.9		0.5	1698	1700
Pentadecanal	1.5	1.2	2.7	1715	1713
Methyl tetradecanoate	0.5			1727	1724
Tetradecanoic acid	0.2	1.3	0.4	1770	1768
Octadecanone			0.2	1798	1800
Pentadecanoic acid	1.2	0.8	3.6	1868	1866
Ethyl linoleolate	2.1	1.0	0.9	1892	1891
Methyl hexadecanoate	1.1	0.5	0.5	1924	1924
Palmitic acid	20.1	10.5	26.3	1987	1982
Methyl linoleate	0.6	0.7	1.5	2095	2096
Methyl octadecanoate	0.3			2127	2125
Oleic acid		1.1	1.2	2141	2144
Ethyl octadecanoate	4.8	2.3	15.2	2197	2197
Docosane[c]	1.0	0.4	5.4	2198	2200
Tricosane[c]	0.8	0.7	0.2	2300	2300
Tetracosane[c]	0.7	0.3	0.1	2399	2400
Pentacosane[c]	2.3	0.6	2.1	2501	2500

[a]RI calculated from retention times relative to that of *n*-alkanes (C_6-C_{32}) on the non-polar HP-5 column. [b]Percentages obtained by FID peak-area normalization. [c]Identified by authentic samples.

TABLE-2
CHEMICAL CLASS DISTRIBUTION IN THE ESSENTIAL OILS OF *A. olympica*

Constituents	Flower		Leaf		Stem	
	% Area	NC[a]	% Area	NC[a]	% Area	NC[a]
Terpenoids						
Monoterpene hydrocarbons	0.5	3	-	-	1.7	3
Oxygenated monoterpenes	9.9	8	33.6	6	14.8	9
Sesquiterpene hydrocarbons	9.5	14	5.1	5	0.8	4
Oxygenated sesquiterpenes	3.0	6	-	-	-	-
Diterpene hydrocarbons	1.7	2	1.3	1	1.6	2
Oxygenated diterpene	-	-	-	-	0.2	1
Terpene related compounds	5.1	6	22.9	8	5.2	8
Aldehydes	3.2	6	3.3	4	5.2	6
Carboxylic acids	21.5	3	14.0	5	31.5	4
Esters	9.4	6	4.5	4	18.1	4
Hydrocarbons	6.9	7	2.1	5	8.8	7
Others	17.7	3	0.5	2	7.4	4
Total	88.4	64	87.3	40	95.3	52

[a]NC = Number of compounds.

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