ESSENTIAL OILS OF TWO Hypericum SPECIES FROM UZBEKISTAN*

K. H. C. Baser, T. Ozek, H. R. Nuriddinov, and A. B. Demirci

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The water-distilled essential oils from aerial parts of two Hypericum species (Hypericaceae) have been analyzed by GC/MS. The main components of the essential oils of Hypericum scabrum L. were α -pinene - 11.2%; spathulenol - 7.2%; p-cymene - 6.1%; acetophenone - 4.8%; carvacrol - 4.7%. The essential oil of Hypericum perforatum L. contains as the main components β -caryophyllene - 11.7%; caryophellene oxide - 6.3%; spathulenol - 6.0%; α -pinene - 5.0%.

Key words: *Hypericum scabrum*, *Hypericum perforatum*, essential oil, GC/MS.

Hypericum (Hypericaceae) species have been used for a long time in folk medicine. In recent years H. perforatum has been the ingredient of modern medicines for the treatment of mild depression. The essential oil of H. perforatum has previously been investigated [1-5]. In a recent study [3], α -pinene (61.7%) was reported as the main constituent of the oil in the plant material of Turkish origin. Hypericum perforatum L is included in the Pharmacopoeias of Russia, Chekhiya, Romania, Poland, and France [4]. In Uzbekistan, a skin remedy is prepared from ashes of its herbal parts. It is used as an antihelminthic in veterinary medicine.

The yield and physicochemical properties and oil composition of *Hypericum scabrum L*. of Turkish origin has previously been reported [3, 6]. It was found to contain α -pinene (71.6%) as the main constituent [3].

Here we report our results on the essential oil composition of *H. scabrum* and *H. perforatum* from Uzbekistan. *H. scabrum* collected in Khisor mountain in the Kashkadar'ya region of Uzbekistan yielded 0.2% essential oil and *H. perforatum* collected in Nanai village in Chimgan mountains in Tashkent region yielded 0.1% essential oil. The composition of the oils is given in Table 1.

A total of 104 and 106 components were characterized representing 85.9% and 89.6% of the essential oils in H. scabrum L. and H. perforatum L., respectively. α -Pinene (11.2%), spathulenol (7.2%), p-cymene (6.1%), acetophenone (4.8%), carvacrol (4.7%) were the main constituents of the essential oil of H. scabrum. The main components of the essential oil of H. perforatum were β -caryophyllene (11.7%), caryophyllene oxide (6.3%), spathulenol (6.0%), α -pinene (5.0%).

Caryophyllene and pinene rich oils of *H. perforatum* have been reported [1-5]. Our results are in agreement with the results reporting sesquiterpenes as the main constituents [1].

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¹⁾ Medicinal and Aromatic Plant and Drug Research Centre (TBAM), Anadolu University, 26470, Eskisehir, Turkey. 2) Institute of the Chemistry of Plant Substances, Academy of Sciences, 700170, Tashkent, Republic of Uzbekistan. Published in Khimiya Prirodnykh Soedinenii, No. 1, pp. 43-45, January-February, 2002. Original article submitted February 12, 2002.

TABLE 1. The Composition of the Essential Oil of *Hypericum* Species

RRI	Compound	A, (%)	B,(%)	RRI	Compound	A, (%)	B, (%)
965	3-Methylnonane	-	0.1	1628	Aromadendrene	0.6	0.6
1032	lpha-Pinene	11.2	5.0	1638	cis-p-Menth-2-en-1-ol	0.1	-
1065	2-Methyldecane	-	0.2	1648	Myrtenal	1.1	0.1
1076	Camphene	0.2	-	1668	(Z) - β -Farnesene	-	1.8
1093	Hexanal	Tr.	-	1671	Acetophenone	4.8	-
1100	Undecane	0.3	0.2	1674	<i>p</i> -Mentha-1,5-dien-8-ol	0.6	0.1
1118	eta-Pinene	0.4	0.9	1683	trans-Verbenol	1.6	0.2
1174	Myrcene	0.1	0.5	1687	lpha-Humulene	-	0.6
1188	α-Terpinene	0.2	Tr	1700	p-Mentha-1,8-dien-4-ol	0.3	-
1203	Limonene	0.9	0.6		(limonen-4-ol)		
1213	1,8-Cineole	0.1	Tr.	1704	γ-Muurolene	1.1	3.6
1218	β -Phellandrene	-	Tr.	1706	α -Terpineol	0.7	-
1224	o-Mentha-1(7),5,8-triene	0.1	-	1711	γ-Himachalene	-	0.1
1225	(Z)-3-Hexenal	0.2	_	1719	Borneol	1.5	-
1244	Amylfuran(2-pentylfuran)	Tr.	Tr.	1725	Verbenone	2.7	_
1246	(Z) - β -Ocimene	-	0.1	1726	Germacrene D	0.4	2.2
1255	γ-Terpinene	0.9	0.2	1740	α -Muurolene	1.1	-
1266	(E)- β -Ocimene	-	0.7	1742	β -Silenene	-	1.8
1280	<i>p</i> -Cymene	6.1	0.7	1744	α -Silenene	_	1.8
1290	Terpinolene	0.2	0.2	1751	Carvone	0.3	-
1296	Octanal	Tr.	-	1755	Bicyclogermacrene	-	0.2
1391	(Z)-3-Hexenol	-	Tr.	1758	(E,E)-α-Farnesene	-	0.2
1391	2-Nonanone	0.1	-	1758	(E)-2-undecenal	-	0.1
1400	2-Nonanone Nonanal	0.1	0.4	1764	Decanol	0.2	
1400		0.1	0.4	1700	δ -Cadinene	1.0	2.1
	γ-Campholene aldehyde						
1441	(E)-2-Octenal	- 0.1	0.1	1776	γ-Cadinene	1.2	2.0
1451	β -Thujone	0.1	-	1797	<i>p</i> -Methyl acetophenone	0.4	-
1466	α-Cubebene	- 0.1	0.1	1798	Methyl salicylate	-	Tr.
1467	6-Methyl-5-hepten-2-ol	0.1	-	1804	Myrtenol	1.1	0.4
1478	cis-Linalool oxide (furanoid)	Tr.	-	1810	3,7-Guaiadiene	-	0.3
1479	(E,Z)-2,4-Heptadienal	Tr.	-	1815	2-Tridecanone	Tr.	-
1493	α-Ylangene	-	0.2	1827	(E,E)-2,4-Decadienal	0.1	0.1
1496	3-Nonanol	Tr.	-	1845	trans-Carveol	1.4	0.1
1497	α-Copaene	-	0.7	1853	cis-Calamenene	-	0.7
1499	α-Campholene aldehyde	2.3	0.5	1857	Geraniol	-	0.1
1503	Isomenthone	-	0.6	1864	<i>p</i> -Cymen-8-ol	2.3	-
1521	2-Nonanol	0.1	-	1868	(E)-Geranyl acetone	0.1	0.2
1532	Camphor	1.3	0.1	1882	cis-Carveol	0.1	-
1535	eta-Bourbonene	0.2	0.1	1896	cis-p-Mentha-1(7),8-diene-2-ol	Tr.	-
1548	(E)-2-Nonenal	-	0.2	1902	Benzyl isovalerate	-	0.1
1553	Linalool	0.3	0.2	1929	2-methyl butyl benzoate	-	0.1
1562	Isopinocamphone	0.1	-	1941	lpha-Calacorene	0.9	0.6
1562	Octanol	-	0.1	1945	1,5-Epoxy-salvial(4)14-ene	0.1	0.4
1565	Linalyl acetate	-	Tr.	1958	(E)- β -Ionone	-	0.2
1571	trans-p-Menth-2-en-1-ol	Tr.	Tr.	1969	cis-Jasmone	-	0.1
1586	Pinocarvone	0.7	0.2	1973	Dodecanol	0.2	1.4
1587	eta-Funebrene	-	1.1	1981	Heptanoic acid	0.2	-
1591	Fenchyl alcohol	0.5	-	1984	γ-Calacorene	0.2	0.1
1599	(E,Z)-2,6-Nonadienal	0.1	-	1988	2-Phenylethyl-2-methyl-butyrate	-	Tr.
1602	6-Methyl-3,5-heptadien-2-one	0.1	_	2001	Isocaryophyllene oxide	0.9	-
1611	Terpinen-4-ol	0.9	0.4	2008	Caryophyllene oxide	0.1	6.3
1612	eta-Caryophyllene	0.3	11.7	2030	Methyl eugenol	-	0.1

TABLE 1. (Continued)

RRI	Compound	A, (%)	B,(%)	RRI	Compound	A, (%)	B, (%)
2037	Salvial-4(14)-en-1-one	0.6	0.6	2239	Carvacrol	4.7	0.5
2050	(E)-Nerolidol	-	2.2	2245	Elimicine	0.1	-
2057	Ledol	0.2	0.8	2247	<i>trans-α</i> -Bergamotol	0.2	0.3
2071	Humulene epoxide-II	0.2	0.4	2255	lpha-Cadinol	-	1.3
2077	Tridecanol	-	3.9	2256	Cadalene	1.6	-
2080	Cubenol	0.1	0.3	2273	Selin-11-en-4 α -ol	-	0.5
2084	Octanoic acid	2.4	-	2289	Oxo- α -Ylangene	0.5	-
2088	1-epi-Cubenol	-	0.6	2296	Myristicine	Tr.	-
2098	Globulol	0.5	0.3	2300	Decanoic acid	1.3	0.5
2100	Heneicosane	0.1	-	2300	Tricosane	0.1	-
2104	Viridiflorol	-	0.2	2316	Caryophylla-2(12),6(13)-dien-5 β -ol	0.1	-
2113	Cumin alcohol	0.1	-		(caryophylladienol I)		
2144	Spathulenol	7.2	6.0	2324	Caryophylla-2(12),6(13)-dien-5 α -ol	-	0.3
2148	(Z)-3-Hexen-1-yl benzoate	-	0.6		(caryophylladienol II)		
2179	3,4-Dimethyl-5-pentylidene-	Tr.	0.2	2341	(2Z,6E)-Farnesol	-	0.3
	2(5H)-furanone			2389	Caryophylla-2(12),6-dien-5 α -ol	0.5	0.4
2179	Tetradecanol	-	2.5		(caryophyllenol I)		
2181	Isothymol(2-isopropyl-4-methylphenol)	0.4	-	2392	Caryophylla-2(12),6-dien-5 β -ol	0.3	-
2187	T-Cadinol	-	0.6		(caryophyllenol II)		
2192	Nonanoic acid	0.4	0.3	2419	4-Isopropyl-6-methyl-1,2,3,4-	0.3	-
2198	Thymol	1.2	0.5		tetrahydronaphthalen-1-one		
2209	T-Muurolol	0.3	0.5	2503	Dodecanoic acid	1.8	1.2
2219	δ -Cadinol	0.1	0.2	2622	Phytol	-	1.2
2221	Isocarvacrol	0.1	-	2655	Benzyl benzoate	0.3	0.3
	(4-isopropyl-2-methylphenol)			2713	Tetradecanoic acid	0.7	1.0
2232	lpha-Bisabolol	0.1	0.2	2931	Hexadecanoic acid	2.8	3.8
					Total	85.9	89.6

A: Hypericum scabrum.

EXPERIMENTAL

The dry aerial parts of the plants were hydrodistilled for 3 h using a Clevenger type apparatus to produce the essential oils. The percentage yields of the oils were calculated on a moisture-free basis.

The essential oils were analyzed by GC/MS using a Hewlett-Packard GCD system. An HP-Innowax FSC column (60 m \times 0.25 mm \varnothing) was used with helium as carrier gas. The GC oven temperature was kept at 60°C for 10 min and programmed to 220°C at a rate of 4°C/min, and then kept constant at 220°C for 10 min and programmed to 240°C at a rate of 1°C/min. Alkanes were used as reference points in the calculation of relative retention indices (RRI). The split ratio was adjusted at 50:1. The injector temperature was 250°C. MS were taken at 70 eV. The mass range was from 35 to 425 m/z. Library search was carried out using the Wiley GC/MS Library and the TBAM Library of Essential Oil Constituents [7-9]. The relative percentage amounts of the separated compounds were calculated from total ion chromatograms by a computerized integrator.

B: Hypericum perforatum.

RRI: Relative retention indices calculated against *n*-alkanes.

^{%:} calculated from TIC data.

Tr.: Trace (< 0.1%).

REFERENCES

- 1. C. Mathis and G. Qurisson, *Phytochemistry*, **3**, 115, 133, 377 (1964).
- 2. F. Chialva, G. Gabri., P. A. Liddle, and F. Vilan, Rev. Ital. Essenze, Profumi, Piante Offic, Aromi, Saponi, Cosmet, Aerosol, 63, 286 (1982).
- 3. A. Cakir, M. E. Duru, M. Harmandar, R. Ciriminna, S. Passannanti, and F. Piozzi, *Flavour Fragr. J.*, **12**, 285 (1987)
- 4. M. D. Mashkovski, *Medicinal Remedies* [in Russian], M.,1977, 1, 624, 2, 552.
- 5. P. Weyerstahl, U. Splittgerber, H. Marchal, and U. K. Kaul, *Flavour Fragr. J.*, **10**, 365(1995).
- 6. N. Tanker, J. Fac. Pharm., Ankara, **1**, 10 (1971).
- 7. F. W. McLafferty and D. B. Stauffer, *The Wiley / NBS Registry of Mass Spectral Data*, John Wiley and Sons, New York, USA, 1988, Vols. 1-7.
- 8. R. P. Adams, *Identification of Essential Oils by Ion Trap Mass Spectroscopy*, Academic Press, New York, USA, 1989.
- 9. R. P. Adams, *Identification of Essential Oil Components by Gas Chromatography /Mass Spectroscopy*, Allured, USA, 1995.