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ESSENTIAL OIL COMPOSITION OF FOUR *Hypericum* SPECIES FROM IRAN

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The genus *Hypericum* L. comprises about 450 species which occur in all temperate parts of the world [1]. In Iran, 19 species of 5 sections exist, two of which are endemic [2]. The most commercially important member of this genus, *H. perforatum* L., is used as a valuable medicinal plant for nervous exhaustion, depression, and seasonal affective disorders [3]. This genus contains a wide range of different natural product classes, including naphthodianthrones (e.g., hypericin), prenylated phloroglucinols (e.g., hyperforin), xanthones, flavonoids, biflavonoids, tannins, proanthocyanidins, and phenolic acids [4]. *Hypericum helianthemoides* (Spach) Boiss., *H. hirtellum* (Spach) Boiss., *H. scabrum* L., and *H. dogonbadanicum* Assadi. are four *Hypericum* species whose oils have been subjected to analysis in this article. *H. dogonbadanicum*, the only member of the section Campylusporus in Iran, is a narrow endemic plant confined to mountainous regions NE of Gachsaran city, SW of Iran; the other three species belong to the Hirtella section and are distributed W and NW of Iran [2]. Here we report on the chemical composition of these four species, two of which, *Hypericum helianthemoides* and *H. hirtellum,* have not been subjected to any previous phytochemical analysis.

Data on the constituents of the four *Hypericum* oils are shown in Table 1. According to Table 1, monoterpenes are the major constituents of *H. scabrum* (Fars, Doshman Ziari, 2005; 73.7%) and *H. dogonbadanicum* (Kohkilooyeh, Gachsaran, 2006; 59.4%), while the major compounds in *H. helianthemoides* (Fars, Hesami, Roshan Kuh, 2005) and *H. hirtellum* (Fars, Neyriz, 2006) are sesquiterpenes with 74.1% and 53.0% of the total oils, respectively.

The first major compound of *H. scabrum* and *H. dogonbadanicum* is α-pinene, which is a major and characteristic constituent of many *Hypericum* species like *H. perforatum* [5], *H. forrestii* [6], *H. perfoliatum* [7], *H. triquetrifolium* [8], *H. hircinum* [9], *H. hyssopifolium,* and *H. heterophyllum* [10]. In three previous works on *H. scabrum* oil, α-pinene was also shown to be the first major compound and in two of them, like ours, α-pinene constituted more than 40% of the total oil [11, 12]. However, in the other report α-pinene only comprised 11.2% of the total oil [13]. Comparison of the other constituents of these reports and ours show that the other major compounds are completely different from each other, which could be attributed to different localities where the plant materials were collected.

The major constituents of *H. dogonbadanicum* oils of our work and previous work [14] were the same but differ in order and percentage. α-Pinene (34.7%), β-pinene (32.1%), limonene (12.1%), and camphene (6.6%) were the first four major compounds of previous work that were the first (12.8%), third (4.7%), second (8.2%), and sixth (3.9%) majors of ours. Major compound percentages in our work were totally less than the previous work. Because of the very limited distribution range of this species, locality could not be an important factor in this difference. Our plant material was collected before bud blooming; different stages of flowering may resulted in different chemical compositions of these two oils.

Two first major compounds of *H. helianthemoides* and *H. hirtellum* are the same; β-caryophyllene (23.3%, 14.1%) and spathulenol (17.4%, 12.3%) with respective percentage. β-Caryophyllene was also among the major constituents of *H. perforatum* [5], *H. triquetrifolium* [8], *H. bupleuroides* [15], *H. carinatum* [16], *H. maculatum* [17], *H. foliosum* [18], and *H. brasiliense* [19]; and spathulenol was one of the main compounds of *H. perforatum* [5], *H. hissopifolium* [20] and *H. linarioides* [21]. α-Pinene is also the fourth and third major compounds of *H. helianthemoides* (6.7%) and *H. hirtellum* (9.8%), respectively. The third major constituent of *H. helianthemoides* is 14-hydroxy-9-epi-(*E*)-carophyllene, with the caryophyllene skeleton. Compounds with this skeleton comprise 47.9% of *H. helianthemoides* total oil. Nonane was a characteristic constituent of *H. perfoliatum* [7], *H. triquetrifolium* [8], *H. hircium* [9], *H. scabrum* [11], *H. caprifoliatum* [16], *H. foiosum* [18], and *H. richeri* [22] oils, the amount of which was not considerable in the four *Hypericum* oils of our work.

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TABLE 1. The Chemical Constituents of Four *Hypericum* Oils

Compound	RI	1	2	3	4	Compound	RI	1	2	3	4
Hexanal	800	Tr.	0.1	0.1	0.3	*cis*-Carveol	1230	-	-	0.1	-
2-(*E*)-Hexenal	852	Tr.	0.2	0.2	-	Neral	1238	-	-	-	0.5
3-(*Z*)-Hexenol	861	-	Tr.	-	-	Carvone	1243	Tr.	-	-	0.2
Nonane	900	-	0.1	1.7	1.1	Geraniol	1256	-	-	-	0.6
Santolinatriene	909	-	-	-	Tr.	Geranial	1268	-	-	-	1.0
Tricyclene	926	-	-	-	Tr.	Isobornyl acetate	1286	-	0.1	-	0.1
α-Thujene	929	-	Tr.	-	-	Lavandulyl acetate	1293	-	Tr.	-	-
α-Pinene	936	6.7	9.8	59.3	12.8	2-Undecanone	1295	-	-	-	0.2
Camphene	950	0.2	0.4	0.5	3.9	Tridecane	1300	-	-	-	0.1
Thuja-2,4(10)-diene-2	957	Tr.	0.1	0.1	0.2	2*E*,4*E*-Decadienal	1318	-	-	-	0.3
Benzaldehyde	960	-	-	-	Tr.	Bicycloelemene	1337	-	0.1	0.3	-
β-Pinene	978	0.1	0.6	4.1	4.7	α-Cubene	1350	-	0.1	-	-
6-Methyl-5-hepten-2-one	984	Tr.	Tr.	-	1.4	α-Longipinene	1351	0.1	-	-	-
Myrcene	989	0.1	1.1	1.8	0.1	α-Terpinyl acetate	1351	-	-	0.2	Tr.
Dehydroxy-*trans*-linalool oxide	995	-	-	-	0.1	α-Ylangene	1372	Tr.	0.1	0.7	Tr.
α-Phellandrene	1004	-	-	0.2	0.3	α-Copaene	1376	0.2	0.4	0.4	0.4
3-(*Z*)-Hexenyl acetate	1005	Tr.	0.3	Tr.	-	β-Bourbonene	1385	Tr.	0.1	-	-
2*E*,4*E*-Heptadienal	1015	-	0.1	-	-	β-Cubebene	1390	-	0.1	0.1	-
α-Terpinene	1017	Tr.	0.5	0.3	0.3	β-Elemene	1393	-	0.3	-	-
p-Cymene	1024	0.1	0.1	0.6	0.1	(*Z*)-Jasmone	1396	-	0.2	Tr.	-
Limonene	1029	1.2	4.6	2.1	8.2	(*Z*)-Isoeugenol	1405	-	-	-	-
1,8-Cineol	1031	-	2.0	0.1	-	Isocaryophyllene	1406	0.1	-	-	-
(*Z*)-β-Ocimene	1038	0.3	0.5	0.1	-	Longifolene	1406	-	0.2	-	-
(*E*)-β-Ocimene	1047	0.1	4.0	0.2	0.3	Methyl eugenol	1408	-	0.1	0.1	-
γ-Terpinene	1058	Tr.	1.1	0.9	0.5	α-Gurjunene	1410	-	-	-	-
Acetophenone	1064	Tr.	-	0.1	1.3	Dodecanal	1410	-	-	0.7	0.4
trans-Linalool oxide (furanoid)	1075	-	-	-	3.7	β-Caryophyllene	1417	23.3	14.1	-	0.4
Terpinolene	1086	Tr.	0.4	0.4	1.6	6-epi-α-Cubebene	1430	0.2	-	0.5	-
p-Cymenene	1089	Tr.	-	-	-	β-Copaene	1430	-	0.3	-	-
cis-Linalool oxide (furanoid)	1090	-	-	-	1.6	α-Guaiene	1437	0.2	0.5	1.2	-
Undecane	1100	Tr.	0.3	0.4	1.2	Aromadendrene	1440	-	-	0.2	0.9
Linalool	1101	Tr.	0.5	0.1	3.0	α-Humulene	1452	0.5	0.7	0.8	-
Nonanal	1103	Tr.	-	-	0.7	*E*-(β)-Farnesene	1456	0.3	1.5	Tr.	-
α-Fenchol	1116	Tr.	-	-	-	Allo-aromadendrene	1463	-	-	-	-
β-Fenchol	1122	-	-	-	1.3	2-(*E*)-Dodecenal	1468	-	-	-	0.9
cis-*p*-Menth-2-en-1-ol	1124	-	0.1	-	-	*trans*-Cadina-1(6)-4-diene	1475	0.5	-	3.4	-
α-Campholenal	1125	0.1	0.1	0.7	1.2	γ-Muurolene	1478	0.2	-	0.8	-
Nopinone	1140	-	-	-	0.4	Germacrene-*D*	1484	-	9.0	0.4	1.0
trans-Pinocarveol	1142	0.1	-	0.3	0.7	β-Selinene	1487	0.1	-	-	-
Camphor	1143	Tr.	0.8	-	1.2	(*E*)-β-Ionone	1488	-	0.1	-	Tr.
trans-Chrysanthenol	1147	0.1	-	-	-	γ-Amorphene	1495	-	-	1.8	0.5
Camphene hydrate	1152	-	-	0.3	1.1	Valencene	1497	-	-	0.4	-
trans-Pinocamphone	1163	-	-	0.1	0.1	Bicyclogermacrene	1499	0.3	3.0	0.4	-
Pinocarvone	1166	Tr.	0.1	0.2	0.7	α-Muurolene	1502	0.1	0.3	-	0.9
p-Mentha-1,5-dien-8-ol	1170	-	0.1	0.2	-	Eudesma-2,4(15),11-triene	1505	-	0.1	2.0	-
Borneol	1172	0.1	-	0.4	4.0	γ-Cadinene	1512	0.7	1.0	3.5	1.8
Terpinen-4-ol	1180	-	0.7	-	0.9	δ-Cadinene	1522	0.6	2.5	0.2	1.2
p-Cymen-8-ol	1185	Tr.	-	-	-	*trans*-Cadina-1,4-diene	1535	-	0.2	0.3	-
α-Terpineol	1190	0.2	1.0	0.4	4.2	α-Cadinene	1537	0.1	0.4	0.3	Tr.
Myrtenol	1195	Tr.	-	0.2	-	α-Calacorene	1544	0.9	0.3	0.4	Tr.
Myrtenal	1196	-	-	Tr.	-	β-Calacorene	1565	-	0.1	0.1	-
Methyl chavicol	1197	-	-	-	Tr.	3-(*Z*)-Hexenyl benzoate	1570	-	-	0.4	0.3
Decanal	1202	-	-	-	1.0	Caryolan-1-ol	1572	-	3.2	-	-
Verbenone	1208	0.1	-	0.2	0.3	Caryophyllenyl alcohol	1574	4.4	-	-	-

TABLE 1 (continued)

Compound	RI	1	2	3	4	Compound	RI	1	2	3	4
Spathulenol	1579	17.4	12.3	1.7	-	Hexadecanoic acid	1978	0.5	1.0	-	1.1
Dodecanoic acid	1581	-	-	-	0.6	Eicosane	2000	-	-	-	0.5
Caryophyllene oxide	1583	1.9	-	-	-	Hexadecyl acetate	2006	-	0.2	-	-
Salvia-4(14)-en-1-one	1596	0.6	0.9	0.1	-	Geranyl linalool	2032	-	0.1	-	-
Humulene epoxide II	1610	0.6	0.2	-	-	Heneicosane	2100	-	0.1	-	1.9
Caryophylla-4(14),8(15)-dien-5-β-ol	1643	2.6	1.1	-	-	Phytol	2123	Tr.	-	-	-
α-Muurolol	1646	-	-	0.3	-	Docosane	2200	Tr.	-	-	0.3
β-Eudesmol	1653	2.4	-	-	-	Tricosane	2300	0.1	-	-	-
α-Cadinol	1656	-		0.2	-	Tetracosane	2400	Tr.	-	-	-
14-Hydroxy-9-epi-(*E*)-caryophyllene	1669	15.6	-	-	-	Pentacosane	2500	0.1	-	-	-
Eudesma-4(15),7-dien-1-β-ol	1690	1.1	2.3	-	-	**Total**		85.5	87.6	98.3	86.0
Heptadecane	1700	-	-	-	0.3	Number of identified		71	72	67	74
Montsulfide	1739	-	-	0.1	-	compounds					
Benzyl benzoate	1761	0.1	Tr.	0.1	-	Yield of the oil, %		0.06	0.07	0.05	0.1
Tetradecanoic acid	1782	0.1	0.2	-	-	Color of the oil		yellow	yellow	yellow	yellow
Bicyclovetivenol	1791	-	-	-	1.2	Monoterpenes		9.5	28.7	73.7	59.4
Octadecane	1800	-	-	-	1.0	Sesquiterpenes		74.1	53.0	20.3	7.1
6,10,14-Trimethyl-2-pentadecanone	1845	0.1	0.2	0.1	1.2	Other compounds		1.9	5.9	4.0	19.5
Nonadecane	1900	-	-	Tr.	1.2						
Farnesyl acetone	1916	Tr.	0.2	-	0.5						

1 - *Hypericum helianthemoides*, 2 - *H. hirtellum*, 3 - *H. scabrum*, 4 - *H. dogonbdanicum*.
The components are listed in order of elution from the HP-5 column.
Tr.: trace (<0.05%); RI: retention indices relative to C_8-C_{28} *n*-alkanes on HP_5.

According to Cakir et all. [21], *Hypericum* species can be divided in two groups, based on the monoterpene and sesquiterpene content with emphasis on β-caryophyllene and α-pinene as the major and characteristic compounds. In the light of this conclusion and despite the morphological characters, *H. scabrum* and *H. dogonbadanicum* could be placed in the α-pinene group, and *H. helianthemoides* and *H. hirtellum* in the β-caryophyllene group. The relation between the morphological and chemical characters of these species needs more chemical investigation.

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