

Essential Oils of the Aerial Parts of *Hypericum apricum* Kar. and Kir. and *Hypericum davisii* Robson (Guttiferae) Species from Turkey

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In this study, essential oil composition of *Hypericum apricum* Kar. and Kir. and *H. davisii* Robson species grown in Turkey were determined by using GC and GC-MS system. The essential oils obtained by hydrodistillation from the aerial parts of plants. Forty-two compounds were identified in the essential oils of *H. apricum*; α -pinene (22.2 %), caryophyllene oxide (8.0 %), nonacosane (6.3 %), β -myrcene (5.9 %) and nonane (5.9 %) (as the major). Thirty compounds were identified in the essential oils of *H. davisii*; nonacosane (23.8 %), α -pinene (17.8 %), caryophyllene oxide (9.5 %) and β -caryophyllene (4.4 %) (as the major). Distribution of the major compounds in essential oil were discussed among the *Hypericum* genus patterns.

Key Words: *Hypericum*, Guttiferae, GC-MS, Essential oil, α -Pinene.

INTRODUCTION

The genus *Hypericum* L. belongs to the Hypericaceae (Guttiferae-Clusiaceae) family and encompasses approximately 460 species accommodated in 36 sections¹. In Turkey, the genus is represented by 89 species of which 43 are endemic^{2,3}. *Hypericum apricum* and *H. davisii* belongs to Section *Drosanthe* Robson, which includes 23 taxa, distributed mostly in the Centre Anatolia of Turkey².

The *Hypericum* species known as "Saint- Johns. Wort." or "centaury" in Turkish are used for their wound healing, antgastritis and antiseptic effects⁴. *Hypericum* species have been reported to contain many bioactive compounds namely naphthodianthrones, phloroglucinols, flavonoids, phenylpropanes, essential oils, amino acids, xanthenes, tannins, procyanidins and other water soluble components that possess a wide array of biological properties⁵⁻⁷.

H. apricum. and *H. davisii* are two *Hypericum* species whose oils have been subjected to analysis for present studies. Herein, we reported the chemical composition of these two species, which have not been cited to any previous phytochemical analysis.

EXPERIMENTAL

Hypericum apricum and *Hypericum davisii* specimens were collected in Sivas, in 2008 Yüce-1096 and 1092. Voucher specimens are kept at the Firat University Herbarium (FUH).

Isolation of the essential oils: Air-dried aerial parts of the plant materials (100 g) were subjected to hydrodistillation using a Clevenger-type apparatus for 3 h to yield, explained in different studies.

Gas chromatographic (GC) analysis: The essential oil was analyzed using HP 6890 GC equipped with and FID detector and an HP-5 MS column (30 m × 0.25 mm i.d., film thickness 0.25 µm) capillary column was used. The column and analysis conditions were the same as in GC-MS. The percentage composition of the essential oils was computed from GC-FID peak areas without correction factors.

Gas chromatography/mass spectrometry (GC-MS) analysis: The oils were analyzed by GC-MS, using a Hewlett Packard system. HP-Agilent 5973 N GC-MS system with 6890 GC in Plant Products and Biotechnology Res. Lab. (BUBAL) in Firat University. HP-5 MS column (30 m × 0.25 mm i.d., film thickness 0.25 µm) was used with helium as the carrier gas. Injector temperature was 250 °C, split flow was 1 mL/min. The GC oven temperature was kept at 70 °C for 2 min and programmed to 150 °C at a rate of 10 °C/min and then kept constant at 150 °C for 15 min to 240 °C at a rate of 5 °C/min. Alkanes were used as reference points in the calculation of relative retention indices (RRI). MS were taken at 70 eV and a mass range of 35-425. Component identification was carried out using spectrometric electronic libraries (Wiley, NIST). The identified constituents of the essential oils are listed in Table-1.

TABLE-1
CONSTITUENTS OF THE ESSENTIAL OILS FROM *H. apricum* AND *H. davisii*

Compounds	RRI	<i>H. apricum</i>	<i>H. davisii</i>
Nonane	996	5.9	2.1
α-Pinene	1021	22.2	17.8
β-Pinene	1055	2.6	3.1
β-Myrcene	1064	5.9	3.4
Decane	1072	0.5	–
<i>p</i> -Cymene	1091	0.7	0.7
Limonene	1095	0.8	0.6
<i>cis</i> -Ocimene	1100	–	1.7
δ-3-Carene	1108	–	3.8
Undecane	1148	–	1.7
<i>trans</i> -Pinocarvone	1178	–	0.5
Camphor	1182	–	1.3
Pinocarvone	1192	0.1	–
α-Terpineol	1215	0.9	1.8
Chrysanthenone	1223	–	0.6
Cyclohexasiloxane	1296	0.2	–
α-Cubebene	1337	0.9	–
α-Longipinene	1340	1.2	–
α-Ylangene	1355	0.2	–

α -Copaene	1360	1.5	0.8
β -Bourbonene	1366	0.2	–
β -Caryophyllene	1393	3.8	4.4
β -Cubebene	1400	0.2	–
β -Farnesene	1416	2.4	1.6
α -Humulene	1418	0.9	–
Octadecane	1421	0.2	–
Cycloheptasiloxane	1425	1.1	2.3
α -Amorphen	1430	1.1	0.6
Germacrene D	1436	0.8	1.0
δ -cadinene	1442	2.6	–
Bicyclogermacrene	1445	–	0.4
Naphtalene	1456	–	0.9
δ -Cadinene	1458	–	1.1
Epibicyclosesquiphllendrene	1460	2.1	–
Spathulenol	1495	1.6	2.9
Caryophyllene oxide	1498	8.0	9.5
Silane	1505	0.5	–
Cyclosativene	1514	–	1.3
Benzoic acid	1523	1.8	2.6
α -Cadinol	1539	1.8	1.7
Dehydroaromadendrene	1558	0.2	–
Tetradecanoic acid	1592	0.2	–
Benzilbenzoate	1596	0.7	–
2-Pentadecanol	1631	0.2	–
Cyclotetradecane	1650	0.2	–
Nonadecane	1660	0.9	–
Cyclodecasiloxane	1672	1.2	1.8
<i>n</i> -Decanoic acid	1692	1.0	–
Heneicosane	1789	0.4	–
Cyclononasiloxane	1853	0.6	0.5
Tricosane	1903	0.3	–
Nonacosane	1942	6.3	23.8
Total		84.9	86.8

RESULTS AND DISCUSSION

The hydrodistillation of the aerial parts of *H. apricum* and *H. davisii* yielded 0.15 % (w/w) of pale yellowish oils. The yields are nearly similar to that observed in other *Hypericum* species under investigation in our laboratory, like *H. scabrum*, *H. scabroides*⁸, *H. thymbrifolium* and *H. pseudolaeve*⁹, *H. salsolifolium* and *H. retusum*¹⁰, *H. capitatum* varieties¹¹, *H. sorgerae*¹² and *H. thymopsis*¹³.

The identified oil components from *H. apricum*, *H. davisii*, representing 84.9 and 86.8 % of the total oils, are listed in Table-1. Table includes their relative retention indices and the percentage composition. The isolated essential oils were complex

mixture of non-terpenes, monoterpenes and sesquiterpenes; 52 components were identified from which 20 are common to both oils (Table-1).

Forty two compounds were identified in the essential oils of *H. apricum*; α -pinene (22.2 %), caryophyllene oxide (8.0 %), nonacosane (6.3 %), β -myrcene (5.9 %) and nonane (5.9 %) (as the major). Thirty compounds were identified in the essential oils of *H. davisii*; nonacosane (23.8 %), α -pinene (17.8 %), caryophyllene oxide (9.5 %) and β -caryophyllene (4.4 %) (as the major).

The first major compound of *H. apricum* and the second major compound *H. davisii* is α -pinene, which is the dominant constituent of *H. scabrum* L.⁸, *H. salsolifolium* Hand.-Mazz. and *H. retusum* Aucher.¹⁰, *H. capitatum* var. *capitatum*¹¹, *H. thymbrifolium* Boiss. and Noë⁹, *H. perfoliatum*¹⁴⁻¹⁶, *H. tomentosum*, *H. humifusum*, *H. linarifolium*¹⁷ and *H. pulchrum*¹⁶ essential oils.

The first major compound of *H. davisii* is nonacosane, which is reported as to be the fourth major compound in *H. apricum*. Nonacosane was also among the major constituents of *H. barbatum*, *H. maculatum*, *H. richeri*, *H. rumeliacum* and *H. tetrapterum*¹⁸.

Caryophyllene oxide is the second major compound in *H. apricum* (8.0 %) and the third *H. davisii* (9.5 %), respectively. Regarding the qualitative pattern of the essential oils of *Hypericum* species, there are similar results for caryophyllene oxide, major/high component reported for Southeastern Serbia and Greece specimens of *H. barbatum*, *H. maculatum*, *H. richeri*, *H. rumeliacum* and *H. tetrapterum*¹⁸, for *H. perforatum* and *H. tetrapterum*¹⁹.

The major components δ -3 carene, camphor, *cis*-ocimene, cyclosativene and δ -cadinene, determined in the essential oils of *H. davisii* were not determined in the essential oils of *H. apricum*.

This study demonstrates the occurrence of α -pinene/caryophyllene oxide chemotype of *H. apricum* and nonacosane/ α -pinene chemotype of *H. davisii* in Central Anatolian region of Turkey.

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