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# Essential oil composition of *Hypericum uniglandulosum* Hausskn. ex Bornm. and *Hypericum lydium* Boiss. from Turkey

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**Abstract**
*Hypericum uniglandulosum* Hausskn. ex Bornm. and *Hypericum lydium* Boiss. are growing naturally in the Eastern Anatolian region of Turkey and both are represented in the same section, *Drosanthe* Robson. The essential oils obtained by hydrodistillation from the aerial parts of Turkey native *H. uniglandulosum* and *H. lydium* were analyzed by GC, GC–MS. Twenty-six compounds were identified in the essential oils of *H. uniglandulosum* with α–pinene (35.1%), undecane (19.2%), benzoic acid (2.7%) and cyclohexasiloxane (2.3%) as main constituents. Fifty-one components were identified in the oil of *H. lydium* with α–pinene (58%), β–pinene (%5.10) and β–myrcene (3.1%) as the most abundant components. The essential oil compositions of both species have given some clues on the chemotaxonomy of genus and as a resource of natural product.

**Key words:** *Hypericum uniglandulosum, Hypericum lydium,* GC-MS, essential oil, α-pinene.

## 1. Introduction

The genus *Hypericum* L. comprises about 450 species which occur in all temperate parts of the World (Robson, 1977). In Turkey, approximately 95 taxa of 19 sections exist, 45 of which are endemic to Turkey. Both species *Hypericum uniglandulosum* and *Hypericum lydium* are growing naturally in the eastern Anatolian region of Turkey. It is represented in section *Drosanthe* Robson in genus *Hypericum. H. uniglandulosum* is a herbaceous perennial plant which is an endemic species to Turkey and is not shown wide distribution in Turkey. *H. lydium* Boiss. is also a herbaceous perennial plant, the distribution area of which is limited to Turkey and Northern Iraq (Davis, 1967).

Both taxa are perennial or suffruticose herbs and have black glands confined usually to sepal and petal margins. *H. lydium* have linear or narrowly oblong-lanceolate leaves and inflorescence cylindric or narrowly pyramidal to subspicate. *H. uniglandulosum* have leaves linear, acutely mucronate, inflorescence very triangular or subspicate. *H. lydium* differs from *H. uniglandulosum* in having capsule ovoid, acuminate or markedly rostrate; stems red and amber glands; sepal equal (Davis, 1967).

*Hypericum* species have been used in traditional medicine for the treatment of external wound, gastric ulcer, antidepressant, antiseptic and antispasmodic (Smelcerovic et al., 2007). Essential oils of *Hypericum* species were complex mixture of volatile compounds of which many (namely oxygenated components) are used as flavouring agents in food, pharmaceutical and perfume industries.

There are several reports on the essential oil composition of *Hypericum* species from Turkey (Bagci and Bekci, 2010; Bagci and Yüce, 2010; Bagci and Yüce, 2011a; Bagci and Yüce, 2011b; Bagci and Yüce, 2011c) and the world (Bertoli et al., 2000; Wolski et al., 2003; Demirci et al., 2005; Ferraz et al., 2005; Nogueira et al., 2007; Smelcerovic et al., 2007; Javidnia et al., 2008; Yüce, 2009). The chemical composition of the essential oils isolated from wild-growing *H. uniglandulosum* and *H. lydium* was reported. The current study presents the results of GC- MS analysis of the essential oils from the aerial parts of *H. uniglandulosum* and *H. lydium* for the first time from Turkey.

## 2. Material and Methods

### *2.1. Plant material*

*H. uniglandulosum* specimens were collected at the flowering stage from natural habitats in Keban (Elazığ), 780 m and *H. lydium* specimens were collected in Narli (Gaziantep), 850 m. in 2008. These specimens were initially identified with the help of the Flora of Turkey (Davis, 1967). Voucher specimens (FUH-9664 and FUH-9675) are kept at the Fırat University Herbarium (FUH), Elazığ, Turkey.

### *2.2. 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.

### *2.3. Gas chromatographic (GC) analysis*

The essential oil was analyzed using Hewlett Packard system (HP) 6890 GC equipped with and FID detector and an HP-5 MS column (30 m x 0.25 mm i.d., film tickness 0.25 µm) capillary column was used. The column and analysis conditions are the same as in GC-MS. The percentage composition of the essential oils was computed from GC–FID peak areas without correction factors.

### *2.4. 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 x 0.25 mm i.d., film tickness 0.25 µm) was used with Helium as the carrier gas. Injector temperature was 250 $^{o}$C, split flow was 1 ml / min. The GC oven temperature was kept at 70 $^{o}$C for 2 min and programmed to 150 $^{o}$C at a rate of 10 $^{o}$C / min and then kept constant at 150 $^{o}$C for 15 min to 240 $^{o}$C at a rate of 5 $^{o}$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 *Hypericum uniglandulosum* (a) and *H. lydium* (b).

| No | Compounds | RRI | a - % | b - % |
|---|---|---|---|---|
| 1 | Nonane | 996 | -- | 0.1 |
| 2 | α–thujene | 1016 | -- | 0.1 |
| 3 | α–pinene | 1021 | 35.1 | 58.0 |
| 4 | Camphene | 1034 | -- | 0.1 |
| 5 | Verbenene | 1037 | -- | 0.2 |
| 6 | β–pinene | 1055 | 2.2 | 5.1 |
| 7 | β–myrcene | 1064 | -- | 3.1 |
| 8 | α–terpinene | 1086 | -- | 0.1 |
| 9 | p-cymene | 1091 | 1.1 | 0.4 |
| 10 | Limonene | 1095 | 1.6 | 1.8 |
| 11 | *Cis*-ocimene | 1100 | -- | 0.1 |
| 12 | δ–3-carene | 1108 | -- | 0.05 |
| 13 | γ– terpinene | 1117 | -- | 0.2 |
| 14 | α–terpinolene | 1137 | 0.5 | 0.7 |
| 15 | Undecane | 1148 | 19.2 | 1.7 |
| 16 | Alloocimene | 1167 | 2.6 | 1.2 |
| 17 | *Trans*- pinocarveol | 1178 | -- | 0.5 |
| 18 | Thymol | 1210 | -- | 0.1 |
| 19 | α–terpineol | 1215 | 0.9 | -- |
| 20 | Chrysanthenone | 1223 | -- | 0.2 |
| 21 | *Trans*- carveol | 1231 | -- | 0.3 |

| | | | | |
|---|---|---|---|---|
| 22 | 2-cyclohexen-1-on | 1249 | -- | 0.04 |
| 23 | α– cubebene | 1337 | -- | 0.06 |
| 24 | α– longipinene | 1340 | -- | 2.7 |
| 25 | α– ylangene | 1355 | -- | 0.1 |
| 26 | α– copaene | 1360 | 0.2 | 0.2 |
| 27 | *β*–elemene | 1370 | -- | 0.09 |
| 28 | l-decanol | 1384 | -- | 0.2 |
| 29 | β–caryophyllene | 1393 | -- | 2.6 |
| 30 | β–cubebene | 1400 | -- | 0.1 |
| 31 | Aromadendrene | 1406 | 1.4 | 0.1 |
| 32 | β–pharnesene | 1416 | -- | 0.9 |
| 33 | Cyclohexansiloxane | 1425 | 2.3 | -- |
| 34 | Naphtalene | 1430 | 1.9 | 0.8 |
| 35 | Germacrene D | 1436 | -- | 1.6 |
| 36 | Bicyclogermacrene | 1445 | -- | 0.5 |
| 37 | α–amorphene | 1456 | 0.3 | 0.4 |
| 38 | δ–cadinene | 1458 | -- | 1.7 |
| 39 | *Cis*-calamene | 1460 | 0.2 | -- |
| 40 | α–cadinene | 1470 | -- | 0.1 |
| 41 | Calacorene | 1473 | -- | 0.1 |
| 42 | Dodecanoicacid | 1486 | 0.3 | -- |
| 43 | 3-hexen-1-ol | 1491 | 1.6 | 0.2 |
| 44 | Spathulenol | 1495 | 1.2 | 1.8 |
| 45 | Caryophyllenoxide | 1498 | 0.5 | 0.7 |
| 46 | Cyclododecane | 1512 | 0.5 | 0.3 |
| 47 | Benzoic acid | 1523 | 2.7 | -- |
| 48 | α-cadinol | 1539 | -- | 0.5 |
| 49 | Tetradecanoic acid | 1592 | 0.2 | -- |
| 50 | Benzylbenzoate | 1596 | 0.1 | 0.05 |
| 51 | 2- pentadecanone | 1631 | 0.3 | 0.04 |
| 53 | Cyclotetradecane | 1650 | 0.8 | 0.06 |
| 54 | Nonadecane | 1660 | -- | 0.1 |
| 55 | Cyclodecasiloxane | 1672 | 2.3 | -- |
| 56 | n-decanoic acid | 1692 | -- | 0.4 |
| 57 | Heneicosane | 1789 | -- | 0.1 |
| 58 | Tricosane | 1903 | 0.3 | 0.06 |
| 59 | Nonacosane | 1942 | -- | 0.2 |
| Total | | | %81.5 | %92.4 |

**3. Results and Discussion**

The essential oils of two *Hypericum* species from Turkey were investigated in means of qualitative and quantitative composition. The identified oil components from *H. uniglandulosum* and *H. lydium,* representing 81.5 and 92.4% of the total oils, are listed in Table 1 in order of their elution on the HP-5 MS column. Table 1 also includes their retention indices and the percentage composition. The isolated essential oils were complex mixture of non-terpenes, monoterpenes and sequiterpenes: 59 components were identified from which 19 are common to both oils.

Twenty-six compounds were identified in the essential oils of *H. uniglandulosum* with α–pinene (35.1%), undecane (19.2%), benzoic acid (2.7%) and cyclohexasiloxane (2.3%) as main constituents. Fifty-one components were identified in the oil of *H. lydium* with α–pinene (58%), β–pinene (%5.10) and β–myrcene (3.1%) as the most abundant components.

In the essential oil of *H. uniglandulosum* and *H. lydium*, the monoterpene hydrocarbons made up the high contribution (ca. 40%, 65%); α-pinene (35.1%, 58%, respectively) being the most abundant compound.

The first major compound of *H. uniglandulosum* and *H. lydium* is α-pinene, which is a major and characteristic constituent of many *Hypericum* species like, *H. Hircinum* (Bertoli et al., 2000), *H. Perfoliatum* (Couladis et al., 2001), *H. perforatum* (Wolski et al., 2003), *H. triquetrifolium* (Bertoli et al., 2003), *H. hyssopifolium* and *H. heterophyllum* (Cakir et al., 2004), *H. forrestii* (Demirci et al., 2005), *H. apricum* (Bagci and Yüce, 2010), *H. thymbrifolium* (Bagci and Yüce, 2011a). The second major compound of *H. uniglandulosum* is undecane (19.2%). Undecane is also found in the oils of *H. lydium* (1.7 %), *H. perforatum* (3.9%) (Gudzic et al., 2001), *H. perfoliatum* (3.8–2.9%) (Nogueira et al., 2007), *H. maculatum* (8.2%) and *H. rumeliacum* (3.5%) (Smelcerovic et al., 2007). The second major compound of *H. lydium* detected as β−pinene (19.2%). β−pinene was also among the major constituent of *H. uniglandulosum* (2.2%), *H. perfoliatum* (1.9-3.2%), *H. humifosum* (4.0-7.7%), *H. linarifolium* (5.0-11.0%) and *H. pulchrum* (9.0-12.5%) (Nogueira et al., 2007). β−caryophyllene was a characteristic constituent of *H. pseudolaeve* (Bagci and Yüce, 2011a), *H. humifosum*, *H. linarifolium* and *H. Pulchrum* (Nogueira et al., 2007) oils. But it was not found in *H. uniglandulosum* oil studied in here. In contrast, β−caryophyllene was one of the major compounds of *H. lydium* (2.6%) (Table 1).

The predominant compounds, α−pinene, β−pinene that are common to both species essential oils were reported in (Smelcerovic et al., 2007), *H. myrianthum* (Ferraz et al., 2005), *H. scabrum* and *H. dogonbdanicum* (Javidnia et al., 2008). It will be said that the high concentration of the α- pinene component have chemotaxonomical importance in section *Drosanthe* (Yüce, 2009).

This richnes of the α- pinene in both species has shown that they will be used as α-pinene sources for some purposes. α-pinene enantiomers can be widely found in nature, they were used by the fragrance industry as a starting material in the synthesis of terpineols, borneol, and camphor. (+)-α-pinene has a slight minty-terpene odor while (-)-α-pinene has a coniferous odor (Bauer et al., 1997).

This study demonstrates the occurrence of α–pinene chemotype of *H. uniglandulosum* and *H. lydium* in Turkey. The results were also supplied some contributions in means of chemotaxonomy and renewable resources in genus *Hypericum.* As a consequence, this study needs to be continued and extended to other Turkey native species and populations of the genus *Hypericum* for a better phytochemical characterization and their industrial applications in order to improve their rational uses.

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