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Research Pape

Volatile Constituents of *Hypericum tetrapterum* Fries. Plants Growing Wild in Iran

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Abstract: Foliage part of *Hypericum tetrapterum* Fries. contains essential oil was collected from north part of Iran. Essential oil was extracted by hydrodistillation method and its components were identified using GC and GC-MS. In this study, thirty-six components (67.21% of total essential oil compositions) were characterized. Alkans (50.07%) and sesquiterpene hydrocarbons (14.42%) were identified as the main fractions of the essential oil together with small amount of monoterpens (0.5 %). The most abundant constituents were *n*-undecane (30.84%), *n*-nonane (9.99%), *n*-tridecane (3.55 %) and β-funebrene (2.79 %).

Key words: *Hypericum tetrapterum* Fries., alkans, sesquiterpene hydrocarbons, *n*-undecane, *n*-nonane, *n*-tridecane

Introduction

The genus *Hypericum* belongs to the Hypericaceae (Clusicaceae) family and comprises more than 469 species worldwide. This genus exists in the flora of Iran with 19 species (Azadi, 1999; Crockett 2010). From therapeutic point of view, among those species *H. perforatum* is the most important medicinal species which had been used in traditional medicine for more than two thousand years ago (Zobayed, 2005). The plant is widely used as an herbal drug for treatment of mild to moderate depression. The genus of *Hypericum* contains a wide variety of secondary metabolites including flavonoids, xanthones, tannins, naphthodianthrones, acylphloroglucinols and essential oil (Zobayed, 2005; Paul, 2009; Crockett 2010; Morshedloo, 2010), which present various biological activities such as antiviral, antioxidant, antifungal and antimicrobial effects. St Peter's wort (*H. tetrapterum* Fries.) is an herbal species of the genus *Hypericum*. This perennial plant has been found in Europe, Turkey, Caucasus, Iraq, Iran (north, North West, and center of Iran) as well as east Mediterranean (Azadi, 1999). Compared with *H. perforatum* this species contains a little amount of hypericin, pseudohypericin, hyperoside and quercitrin (Kosuth, 2011). Essential oils include a large number of volatile secondary metabolites such as terpens, terpenoids, phenolic and aliphatic derivatives. These metabolites are well known as important therapeutic drugs (Burt, 2004).

The family Hypericaceae is a valuable source of plant species, containing essential oil, has been subjected to many phytochemical and biological studies which is reviewed recently (Crockett 2010; Pavlović, 2006).

Pavlovic et al. (2006) reported the essential oil for *H. tetrapterum* in Greece including sesquiterpene hydrocarbons (43.6%), oxygenated sesquiterpenes (19.5%) and monoterpene hydrocarbons (21.9%) as the main constituent of essential oil in dry flowering aerial part of plant. Fore there more Maggi et al. (2010) reported that α-copaene (12.7%) and α-longipinene (8.1%) were the main fraction of essential oil of dry flowering aerial part of *H. tetrapterum*.

Material and methods

Plant material: aerial parts of the Plants were collected at the flowering stage from north part of Iran (Golestan province, Shirgah) in August 2011. A voucher specimen (6405) was deposited at the Herbarium of Department of Horticultural Sciences, College of Agricultural, The University of Tehran.

Essential oil isolation: dry plant materials were subjected to hydrodistillation using a Clevenger-type apparatus for 4 h. The essential oil was collected, dried over anhydrous sodium sulphate and kept in dark vials at 4oC prior to GC and GC-MS analysis.

Gas Chromatography–Mass Spectrometry: The essential oil of *H. tetrapterum* was analyzed using an Agilent 6890 GC with Agilent 5973 mass selective detector operated in the EI mode, electron energy = 70 eV, scan range = 50-550 amu, and an Agilent ChemStation data system. The GC column was an HP-5ms fused silica capillary with a film thickness of 0.25 µm, a length of 30 m, and an internal diameter of 0.25 mm. The carrier gas was helium with a flow rate of 0.8 ml/min. Injector temperature was 290°C. The GC oven temperature program was managed as follows: 50°C initial temperature, hold for 5 min (temperature gradient was 3°C); increased at 15°C/min to 240°C; increased to 300°C and held for 3 min.
Identification of the oil components was based on their retention indices determined by reference to a homologous series of n-alkanes, and by comparison of their mass spectral fragmentation patterns with those reported in the literature (Adams, 2001), and stored on the MS library [Chemstation data system]. The essential oil composition is summarized in Table 1.

Results and discussion

Hydrodistillation of *H. tetrapterum* dry flowering aerial parts produced 0.12% (v/w) of a yellowish oil. In total thirty-six components comprising about 67.21% of the total oil composition were identified (Table 1). Alkans (50.07%) with *n*-undecane

(30.84%), and *n*-nonane (9.99%) as the main constituent of the essential oil fraction and followed by sesquiterpene hydrocarbons (14.42%) with β-funebrene (2.79%) as the major constituent.

Table 1.The chemical constituent of the essential oil of *Hypericum tetrapterum* Frise

No	Compound	RI[1]	Percentage
1	*n*- nonane	896	9.99
2	*α*- Pinene	927	0.31
3	6- methyle-5- heptanone	981	0.18
4	*n*- decane	996	0.29
5	Limonene oxaide	1068	0.19
6	*n*- undecane	1103	30.84
7	*n*- tridecane	1298	3.55
8	*α*- copaene	1373	0.82
9	*β*- bourbonene	1391	0.6
10	*β*- elemene	1394	0.43
11	*β*- funebrene	1410	2.79
12	*β*- cedrene	1416	1.11
13	*β*- duprezianene	1426	0.33
14	*β*- acaradiene	1464	1.59
15	Murula- 4,5 diene (cis)	1474	1.51
16	Curcumene (ar)	1479	0.41
17	*β*- selinene	1483	0.22
18	Valencene	1491	0.72
19	*n*- pentadecane	1496	0.97
20	*γ* –Cadinene	1511	1.47
21	*Δ-Cadinene*	1520	1.91
22	*α* –Cadinene	1534	0.18
23	*α*- calacorene	1539	0.33
24	Dodecanoic acid	1565	0.55
25	Spathulenol	1574	0.38
26	Caryophyllene oxide	1579	0.59
27	n- hexadecane	1596	0.44
28	Humulene epoxide II	1605	0.25
29	Eudesmol-4, 7- dien	1682	0.27
30	*n*- heptadecane	1695	0.59
31	*n*- octadecane	1795	0.57
32	Nonadecane	1895	0.9
33	Eicosane	1994	0.52
34	Heneicosane	2095	1.07
35	*n*- docosane	2193	0.17
36	*n*- tricosane	2293	0.17
No	**Compound**	**RI**	**Percentage**
	Monoterpenes		0.5
	Sesquiterpene hydrocarbons		14.42
	Oxygenated sesquiterpenes		1.49
	Alkans		50.07
	Others		0.73
	Total		67.21

To the best of our knowledge, there are only two reports about essential oil composition of *H. tetrapterum* in Greece and Italy. In that research work, α-copaene (11.3%), α-longipinene (9.7%), caryophyllene oxide (8.9%) and *n*-undecane (7.4%) in Greece populations and α-copaene (12.7%) and α-longipinene (8.1%) in Italy populations were identified as the major components of the

[1]RI, retention indices on the HP5ms column

essential oil of *H. tetrapterum* dry flowering aerial parts. Although *n*-undecane was one of the main constituent of the essential oil this plant in Greece but in comparison, in present study, the amount of this fraction was low, and in fact there were no similarities between the main constituents of these two reports. *n*-undecane (30.84%) and *n*- nonane (9.99%) were the main constituent of the essential oil from Iran which was not detected in the essential oil from Italy population. The difference between main constituent of the essential oil in different part of world could be due to different parameters such as method of oil extraction, extraction of essential oil in different phenological stage, various environmental conditions, genetic background, different sampling part of the plant such as fruit and etc.

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