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Short communication

Hypericum origanifolium Willd.: The essential oil composition of a new valuable species

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ABSTRACT

Turkish *Hypericum origanifolium* Willd has been recently considered for its hypericin and phenolic content as a potential substitute of the well-established EU market position *Hypericum perforatum*. However, a complete phytochemical characterization of *H. origanifolium* has not carried out yet in order to assert its potential industrial value. The present paper represents the first attempt to define the aromatic fingerprint of a representative wild Turkish *H. origanifolium* Willd. population. In addition, its volatiles were studied as potential discriminating constituents between *H. perforatum* and *H. origanifolium* with a similar hypericin and phenolic composition.

1. Introduction

The genus *Hypericum* (Guttiferae) is one of the most representative in temperate zones (Davis, 1988; Tutin, 1993; Robson, 2003). Due to the increasing commercial value of Hyperici herba, *Hypericum* species have received considerable renewed interest in the last years. Many studies have been carried out on the polar extracts of *Hypericum* spp. in order to compare their chemical composition and biological activities with those of the well-known *Hypericum perforatum* (Çirak et al., 2006, 2007a; Nogueira et al., 2013). In addition, the current research interest has been more and more addressed also towards the essential oils of *Hypericum* species and their volatile constituents as important chemotaxonomic markers (Bertoli et al., 2011; Crockett, 2010). Turkey represents one of the most important sites of *Hypericum* populations as the genus is represented by 89 species of which 43 are endemic (Davis, 1988). These plants are generally used as sedatives, antiseptics and antispasmodics in Turkish folk medicine under the names: "kantaron, peygamber çiçeği, kılıçotu, kanotu, kuzukıran and binbirdelik otu" (Baytop, 1999). However, in the last decade some companies interested in hypericins, hyperforins, phloroglucinols have collected wild Turkish plant materials for exporting to European herbal industry which is increasingly devoted to herbal treatments for depression (Çirak et al., 2004). In the last few years, a great pharmaceutical potential has been addressed to Turkish *Hypericum origanifolium* for its phenolic and hypericin content which is comparable to *H. perforatum*, the valuable marketable raw source of these compounds (Çirak et al., 2007b; Ayan et al., 2004; Ozen et al., 2005; Öztürk et al., 2009).

In the present work, the leaf (HOL) and flower (HOF) essential oils (EOs) of wild Turkish plant samples were hydrodistilled separately and analyzed by GC–MS for the first time. In addition, these results were compared to the EO fingerprints obtained from different plant parts (leaves, HPL and flowers, HPF) of a wild Turkish *H. perforatum* population collected in the same region (Samsun region). Due to the recent interest in Turkish *H. origanifolium* as a potential substitute of *H. perforatum* for its similar content in hypericins and flavonoids, the present work pointed out other target compounds and volatile chemical classes as discriminating phytochemicals for *H. origanifolium* and *H. perforatum* raw plant material.

2. Material and methods

H. origanifolium stems are 5–30 cm long, suberect to sometimes rooting at the base. The leaves are opposite, 5–30 mm in height; with intramarginal and sometimes superficial black glandular dots.

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Fig. 1. Turkish wild *H. origanifolium* sample at flowering period.

The flowers are numerous and of a golden yellow colour, forming inflorescence (Davis, 1988; Fig. 1). *Sampling procedures:* The aerial parts were collected at Çakallı district (Samsun province, 41°04′N; 36°01′E; 470 m sea level) in May at flowering period. The identification was carried out by Dr. Hasan Korkmaz, Department of Biology, University of 19 Mayıs, Samsun, Turkey. Voucher specimen was deposited in the herbarium of Ondokuz Mayis University Agricultural Faculty (OMUZF # 109). The air-dried aerial parts (150 g) were hydrodistilled and analyzed by both GC-FID and GC–MS at the same experimental condition reported in Çirak et al. (2010) (Table 1). Principal component analysis (PCA) was carried out using the statistical software package SPSS Version 13.0. The obtained data were used to create scatter plot diagrams (Backhaus et al., 1989). Therefore, a factor analysis was performed, whereby each variable was used to calculate relationships between variable and investigated factors.

3. Results and discussion

The development of reproductive parts, especially floral buds and flowers in *Hypericum* plants has been followed by the acceleration of secondary metabolism which has generally resulted in enhanced accumulation of different chemical compounds such as hyperforin, hypericins (Çirak et al., 2008), rutin, hyperoside, quercitrine (Hosni et al., 2011) and essential oils (Schwob et al., 2004). Further relationship between chemical content of plant material and harvesting time in different *Hypericum* plants was mathematically formulized and results of these studies indicated flowering time as the most suitable harvesting time for the highest chemical content (Odabas et al., 2008, 2009). Therefore, in the present study, the leaves (HOL) and flowers (HOF) of *H. origanifolium* were collected during the balsamic time in order to evaluate and compare the volatile levels at the same harvesting time generally considered for the valuable market *H. perforatum* raw material. In addition, Turkish *H. perforatum* has not yet been domesticated and it has been generally collected from its natural habitat. However, in the last decade some companies interested in hypericins, hyperforins, phloroglucinols content have collected Turkish plant materials for exporting to herbal industry, which is increasingly devoted to EU market of herbal treatments for depression (Çirak and Kevseroğlu, 2004). Therefore, lots of these wild Turkish *Hypericum* spp. have to be taken into consideration as a potential contaminating raw plant material of the well-established valuable crops *H. perforatum*. In this situation, the availability of Turkish *Hypericum* species with similar content of the standardized active principles (hypericins, hyperphorins, flavonoids) such as *H. origanifolium* should require a constant performed monitoring activity also based on other different markers (Çirak et al., 2004).

Table 1
GC–MS main composition of wild *H. origanifolium*.

Compounds	LRI[a]	HOL[b]	HOF	HPL	HPF
2-E-hexenol	860		0.03	0.97	1.72
α-Pinene	941	0.74	1.27	0.29	1.60
α-Cubebene	1351	0.74	1.10	0.14	0.21
a-Copaene	1377	4.82	3.86	1.02	1.19
β-Elemene	1392	2.26	1.65	0.17	0.17
β-Longipinene	1401			0.12	0.17
Isocaryphyllene[c]	1404			0.17	0.17
α-Gurujene	1409	2.60	1.83	0.11	0.08
β-Caryophyllene	1420	2.66	2.49	4.56	7.10
β-Gurjunene	1432	1.72	1.51	0.56	0.59
Aromadendrene	1440	2.72	1.96	0.42	0.38
E-β-farnesene	1455	0.68	tr[d]	1.13	2.25
Alloaromadendrene	1461	1.86	1.33	0.49	0.44
γ-Gurjunene		2.83	1.89		tr
γ-Muurolene	1479	4.65	4.71	3.40	3.74
Dodecanol	1482			5.55	1.01
Germacrene D	1482	2.65	3.32	0.14	0.26
β-Selinene	1486	16.12	15.34	5.70	4.96
Valencene	1493	0.96	2.76		
γ-Amorphene[c]	1491	1.70		0.58	0.79
trans-Muurolene-4 (14), 5-diene#	1493	1.70	tr		
α-Selinene	1496	19.62	18.71	4.33	3.79
Germacrene A	1501	1.39	1.94		
E.E-α-farnesene	1503	1.39	1.94		0.16
cis -γ-Cadinene	1511	2.60	2.51	1.92	2.41
δ-Cadinene	1524	8.21	7.74	1.91	2.62
trans-Nerolidol	1563			1.23	2.43
Spathulenol	1577	4.21	5.15	4.58	2.25
Caryophyllene oxide	1582	0.03	0.04	11.13	14.35
	0.36	0.08	6.11	4.23	
t-Cadinol	1640	0.56	0.76	1.18	1.80
t-Muurolol	1643		0.08	1.01	
α-Cadinol	1653	0.68		1.18	1.80
Himachalol	1654			1.02	
α-Eudesmol	1655		1.19	0.57	
Selina-11-en-6-a-ol[c]	1660	1.53	2.45	0.70	1.57
β-Bisabolol	1672			1.18	1.80
Cadalene[c]	1677			1.07	1.81
n-Tetradecanol	1677			11.87	1.71
Trimethylpentadecanone	1843		0.69	1.96	2.59
Hexadecanol				1.04	0.09
n-Heneicosane	2100		0.64	0.17	1.26
Total		**99.13**	**98.27**	**98.53**	**99.78**
Main volatile chemical classes					
Hydrocarbons		0.21	1.59	1.24	2.55
Oxygenated non-terpenoids		0.23	1.55	24.22	9.80
Aldhehydes		0.05	0.13	1.58	3.52
Hydrocarbon Monoterpenes		1.23	1.49	1.08	2.80
Oxygenated Mononoterpenes		0.03	0.20	0.85	4.12
Hydrocarbon Sesquiterpenes		84.85	79.08	33.32	39.77
Oxygenated Sequiterpenes		9.81	12.27	34.44	34.18

[a] Linear retention index on a non-polar column (LRIa).
[b] Percentage values (≥1.00%) are means of three values with *se* for the components below 5% in all cases.
[c] Tentative identification.
[d] tr = less than 0.01%. (HOF = flowers and HOL = leaves) and *H. perforatum* (HPF = flowers and HPL = leaves).

According to the present paper, the volatile fingerprints of leaf and flower *H. origanifolium* could be addressed as useful key quality parameters to distinguish the raw plant material of these two *Hypericum* species. Very similar aromatic fingerprints characterized the two different *H. origanifolium* plant organs. In fact, very few quali-quantitative differences were found between the leaf and flower EOs fingerprints of *H. origanifolium* (Table 1). Hydrocarbon sesquiterpenes were the main volatiles (84.8% HOL–79.1% HOF) in the both essential oil samples (Fig. 2). The target volatiles