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Essential oil composition of *Hypericum perforatum* L. and *Hypericum scabrum* L. growing wild in Tajikistan

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ABSTRACT

The essential oils obtained by hydrodistillation from the aerial parts of Hypericum perforatum L. and Hypericum scabrum L. from plants growing wild in Tajikistan were analyzed by GC-MS. Sixty-six compounds were identified in the essential oils of H. perforatum with germacrene D (13.7%), α-pinene (5.1%), (E)-caryophyllene (4.7%), n-dodecanol (4.5%), caryophyllene oxide (4.2%), bicyclogermacrene (3.8%), and spathulenol (3.4%) as the main constituents. Twenty-six components were identified in the oil of H. scabrum L. with α-pinene (44.8%), spathulenol (7.1%), verbenone (6.0%), trans-verbenol (3.9%), and γ-muurolene (3.5%) as the most abundant components. A cluster analysis based on the major components of H. perforatum reveals a large degree of variability in composition of samples from different geographical locations.

Keywords: *Hypericum perforatum*, *Hypericum scabrum*, essential oil composition, α-pinene, germacrene D, spathulenol, verbenone.

INTRODUCTION

The genus *Hypericum* of the Hypericaceae consists of over 450 species, with worldwide distribution in warm temperate, subtropical and mountainous tropical regions [1,2], and a number of *Hypericum* species are widely used in folk and modern medicine. Hypericin, an aromatic polycyclic anthrone, extracted from *Hypericum perforatum* L., has been shown to have potent, broad spectrum antimicrobial activity. This compound significantly inhibited the replication of several viruses, including HIV, influenza A, cytomegalovirus (CMV), Herpes

simplex 1 and 2 (HSV-1 and HSV-2), and Epstein-Barr virus (EBV. *H. perforatum* L. oils have also shown notable biological activities including antiviral, wound healing, antioxidant, antimicrobial, antifungal, anxiolytic and anticonvulsant activities [3,4]. The essential oil compositions and antimicrobial activities of *Hypericum* have been recently reviewed [5].

There have been numerous investigations of *H. perforatum* essential oils and they have show a wide variability in composition [6-15]. Thus, for example, the main constituents of the essential oil of *H. perforatum* from northern Turkey were sesquiterpenoids such as (*E*)-caryophyllene (4.1-5.9%), γ-muurolene (5.0-9.6%), β-selinene (5.1-19.6%), α-selinene (4.1-10.4%), δ-cadinene (3.0-4.9%), spathulenol (2.3-5.1%), and caryophyllene oxide (6.0-12.2%) [6]. A different sample from Turkey was dominated by α-pinene (61.7%) with lesser amounts of δ-3-carene (7.5%), (*E*)-caryophyllene (5.5%), myrcene (3.6%), and cadalene (3.2%) [15]. Lithuanian *H. perforatum* was dominated by oxygenated sesquiterpenoids caryophyllene oxide (7.7-34.0%), spathulenol (4.5-11.0%) and viridiflorol (0.5-11.1%) [7], while *epi*-bicyclosesquiphellandrene (10%) and *n*-alkanes were the major components of the essential oil from Bulgarian *H. perforatum* [8]. The main constituents of the volatile oils of *H. perforatum* from southeastern France were (*E*)-caryophyllene (0.2-28.4%), *ar*-curcumene (0.6-13.0%), spathulenol (0.5-21.5%), and caryophyllene oxide (0.5-18.4%) [9], but 2-methyloctane (21.1%), germacrene D (17.6%) and α-pinene (15.8%) were the major compounds in Sardinian *H. perforatum* oil [10]. α-Pinene (29.3%) was the main component of the volatile oil from Iranian *H. perforatum* [11]. Greek *H. perforatum* oils were rich in germacrene D (16.9-22.8%), 2-methyloctane (10.8-17.8%), (*E*)-caryophyllene (6.6-10.3%), α-pinene (5.2-10.1%), and bicyclogermacrene (4.1-4.8%) [12]. *H.perforatum* growing in Uzbekistan showed (*E*)-caryophyllene (11.7%), caryophyllene oxide (6.3%), spathulenol (6.0%), α-pinene (5.0%) as the most abundant components [13].

Hypericum scabrum L. essential oils have generally shown an abundance of α-pinene. The major components of the essential oil of *H. scabrum* from Uzbekistan, for example, were α-pinene (11.2%), spathulenol (7.2%), *p*-cymene (6.1%), acetophenone (4.8%), and carvacrol (4.7%) [14]. Turkish *H. scabrum* oil contained α-pinene (71.6%), (*E*)-caryophyllene (4.8%), myrcene (3.8%), cadalene (3.4%) and β-pinene (2.9%) [15], while Iranian *H. scabrum* oil was composed of α-pinene (45.3%), *n*-nonane (5.6%) and thymol (5.3%) [16].

Because of the medicinal importance of *Hypericum* species and the variation in composition with geographical location, in this study we have examined the essential oil compositions of *H. perforatum* and *H. scabrum* growing wild in Tajikistan. To our knowledge, Tajik *Hypericum* essential oils have not been previously reported. In addition, we have carried out a cluster analysis of *H. perforatum* based on essential oil composition.

EXPERIMENTAL SECTION

Plant Material

Aerial parts of *H. perforatum* and *H. scabrum* were collected in Chormaghzak village, Yovon region, Tajikistan (38.4055 N, 69.1701 E, 1500 m above sea level), on 25 July 2010 and 2 May 2008. The plants were identified by F.S. Sharopov. Voucher specimens have been deposited in the herbarium of the Chemistry Institute of the Tajikistan Academy of Sciences herbarium, voucher numbers TJ2010-017 (*H. perforatum*) and TJ2008-023 (*H. scabrum*). The plants were

air dried and the dried samples were crushed and hydrodistilled for 3 h to give yellow essential oils in 0.1% and 0.4% yield, respectively.

Gas Chromatography – Mass Spectrometry

GC-MS analysis was performed on the essential oils of *H. perforatum* and *H. scabrum* using an Agilent 6890 GC, Agilent 5973 mass selective detector, HP-5ms column as described previously [17]. 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 [18], and stored on the MS library [NIST database (G1036A revision D.01.00)/ChemStation data system (G1701CA, version C.00.01.080)]. The percentages of each component are reported as raw percentages based on total ion current without standardization. The chemical compositions of the *H. perforatum* and *H. scabrum* oils are summarized in Tables 1 and 2, respectively.

Numerical Cluster Analysis

A total of 67 different *H. perforatum* samples [7-9,11,14,19-26] were treated as operational taxonomic units (OTUs). The percentage composition of 50 main essential oil components was used to determine the chemical relationship between the different *H. perforatum* essential oil samples by cluster analysis using the NTSYSpc software, version 2.2 [27]. Correlation was selected as a measure of similarity, and the unweighted pair-group method with arithmetic average (UPGMA) was used for cluster definition.

RESULTS AND DISCUSSION

A total of 66 compounds were identified in the essential oil of *H. perforatum*, representing 89.2% of the composition (Table 1). The major components were germacrene D (13.7%), α-pinene (5.1%), (*E*)-caryophyllene (4.7%), *n*-dodecanol (4.5%), caryophyllene oxide (4.2%), bicyclogermacrene (3.8%), and spathulenol (3.4%). The cluster analysis (Fig. 1) shows some, albeit not close, relationship to a sample from Serbia, both rich in α-pinene and spathulenol [14,21]. In her review of *Hypericum* essential oils [5], Crockett noted the enormous variability in the chemical compositions of *H. perforatum*, and this conclusion is supported by the cluster analysis (Fig. 1). In spite of the variability, there are some apparent chemical constituent clusters. Not only are there (*E*)-caryophyllene-rich, caryophyllene-oxide-rich, germacrene-D-rich, and α-pinene-rich chemotypes as previously noted by Crockett [5], but also clusters dominated by β-selinene, spathulenol, and tetradecanol (Fig. 1). The *H. perforatum* essential oil in this current study is notable in that it is rich in both germacrene D as well as pinenes.

Table 1: Chemical composition of *Hypericum perforatum* L. from Tajikistan

RI	Compound	%	RI	Compound	%
940	α-Pinene	5.1	1439	Unidentified	4.2
978	β-Pinene	2.8	1453	α-Humulene	0.7
992	Myrcene	1.2	1458	(*E*)-β-Farnesene	0.5
1004	α-Phellandrene	0.2	1463	Sesquisabinene	0.4
1024	*p*-Cymene	0.9	1467	(2*E*)-Dodecenal	1.6

1028	Limonene	0.2	1475	*n*-Dodecanol	4.5
1030	1,8-Cineole	0.4	1477	γ-Muurolene	1.1
1036	Santolina alcohol	1.1	1482	Germacrene D	13.7
1048	(*E*)-β-Ocimene	0.2	1486	β-Selinene	1.8
1058	γ-Terpinene	0.4	1492	*trans*-Muurola-4(14),5-diene	0.3
1100	Linalool	0.4	1496	Bicyclogermacrene	3.8
1105	*cis*-Thujone (= α-Thujone)	0.7	1500	α-Muurolene	0.5
1116	*trans*-Thujone (= β-Thujone)	1.6	1505	Germacrene A	0.5
1133	Octyl formate	0.4	1509	(*E*,*E*)-α-Farnesene	0.6
1153	Menthone	0.3	1514	γ-Cadinene	1.0
1164	Borneol	0.5	1523	δ-Cadinene	2.2
1170	(2*E*)-Nonenol	0.8	1563	(*E*)-Nerolidol	3.2
1176	Terpinen-4-ol	0.5	1569	(3*Z*)-Hexenyl benzoate	0.5
1189	α-Terpineol	0.7	1576	Spathulenol	3.4
1237	Pulegone	1.9	1582	Caryophyllene oxide	4.2
1242	Carvone	0.4	1590	Globulol	0.8
1253	*cis*-Piperitone epoxide	0.7	1602	Ledol	1.0
1256	Linalool acetate	0.3	1611	Unidentified	1.2
1260	*cis*-Chrysanthenyl acetate	0.6	1617	Junenol	0.4
1277	Citronellyl formate	0.3	1628	1-*epi*-Cubenol	0.3
1292	Thymol	1.8	1639	Unidentified	4.7
1301	Carvacrol	1.4	1646	α-Muurolol (= Torreyol)	0.8
1349	a-Cubebene	0.2	1649	β-Eudesmol	0.3
1368	Piperitenone oxide	0.5	1654	α-Cadinol	3.5
1374	(2*E*)-Undecenol	0.5	1670	14-Hydroxy-9-*epi*-(*E*)-caryophyllene	0.8
1386	β-Bourbonene	0.3	1676	*n*-Tetradecanol	1.4
1393	β-Elemene	1.2	1685	Germacra-4(15),5,10(14)-trien-1α-ol	0.6
1412	2-*epi*-β-Funebrene	0.6	1844	Phytone	0.5
1420	(*E*)-Caryophyllene	4.7	1948	Unidentified	0.7
1429	β-Copaene	0.3	2107	(*E*)-Phytol	0.3
				Total Identified	89.2

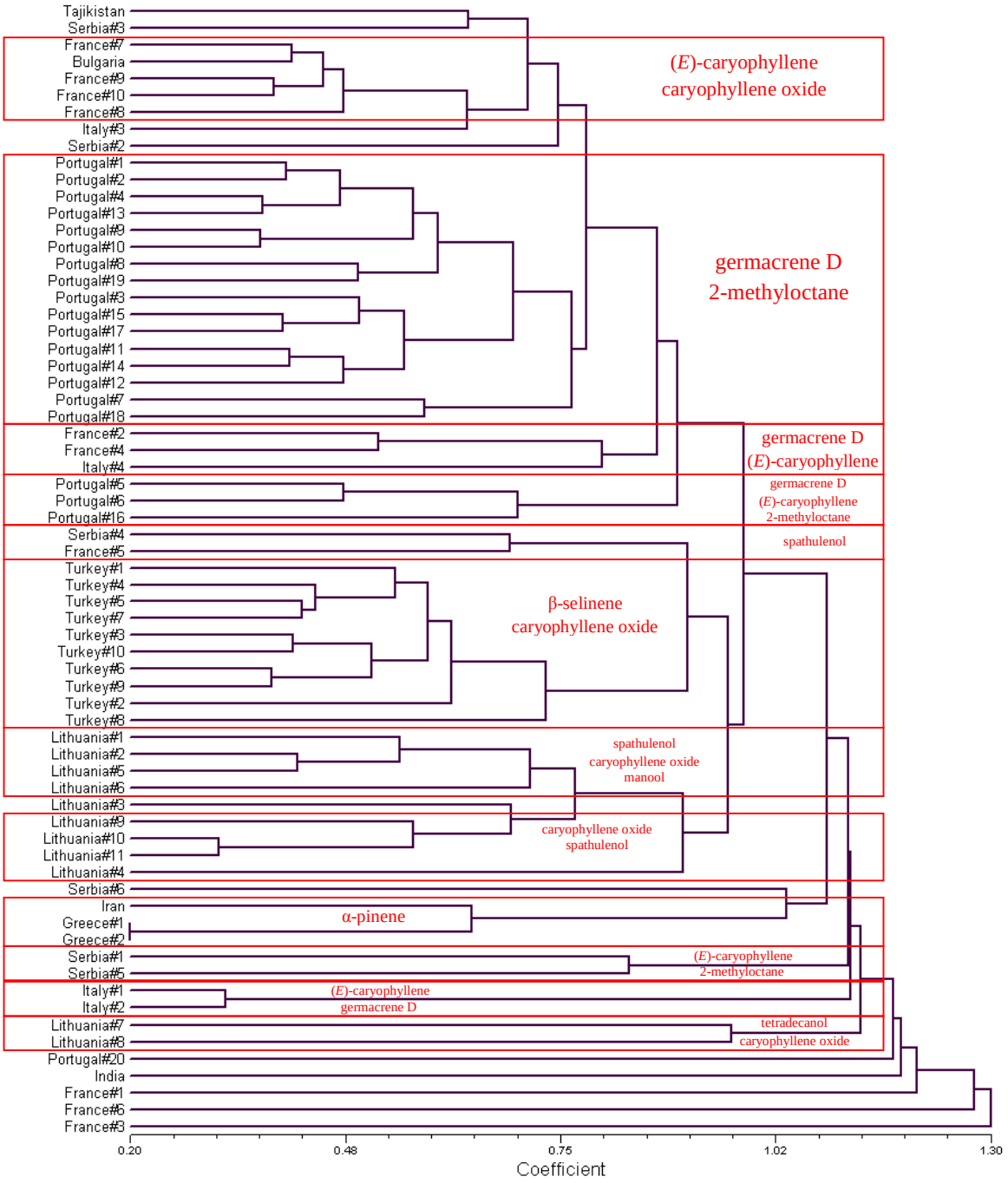

Figure 1. Dendrogram obtained by cluster analysis of the percentage composition of essential oils from 67 *Hypericum perforatum* samples, based on correlation and using the unweighted pair-group method with arithmetic average (UPGMA).

Twenty-six components were characterized in the *H. scabrum* oil, accounting for 95.6% of the oil, which was dominated by α-pinene (44.8%). Other major components in *H. scabrum* oil were spathulenol (7.1%), verbenone (6.0%), *trans*-verbenol (3.9%), and γ-muurolene (3.5%). Thus, the *H. scabrum* oil from Tajikistan is qualitatively similar to essential oils from previous studies

in that α-pinene was the major component [13,15,16,28,29], but does show some differences such as the absence of thymol, carvacrol [13,16], myrcene [15], or limonene [28,29].

Table 2: Chemical composition of *Hypericum scabrum* L. from Tajikistan

RI	Compound	%	RI	Compound	%
941	α-Pinene	44.8	1294	α-Campholenic acid	1.5
958	Thuja-2,4(10)-diene	1.1	1378	*trans*-Soberol	1.6
978	β-Pinene	2.8	1439	α-Guaiene	1.0
1126	α-Campholenal	1.9	1477	γ-Muurolene	3.5
1137	*trans*-Pinocarveol	2.3	1485	β-Selinene	1.0
1144	*trans*-Verbenol	3.9	1500	α-Muurolene	0.6
1163	Pinocarvone	1.3	1513	γ-Cadinene	1.7
1184	*p*-Cymen-8-ol	1.2	1522	*trans*-Calamenene	1.3
1189	α-Terpineol	1.2	1552	Unidentified	0.8
1194	Myrtenol	1.9	1569	(3*Z*)-Hexenyl benzoate	1.0
1207	Verbenone	6.0	1576	Spathulenol	7.1
1217	*trans*-Carveol	2.1	1581	Caryophyllene oxide	2.1
1221	Unidentified	2.3	1611	Unidentified	1.3
1273	*cis*-Tetrahydrojasmine	1.2	1653	α-Cadinol	0.8
1285	*cis*-Verbenyl acetate	0.7		Total Identified	95.6

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