Essential Oil Composition of *Hypericum* 'Hidcote'

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Abstract

The essential oil of the artificial hybrid *Hypericum* 'Hidcote', one of the most cultivated St. John's worts in European and American gardens, was analyzed for the first time by GC and GC/MS. Forty-six components were identified, representing 91.5% of the oil. The sesquiterpene fraction gave the highest contribution (68.4%), whilst monoterpenes amounted to 22.5%. The major constituents were β-pinene (11.9%), α-humulene (7.4%), β-caryophyllene (6.5%) and α-selinene (5.4%). Results confirm that hybridization may generate novel secondary chemistry in plants.

Key Word Index

Hypericum 'Hidcote', Guttiferae, essential oil composition, β-pinene.

Introduction

The genus *Hypericum* (Guttiferae family) comprises mainly perennial herbs, but also several shrubs producing large and showy flowers, and for this reason it is used as ornamental garden plants. Among them, *Hypericum* 'Hidcote' is certainly one of the most commonly cultivated St. John's worts in European and American gardens (1). In past times this plant was called *H. patulum* 'Hidcote', but now it is believed to be an artificial hybrid derived from *H. calycinum* L. and *H.* x *cyathiflorum* N. Robson, itself a hybrid between *H. addingtonii* N. Robson and *H. hookerianum* Wight et Arn. (2–4). *Hypericum* 'Hidcote' is a semi-evergreen, very showy shrub up to six feet tall, which produces an abundance of large golden yellow flowers until the first frosts of the autumn. This hybrid is very similar to *H. calycinum*, although it differs for its decussate, ovate-lanceolate shaped leaves and shorter non reddish stamens (Figure 1).

Because of its large distribution in many gardens of Europe and United States, *H.* 'Hidcote' may represent an easily reached and available source of pharmaceutical compounds. For this reason we decided to investigate its essential oil composition. Data about phytochemical analysis of *H.* 'Hidcote' are not well-known; to the best of our knowledge, the present work represents the first investigation of this plant.

Experimental

Plant material and oil isolation: *Hypericum* 'Hidcote' was collected during flowering in September 2006 in a garden located in front of the Institute of Botany, Slovak Academy of Sciences, Bratislava (Slovakia). A voucher specimen was identified by Prof. Mártonfi at the Institute of Biology and Ecology, Department of Botany, P. J. Šafárik University, Košice (Slovakia); then it was deposited in the Herbarium Camerinensis, Department of Environmental Sciences, Section of Botany and Ecology, University of Camerino (Italy), under the accession code CAME 9606. Air dried leaves, with flowers and fruits (25 g), were subjected to hydrodistillation for 3 h, using a Clevenger-type apparatus with hexane (10 mL) as collector solvent. After evaporation of the solvent under a N_2 flow, the oil (yield 0.24%) was dried over anhydrous sodium sulphate and stored in sealed vials under refrigeration before GC-FID and GC/MS analyses.

Gas chromatography: GC analysis of the oil was carried out using an Agilent 4890D instrument with FID detector and a HP-5 column (25 m x 0.32 mm, 0.17 μm film thickness), working with the following temperature program: 5 min at 60°C, and subsequently at 4°C/min up to 220°C, then 11°C/min up to 280°C held for 15 min; injector and detector temperatures: 280°C; carrier gas: He; flow rate: 1.4 mL/min; injection volume: 1 μL; split ratio: 1:34.

Gas chromatography-mass spectrometry: GC/MS analysis was performed using an Agilent 6890N-5973N GC/MS system operating in the EI mode at 70 eV, using a HP-5MS (30 m x 0.25 mm, 0.1 μm film thickness) capillary column which was programmed at 40°C for 5 min, then ramp at 4°C/min to 220°C, then 11°C/min up to 280°C held for 15 min,

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finally 11°C/min up to 300°C held for 5 min; carrier gas: He; flow rate: 1.0 mL/min; injector and transfer line temperatures: 280°C; injection volume: 2 μL; split ratio: 1:50; scan time: 75 min; acquisition mass range: 29–400.

Identification of the components: The identification of the components was based on computer matching with the WILEY275 and NIST02 libraries, as well as by comparison of the mass spectra with those reported in the literature (5–6). Retention indices relative to n-alkanes were also considered and whenever possible authentic compounds were used. Area percentages were obtained electronically from the GC-FID response without the use of an internal standard or correction factors.

Results and Discussion

Composition of the oil of *H.* 'Hidcote' is given in Table I. Forty-six components were identified, representing 91.5% of the oil under study. β-Pinene (11.9%), α-humulene (7.4%), β-caryophyllene (6.5%) and α-selinene (5.4%), were the most abundant components. The sesquiterpenes gave the highest contribution (68.4%) with hydrocarbons dominating (51.7%). The monoterpenes amounted to 22.5% with the hydrocarbons dominating (19.4%). Aliphatic compounds gave the lowest contribution (0.6%). High content of sesquiterpene hydrocarbons was also reported in previous studies of some *Hypericum* oils (7–10).

If we compare our results with data available from relatives of *H.* 'Hidcote' (*H. calycinum* and *H. hookerianum*), we may notice some quantitative and qualitative differences. Mathis and Ourisson (11,12) in the chemotaxonomic investigation of *Hypericum* oils concluded that *H. calycinum* (Sect. Eremanthe) and *H. hookerianum* (Sect. Norysca) may be enclosed in a group with limonene (> 10%), rich in oxygenated monoterpenes (more than 40% and from 10 to 40%, respectively) and poor in sesquiterpenes, whilst our results showed the sesquiterpene fraction (68.4%) as predominant in *H.* 'Hidcote' oil and a content of limonene (3.0%) not typical of Eremanthe and Norysca sections.

Recently, in two investigations of the oil of *H. calycinum* growing in Turkey (13) and China (14), 32 and 37 components were identified by microdistillation, respectively, with β-pinene (29.2%) and α-terpineol (11.5%) (13), and α-pinene (24%) and β-pinene (14%) (14), reported as the main constituents, respectively. We also detected β-pinene (11.9%) as the predominant compound, whilst α-terpineol (2.5%) and α-pinene (3.4%) were not as abundant as in the studies cited above. The oil of *H.* 'Hidcote' shared 8 of 32 and 20 of 37 components with the oil of *H. calycinum* from Turkey and China, respectively, supporting the hypothesis that the chemistry of parental species can be partially repeated in its hybrids. However, the higher number of components detected (46) confirms that hybridization may generate also a novel secondary metabolite chemistry (15). Among new major components detected in *H.* 'Hidcote' with respect to its relatives, there were α-selinene (5.4%), *trans*-dihydro-occidentalol (4.5%), β-selinene (4.4%) and γ-muurolene (4.0%). Therefore, analysis of the essential oil may be very useful in the identification of the hybrids, especially when they have a morphology very similar to their relatives to make the identification quite doubtful.

Table I. Chemical composition of *Hypericum* 'Hidcote' essential oil

Compound	RI*	(%)	Method of Identification
nonane	900	0.2	1,2
α-pinene	934	3.4	1,2
β-pinene	977	11.9	1,2
myrcene	994	0.4	1
limonene	1032	3.0	1,2
γ-terpinene	1063	0.4	1
terpinolene	1090	0.4	1
linalool	1098	0.3	1,2
terpinen-4-ol	1180	0.3	1
α-terpineol	1192	2.5	1,2
α-cubebene	1356	0.3	1
α-copaene	1377	1.4	1
β-bourbonene	1384	0.6	1
β-isocomene	1400	0.3	1
β-caryophyllene	1416	6.5	1,2
β-copaene	1426	0.3	1
aromadendrene	1434	0.5	1,2
α-humulene	1451	7.4	1,2
allo-aromadendrene	1459	0.2	1,2
(E)-β-farnesene	1461	3.2	1
β-chamigrene	1468	0.2	1
γ-muurolene	1476	4.0	1
β-selinene	1484	4.4	1
cis-β-guaiene	1487	0.3	1
α-selinene	1492	5.4	1
trans-β-guaiene	1498	0.2	1
(E,E)-α-farnesene	1506	3.7	1
γ-cadinene	1511	2.2	1
(Z)-γ-bisabolene	1516	3.0	1
δ-cadinene	1524	4.2	1
zonarene	1532	2.0	1
α-calacorene	1543	0.2	1,2
germacrene B	1555	0.9	1
spathulenol	1577	0.8	1
caryophyllene oxide	1581	0.9	1
guaiol	1598	1.4	1,2
humulene epoxide II	1612	0.3	1
10-epi-γ-eudesmol	1618	1.4	1
1-epi-cubenol	1630	1.4	1
γ-eudesmol	1632	1.1	1
cis-cadin-4-en-7-ol	1640	0.4	1
epi-α-cadinol	1645	1.0	1
β-eudesmol	1650	2.4	1
trans-dihydro-occidentalol	1654	4.5	1
bulnesol	1669	1.0	1
hexadecanoic acid	1974	0.4	1

*: Retention Indices relative to C9-C24 alkanes on the HP-5MS column; 1: mass spectra, 2: authentic sample.

Finally, novel chemistry of artificial hybrids may be of interest for future larger scale phytochemical and pharmaceutical applications, since these plants could be easily cultivated.

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Figure 1. *Hypericum* 'Hidcote'

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