

裂叶荆芥不同部位香精油组成研究

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摘要: 采用水蒸气蒸馏法, 分别从裂叶荆芥的叶、茎和花三个不同部位提取香精油并进行气相色谱/质谱分析。结果发现, 叶、茎、花的香精油分别含有 23、29、26 种组分。叶和花香精油的组成和含量基本相似, 主要成分是含量分别为 15.09%、14.51% 的薄荷酮和 29.26%、31.36% 的 (+) 胡薄荷酮等单萜化合物以及含量分别为 17.09%、5.00% 的 1-萜草烯等倍半萜。而茎香精油的萜类化合物含量较低, 含薄荷酮为 4.15%, (+) 胡薄荷酮为 7.68%, 但其乙酯含量相对较高, 如 (E)-9-十六碳烯酸乙酯含量为 11.92%, 异戊酸乙酯为 9.38%。

关键词: 裂叶荆芥; 香精油; 组成

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Composition of Essential Oil from the Aerial Part of *Schizonepeta tenuifolia*XIE Lian-wu^{1,2}, DAI Shi-kun^{1,2}, WANG Guang-hua^{1,2}, ZHANG Jun-zeng³, CHEN Min-jie^{1,2}, LI Xiang^{1*}¹South China Sea Institute of Oceanology, Chinese Academy of Sciences, Guangzhou 510301, China;²Graduate University of the Chinese Academy of Sciences, Beijing 100049, China;³Institute for Nutritional Sciences and Health, National Research Council of Canada, Charlottetown PEI C1A 4P3, Canada

Abstract: *Schizonepeta tenuifolia* (Benth.) Briq. of Labiatae family is widely used as a key components of traditional Chinese medicine in China. The compositions of essential oil extracted by hydrodistillation from the leaf, stem and fascicled flower (spike) of *Schizonepeta tenuifolia* were identified using GC/MS. The leaf oil comprised of 23 components, while the stem and spike oil contained 29 and 26 components, respectively. The constituents and their level of contents in essential oil extracted from the leaf and spike were similar with the major components of (1) monoterpene: menthone (15.09% from leaf and 14.51% from spike), (2) (+)-pulegone (29.26% from leaf and 31.36% from spike) and (3) sesquiterpene: α -humulene (17.09% from leaf and 5.00% from spike). The stem oil contains a higher content of ethyl esters [ethyl-(E)-9-hexadecenoate, 11.92%; ethyl isovalerate 9.38%] and a lower level of monoterpenes (menthone of 4.15% and (+)-pulegone of 7.68%) than the leaf and spike oil.

Key words: *Schizonepeta tenuifolia* Labiatae; essential oil; composition

Introduction

The plant *Schizonepeta tenuifolia* (Benth.) Briq. (Jingjie in Chinese) is a member of Labiatae family, and mainly grows in Southern and Central China. It is the dried aerial part including the spike, leaf and stem

of *Schizonepeta tenuifolia* that are often used in traditional Chinese medicine (TCM)^[1]. With the increasing use of herbal products, *S. tenuifolia* has been commonly marketed for the treatment of common cold and fever with headache, sore throat^[2], allergic dermatitis, pruritus^[3], and eczema^[4] in TCM. *In vitro* and *in vivo* studies on its pharmacological activities have also been carried out^[2-5]. In addition, the carbonized herb is recommended and used as a remedy for stopping bleeding due to its hemostatic property^[6]. It had been known that the essential oils from many aromatic plant and herb possess bioactivity such as antimicrobial^[7], antifungal^[8] and antioxidant properties^[9]. So research on

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compositions of essential oil from TCM had become increasingly important. Several major components and structures such as glycosides (schizonepetoside A, B, C, D and E), schizonol, schizonodiol^[10,11], volatile oils (menthone and pulegone)^[12,13], and flavonoids^[10] (diosmetin, hesperetin, and luteolin) have been isolated and identified from *S. tenuifolia*. Although as mentioned above that many studies on its pharmacological activities have been carried out, but no detailed analysis of the essential oil from its spike, leaf and stem has been reported. Therefore, as part of fingerprint research on *S. tenuifolia*, the present investigations were designed to identify the compositions of the essential oils from the leaf, stem and spike of *S. tenuifolia*.

Experimental

Plant material and extraction

The aerial part including the spikes, leaves and stems of *S. tenuifolia* were collected from mature plants (in anthesis) growing in Hongan County, Hubei Province, China. After air-dried, about 200 g each of spikes, leaves and stems were subjected to hydrodistillation in 3 L boiling distilled water with an essential oil collector. The process was performed until there was no significant increase in volume of oil within 6 h, yielding 2.92 g spike oil, 1.56 g leaf oil and 0.83 g stem oil. All oil samples were dried over anhydrous sodium sulphate and stored at 10 °C in the absence of light.

GC-MS analysis

Analysis of essential oil extract employed a Thermo Finnigan TRACE gas chromatography (GC), equipped with Thermo Finnigan TRACE MS^{plus} and HP-5 silica fused capillary column (30 m × 0.25 mm i.d. with 0.25 μm membrane thickness, Agilent Technology). Splitless surge injection of 1 μL of extract was manually conducted. The injector and the transfer line temperature were maintained at 250 °C and 280 °C, respectively. Column temperature was programmed from 40 °C (hold for 1 min) to 100 °C at a rate of 10 °C/min, 100 °C for 2 min, followed by an increase to 180 °C at a rate of 4.0 °C/min, 180 °C for 2 min, then increased to 280 °C at a rate of 5.0 °C/min (hold for 8 min). Ul-

tra-purified helium was used as the carrier gas with split flow 50 mL/min for 2 min, flow rate at 1 mL/min, surge pressure 300 kPa for 2 min, and gas saver flow 20 mL/min for 2 min.

Mass spectra were acquired at the electron ionization (EI) mode with an electron multiplier voltage of 2200 V and an ionization voltage of 70 eV. The mass scanning ranged between m/z 45 and m/z 550 under scan mode.

Identification of components

Identifications of components were achieved by matching their mass spectra with those in the WILEY, MARLB, REPLB and NISTDEMO libraries with similar index (SI) > 800 or with published MS data bank^[14]. The components were confirmed by comparing their Kovats retention indices with those of authentic compounds. The Kovats retention indices of the components were determined relative to the retention times of a series of n-alkanes. Quantification was performed by integration of the selected ion chromatograms extracted from the total ion current. Quantitative data were obtained from the total ion current chromatogram (TIC) peak area percentages without the use of correction factors.

Results and Discussion

The constituents of the leaf oil, the stem oil and the spike oil of *S. tenuifolia* were given in Table 1, together with experimental Kovats retention indices (RI) on HP-5 column, including their percentage peak areas. Distinct qualitative and quantitative differences were observed in three kinds of essential oils studied. Major compounds over 5% of each of the essential oils were described below.

There were 18 terpenoids of the 23 volatile compounds from the leaf oil, making up 86.92% of the total oil composition. Major terpenoid compounds were (+)-pulegone (29.26%), -humulene (17.09%) and menthone (15.09%). Non-terpenoids identified from the leaf oil only represented 13.08% of the oil. Terpenoids were one group of interesting components because of their broad bioactivities, notably antibacterial and

Table 1 Composition of essential oil from *Schizonepeta tenuifolia*^a

Compound	R ^b	Leaf	Stem	Spike	Method of identification ^c
Ethyl isovalerate	859	1.28	9.38	-	RIMS
3-Octanone	968	0.21	0.23	0.38	MS
1-Octen-3-one	982	0.05	0.43	0.21	MS
Myrcene	991	0.23	0.16	0.35	RIMS
3-Octanol	993	0.85	1.12	0.31	MS
Limonene	1022	2.98	3.00	4.50	RIMS
1-Ocrenyl acetate	1048	2.26	1.84	2.15	RIMS
<i>cis-p</i> -Menth-2,8-dien-1-ol	1123	-	1.31	1.53	RIMS
Menthone	1157	15.09	4.15	14.51	RIMS
Menthofuran	1165	2.43	2.53	2.95	RIMS
Isopulegone	1187	1.49	1.11	2.29	RIMS
(<i>E, E</i>)-5,7-Dodecadiene	1201	-	4.36	5.08	RIMS
(+) Pulegone	1225	29.26	7.68	31.36	RIMS
(-) Pulegone	1236	4.21	2.49	1.90	RIMS
4,5-Epoxy-carane	1290	0.51	0.40	-	RIMS
Cineol	1292	-	-	0.60	RIMS
2-Undecenal *	1350	-	1.68	1.96	MS
(<i>E</i>)- γ -Famesene	1458	1.73	1.02	2.19	RIMS
γ -Acoradiene	1463	2.38	2.12	2.47	RIMS
(<i>Z, E</i>)- γ -Famesene	1491	1.31	1.65	0.93	RIMS
Cadina-1,4-diene	1532	0.25	0.23	0.49	RIMS
γ -Humulene	1558	17.09	21.42	5.00	RIMS
Cedrenol	1696	0.05	0.28	0.32	MS
6,10,14-Trimethyl-2-pentadecanone	1849	0.22	0.43	0.29	RIMS
Hexadecanoic acid	1995	0.36	0.16	0.09	RIMS
Ethyl-(<i>E</i>)-9-hexadecenoate	2027	3.98	11.92	2.78	RIMS
Ethyl, linoleate	2155	-	1.48	1.73	RIMS
Famesyl acetate *	2283	0.22	0.29	0.32	RIMS
Tetracosane	2400	-	0.11	-	RIMS
Heptacosane	2700	-	0.14	-	RIMS

Note: ^a shows percentage of compounds of essential oils; ^b Kovats retention indices on HP-5 GC column; ^c Compounds were identified by comparison with the authentic standards on the following criteria: RI on HP-5 GC column and mass spectra at the electron ionization mode; * *cis-trans* isomer not identified

antioxidant properties

Although 29 compounds from the stem oil were analyzed, only two compounds γ -humulene (21.42%) and (+) pulegone (7.68%) were predominated ones in 19 terpenoids components. The other two major component ethyl-(*E*)-9-hexadecenoate (11.92%) and ethyl isovalerate (9.38%) were both ethyl esters. The

content of all terpenoids of stem oil (58.73%) was 30% less than that of the leaf oil.

The analysis of the spike oil revealed that (+) pulegone (31.36%), menthone (14.51%), (*E, E*)-5,7-dodecadiene (5.08%) and γ -humulene (5.00%) as the major components. The content of 17 terpenoids from 26 compounds identified from the spike oil was

similar to that of leaf oil, making up 81.37% of the total extract

Among the 6 main components mentioned above, 4 of them, such as menthone, (+)-pulegone, α -humulene, and ethyl-(*E*)-9-hexadecenoate presented in all three kinds of oils. Ethyl isovalerate was not detected in the spike oil, with only 1.28% ethyl isovalerate in the leaf oil compared with that of the stem oil. In addition, the leaf oil did not contain (*E, E*)-5,7-dodecadiene, whereas it showed both in stem oil (4.36%) and spike oil. The stem oil was characteristic of having a higher content of ethyl esters (ethyl-(*E*)-9-hexadecenoate and ethyl isovalerate) and a lower content of monoterpenes (menthone 4.15% and (+)-pulegone 7.68%), when compared with leaf and spike oil. The constituents and contents of essential oil extracted from the leaves and spikes were similar, with the major components being monoterpenes (menthone and (+)-pulegone) and sesquiterpene (α -humulene).

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