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ANALYSIS OF VOLATILES IN THE FLOWERS OF *Patrinia scabiosifolia* BY HS-SPME-GC-MS

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Patrinia, a genus of about 20 species, which belongs to the family Valerianaceae, is an herbaceous perennial plant growing locally in temperate eastern Asia [1]. According to the Chinese herbology, *Patrinia scabiosifolia* Fisch., which grows in northeastern China, is latent heat clearing, antipyretic, detoxicant, anti-inflammatory, stasis-eliminative, and pus-discharging; it is used traditionally in the treatment of intestinal carbuncle, including acute appendicitis, abscess of the liver, dysentery in enteritis, postpartum abdominal pain due to blood stasis, carbuncle, and deep-rooted ulcer [2]. The herb is also used in folk remedy in combination with other medicinal herbs for treating gastrointestinal cancer and has been reported to inhibit murine ascites cancer [3].

Phytochemical research showed that triterpenoids [4, 5], sterols [6], and coumarins [7] were the main constituents in *P. scabiosifolia* roots. Pharmacological studies and clinical practice have demonstrated that *P. scabiosifolia* has antibacterial, antiviral, antitumor, sedative-hypnotic, hepatoprotective, and choleretic action [8–11]. To the best of our knowledge, there is no research on the volatiles from the flowers. We studied the volatiles in *P. scabiosifolia* flowers using solid-phase micro-extraction coupled with GC-MS for the first time.

The volatiles in *P. scabiosifolia* flowers and their percentages are given in Table 1. Twelve compounds were identified in *P. scabiosifolia* flowers, which comprised 96.21% of the total volatiles. Esters (87.40%) were dominant in the flowers. The most abundant compound is *cis*-3-hexenyl isovalerate (28.91%), followed by pentanoic acid phenylmethyl ester (20.79%), hexyl *n*-valerate (10.44%), 3-methyl-2-phenylethyl butanoic acid ester (9.80%), 3-methylbutanoic acid 3-methylbutyl ester (8.75%), and *trans*-2-hexenyl valerate (5.79%).

cis-3-Hexenyl isovalerate, which has a flowery fragrance and new fresh fruit fragrant and the ripe apple fragrance, is often used in tobacco and flavoring. 3-Methylbutanoic acid 3-methylbutyl ester is used widely as a food odorant in imitation apple, banana, and fruit odor type essences. It can also be used in synthesizing some medicine. *trans*-2-Hexenyl valerate has a fruity fragrance, while 3-methyl-2-phenylethyl butanoic acid ester has a strong fruit and rose fragrance and is commonly used in flavoring and cosmetics [12]. Eugenol which has an intense clove smell, is used to make the essences, isoeugenol and vanillin. It may also be used as a pesticide and antiseptic. So it is considered that these ingredients are the main source of fragrance of *P. scabiosifolia* flowers.

Plant Material. The air-dried *P. scabiosifolia* flowers were collected in Henan, China, in July 2009. They were identified by Prof. Changqin Li, and voucher specimens were deposited in the Institute of Natural Products, Henan University.

Extraction of Volatile Constituents. Volatile organic compounds were extracted by a manual SPME holder together with 5 mL vials and PDMS-DVB fibers purchased from Supelco Inc. (Bellefonte, USA). Prior to extraction, the fiber was activated for 10 min in the GC 6890 system (Agilent, USA). The powder of *P. scabiosifolia* flowers, about 0.7 g, was placed in vials (5 mL), then the SPME fiber was exposed in the upper space of the sealed vial for 30 min at 80°C to adsorb the analytes. After that, the fiber was withdrawn and directly inserted into the GC-MS inlet for desorption of the volatiles for 1 min.

HS-SPME-GC-MS Analyses. The volatile constituents were analyzed by HS-SPME-GC-MS. Analysis was carried out using an Agilent 6890 N gas chromatograph equipped with a DB-5 MS capillary column (5% phenylmethylsiloxane, 30 m × 0.25 mm, film thickness 0.25 μm, Agilent Technologies, USA) coupled with a 5975B mass selective detector spectrometer from the same company. The front inlet was kept at 250°C in splitless mode. The temperature program was as follows: initial column temperature 50°C, held for 1 min, then programmed to 120°C at a rate of 3 min^{-1} and held for 2 min; finally programming to 210°C at a rate of 4 min^{-1}, then held at 210°C for 10 min. As a carrier gas, helium at 1.0 mL min^{-1} was used.

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TABLE 1. The Volatiles in *P. scabiosifolia* Flowers

Compound	RI	%	Compound	RI	%
3-Methylbutanoic acid, methyl ester	618	1.53	*trans*-2-Hexenyl valerate	1148	5.79
3-Methylbutanoic acid, ethyl ester	744	2.38	Eugenol	1247	3.02
3-Methylbutanoic acid, 2-methylpropyl ester	912	0.42	Pentanoic acid, phenylmethyl ester	1287	20.79
3-Methylbutanoic acid, 3-methylbutyl ester	1013	8.75	3-Methyl-2-phenylethyl butanoic acid ester	1371	9.80
Valeric acid, 3-methylbut-2-enyl ester	1052	1.24	3-Methyl-1-ethenyl-1,5-dimethyl-4-hexenyl butanoic acid ester	1513	3.14
cis-3-Hexenyl isovalerate	1139	28.91			
Hexyl *n*-valerate	1145	10.44	Total		96.21

RI: retention indices relative to C_8-C_{26} *n*-alkanes on the DB-5MS column.

MS conditions: the detector was used in the EI mode with an ionization voltage of 70 eV. The ion source temperature was at 230°C. The transfer line was at 280°C. The spectra were collected at 3 scans/s over the mass range (*m*/*z*) 30–440. The volatile constituents (Table 1) were identified by comparison of their linear retention indices (relative to C_8-C_{26} alkanes on the DB-5MS column and their mass spectra with those of authentic standards, as well as those from RTLPEST3.L and NIST05.L). The percentage composition of the volatile was computed from the GC peak areas normalization without any corrections [13–15].

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