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蒜香藤的挥发性成分分析

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摘 要:采用采用气相色谱-质谱联用技术对蒜香藤不同部位叶、茎与果的挥发性成份进行分析。结果发现,叶、茎、果中可定性定量的化合物分别占挥发性成份总量的97.6%、95.4%与97.4%。在不同部位中,主要的化合物是含硫化合物,分别占挥发性总量的78.4%、54.0% 与81.0%。叶、茎、根中主要的挥发性成份有二烯丙基二硫化物(48.9%、25.4%、34.2%)和二烯丙基三硫化物(18.4%、14.0%、29.8%)。蒜香藤的挥发性化学成份与大蒜的相似,尤其体现在含硫化合物上,因此,蒜香藤可以作为大蒜的潜在替代物,其药理活性需要进一步开发研究。

关键词:蒜香藤;含硫化合物;二烯丙基二硫化物;挥发性成份;气相色谱-质谱联用技术;

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Essential Oil Composition of A Novel Garlic Vine *Pseudocalymma alliaceum*

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Abstract:In this study,the leaf,stem,and fruit of *Pseudocalymma alliaceum* were distilled and the essential oil composition was studied by GC-MS. The identified components constituted 97.6%,95.4% and 97.4% of the leaf,stem,and fruit oils,respectively. The major components of different parts of *P. alliaceum* were sulfur-containing compounds,amounting to 78.4%,54.0% and 81.0% of essential oil composition in leaves,stems,and fruits,respectively. The result showed that the main constituents of the essential oil of leaves,stems,and fruits oils were diallyl disulphide(48.9%,25.4% and 34.2%) and diallyl trisulfide(18.4%,14.0% and 29.8%). It was concluded that the essential oil composition of *P. alliaceum* was similar with the garlic *Allium sativum*,especially to sulfur-containing compounds. The garlic vine *P. alliaceum* is a potential substitute of *A. sativum* and its pharmaceutical effects need to be studied in the future.

Key words:*Pseudocalymma alliaceum*;diallyl disulphide;diallyl trisulfide;essential oil;GC-MS

Introduction

Garlic (*Allium sativum* L.) has played an important role in human life for centuries. In the pharmaceutical industries,garlic is widely used for the treatment different diseases,including cancer,obesity,diabetes,pneumonia,and rheumatism [1]. Over the past decades,China has been the highest producing country of garlic in the world. Garlic production in China was 13.7 million tons and the value was 7.2 billion dollars in 2010(data from Food and Agriculture Organization of the United Nations,http://faostat.fao.org). Previous studies have established that the chemical composition of garlic was complex with more than 100 compounds including high amounts of volatile organosulfur compounds[2].

Pseudocalymma alliaceum Sandw. (Bignoniaceae) is an evergreen vine,which is native to Guyana and Brazil. The species was introduced as an ornamental flower in China in the last century. We found that the leaves of *P. alliaceum*,planted in the Yunnan Branch,Institute of Medicinal Plant,Chinese Academy of Medical Sciences,have a typical garlic odor. Hence,it was hypothesized that the volatiles of garlic vine,*P. alliaceum*,may be similar to garlic(*Allium sativum*). It was found that only a fewer reports about essential oil composition and larvicidal activity of *P. alliaceum* were published

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compared to 392 publishes about essential oil and its functions of garlic (*A. sativum*) [3,4].

In this study, the essential oil composition of leaves, stems, and fruits of *P. alliaceum* were investigated. The objective of the work was to address three questions: (1) is essential oil composition of *P. alliaceum*, similar with *A. sativum*, especially to sulfur-containing compounds? (2) does essential oil composition and content differ in different parts of *P. alliaceum*? (3) can *P. alliaceum* be used as a substitute of *A. sativum*?

Materials and Methods

Plant materials

Aerial parts of three year old *P. alliaceum*, at fruit stage were collected and weighed from Yunnan Branch, Institute of Medicinal Plant, Chinese Academy of Medical Sciences, in March 2011. The plant was identified and collected by Ling Tang. A voucher specimen was kept at the Kunming Botanical Garden, Kunming Institute of Botany, The Chinese Academy of Sciences.

Collection of essential oil of *P. alliaceum*

Essential oil of *P. alliaceum* was collected by using steam distillation method. Fresh aerial parts (leaves, stems, and fruits) of *P. alliaceum* (150 g for each sample and two replicates for each material, respectively) were separately ground and blended with 450 mL deionized water, then submitted for hydrodistillation for 1.5 h using a clevenger-type apparatus. The light yellow oils obtained were dried over anhydrous sodium sulfate.

Identification of essential oil composition of *P. alliaceum*

Essential oil from leaves, stems, and fruits of *P. alliaceum* were analyzed using a HP 6890 gas chromatograph (Agilent Technologies, USA), equipped with a HP-5MS column, and linked to a HP 5973 mass spectrometer (Agilent Technologies, USA). Helium was used as carrier gas at a flow of 1 mL/min, and injector temperature was set to 250 ℃. Column temperature was from 50 ℃ to 280 ℃ at a rate of 3 ℃ /min after the injection of sample. Compounds were tentatively identified by comparing their retention times, retention indices, and mass spectra with those obtained from the authentic samples and/or the MS library. The percentage composition of the essential oils was computed according to peak areas. The linear retention indices were calculated with hydrocarbons (C_8-C_{30}) (Aldrich Chemical Company) as references.

Results and Discussion

The essential oils of *P. alliaceum* exhibited in light yellow color and typical garlic odor. The yields of the essential oil of leaves, stems, and fruits were 0.06%, 0.05% and 0.07% (w/w; based on fresh weight), respectively. GC-MS analysis identified 42 compounds from the essential oil of leaves, stems and fruits of *P. alliaceum*. The identified compounds were divided into five chemical classes based on their biosynthetic origin: sulfur-containing compounds, fatty acid derivatives, benzenoids, terpenes, and miscellaneous cyclic compounds (Table 1). Essential oil composition of *P. alliaceum* was dominated by 13 sulfur-containing compounds (Table 1). The fatty acid derivatives, benzenoid, terpenes and miscellaneous cyclic compounds were minor components.

A total of 27, 30, and 33 compounds were identified in essential oil of leaves, stems and fruits of *P. alliaceum*, amounting to 97.6%, 95.4% and 97.4% of the total compositions of essential oil, respectively. The major components of different parts of *P. alliaceum* were sulfur-containing compounds, amounting to 78.4%, 54.0%, and 81.0% of essential oil composition in leaves, stems and fruits, respectively (Table 1). The main constituents of leaves oil were diallyl disulphide (48.9%), diallyl trisulfide (18.4%), mushroom alcohol 1-octen-3-ol (10.2%) and propyl 2-methylpropylsulfide (5.4%). The results were different to the previous study by Na [3], where sulfur-containing compounds only accounted for 18.8% of the total essential oil. This may be caused by the different environment and experiment. The oil sample of stems was dominated by diallyl disulphide (25.4%), diallyl trisulfide (14.0%), hexadecanoic acid (11.0%), propyl 2-methylpropylsulfide (10.5%) and 1-octen-3-ol (10.2%), while diallyl trisulfide (34.2%), diallyl disulphide (29.8%) and propyl 2-methylpropylsulfide

(9.3%) were established as the main components of fruit oil. There was no obvious difference in essential oil composition in the different parts of *P. alliaceum*.

The abundance and content of sulfur-containing compounds, detected in *P. alliaceum*, such as diallyl disulphide and diallyl trisulfide, agreed with previous studies on garlic *Allium sativum* essential oil[2,5]. From these results it is evident that *P. alliaceum* is a good source for the production of essential oil, and resembles in composition to a great extent the oil obtained from garlic bulbs. The essential oil composition of *P. alliaceum* is similar with garlic *Allium sativum*, especially to sulfur-containing compounds. However, garlic essential oil composition of cryogenic or solvent extraction methods is different with hydrodistillation [6]. A reasonable explanation was thiosulfinates were very unstable compounds and gave rise to further structural rearrangements under high temperature and lead to a wide variety of derived sulfur compounds[1,6].

In this study, diallyl disulfide and diallyl trisulfide were abundant in all parts of *P. alliaceum*. It has been reported the presence of allyl group-containing compounds is very important for the anticarcinogenic effect, especially diallyl disulfide [7]. Shenoy & Choughuley [8] indicated that diallyl sulfur compounds in garlic essential oil might also act as nitrite scavengers. Diallyl disulfide and diallyl trisulfide also can be used to inhibit platelet thromboxane or tumor cell formation, decrease atherosclerosis, or intestinal damage[9,10]. In conclusion, we suggested that garlic vine *P. alliaceum* is a potential substitute of *A. sativum*, and more work of pharmaceutical effects of *P. alliaceum* need to be carried out in future.

Table 1 Average relative concentrations (%) of essential oil composition of *P. alliaceum*

Compounds	RT	KI	Relative amounts (%)		
			Leaf	Stem	Fruit
Sulfur-containing compounds			78.4	54.0	81.0
1,2-dithiolane	6.68	832	0.3	–	0.1
methyl 2-propenyl disulfide	9.33	910	0.4	0.3	0.3
1-(1-propenylthio) propane	9.62	917	0.4	0.5	0.6
propyl 2-methylpropylsulfide	16.41	1082	5.4	10.5	9.3
diallyl disulphide	16.61	1087	48.9	25.4	34.2
trisulfide, methyl 2-propenyl	18.53	1139	0.2	0.6	0.4
2-propenyl propyl disulfide	19.40	1163	0.4	–	–
3-vinyl-1,2-dithiacyclohex-4-ene	20.32	1189	0.7	–	0.8
3-vinyl-1,2-dithiacyclohex-5-ene	21.21	1217	1.1	0.7	2.2
benzosulfonazole	21.50	1226	–	0.5	–
diallyl trisulfide	23.93	1306	18.4	14.0	29.8
diallyl tetrasulphide	30.26	1543	2.2	1.5	2.9
cyclic octaatomic sulfur	40.85	2048	–	–	0.4
Fatty acid derivatives			17.5	31.1	13.0
trans-5-hexenal	5.12	777	1.0	1.8	1.2
2,2-dimethyl-4-pentenal	5.43	791	0.1	0.4	0.1
1-hexanal	5.44	792	–	0.3	0.3
trans-2-hexenal	7.05	843	0.6	2.4	0.5
3-hexen-1-ol	7.21	848	2.4	2.7	1.4
5-hexen-1-ol	7.39	854	–	0.3	–
1-hexanol	7.62	861	0.3	0.5	0.2
1-octen-3-one	11.98	976	0.4	–	–

1-octen-3-ol	12.34	984	10.2	7.1	1.3
3-octanone	12.41	986	0.4	1.4	0.2
3-octanol	12.89	998	1.7	1.4	0.5
cis-2,6-nonadien-1-al	19.10	1155	-	0.7	0.3
trans-2-nonenal	19.32	1161	-	0.5	0.6
cis-13-octadecen-1-al	37.90	1895	-	0.6	1.0
hexadecanoic acid	39.42	1972	0.4	11.0	5.2
oleic acid	42.61	2144	-	-	0.2
Benzenoid compounds			0.7	3.3	1.4
benzeneacetaldehyde	14.92	1046	0.1	2.0	0.5
methyl salicylate	20.54	1196	0.3	1.3	0.9
2-methoxy-4-vinylphenol	24.29	1319	0.3	-	-
Terpenes			0.7	4.8	1.2
linalool	17.18	1100	0.3	1.4	0.1
α-cedrene	27.02	1418	-	-	0.1
trans-α-ionone	27.34	1431	-	0.4	-
trans-geranylacetone	27.94	1454	-	0.2	-
β-ionone	28.85	1489	-	1.1	-
β- guaiene	32.31	1634	-	-	0.9
neophytadiene	42.06	2113	0.4	1.7	0.1
Miscellaneous cyclic compounds			0.3	2.2	0.8
2-ethylfuran	3.39	708	-	0.4	-
2,4-dimethyl-furan	4.33	741	0.3	0.7	0.4
trans-7-methyl-1,6-dioxaspior[4.5] decane	15.38	1100	-	1.1	0.4
Total			97.6	95.4	97.4

RT and KI, retention time and retention index on HP-5MS column。
"-", not detected.

References

1 Lanzotti V. The analysis of onion and garlic. *J Chromatogr*, 2006, 1112: 3-22.

2 Block E. The organosulfur chemistry of the Genus *Allium* - implications for the organic chemistry of sulfur. *Angew Chem*, 1992, 31: 1135-1178.

3 Na Z(纳智). Components in the volatile oil from *Pseudocalymma alliaceum* leaf. *J Plant Resour Environ* (植物资源与环境学报), 2005, 14: 57-58.

4 Charma SP, Mohan L, Srivastava CN. Larvicidal activity of *Pseudocalymma alliaceum* and *Allium sativum* against *Culex quinquefasciatus* (Say). *Entomol Res*, 2011, 41: 216-220.

5 Block E. The chemistry of garlic and onions. *Sci Am*, 1985, 252: 114-119.

6 Abu-lafi S, Dembicki JW, Goldshlag P, *et al*. The use of the 'Cryogenic' GC/MS and on-column injection for study of organosulfur compounds of the *Allium sativum*. *J Food Compos Anal*, 2004, 17: 235-245.

7 Wattenberg LW, Sparnins VL, Barany G. Inhibition of N-nitrosodiethylamine carcinogenesis in mice by naturally occurring organosulfur compounds and monoterpenes. *Cancer Res*, 1989, 49: 2689-2692.

8 Shenoy NR, Choughuley ASU. Inhibitory effect of diet related sulphydryl compounds on the formation of carcinogenic nitrosamines. *Cancer Lett*, 1992, 65: 227-232.

9 Bordia A, Verma SK, Srivastava KC. Effect of garlic (*Allium sativum*) on blood lipids, blood sugar, fibrinogen and fibrinolytic activity in patients with coronary artery disease. *Prostaglandins Leukot Essent Fatty Acids*, 1998, 58: 257-263.

10 Wu CC, Chung JG, Tsai SJ, *et al*. Differential effects of allyl sulfides from garlic essential oil on cell cycle regulation in human liver tumor cells. *Food Chem Toxicol*, 2004, 42: 1937-1947.