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Hyphenated GC-MS Determination of Volatile Constituents in Lilium

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Volatile components of lilium were extracted by water steam distillation and analyzed by using gas chromatography-mass spectrometry (GC-MS). A total of 72 volatile oil components were identified and the relative content of each component was determined by area normalization. Among 72 volatile oil components, 48 compounds identified amount to 77.28 % of the total amount of volatile oil. The major compounds were found to be 1-dodecene (8.04 %), 1-docosene (7.35 %), 1-hexadecanol (5 %), ethanol, 2-(9-octadecenyloxy)-, (Z)- (4.22%), *n*-hexadecanoic acid (3.27 %), benzofuran, 4,7-dimethyl- (3.26%) and hexadecane-1,2-diol (3.09 %).

Keywords: Lilium, Volatile oil, Water steam distillation, Gas chromatography-mass spectrometry.

INTRODUCTION

Lilium is the dried bulb of *Lilium lancifolium Thunb, Lilium brownii* F.E. Brown var. *viridulum* Baker or *Lilium pumilum* DC., which belongs to liliaceous plants and has been recorded in China pharmacopoeia[1]. Lilium is a perennial herb and main ornamental plant. In traditional medicine, lilium is well known to treat chronic cough, palpitation, insomnia, *etc*.

Chemical constituents in lilium were begun to study since 1980's. The bulb of lily is rich in nutrient content, such as protein, starch, fat, vitamin B_1, B_2 and many trace elements. In addition, there are many active matter in the bulb of lily, therefore, lily have extensive pharmacological activity. Besides, steroidal saponins from the bulbs of lilium longiflorum have antitumour-promoter activity[2] and trace colchicine in lily can inhibit the growth and proliferation of cancer cell[3] and have anticancer pharmacological activity. Recently, the researchers gradually pay attention to secondary metabolites in lilium, which can be divided into five groups: glycoside[4-11], phenolic glycerides, steroidal saponin[12,13], alkaloid[14] and flavonoids[15]. Compared to the studies on soluble constitutions, the volatile components of lilium have received little attention. Only several volatile components of lilium have been reported using gas chromatography-mass spectrometry[16-20].

GC-MS analysis is a popular and effective method in the qualitative and quantitative analysis of volatile components. However, using only GC-MS, it has not been possible to identify all volatile components. Isolation and identification of volatile components need further work. In addition, the appropriate sample preparation technique is also important before GC-MS analysis. For the extraction of volatile components, several methods including water steam distillation, solid phase micro-extraction[21], static headspace extraction[22], accelerated solvent extraction[23] and simultaneous distillation extraction are usually employed. The aim of present work was to identify the main volatile compounds of lilium extracted by water steam distillation using GC-MS analysis.

EXPERIMENTAL

All analytical grade solvents were from Tianjin Fuyu Fine Chemicals Co. Ltd (Tianjin, China). Anhydrous sodium sulfate was purchased from Beijing Tongguang Fine Chemicals Company (Beijing, China). Lilium purchased from a local drugstore was ground with a commercial mill to obtain a relatively homogenous drug powder. To determine oil yield of the materials used in the extractions, the powder was dried at 55 °C until constant weight.

Extraction procedure: Lilium was ground and steam-distilled according to the method recommended by the China Pharmacopoeia. A 100 g lilium was submerged in 500 mL distilled water for 24 h and distilled for 10 h. The time of distillation was measured from the beginning of vapour condensation on the walls of condenser. We checked in preliminary experiments that the amount of essential oil collected in separator did not further increase after 8 h of distillation. Distillate was transferred to separating funnel and was extracted with diethyl ether for 3 times. Extract liquid was collected and reagent was recovered by rotary evaporator. The essential oils were dried over anhydrous sodium sulfate and stored at 4 °C in the refrigerator. Extractions were performed at least three times and the mean value of the oil yield from lilium was 1.3 % based on the dried weight.

Analysis of the volatile oils: The volatile oil extracts were analyzed by using gas chromatography-mass spectrometry. The GC-MS conditions were optimized on the basis of the property of the essential oil extracts. Gas chromatography with mass spectrometry was used for identification of volatile compounds in the volatile oil after its isolation by steam-distilled method, equipped with a capillary column ZB 5 MS (length 30 m × I.D. 0.25 mm × thickness 0.25 μm), injector temperature 230 °C, column temperature 50 °C, temperature gradient 50 °C (1 min), programming 10 °C/min to final temperature 230 °C (held for 3 min). Helium was used as a carrier gas flowed at a rate of 1 mL/min. A 1 μL of the sample extract was injected using the discharge ratio. Discharge ratio was set at 1:50. The first GC column was used for obtaining the residence time for identification, while the second column and MS detection was used the confirmation. Mass spectra were recorded in EI-source scanning mode with a mass range of 60-400 AMU. Ion source temperature was set at 210 °C and ionization voltage 70 eV.

TABLE-1
VOLATILE CONDTITUENTS IN LILIUM

Peak	Residence time (min)	Compound	Content (%)
1	6.26	5-Methyl-2-furancarboxaldehyde	1.13
2	7.70	N-Benzyloxycarbonyl-L-tyrosine	0.88
3	8.02	4-Methyl-phenol	0.64
4	8.11	2-(Cyclohex-1-enyl) furan	0.46
5	8.54	2-Methyl-benzofuran	1.82
6	8.99	2,4-Dimethylstyrene	0.42
7	9.11	2,3-Dimethyl phenol	1.51
8	9.39	3,4-Dimethyl phenol	1.31
9	9.55	2-(2-Furanylmethyl)-5-methyl furan	1.75
10	9.73	1,2-Dihydro-acetate 2-naphthalenol	0.66
11	10.13	4,7-Dimethyl-benzofuran	3.26
12	10.25	5,7-Dimethyl-1*H*-indazole	1.14
13	10.44	3-(1-Methylethyl) phenol	0.71
14	10.81	1,2,3,4-Tetrahydro-3-methyl-1-naphthalenol	0.56
15	10.91	2,2'-Methylenebis[5-methyl furan]	2.18
16	11.13	1-Methoxy-4-(1-propenyl) benzene	1.87
17	11.32	2,3,3,4,7-Pentamethyl-2,3-dihydro-benzofuran	2.68
18	11.49	2,3-Dihydro-3,3-dimethyl-1*H*-inden-1-one	2.48
19	11.57	1,3,3-Trimethyl-1-phthalanol	1.93
20	12.04	3-Methyl-4-phenyl-3-buten-2-one	1.08
21	12.11	1,4-*Bis*(1,1-dimethylethyl) benzene	0.95
22	12.71	1,2,3,4-Tetrahydro-1,6,8-trimethyl-naphthalene	0.87
23	12.80	1,4-Dimethyl-naphthalene	0.93
24	13.35	2,3-Dihydro-3,4,7-trimethyl-1*H*-inden-1-one	0.35
25	13.54	1-Dodecene	8.04
26	13.94	2-Methyl-5-(butin-1-yl)pyridine	0.27
27	14.41	2,3,6-Trimethyl naphthalene	0.47
28	14.62	α-1-Cyclohexen-1-yl-benzenemethanol	0.64
29	14.81	6-Methoxy-α-methyl-2-naphthaleneacetic acid methyl ester	0.35
30	15.12	2-Fluorodiphenylmethane	0.89
31	15.52	2-Hydroxyfluorene	0.36
32	15.90	1-Hexadecanol	5.00
33	16.07	2-(2-Methoxynaphthalen-1-yl)-2-methylpropionaldehyde	0.51
34	16.17	1,2,3-Trichloro-4,5-dimethoxy benzene	2.80
35	16.40	1-Docosene	7.35
36	17.15	Docosane	0.37
37	18.48	Hexadecane-1,2-diol	3.09
38	18.62	8,9-Dihydrocyclopenta[d,e,f]phenanthrene	0.65
39	18.89	*n*-Hexadecanoic acid	3.27
40	19.22	2-(9-Octadecenyloxy)-(*Z*)-ethanol	4.22
41	20.05	7-Isopropyl-1,1,4a-trimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene	1.51
42	20.14	Cyclic octaatomic sulfur	0.64
43	20.51	(*Z*,*Z*)-9,12-Octadecadienoic acid	1.99
44	20.72	Octadecanoic acid	0.48
45	21.57	Dodecyl hexadecanoic acid ester	1.28
46	24.99	α-Sitosterol acetate	0.26
47	25.74	Linoleic acid ethyl ester	0.81
48	26.19	Tetradecyl hexadecanoic acid ester	0.46

RESULTS AND DISCUSSION

The volatile oil of lilium was analyzed by using GC-MS analyses and the constituents were identified according to their retention times and mass spectra. The relative content of volatile oil components extracted from lilium was determined by area normalization. More than 72 components were separated and 48 components were identified from volatile oil in lilium by comparing the obtained mass spectra of the analytes with by retrieving and comparison with NIST (National Institute of Standards and Technology) mass spectral database and standard spectra, among these compounds most of them were alkenes, alcohol and furans (Table-1).

Table-1 presents the summary results. The relative content of these constituents determined with area normalization method amount to 77.28 % of the total amount of volatile oil. Comparison of the oil compositions of the extract showed that the percentage of volatile chemical compounds from lilium were different. The amount of 1-dodecene which was significantly higher than other chemical compounds was up to 8.04 %.

As can be seen from Table-1, constituents determined concluded alkenes, alcohol and furan, *etc.*, among which alkenes account for 15.39 % of chromatographic peak area, alcohol compounds account for 12.95 %, furan compounds account for 12.15 %, acids account for 5.74 %. Compounds in which content was more than 3 % concluded 1-dodecene (8.04 %), 1-docosene (7.35 %), 1-hexadecanol (5 %), ethanol, 2-(9-octadecenyloxy)-, (Z)- (4.22 %), *n*-hexadecanoic acid (3.27 %), benzofuran, 4,7-dimethyl-(3.26 %), hexadecane-1,2-diol (3.09 %). Other compounds identified in the sample extracts are listed in Table-1.

As to volatile compounds in lilium, 1-dodecene was used to produce surfactant, detergent, lubricating oil additive and plasticizer *etc*. 1-Hexadecanol was used as emollient and emulsifier in preparation of cosmetic. At the same time, 1-hexadecanol was also used as emulsifier, hardener in pharmaceutical preparations and was sprayed on plant surface to preventing water evaporation. *n*-Hexadecanoic acid has the action of moistening the intestines and freeing the stool. The results showed that, lilium volatile oil is of certain medicinal value. However, it is thought that interaction of multiple chemical compounds contributes to the therapeutic effects of Chinese medicines. The contents of the compounds investigated volatile components in lilium are obviously different and pharmacological activities of different compounds are various. Therefore, study on interaction of volatile chemical compounds from lilium is very important .The details need to be further investigated. In addition, the overall clinical efficacy of the extract has not been determined.

Conclusion

In this paper, the volatile oil of lilium has been investigated. By applying GC-MS, the volatile oil sample of lilium was analyzed and compared regarding their qualitative and relatively quantitative characteristics. The contents of volatile components extracted from lilium are obviously different, which suggests that the identification of the volatile oil components is helpful to elucidate which are the active components and pharmacological activities. The information about the chemical constituents of volatile oils is useful and necessary to the further study of lilium, which will certainly help us to utilize the traditional Chinese herb.

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