Available online at www.sciencedirect.com
ScienceDirect
Journal of Pharmaceutical and Biomedical Analysis 44 (2007) 464–470
JOURNAL OF PHARMACEUTICAL AND BIOMEDICAL ANALYSIS
www.elsevier.com/locate/jpba

Analysis of the volatile compounds in *Ligusticum chuanxiong* Hort. using HS-SPME–GC-MS

Cong Zhang [a], Meiling Qi [a,*], Qinglong Shao [a], Shan Zhou [b], Ruonong Fu [a]

[a] *Department of Chemistry, School of Science, Beijing Institute of Technology, Beijing 100081, China*
[b] *Beijing Municipal Center for Disease Prevention and Control, Beijing 100020, China*

Received 20 November 2006; received in revised form 5 January 2007; accepted 9 January 2007
Available online 20 January 2007

Abstract

A headspace solid-phase microextraction (HS-SPME) method followed by gas chromatography–mass spectrometry (GC–MS) is described for the analysis of volatile compounds in the dry rhizome of *Ligusticum chuanxiong* Hort. Three types of SPME fibers including PDMS, PDMS–DVB and DVB–CAR–PDMS were investigated and the best extraction was achieved with the mixed fiber DVB–CAR–PDMS. Parameters for HS-SPME in terms of temperature and time, sample amount and particle size, and desorption time were also investigated. A polar capillary column was used for the chromatographic separation. As a result, 73 compounds were determined and identified by the HS-SPME–GC–MS method with at least 20 more compounds than those in the methods available. Comparison was made between HS-SPME–GC–MS and steam distillation (SD)-GC–MS methods. Using much less sample amount, shorter extraction time and simpler procedure, HS-SPME method can achieve similar results with those by SD. In conclusion, the present method is simple, rapid and effective and can be used for the analysis of volatile compounds in medicinal plants.

Keywords: Solid phase microextraction; *Ligusticum chuanxiong*; Volatile compounds; Medicinal plants; Gas chromatography–mass spectrometry

1. Introduction

The dry rhizome of *Ligusticum chuanxiong* Hort. (chuanxiong) is a typical traditional Chinese medicine and has been used for the clinical treatment of headache, rheumatic arthralgia and coronary heart diseases in China over hundreds of years [1]. The volatile compounds in this medicinal plant are recognized as an important part for its pharmacological activities mentioned above. For the analysis of the volatile compounds in chuanxiong, some publications are available using gas chromatography–mass spectrometry (GC–MS) following steam distillation (SD) extraction or supercritical fluid extraction and around 50 volatile compounds were reported [2–4]. Steam distillation is a conventional extraction method for essential oils from medicinal plants. However, it often needs large amount of sample and is time-consuming and laborious. Nowadays, modern sample preparation in analytical chemistry is characterized by simplification, miniaturization, high enrichment and minimization of sample amount and solvent.

In recent years, headspace solid phase microextraction (HS-SPME) [5] has gained wide acceptance as an effective extraction technique for a wide variety of samples [6–9]. HS-SPME is performed by exposing a fiber coated with single or multiple polymers to the headspace of a sample matrix until equilibrium is reached between the analyte partitioned in the fiber coating and the analyte in the sample matrix. The amount of the analyte extracted onto the fiber is linearly proportional to its initial concentration in the sample matrix. The polymeric film on the fiber concentrates organic analytes on its surface through either adsorption or absorption. The fiber selection is often based on the principle "like dissolves like".

There are two major types of polymers used for SPME fibers. One is liquid for nonpolar and less polar compounds (e.g. polydimethylsiloxane, PDMS) and the other is solid for semipolar or polar compounds (e.g. divinylbenzene, DVB; carboxen, CAR; or both). A number of SPME fibers of different polarity and coating thickness are commercially available and have been used for extraction of the volatile compounds in medicinal plants [10–18]. Among the fibers, PDMS or PDMS-based mixed fibers

* Corresponding author. Tel.: +86 10 68912667; fax: +86 10 68913293.
E-mail addresses: mlqi2006@yahoo.com.cn, mlqi@bit.edu.cn (M. Qi).

0731-7085/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jpba.2007.01.024

are most commonly used. For a complex sample, mixed fibers including PDMS–DVB, PDMS–CAR and DVB–CAR–PDMS showed better extraction efficiency for a wide variety of compounds in comparison with "single fiber" due to their higher retention capacity [7,16–18].

The aim of this research was to develop a HS-SPME method in combination with GC–MS that can be used for the analysis of the volatile compounds of *Ligusticum chuanxiong* Hort. To the best of our knowledge, no related publications are available for the purpose. The effects of the various parameters on the extraction were investigated, including fiber types (PDMS, PDMS–DVB and DVB–CAR–PDMS), extraction temperature and time, sample amount and particle size, and desorption time. For the optimization process, both the total peak areas of all the obtained compounds and the individual peak areas of five target compounds including eudesma-4(14),11-diene,3-butylidenephthalide, 1-(2,4-dimethylphenyl)-1-propanone, ligustilide and fenipentol (numbered as **1**–**5** in the order in the following figures 2∼6), were employed to evaluate the effects of the HS-SPME parameters on the extraction of the volatile compounds in *Ligusticum chuanxiong* Hort. These five target compounds were chosen on the basis of either characteristic compounds of the plant or their recognized contributions to the pharmacological activities of chuanxiong for the cardiovascular system illness [19,20].

2. Experimental

2.1. Materials

The dry rhizome samples of *Ligusticum chuanxiong* Hort. were purchased from An'guo traditional Chinese medicine market in Hebei province of China and were authenticated by the Institute of Medicinal Plants, Academy of Medical Science of China. The samples were ground to certain particle sizes (40–120 mesh). After that, the powdered samples were stored in tightly sealed amber vials until analysis.

2.2. GC–MS conditions

Chromatographic separation was performed on HP5973 GC-MSD (Agilent Technologies, Palo Alto, CA, USA) using a HP-INNOWAX capillary column (30 m × 0.25 mm i.d., film thickness 0.25 μm). The GC oven temperature was programmed as follows: from 50 to 80 °C at a rate of 2 °C/min and then to 180 °C at a rate of 5 °C/min and held for 1 min and finally to 210 °C at a rate of 2 °C/min and held for 10 min. The injector temperature were 250 °C. Nitrogen of high-purity was used as the carrier gas at a flow rate of 1 ml/min. The split ratio was 1:50.

The mass spectrometer was fitted with an EI source operated at 70 eV with a source temperature of 250 °C, and mass spectra were recorded in the range of *m*/*z* 30–500 amu in the full-scan acquisition mode. The interface temperature was 280 °C. Volatile compounds were identified by comparing the obtained mass spectra of the analytes with those of authentic standards from the NIST and Wiley libraries with a resemblance percentage above 85%.

2.3. SPME fibers and extraction procedure

A manual SPME holder and three different fibers, 100 μm PDMS, 65 μm PDMS–DVB and 50/30 μm DVB–CAR–PDMS from Supelco (Bellefonte, USA), were used for the SPME procedure. All the fibers were of the same length (1 cm) and conditioned prior to use by insertion into the GC injector at 250 °C for 0.5 h for PDMS and PDMS–DVB and 270 °C for 1 h for DVB–CAR–PDMS.

The powdered samples were placed in 15 ml sample vials sealed with septum-type caps from Supelco (Bellefonte, USA). For each extraction, after the SPME needle pierces the septum, the fiber was extended through the needle and exposed to the headspace above a sample (0.3–1.2 g, 40–120 mesh) under a temperature (40–90 °C). After an extraction time (10–60 min), the fiber was withdrawn into the needle, and then the needle was removed from the septum and inserted directly onto the injection port of the GC. The desorption of analytes from the fiber coating was performed by heating the fiber in the injection port at 250 °C for 1–5 min. At last the analytes were transferred directly onto the chromatographic column for analysis.

2.4. Steam distillation procedure

The essential oil was extracted by steam distillation following the Chinese Pharmacopoeia (2005). The powdered sample (50 g) was weighed into a 2 l round-bottom distillation flask and then 400 ml of water was added. After that, the mixture was distilled for 5 h. The essential oil was collected from the condenser and dried with anhydrous sodium sulfate. The 0.7 μl of the obtained essential oil was injected onto GC–MS system without further dilution.

3. Results and discussion

3.1. SPME fibers

Three types of fibers (PDMS, PDMS–DVB and DVB–CAR–PDMS) were used to evaluate the effect of fiber types on the extraction of volatile compounds in chuanxiong. Fig. 1 shows

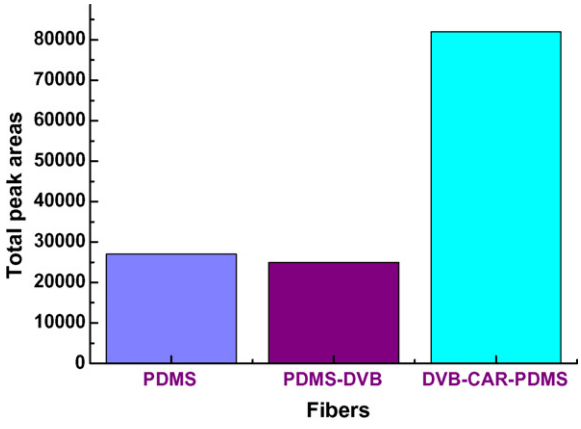

Fig. 1. Effect of SPME fibers on the total peak areas of all the obtained compounds from *Ligusticum chuanxiong* Hort.

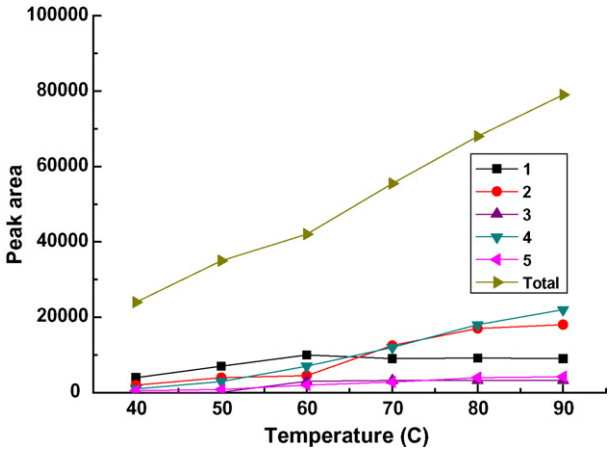

Fig. 2. Effect of extraction temperature on the total peak areas of all the obtained compounds from *Ligusticum chuanxiong* Hort. and on the individual peak areas of the five target compounds. (**1**) Eudesma-4(14),11-diene; (**2**) 3-butylidene-phthalide; (**3**) 1-(2,4-dimethylphenyl)-1-propanone); (**4**) ligustilide; (**5**) fenipentol.

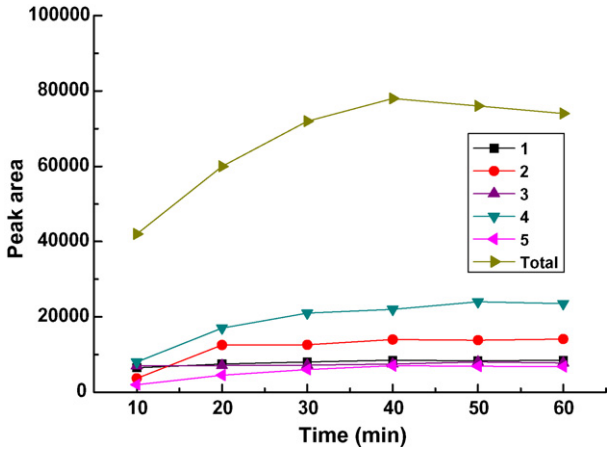

Fig. 3. Effect of extraction time on the total peak areas of all the obtained compounds from *Ligusticum chuanxiong* Hort. and on the individual peak areas of the target compounds: (**1**) Eudesma-4(14),11-diene; (**2**) 3-butylidene-phthalide; (**3**) 1-(2,4-dimethyl-phenyl)-1-propanone); (**4**) ligustilide; (**5**) fenipentol.

the total peak areas of the obtained compounds by the three types of fibers. It can be clearly observed that DVB–CAR–PDMS fiber achieved almost two times higher extraction of the analytes than the PDMS and PDMS–DVB fibers. This suggested that the retention ability of the DVB–CAR–PDMS fiber for the volatile compounds in the medicinal plant is much stronger than the rest two fibers. One interesting thing about this result is that the fiber PDMS–DVB did not show better extraction for the analytes in this sample than the fiber PDMS as expected. It probably resulted from the fact that most of the analytes in the sample are of low to medium polarity. The polarity of the three fibers were supposed to be in the order of PDMS < DVB–CAR–PDMS < PDMS–DVB. In this case, the fiber DVB–CAR–PDMS has higher extraction ability than the others. On the basis of the above results, the DVB–CAR–PDMS fiber was selected for the extraction of the volatile compounds in this medicinal plant.

3.2. Extraction temperature

The extraction temperature was varied from 40 to 90 °C and the results are shown in Fig. 2, showing the effect of extraction temperature on the total peak areas of all the obtained compounds and the individual peak areas of the five target compounds from *Ligusticum chuanxiong* Hort. It was found that either the total peak areas or the individual peak areas increased steadily with the temperature. The extraction temperature had a significant influence on the extraction because it can influence the distribution coefficients of the compounds between the sample and the headspace and between the headspace and the fiber. From these results, the temperature of 90 °C was finally used for the present work.

3.3. Extraction time

The extraction time varying from 10 to 60 min was investigated and the results are shown in Fig. 3. It can be observed that there are some differences between the total peak area and the individual peak areas of the target compounds in the tendency of peak areas with the extraction time. The profile for the total peak area shows a highest total peak area at 40 min while the individual profiles for the target compounds basically display steadily increasing trend with peak areas within the indicated time range and remain almost unchanged after 40 min except a slight decrease for the target compound **3** (1-(2,4-dimethylphenyl)-1-propanone) after 50 min. The decline of the total peak area after 40 min probably resulted from a partial desorption of some highly volatile compounds from the fiber coating when a longer extraction time than 40 min was used. All the things considered, the extraction time of 40 min was finally selected for the analysis.

3.4. Sample particle size

When SPME is applied for a solid sample, sample particle size often plays an important role in the extraction process. For the present work, sample particle size ranging from 40 to 120 mesh was investigated and the corresponding results are shown in Fig. 4. From the profile of the total peak area, a significant increase was observed at 100 mesh. The same case was found with the target compound **4** while the individual peak areas for the other four target compounds increased steadily with the particle size. Based on the above facts, the particle size of 120 mesh was adopted for the purpose. Less particle size was not tested because of its severe static effects.

3.5. Sample amount

For a given-volume vial, sample amount has a positive effect on the peak areas of the compounds. But this does not mean that the larger the sample amount, the better the results. In the present work, the sample amount varied from 0.3 to 1.2 g and the results of the effects of sample amount on the total peak areas and the individual peak areas of the five target compounds are

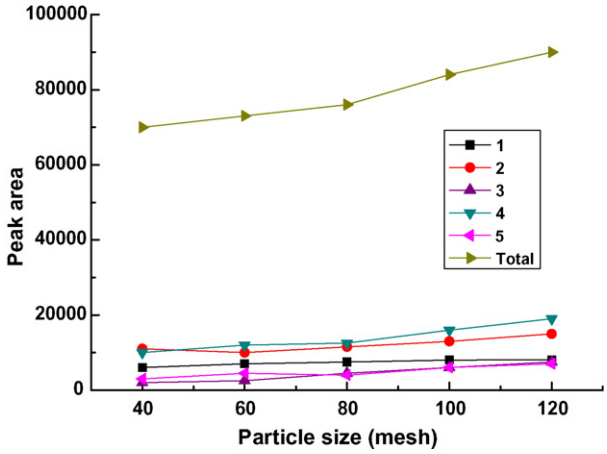

Fig. 4. Effect of sample particle size on the total peak areas of all the obtained compounds from *Ligusticum chuanxiong* Hort. and on the individual peak areas of the five target compounds. (**1**) Eudesma-4(14),11-diene; (**2**) 3-butylidene-phthalide; (**3**) 1-(2,4-dimethylphenyl)-1-propanone); (**4**) ligustilide; (**5**) fenipentol.

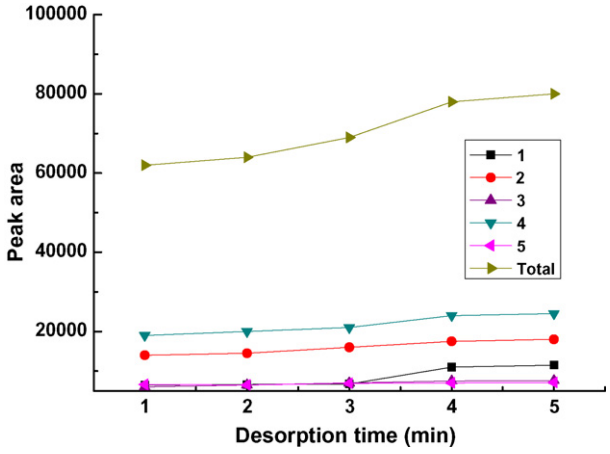

Fig. 6. Effect of desorption time on the total peak areas of all the obtained compounds from *Ligusticum chuanxiong* Hort. and on the individual peak areas of the five target compounds. (**1**) Eudesma-4(14),11-diene; (**2**) 3-butylidene-phthalide; (**3**) 1-(2,4-dimethylphenyl)-1-propanone); (**4**) ligustilide; (**5**) fenipentol.

shown in Fig. 5. Just as expected, the total peak areas increased smoothly with sample amount. For the individual peak areas of the target compounds, the same trends were observed with the compounds **2** and **4** while no significant increase in peak areas were found with the compounds **1**, **3** and **5**. A sample amount is often considered suitable for the analysis if it can satisfy the sensitivity for the purpose. For a HS-SPME procedure, a large sample amount sometimes causes trouble for the sampling process due to static adsorption of the sample powder to the fiber especially when a fine powdered sample is used for the analysis. Taking into account the above results, the sample amount of 0.5 g was chosen for the present work.

3.6. Desorption time

Desorption time in the injection port was investigated in the range of 1–5 min while keeping the fibers at the same injection depth (in the center of the hot injector zone). The effects of desorption time on the total peak area and individual peak areas are shown in Fig. 6. The profile for the total peak area shows an almost complete desorption of the analytes at 4 min and the profiles for the individual five compounds display that with the increase of desorption time, the peak areas for the target compounds **2** and **4** kept growing while the peak areas of the target compounds **3** and **5** remained unchanged. For the compound **1**, no significant increase in peak areas were observed between 1 and 3 min and a sharp increase occurred at 4 min and kept steady after that. Taking into consideration that a longer desorption time may hurt the fiber lifetime, the desorption time of 4 min was employed for the purpose.

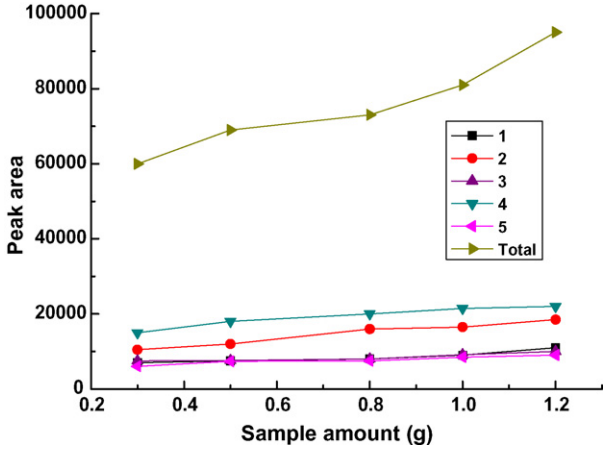

Fig. 5. Effect of sample amount on the total peak areas of all the obtained compounds from *Ligusticum chuanxiong* Hort. and on the individual peak areas of the five target compounds. (**1**) Eudesma-4(14),11-diene; (**2**) 3-butylidene-phthalide; (**3**) 1-(2,4-dimethyl-phenyl)-1-propanone); (**4**) ligustilide; (**5**) fenipentol.

3.7. Repeatability

Under the optimum conditions, the repeatability of the HS-SPME–GC–MS method was determined by 5-day replicate analyses of volatile compounds in chuanxiong and was evaluated on the basis of the peak areas of the five target compounds and expressed as relative standard deviation (RSD), which was found to be 3.2% for eudesma-4(14),11-diene, 2.7% for 3-butylidene-phthalide, 4.7% for 1-(2,4-dimethylphenyl)-1-propanone, 3.6% for ligustilide and 2.2% for fenipentol. The RSD values for the target compounds were below 5%, indicating the satisfactory repeatability of the proposed method.

3.8. Analysis of the volatile compounds in Ligusticum chuanxiong Hort.

The typical total ion chromatograms of the HS-SPME–GC–MS and SD-GC–MS methods are shown in Fig. 7 and the corresponding volatile compounds identified by the two methods are listed in Table 1 . The volatile compounds were identified by matching mass spectra with spectra of reference compounds in NIST and Wiley mass spectral libraries with a resemblance percentage above 85%. The relative amount percent of individ-

Table 1
The volatile compounds in *Ligusticum chuanxiong* Hort. obtained by HS-SPME–GC–MS and SD-GC–MS methods

No.	Retention time (min)	Compounds	SD-GC–MS (RA%)	SPME-GC–MS (RA%)
1	5.37	β-Phellandrene	0.39	0.02
2	5.51	Dodecane	0.10	0.14
3	6.21	α-Pinene	0.03	0.02
4	6.39	γ-Terpinene	3.58	0.53
5	6.67	3-Carene	0.04	–
6	7.12	*p*-Cymene	3.43	–
7	7.46	β-Terpinene	2.21	2.50
8	8.70	Pentadecane	0.29	0.42
9	9.01	Tridecane	–	0.20
10	9.23	6-Butyl-1,4-cycloheptadiene	1.73	2.01
11	11.46	3-Methyl-tridecane	0.05	0.21
12	11.98	2-Carene	0.14	0.24
13	12.58	Pentylbenzene	1.42	1.55
14	12.94	Tetradecane	0.18	0.39
15	13.90	*p*,α-Dimethylstyrene	–	0.28
16	15.10	Acetic acid	–	0.31
17	15.30	Furfural	–	0.33
18	15.62	β-Terpineol	–	0.38
19	15.70	1,2,3,4,4a,5,6,8a-Octahydro-7-methyl-4-methylene-1-(1-methyl)-naphthalene	–	0.12
20	15.99	3-Methylpentyl-benzene	0.08	–
21	16.87	(1-Ethylpropyl)-benzene	–	0.06
22	17.49	Pentadecane	0.21	0.58
23	18.15	2-Tetradecene	–	0.10
24	18.79	1,3-Butanediol	–	0.77
25	19.14	1-Methyl-4-(1-methylethyl)-2-cyclohexen-1-ol	0.20	0.13
26	19.37	β-Cedene	0.13	–
27	19.48	1,2,3,4,4a,5,6,8a-Octahydro-7-methyl-4-methylene-1-(1-ethyl)-naphthalene	–	0.39
28	9.67	1-Ethenyl-1-methyl-2-(1-methylethenyl)-cyclohexane	0.20	0.55
29	19.99	1,2,3,4,4a,7-Hexahydro-1,6-dimethyl-4-(1-methylethyl)-naphthalene	1.84	4.71
30	20.35	4-Methyl-1-(methylethyl)-3-cyclohexen-1-ol	4.52	3.22
31	20.82	(−)-α-Gurjunene	–	0.05
32	20.87	5-(1-Methylethyl)-bicyclo[3.1.0]hexan-2-one	0.03	0.05
33	21.21	Germacrene B	–	0.32
34	21.37	Butanoic acid	–	0.46
35	21.71	α-Caryophyllene	0.06	0.13
36	22.01	Decahydro-4a-methyl-1-methylene-7-naphthalene	0.21	0.46
37	22.53	1,2,3,4,4a,7-Hexahydro-1,6-dimethyl-4-(1-methylethyl)-naphthalene	0.15	1.05
38	22.87	1-Methyl-4-(5-methyl-1-methylene-4-hexenyl)-cyclohexene	–	0.10
39	23.11	Eudesma-4(14),11-diene[a]	6.15	9.22
40	23.25	1,2,3,4,4a,5,6,8a-Octahydro-4a,8-dimethyl-2-(methyl)-naphthalene	1.69	2.25
41	23.85	2,6-Dimethyl-6-(4-methyl-3-pentenyl)-bicyclo[3.1.1]hept-2-ene	0.15	0.25
42	24.16	1,2,3,4,4a,5,6,8a-Octahydro-4a,8-dimethyl-2-(ethyl)-naphthalene	0.35	0.66
43	24.32	3-Methyl-6-(1-methylethyl)-2-cyclohexen-1-ol	0.11	0.19
44	24.56	Decahydro-4a-methyl-1-methylene-7-naphthalene	0.06	0.15
45	24.76	1-(1,5-Dimethyl-4-hexenyl)-4-methyl-benzene	0.04	0.13
46	25.74	Germacrene D	0.22	0.08
47	26.40	1,2,3,4-Tetrahydro-1,6-dimethyl-4-(1-methylethyl)-naphthalene	0.10	0.14
48	26.77	2-Ethyl-4,5-dimethyl-phenol	0.57	0.67
49	27.27	Benzyl alcohol	–	0.13
50	27.72	1-Phenyl-1-pentanone	1.39	1.03
51	28.00	Phenylethyl alcohol	-	0.03
52	29.20	Isopropyl phenyl ketone	0.70	0.51
53	30.04	Carotol	0.29	0.16
54	30.22	1,2-Dimethoxy-4-(2-propenyl)-benzene	0.07	0.11
55	30.36	1,4,5,6,7,7a-Hexahydro-4-methyl-7-2H-inden-2-one	0.04	0.02

Table 1 (*Continued*)

No.	Retention time (min)	Compounds	SD-GC–MS (RA%)	SPME-GC–MS (RA%)
56	31.24	1,2,3,4,4a,5,6,8a-Octahydro-1,8a-dimethyl-7-(1-methylethyl)-naphthalene	0.16	0.13
57	31.82	4-(1-Methylethyl)-benzenemethanol	0.08	0.11
58	31.92	Cedrol	0.12	0.10
59	32.21	(−)-Spathulenol	2.20	1.64
60	33.04	Eugenol	0.07	0.09
61	33.29	Ethyl-cyclohecane	–	0.10
62	33.34	Cyclotetradecane	0.06	–
63	33.61	2-Methoxy-4-vinyl phenol	1.62	2.03
64	33.92	Ethyl-benzenmethanol	–	0.23
65	34.09	Thujopsene	–	0.29
66	34.48	β-Panasinsene	0.15	–
67	34.83	Hexadecanoic acid, ethyl ester	0.12	0.05
68	35.61	Ledene	0.08	0.13
69	36.74	1,4-Diethyl-2-methyl-benzene	0.08	0.15
70	37.22	Acetic acid, 4-methylphenyl ester	1.14	0.89
71	38.19	1H-indol-5-ol	0.03	0.05
72	39.52	9,12-Octadecadienoic acid, methyl ester	0.05	0.08
73	39.89	3-Butylidene-phthalide[a]	18.47	16.00
74	40.17	1-(2,4-Dimethylphenyl)-1-propanone[a]	3.78	4.29
75	41.12	Ligustilide[a]	23.96	18.71
76	41.94	Fenipentol[a]	6.40	12.24
77	42.21	2-Butylidene-phthalide	0.36	0.35
78	42.91	9,12-Octadecadienoic acid	0.02	0.02
79	44.37	Pentadecanoic acid	0.20	0.21
80	44.63	*n*-Hexadecanoic acid	0.22	0.23

[a] Target compounds; RA%: relative amount percent.

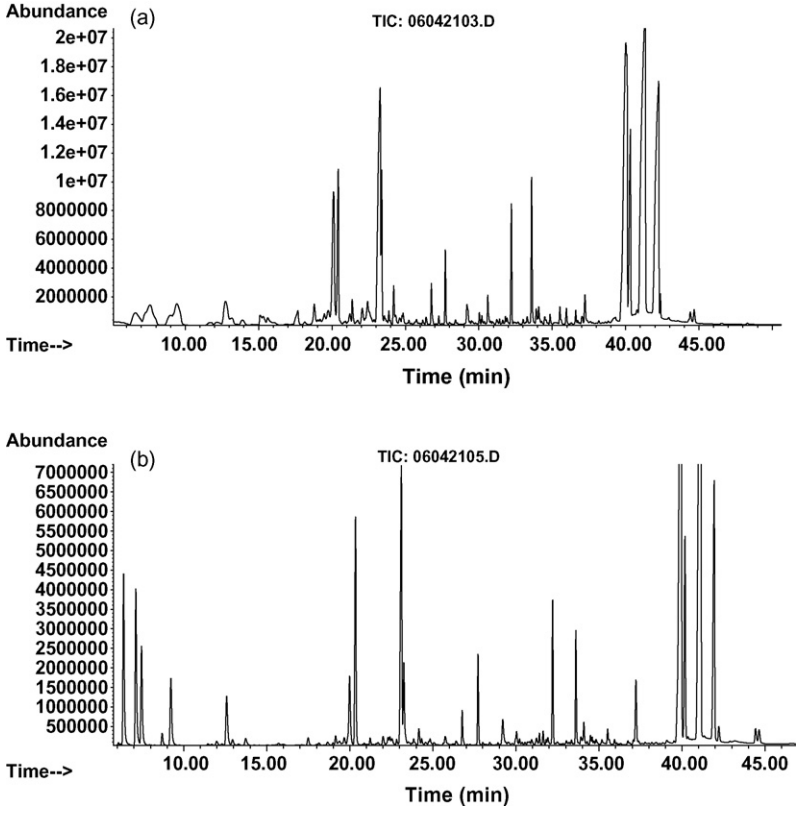

Fig. 7. Typical total ion chromatograms of the volatile compounds from *Ligusticum chuanxiong* Hort. by (a) HS-SPME–GC–MS and (b) SD-GC–MS methods.

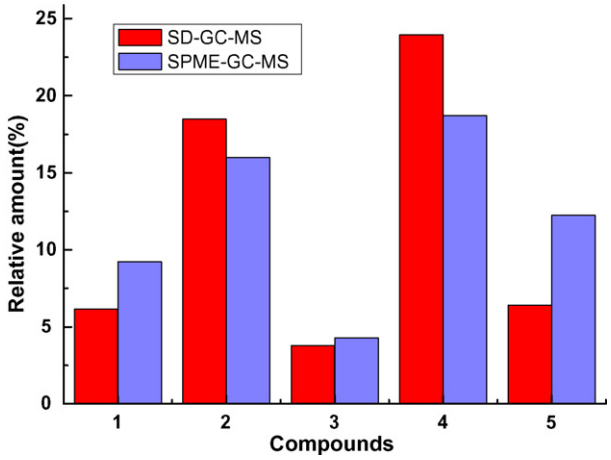

Fig. 8. Comparison of the relative amount percent of the five target compounds by HS-SPME–GC–MS and SD-GC–MS methods. (**1**) Eudesma-4(14),11-diene; (**2**) 3-butylidene-phthalide; (**3**) 1-(2,4-dimethylphenyl)-1-propanone); (**4**) ligustilide; (**5**) fenipentol.

ual components was expressed as percent peak areas relative to total peak areas (RA%).

It can be found that 73 and 61 compounds were identified by HS-SPME–GC–MS and SD-GC–MS methods, respectively, and HS-SPME–GC–MS method shared 57 compounds in common with SD-GC–MS method, accounting for 93.4% of the compounds by SD-GC–MS. In addition, it is observed that 20 more compounds were obtained by the present HS-SPME–GC–MS method than the methods reported. The major compounds by the HS-SPME–GC–MS method include β-terpinene (2.5%), 6-butyl-1,4-cycloheptadiene (2.01%), 4-methyl-1-(methylethyl)-3-cyclohexen-1-ol (3.22%), eudesma-4(14),11-diene (9.22%), 1-phenyl-1-pentanone (1.03%), (−)-spathulenol (1.64%), 2-methoxy-4-vinyl phenol (2.03%), 3-butylidene-phthalide (16.00%), 1-(2,4-dimethylphenyl)-1-propanone (4.29%), ligustilide (18.71%) and fenipentol (12.24%). Fig. 8 showed a clear comparison of the RA% values for the five target compounds by the two methods. Compared with the SD-GC–MS method, the present HS-SPME–GC–MS method obtained much higher RA% for eudesma-4(14),11-diene and fenipentol but lower RA% values for ligustilide, and comparable RA% for 3-butylidene-phthalide and 1-(2,4-dimethylphenyl)-1-propanone.

4. Conclusions

A HS-SPME–GC–MS method for the analysis of the volatile components in the dry rhizome of *Ligusticum chuanxiong* Hort. is described and a comparison between HS-SPME–GC–MS and SD-GC–MS methods is made. Using much less sample amount, shorter extraction time and simpler procedure, HS-SPME method can achieve comparable results with those by SD. For HS-SPME, the obtained optimuml extraction conditions were: 50/30 μm DVB–CAR–PDMS fiber, 0.5 g of the ground sample with a particle size of 120 mesh, 90 °C for 40 min, 4 min for desorption. It was found that the present method can achieve better results than the methods available for the purpose with at least 20 more compounds obtained. In conclusion, the present method is simple, rapid and effective and can be used for the analysis of volatile compounds in medicinal plants.

Acknowledgements

The authors wish to thank the National Natural Science Foundation of China for funding (Grant No. 20475007). The authors also thank Professor Baolin Guo for the authentication of *Ligusticum chuanxiong* Hort.

References

[1] China Pharmacopoeia Committee, Chinese Pharmacopoeia, vol. 1, Chemical Industry Press, Beijing, PR China, 2005, p. 28.
[2] X. Li, Y. Liang, F. Guo, Acta Pharmacopoeia Sin. 27 (2006) 491–498.
[3] M. Liang, L. He, Y. Li, J. Chin. Mass Spectrom. Soc. 25 (2004) 150–154.
[4] Z. Hong, X. Wang, J. Le, D. Zhang, Z. Liu, J. Chin. Pharm. Sci. 11 (2002) 31–34.
[5] C.L. Arthur, J. Pawliszyn, Anal. Chem. 62 (1990) 2145–2150.
[6] C. Bicchi, S. Drigo, P. Rubiolo, J. Chromatogr. A 892 (2000) 469–485.
[7] H. Kataoka, H.L. Lord, J. Pawliszyz, J. Chromatogr. A 880 (2000) 35–62.
[8] S. Ulrich, J. Chromatogr. A 902 (2000) 167–194.
[9] L. Krutz, S.A. Senseman, A.S. Sciumbato, J. Chromatogr. A 999 (2003) 103–121.
[10] J. Cao, M. Qi, L. Fang, S. Zhou, R. Fu, J. Pharm. Biomed. Anal. 40 (2006) 552–558.
[11] M. Liang, M. Qi, S. Zhou, R. FU, J. Huang, Anal. Chim. Acta 531 (2005) 97–104.
[12] F. Guo, L. Huang, S. Zhou, Y. Liang, Anal. Chim. Acta 570 (2006) 73–78.
[13] X. Zheng, C. Deng, G. Song, Y. Hu, Chromatographia 59 (2004) 729–732.
[14] C. Deng, N. Li, X. Zhang, J. Chromatogr. A. 1059 (2004) 149–155.
[15] Q. Wu, C. Deng, S. Shen, G. Song, Y. Hu, D. Fu, J. Chen, X. Zhang, Chromatographia 59 (2004) 763–767.
[16] F. Pellati, S. Benvenuti, F. Yoshizaki, D. Bertelli, M. Rossi, J. Chromatogr. A 1087 (2005) 265–273.
[17] M. Adam, M. Juklov'a, T. Bajer, A. Eisner, K. Ventura, J. Chromatogr. A 1084 (2005) 2–6.
[18] X. Deng, J. Peng, B. Luo, M. Wei, W. Hu, J. Du, Anal. Bioanal. Chem. 380 (2004) 950–957.
[19] T. Natio, K. Kubota, Y. Shimoda, Nat. Med. 49 (1995) 288–292.
[20] J. Xiong, Y. Feng, Acta Pharm. Sin. 35 (2000) 408–412.