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Journal of Pharmaceutical and Biomedical Analysis 40 (2006) 552–558
JOURNAL OF PHARMACEUTICAL AND BIOMEDICAL ANALYSIS
www.elsevier.com/locate/jpba

Solid-phase microextraction–gas chromatographic–mass spectrometric analysis of volatile compounds from *Curcuma wenyujin* Y.H. Chen et C. Ling

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Received 29 May 2005; received in revised form 20 July 2005; accepted 29 July 2005
Available online 21 September 2005

Abstract

A solid-phase microextraction coupled with gas chromatography–mass spectrometry (SPME–GC–MS) for analysis of the volatile compounds from *Curcuma wenyujin* Y.H. Chen et C. Ling is described. SPME parameters (fiber type, extraction temperature and time, headspace volume and desorption time) and GC conditions were tested. The powdered sample of *C. wenyujin* Y.H. Chen et C. Ling was directly analyzed by SPME–GC–MS and 72 compounds were identified. The results from SPME–GC–MS were compared with those obtained from steam distillation gas chromatography–mass spectrometry (SD-GC–MS) with a good agreement. The results show that SPME–GC–MS method is a fast, simple and efficient way for the analysis of volatile components from traditional Chinese medicines (TCMs).

Keywords: Headspace solid-phase microextraction; Gas chromatography–mass spectrometry; Volatile components; Traditional Chinese medicines (TCMs)

1. Introduction

Traditional Chinese medicines (TCMs) are well known for their various pharmacological activity, low toxicity and complex components [1]. TCMs are an unimaginable complicated system and often contain tens or even hundreds of components whose identity is only partially known, which makes the quality evaluation of TCMs greatly challenging. Unlike synthetic drugs, the therapeutic effects of a TCM originate from the synergic effects of its numerous components. Therefore, the quality evaluation of a TCM should not just base on its one or a few marker components of pharmacological activity. Chromatographic fingerprints, profiling the global chromatographic pattern of the components, have been internationally accepted as a feasible means for the quality evaluation of TCMs [2–5].

Curcuma wenyujin Y.H. Chen et C. Ling called “Erzhu” in Chinese has been clinically used for suppression of tumors, treatment of cervical cancer, increasing white blood cells, antithrombosis, and increasing motility of the stomach [6,7]. It has been proved that the volatile components in *C. wenyujin* Y.H. Chen et C. Ling are pharmacologically active and often used for its quality evaluation. The principal components include β-elemene, curzerene, curzerenone, germacrone, curcumol, isocurcumenol and curcumenol [8]. As a result of a recent survey, the volatile components from *C. wenyujin* Y.H. Chen et C. Ling was often analyzed by gas chromatography and/or mass spectrometry (GC–MS) using the essential oil extracted by steam distillation (SD) and the analyses focused on one or a few components [9–11]. Steam distillation is often complex and time-consuming. It requires a relatively large amount of sample and takes several hours or days to complete, which further complicates the analytical results due to more influencing factors involved. Besides, because of the instability of the essential oil from *C. wenyujin* Y.H. Chen et C. Ling, it is often required that the oil should be freshly prepared before analysis and sometimes some stabilizing reagent should be added, which causes some trouble for the analysis. The problems mentioned above can be addressed by solid-phase microextraction–gas chromatography–mass spectrometry (SPME–GC–MS).

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doi:10.1016/j.jpba.2005.07.050

SPME is a new solvent-free sample preparation technique introduced by C. Arthur and J. Pawliszyn in 1990 [12], which combines extraction, concentration, and injection in one step and in one device. Combined with gas chromatography–mass spectrometry, SPME has been used for the analysis of semi-volatile and volatile constituents from plant materials [13–19], food [20], biological [21] and environmental [22] samples and TCMs [23–29]. However, no publications are available for the analysis of *C. wenyujin* Y.H. Chen et C. Ling by SPME–GC–MS.

The present study describes a SPME–GC–MS method for the analysis of the volatile components from *C. wenyujin* Y.H. Chen et C. Ling. SPME parameters (fibers, extraction temperature and time, headspace volume and desorption time) were investigated. A comparison between SPME–GC–MS and SD-GC–MS is made. The objective of the present work is to develop a rapid and practical method for the identification and evaluation of *C. wenyujin* Y.H. Chen et C. Ling on the basis of the chromatographic fingerprints. The developed method can also be applied to other traditional Chinese medicines (TCMs) containing the volatile compounds as the pharmacologically active components for their quality evaluation.

2. Experimental

2.1. Apparatus and materials

GC–MS analyses were performed on HP 5973 GC-MSD (Agilent, USA). HP Innowax column (30 m × 0.25 mm × 0.25 μm) was from J&W Scientific (USA). A manual SPME holder and two types of fibers (100 μm polydimethylsiloxane (PDMS), 85 μm polyacrylate (PA) and 5 ml vials from Supelco (Bellefonte, USA) were used for the extraction procedures. Fibers were conditioned following the supplier's instructions prior to use.

The samples of *C. wenyujin* Y.H. Chen et C. Ling were purchased from An'guo traditional Chinese medicine market in Hebei province of China and were authenticated. Samples were ground to fine powder in a high-speed rotary cutting mill and sieved (120 mesh) and stored in a sealed bottle until analysis.

2.2. Extraction

2.2.1. Steam distillation procedure

The essential oil was extracted from the sample powder (55 g) by steam distillation following Chinese Pharmacopeia (2005). The sample powder was weighed into a 2 l distillation flask and then 400 ml 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.

2.2.2. SPME procedure

The sample powder was placed in a 5 ml vial sealed with a septum-type cap. After the SPME needle pierced the septum, the fiber was exposed to the sample headspace. After a suitable extraction time, the fiber was retracted and removed from the vial and was immediately thermally desorpted in the injection port of the GC–MS.

2.3. Selection of SPME parameters

SPME parameters including fiber type, extraction temperature and time, headspace volume (sample amount), and desorption time are optimized. Two types of fibers, PDMS and PA, were determined under the following conditions: extraction temperature, 80 °C; extraction time, 20 min; desorption temperature and time, 230 °C, 5 min; sample amount, 1.5 g. The percentages of relative amount of the main components in *C. wenyujin* Y.H. Chen et C. Ling were used to evaluate the optimal fiber. Extraction temperature (50, 60, 70, 80 and 90 °C) and extraction time (5, 10, 20, 25, 30, 40, 50, 60 min) were tested by using PA fiber. The sum of peak areas was adopted to evaluate the optimal temperature and time. Headspace volume was determined by varying the amount of the powdered sample in a 5 ml vial (1.5, 1.2, 0.9, 0.6 and 0.3 g). The responses of the main components were adopted to choose the right sample amount (inversely proportional to headspace volume). Desorption time was determined by varying desorption time from 1 to 5 min. The sums of peak areas were used to determine the optimal desorption time.

2.4. GC–MS conditions

Chromatographic separation was performed under the following conditions: HP Innowax capillary column (30 m × 0.25 mm × 0.25 μm); oven temperature program, 70 °C (3 min) to 145 °C at a ramp of 20 °C/min and 145 °C to 200 °C (20 min) at a ramp of 2 °C/min; injector temperature, 230 °C; detector temperature, 260 °C; carrier gas, high-purity nitrogen at a pressure of 7 kPa at the column head; split ratio, 1:10; injection volume (for SD-GC–MS), 0.1 μl; sample amount (for SPME–GC–MS), 1.5 g.

The mass spectrometer was fitted with an EI source operated at 70 eV with a source temperature of 180 °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 240 °C and the ion source temperature was 230 °C. Compounds were identified by matching their mass spectra with the NIST and Wiley spectral libraries with a resemblance percentage above 85%.

3. Results and discussion

3.1. Selection of headspace SPME conditions

3.1.1. SPME fiber type

Two types of fibers was used for headspace extraction of *C. wenyujin* Y.H. Chen et C. Ling at the temperature of 80 °C for 20 min. The peak areas of seven main compounds including β-elemene, curzerene, curzerenone, germacrone, curcumol, isocurcumenol, and curcumenol present in the medicinal plant were used for the evaluation of the optimal fiber. The results were shown in Fig. 1, indicating that the PA fiber provided higher

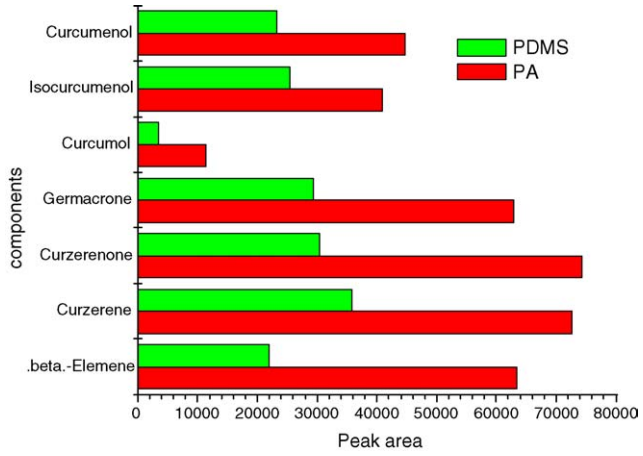

Fig. 1. Effect of SPME fibers on the peak areas of seven main compounds from *C. wenyujin* Y.H. Chen et C. Ling.

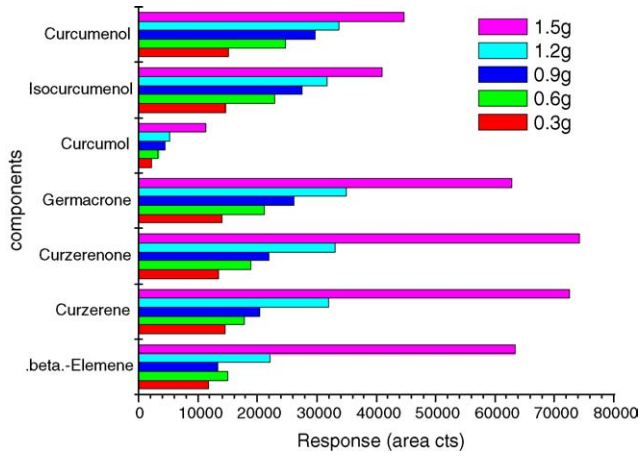

Fig. 3. Effect of sample amount (inversely proportional to headspace volume) on the response of seven main volatile compounds from *C. wenyujin* Y.H. Chen et C. Ling.

extraction efficiency to the seven components than PDMS and was finally adopted for the present work.

3.1.2. Extraction temperature and time

Extraction temperature and time are important factors for the SPME process. SPME is mainly based on the equilibrium among sample, sample headspace and the solid-phase fiber coating. The results for the effect of extraction temperature and time of SPME on the extraction of analytes are shown in Fig. 2, indicating that the sum of peak areas of the volatile components increases with the increase of temperature and time. A significant jump occurred between 70 and 80 °C. When the temperature was further increased from 80 to 90 °C, no significant increase in the response was observed. High temperature is favorable for the release of volatile components from the powdered sample, but exerts a negative effect on distribution constant. A reasonable temperature should balance in these two aspects. Finally, a temperature of 80 °C was used for the analysis.

The extraction time was also determined and the results were shown in Fig. 2. On the basis of Fig. 2, it can be found that the sum of peak areas reach the platform at 30 min after the steep increase from 5 to 25 min at 80 °C and below. Therefore, 30 min at 80 °C was finally adopted for the SPME extraction of the volatile compounds from the powdered sample of *C. wenyujin* Y.H. Chen et C. Ling.

3.1.3. Headspace volume

Headspace volume were determined by using different amount of the powdered sample in a 5 ml vial on the basis that headspace volume is inversely proportional to sample amount in the given volume of container. The results were shown in Fig. 3, indicating that the responses of these seven constituents increase with the quantity of sample or with the decrease of headspace volume. Because of the limited volume of the vial, no more sample amount than 1.5 g was determined and 1.5 g of the powdered sample in a 5 ml vial was finally chosen for the present study.

3.1.4. Desorption time

The desorption time of PA fiber from 1 to 5 min was determined with the injector temperature of 230 °C and extraction time of 30 min at 80 °C. The sums of peak areas were used to evaluate the optimal desorption time. The results shown in Fig. 4 demonstrate that the volatile compounds absorbed on the fiber can be completely desorbed at the time of 3 min, which was finally used for the analysis.

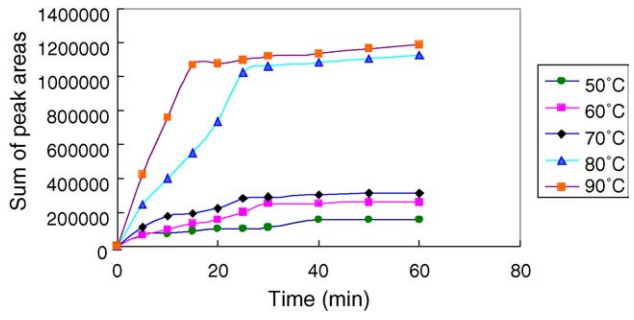

Fig. 2. Effect of extraction temperature and time on the sum of the peak areas of volatile compounds of *C. wenyujin* Y.H. Chen et C. Ling.

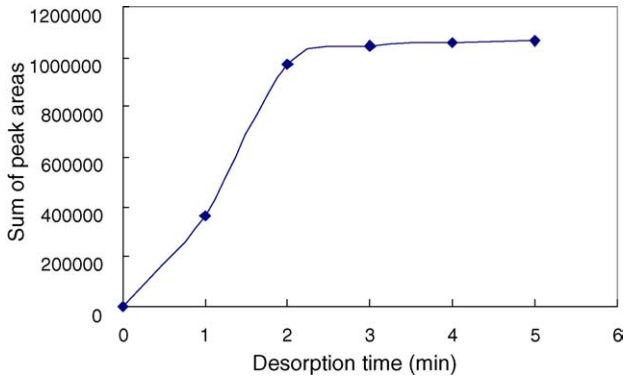

Fig. 4. Effect of desorption time on the sum of peak areas of volatile compounds from *C. wenyujin* Y.H. Chen et C. Ling.

Table 1
Components of *C. wenyujin* Y.H. Chen et C. Ling obtained by SPME–GC–MS and SD-GC–MS.

No.	Retention time(min)	Compounds	Relative amount (%) SPME–GC–MS	SD-GC–MS
1	2.04	*m*-Cymene	0.02	–
2	2.70	1R-.alpha.-Pinene	0.06	–
3	3.03	Camphene	0.46	–
4	3.91	3-Carene	0.03	–
5	4.02	.beta.-Myrcene	0.02	–
6	4.51	D-Limonene	0.09	0.07
7	4.71	Eucalyptol	0.24	0.05
8	5.03	4-Carene, 1S,3R,6R)-(−)-	0.01	0.02
9	5.43	Bicyclo[4.1.0]hept-2-ene,3,7,7,-trimethyl-	0.05	–
10	5.50	2-Octanol	0.03	–
11	5.77	2-Heptanol	0.07	–
12	6.43	2-Undecanone	0.04	–
13	6.59	Bicyclo[2.2.1]heptan-2-one,1,3,3-trimethyl-	0.04	–
14	7.05	Furfural	0.18	–
15	7.13	.delta.-Elemene	0.39	0.93
16	7.31	Ylangene	0.04	0.06
17	7.39	.alpha.-Cubebene	0.04	0.04
18	7.48	2-Nonanol	0.13	0.15
19	7.65	Camphor	1.30	1.50
20	8.16	Isocaryophillene	0.17	0.37
21	8.26	.beta.-Elemene	1.87	3.93
22	8.41	Caryophyllene	0.32	0.46
23	8.66	Epizonarene	0.11	0.20
24	8.76	.gamma.-Elemene	0.11	0.16
25	9.13	Isoborneol	1.19	2.58
26	9.23	.alpha.-Caryophyllene	0.95	3.57
27	9.55	Borneol	0.46	1.99
28	9.67	Naphthalene,1,2,4a,5,6,8a-hexahydro-4,7-dimethyl-1-(1-methylethyl)-,(1.alpha.,4a.alpha.,8a.alpha.)-	0.09	0.56
29	9.74	Azulene,1,2,3,4,5,6,7,8-octahydro-1,4-dimethyl-7-(1-methylethylidene)-,(1S-*cis*)-	0.30	1.08
30	9.87	Eudesma-4(14),11-diene	0.59	1.70
31	10.03	8-Isopropenyl-1,5-dimethyl-cyclode	0.94	1.38
32	10.31	Naphthalene,1,2,3,5,6,8a-hexahydro-4,7-dimethyl-1-(1-methylethyl)-,(1s-*cis*)-	0.22	0.43
33	10.38	Bicyclo[4.4.0]dec-1-ene,2-isopropyl-5-methyl-9-methylene-	0.06	0.09
34	10.47	1H-Benzocycloheptene,2,4a,5,6,7,8-hexahydro-3,5,5,9-tetramethyl-,(R)-	0.27	0.68
35	10.72	Naphthalene,1,2,3,4,4a,5,6,8a-octahydro-4a,8-dimethyl-2-(1-methylethylidene)-,(4aR-*trans*)-	1.16	1.80
36	11.02	Cyclohexane,1-ethehyl-1-methyl-2-(1-methylethenyl)-4-(1-methylethylidene)-	0.35	0.64
37	11.34	Benzene,1-methoxy-4-(1-propenyl)-	5.70	0.12
38	11.53	Germacrene B	0.14	0.20
39	11.60	Cadina-1(10),6,8-triene	–	0.18
40	11.65	Thymol	0.17	0.11
41	11.70	Neoisolongifolene,8,9-dehydro-	–	0.10
42	12.14	Curzerene	2.90	3.24
43	12.40	Benzofuran,6-ethenyl-4,5,6,7-tetrahydro-3,6-dimethyl-5-isopropenyl-, *trans*-	0.15	0.10
44	14.51	Ledol	0.44	0.60
45	15.38	Benzaldehyde, 4-methoxy-	0.73	0.53
46	16.75	Arzingiberone	4.67	5.06
47	17.13	.beta.-Elemenone	2.42	0.62
48	17.42	1,2,3,4-Tetrahydro-.beta..-carbolin,5-methoxy-1-methy1-	0.62	0.72
49	17.56	(−)-Globulol	0.11	0.12
50	18.40	.alpha.-Humulene	0.21	0.19
51	18.51	(E)-β-Farnesene	0.09	0.11
52	18.80	Dihydro-*cis*-.alpha.-copaene-8-01	0.29	0.40

Table 1 (*Continued*)

No.	Retention time(min)	Compounds	Relative amount (%) SPME–GC–MS	SD-GC–MS
53	19.10	3,7-Cyclodecadien-1-one,10-(1-methylethenyl)-, (E,E)-	0.38	0.48
54	19.36	2-Naphthalenemethanol,1,2,3,4,4a,5,6,7-octahydro-.alpha.,.alpha.,4a,8-tetramethyl-, (2R-*cis*)-	0.54	0.92
55	19.50	.tau.-Muurolol	1.24	1.44
56	19.93	Guaia-3,9-diene	0.46	0.52
57	20.08	Neocurdione	0.21	0.22
58	20.29	.alpha.-Cadinol	0.77	0.86
59	20.60	Curzerenone	5.28	4.98
60	20.89	2-Naphthalenemethanol,1,2,3,4,4a,5,6,8a-octahydro-.alpha.,.alpha.,4a,8-tetramethyl-,[2R-(2.alpha.,4a.alpha.,8a.beta.)]-	0.64	0.48
61	21.08	Germacrone	6.68	9.07
62	21.29	Curcumol	1.34	1.69
63	21.65	Ledene oxide-(II)	0.08	0.30
64	21.87	Azulene,1,2,3,3a,4,5,6,7-Octahydro-1,4-dimethyl-7-(1-methylethenyl)-,[1R-(1.alpha.,3a.beta.,4.alpha.,7.beta.)]-	0.66	0.73
65	22.01	(−)-Spathulenol	0.41	0.33
66	22.84	*cis*-Z-.alpha.-Bisabolene epoxide	0.30	0.19
67	23.26	Caryophyllene-(I1)	0.44	0.44
68	23.43	Isoaromadendrene epoxide	0.03	0.04
69	24.04	Furanogermenone	1.11	0.87
70	25.93	Isocurcumenol	8.70	7.48
71	26.62	Curcumenol	8.88	8.53
72	29.76	Cyclopentane,(1-phenyl-1-trimethylsilylmethylene,-	0.25	0.12
73	39.77	2-Nonadecanone	0.17	0.12
74	42.53	9-Octadecenoic acid,(E)-	1.12	–

3.2. Determination of the volatile compounds of C. wenyujin Y.H. Chen et C. Ling

Under the determined conditions mentioned above, the powdered samples of *C. wenyujin* Y.H. Chen et C. Ling were analyzed by SPME–GC–MS and the typical total ion chromatogram is shown in Fig. 5. Seventy-two compounds were identified and listed in Table 1. The main compounds identified include beta-elemene, curcumol, curzerenone, isocumenol, curdione, curcumenol and curzerene, among which beta-elemene, curcumol and curzerenone have been proved to be pharmacologically active. The mass spectrum of beta-elemene is shown in Fig. 6. Other compounds with less relative amount were gamma-elemene, camphene, 1,8-cineol, camphor, isoborneol, borneol, (−)-alpha-cubebene,alpha-curcumene and beta-elemenone. Volatile compounds were identified by comparing the obtained mass spectra of the analytes with those of authentic standards from the NIST and Wiley libraries.

3.3. Repeatability

The repeatability of the developed method was determined by five replicate analyses of volatile compounds in *C. wenyujin* Y.H. Chen et C. Ling under the determined conditions. The repeatability data focused on seven main components in the TCMs and were evaluated by relative standard deviation (R.S.D.) values. The results are listed in Table 2, showing that the R.S.D. values for the peak areas of seven main compounds were below 6%. The results indicate the satisfactory repeatability of the developed method.

3.4. Comparison of SPME–GC–MS and SD-GC–MS

A comparison of the volatile components between SPME–GC–MS and SD-GC–MS methods is made and the results are listed in Table 1. In general, the total ion chromatograms form these two methods are comparable and share many components in common. But there are also some differences between them. More compounds can be detected by SPME–GC–MS (72 compounds) than by SD-GC–MS (62 compounds). Besides, SPME–GC–MS method can greatly simplify and shorten the analytical process for volatile compounds from

Table 2
The repeatability of the developed method

Components	Peak areas					R.S.D. (%)
	Exp. 1.	Exp. 2.	Exp. 3.	Exp. 4.	Exp.5	
.beta.-Elemene	63415	59782	63085	62596	62341	2.3
Curzerene	72583	67435	68342	70348	69472	2.8
Curzerenone	74305	66493	67386	71834	69037	4.6
Germacrone	62833	55768	56790	63452	60648	5.8
Curcumol	11345	9876	10432	9963	10173	5.7
Isocurcumenol	40994	36493	38765	41223	39876	5.0
Curcumenol	44780	39430	40367	43661	42138	5.3

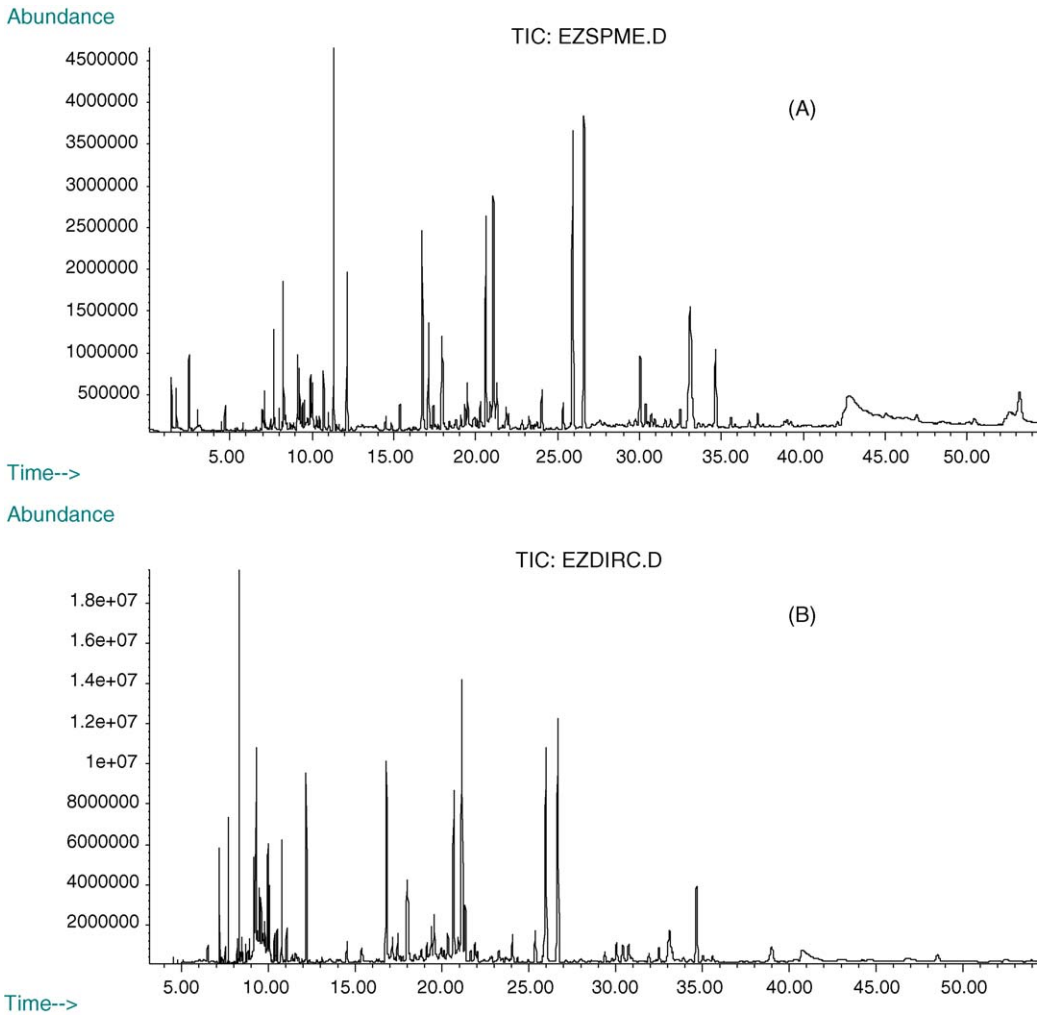

Fig. 5. Typical chromatograms of volatile components from *C. wenyujin* Y.H. Chen et C. Ling by SPME–GC–MS (A) and SD-GC–MS (B).

TCMs. Compared with SD-GC–MS method, SPME–GC–MS method can directly use the ground powder of TCMs for the analysis and need much less sample amount. What is more, SPME is a solvent-free and environmentally friendly technique. Therefore, SPME–GC–MS method is a simple and efficient method for the analysis of the volatile compounds from *C. wenyujin* Y.H. Chen et C. Ling.

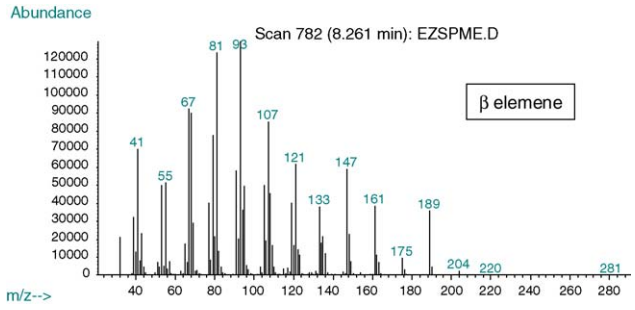

Fig. 6. Mass spectrum of beta-elemene.

4. Conclusions

A SPME–GC–MS method for the analysis of the volatile components of *C. wenyujin* Y.H. Chen et C. Ling is described and a comparison between SPME–GC–MS and SD-GC–MS methods is made. In addition to the comparable results of the two methods, SPME–GC–MS method uses much less sample, shorter time and simpler procedure. What's more, the ground powder of TCMs can be directly used for the analysis by SPME–GC–MS, which minimizes the possible influences of the process factors in SD-GC–MS method. In conclusion, SPME–GC–MS method is a simple, rapid and effective method and can be used for the analysis of volatile constituents from traditional Chinese medicines.

Acknowledgements

This research work was supported by the National Natural Science Foundation (no. 20475007). The authors would like to thank Professor Baolin Guo (Institute of Medicinal Plants,

Academy of Medicinal Science of China) for the help in the authentication of *C. wenyujin* Y.H. Chen et C. Ling.

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