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Headspace solvent microextraction-gas chromatography–mass spectrometry for the analysis of volatile compounds from *Foeniculum vulgare* Mill

Lianghua Fang, Meiling Qi *, Ting Li, Qinglong Shao, Ruonong Fu

Department of Chemistry, School of Science, Beijing Institute of Technology, Beijing 100081, China

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Abstract

A novel and rapid headspace solvent microextraction followed by gas chromatography–mass spectrometry (HSME-GC–MS) for the analysis of the volatile compounds of *Foeniculum vulgare* Mill is described. HSME parameters including extracting solvent, extraction temperature and time, headspace volume and particle size were optimized. As a result, benzyl alcohol was finally used for the extraction at 70 °C for 20 min with headspace volume of 12.1 ml and particle size of 120 mesh. Under the determined conditions, the powered samples of *Foeniculum vulgare* Mill were directly applied for the analysis. A comparison of HSME-GC–MS, solid phase microextraction (SPME)-GC–MS and steam distillation (SD)-GC–MS methods was made and showed that the HSME-GC–MS method was simple, inexpensive and effective and can be used for the analysis of volatile compounds in traditional Chinese medicines (TCMs).

Keywords: Headspace solvent microextraction; Volatile compounds; *Foeniculum vulgare* Mill; Traditional Chinese medicine

1. Introduction

Historically, especially in China, traditional Chinese medicines (TCMs) have played an important role in clinical therapy because of their high pharmacological activity and low toxicity [1,2]. *Foeniculum vulgare* Mill has been used as a TCM for about a thousand year to treat such diseases as dysmenorrhea, vomiting and diarrhea, and deflection of spermary. It has been proven that its pharmacological activity mainly originates from its volatile compounds [3,4].

Traditionally, the analysis of volatile compounds of TCMs is often performed using the essential oil previously extracted by steam distillation (SD) followed by gas chromatography (GC) or gas chromatography–mass spectrometry (GC–MS). The main volatile compounds in *Foeniculum vulgare* Mill include *trans*-anethole, limonene, estragole, fenchone, 4-methoxybenzaldehyde and γ-terpinene [3]. However, the SD method usually requires a large amount of samples and a long time (several hours or even days). We recently reported solid-phase microextraction (SPME)-GC–MS methods for the analysis of the volatile compounds in TCMs [5,6] (and references cited therein). SPME-GC–MS is a rapid and efficient method for the purpose, but SPME fibers are relatively expensive and the fiber types available are limited.

Headspace solvent microextraction (HSME), a new sample preparation technique introduced by Jeannot and co-workers, has attracted increasing attentions [7]. HSME integrates sampling, extraction, concentration and sample introduction into one step and uses only a few microliter solvent and simple laboratory apparatus. This technique was successfully applied for analysis of volatile compounds in environmental and food samples [8–20]. Recently, we reported an HSME-GC–MS method for the analysis of volatile compounds in *Curcuma wenyujin* Y.H. Chen et C. Ling [21]. A recent survey revealed that no publications are available for the analysis of the volatile compounds in *Foeniculum vulgare* Mill by HSME-GC–MS method.

The present study describes an HSME-GC–MS method for the analysis of volatile compounds in *Foeniculum vulgare* Mill. HSME parameters in terms of extracting solvent, extraction temperature and extraction time, headspace volume and particle size

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

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of sample were investigated. A comparison of HSME-GC–MS, SPME-GC–MS and SD-GC–MS methods was made and the results showed that HSME-GC–MS method is simple, inexpensive and effective and can be used for the analysis of the volatile compounds of TCMs.

2. Experimental

2.1. Materials and reagents

Samples of *Foeniculum vulgare* Mill were commercially collected from Anguo traditional Chinese medicine market, Hebei province of China. Prior to use, samples were dried in an oven below 40 °C, and ground into fine powder and sieved (20, 60, 80, 100 and 120 mesh).

Decane, dodecane, tridecane, tetradecane, hexadecane and acetone were purchased from Beijing Chemical Reagents Company (Beijing, China). Squalane was purchased from A.E.C (France). Butyl acetate was obtained from Atoz Fine Chemical Co., Ltd., benzyl alcohol, isobutyl alcohol, 1-octanol were obtained from Ourchem (Shanghai, China). All the reagents except 1-octanol (chromatographic grade) were analytical grade and used as received.

2.2. Optimization of HSME procedure

To achieve the optimum extraction efficiency of HSME-GC–MS method, the following parameters were investigated: extracting solvent, extraction temperature and time, headspace volume and particle size of the powdered sample. The peak area ratios of total chromatographic peak areas to 1-octanol (internal standard) were used to evaluate the influence of each of the parameters on the extraction.

A 15-ml vial (Supclo, USA) with PTFE septum containing the powdered sample was placed at a fixed position for improving precision of method in a water bath. Then a 5 μl GC microsyringe (Hamilton, Reno, NV) was pierced into the headspace of the vial and clamped at a fixed position. One microliter benzyl alcohol containing 0.2% 1-octanol (internal standard) was suspended at the tip of the microsyringe. The microsyringe was washed at least 20 times by extracting solvent between runs. After a pre-set extraction time, the extracting solvent was retracted into the needle and swiftly injected onto GC–MS for the analysis.

2.3. SPME procedure

SPME was performed using a 100 μm PDMS fiber and a SPME holder assembly from Supelco (Sigma Aldrich). The fiber was conditioned following the supplier's instructions. The SPME holder assembly was clamped in a fixed location and the fiber was exposed to the headspace of the powdered sample (0.5 g, 120 mesh) in a 5 ml sealed vial in a water bath at 90 °C. After an extraction time of 30 min, the fiber is withdrawn into the needle, and then the needle is removed from the septum and inserted directly into the injection port of the GC. The desorption of analytes from the fiber coating is performed by heating the fiber in the injection port at 230 °C for 5 min.

2.4. SD procedure

Fifty gram of the ground powder of *Foeniculum vulgare* Mill (20 mesh) and 400 ml water were added into a 1000 ml distillation flask and mixed well. And the mixture was distilled for 6 h following the Chinese pharmacopoeia (2005). The yield of the sample was 0.98%. After the extraction, a small amount of anhydrous sodium sulfate was added into the obtained essential oil to remove the minor water possibly present in the oil. The obtained essential oil was stored at −4 °C until analysis. SD-GC–MS analysis was carried out by directly injecting 1 μl essential oil onto GC–MS apparatus.

2.5. GC–MS procedure

GC–MS analyses of volatile compounds were performed on a HP 5973 GC-MSD (Agilent, USA). HP Innowax column (PEG-20 M) (30 m × 0.25 mm × 0.25 μm) was from J&W Scientific (USA). The column oven temperature was programmed to rise from 50 °C (5 min) to 90 °C (1 min) at 20 °C/min, and then rise to 150 °C (10 min) at 2 °C/min. The injector temperature and ion source temperature were 230 and 250 °C, respectively. The injection volume for SD-GC–MS method was 1 μl essential oil with the split ratio of 100:1. The split ratios for SPME-GC–MS and HSME-GC–MS methods were 10:1. The carrier gas was nitrogen of high purity (99.995%) at a flow rate of 1 ml/min. The electron impact ionization mode was used and ion energy was 70 eV. Total ion chromatograms were obtained with the scan range of 30–500 amu in the full-scan acquisition mode, and compounds were identified using the NIST and Wiley libraries with a resemblance percentage above 85%.

3. Results and discussion

Under the extraction conditions, the volatile compounds of the sample in a vial evaporate and transfer into the headspace where a single drop of an extracting solvent is suspended at the tip of a syringe needle. Over a time period, a dynamic equilibrium will establish among the matrix, headspace and solvent phase. Eq. (1) describes the amount of analytes (n) extracted by the microdrop at equilibrium [8]:

$$n = \frac{K_{ods} V_d C_0 V_s}{K_{ods} V_d + K_{hs} V_h + V_s} \quad (1)$$

$$n = \frac{K_{ods} V_d C_0 V_s}{K_{hs} V_h + V_s} \quad (2)$$

where K_{ods} and K_{hs} are the distribution constants of solvent drop-sample and headspace-sample, respectively; C_0 is the initial concentration of analytes in the sample; V_d, V_s and V_h are the volumes of solvent drop, sample and headspace, respectively. Supposing that K_{hs} is much larger than K_{ods} of volatile compounds in the TCM, Eq. (1) can be simplified as Eq. (2).

3.1. Optimization of HSME procedure

3.1.1. Extracting solvent

Selecting a proper extracting solvent is especially crucial for the analysis of volatile compounds of TCMs because of the great differences of the compounds in polarity and volatility.

Taking into account the extraction efficiency, volatility and chromatographic behaviors, many kinds of solvents were tried, including decane, dodecane, tridecane, tetradecane, hexadecane, squalane, butyl acetate, isobutyl alcohol, decanol, 1-octanol and benzyl alcohol. As a result, benzyl alcohol offered satisfactory extraction, reasonable volatility and satisfactory chromatographic resolution with the analytes of interest in the chromatograms and was finally adopted as the extraction solvent.

From Eq. (1), it can be known that the amount of extracting analytes in the solvent drop increased with the solvent volume. However, the results show that when the volume exceeded 1 μl, the chromatographic peak of the solvent broadened and even covered the peaks of analytes of interest. Furthermore, a microdrop of a larger volume had a great tendency to fall down from the tip of the microsyringe needle. In light of this, 1 μl benzyl alcohol was finally used for the present study.

3.1.2. Extraction temperature

The extraction temperature usually has a double impact on HSME. One is that the diffusion coefficients of the analytes increase with the temperature. The other is that the partition coefficients of the analytes between the microdrop and the headspace decrease with the increase of temperature. In addition, different from SPME method, a high extraction temperature can speed the evaporation of the solvent phase. To find a reasonable extraction temperature, it was investigated in a range from 40 to 80 °C using the powdered samples (120 mesh) for 15 min with a headspace volume of 10.9 ml. The result is shown in Fig. 1, indicating that the peak area ratio of the analytes reaches its maximum at 70 °C. Therefore, a temperature of 70 °C was finally selected for the extraction.

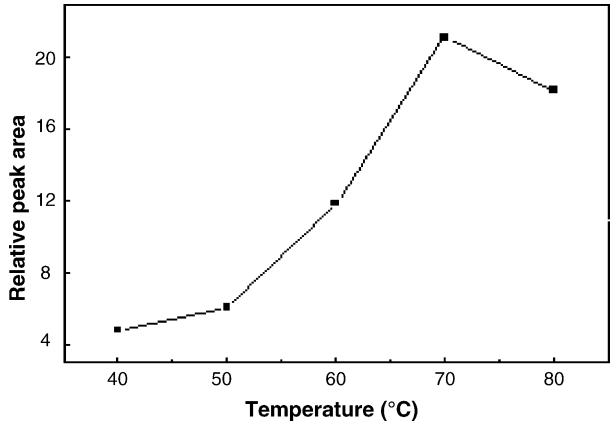

Fig. 1. Graph of peak area ratios of total chromatographic peak areas to 1-octanol (internal standard) vs. extraction temperature. Extraction conditions: microdrop volume, 1 μl; extraction time, 15 min; sample particle size, 120 mesh; headspace volume, 10.9 ml.

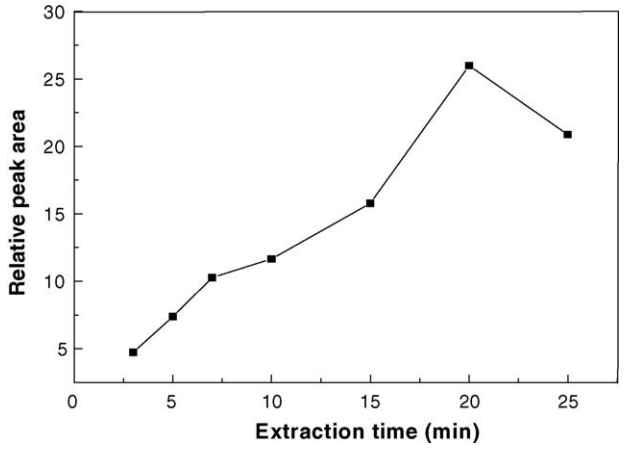

Fig. 2. Graph of peak area ratios of total chromatographic peak areas to 1-octanol (internal standard) vs. extraction time. Extraction conditions: microdrop volume, 1 μl; extraction temperature, 70 °C; sample particle size, 120 mesh; headspace volume, 10.9 ml.

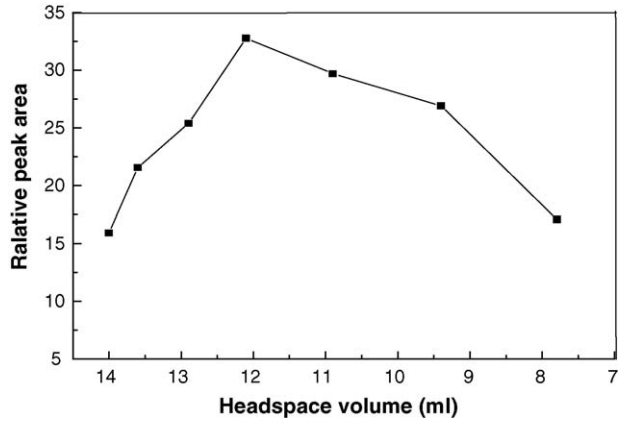

Fig. 3. Graph of peak area ratios of total chromatographic peak areas to 1-octanol (internal standard) vs. headspace volume. Extraction conditions: microdrop volume, 1 μl; extraction temperature, 70 °C; extraction time, 20 min; sample particle size, 120 mesh.

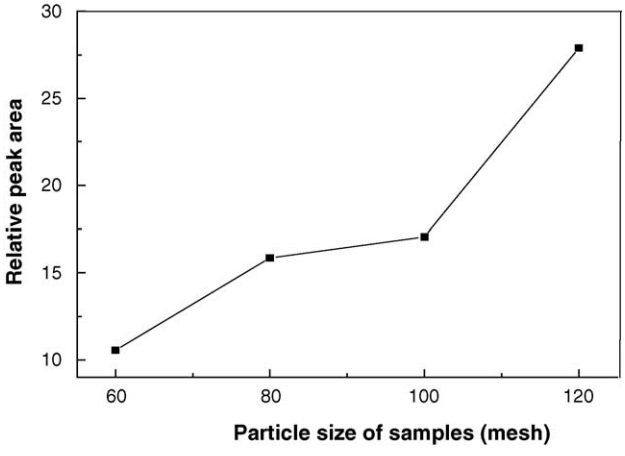

Fig. 4. Graph of peak area ratios of total chromatographic peak areas to 1-octanol (internal standard) versus particle size of sample. Extraction conditions: microdrop volume, 1 μl; extraction temperature, 70 °C; extraction time, 20 min; headspace volume, 12.1 ml.

Table 1
The volatile compounds from *Foeniculum vulgare* Mill tentatively identified by HSME-GC–MS, SPME-GC–MS and SD-GC–MS methods

No.	Retention time (min)	Compounds	RA%		
			SD-GC–MS	SPME-GC–MS	HSME-GC–MS
1	1.76	2-Heptene	–	–	0.32
2	2.33	3-Methyl-butanal	0.51	0.01	0.01
3	4.01	β-Pinene	0.42	0.01	0.11
4	4.99	Camphene	–	–	0.01
5	5.48	Hexanal	–	0.09	0.01
6	5.92	α-Pinene	0.08	0.09	0.02
7	6.19	β-Phellandrene	0.26	–	0.10
8	6.95	α-Phellanrrene	0.33	–	0.08
9	7.02	β-Myrcene	0.01	–	–
10	7.17	4-Carene	0.03	–	0.01
11	7.35	2-Heptanohe	–	–	0.01
12	7.55	Limonene	6.29	0.40	2.02
13	7.66	4-Methyl-bicyclo[3.1.0]hex-2-ene	0.35	–	–
14	7.69	Eucalyptol	0.53	0.05	0.61
15	8.13	α-Pinene	0.88	0.03	0.28
16	8.35	γ-Terpinene	2.53	0.09	0.82
17	8.44	3,7-Dimethyl-1,3,7-octriene	0.44	–	–
18	8.81	1-Methyl-3-(1-methylethyl)-benzene	1.11	0.12	0.57
19	9.05	3-Carene	0.11	–	0.02
20	9.52	2-Methyl-3-methylethyl-butanoic acid	0.02	–	0.02
21	10.11	2-Heptanol	–	–	0.04
22	10.66	2-Propyn-1-ol	–	–	0.03
23	11.09	2,6-Dimethyl-2,4,6-octatriene	0.01	–	0.01
24	11.82	Fenchone	3.28	1.05	5.49
25	12.12	1-Methyl-4-(1-methylethyl)-benzene	–	–	0.01
26	13.46	*Cis*-limonene oxide	0.01	–	0.07
27	13.53	*Trans*-limonene oxide	0.04	0.11	0.07
28	13.84	6-Methylene-bicyclo[3.1.0]hexane	0.03	–	–
29	14.50	Sabinenehydrate	0.03	–	0.11
30	14.65	Fenchyl acetate	0.11	–	0.09
31	15.35	Camphor	0.09	0.04	0.10
32	15.88	Benzaldehyde	–	–	3.81
33	16.76	1,3-Butanediol	–	0.07	0.02
34	17.22	Dicyclopropyl carbinol	–	–	0.16
35	17.64	Fenchol	0.01	–	–
36	17.66	1-Octanol	–	0.01	1.07
37	18.31	5-Methyl-2-heptanol	–	0.02	0.03
38	18.80	Tetradecyl-oxirane	–	0.31	–
39	19.11	4-Methyl-1-(methylethyl)-3-cyclohexen	0.01	–	0.08
40	19.90	*Trans-p*-2,8-menthadien-1-ol	0.03	0.11	0.06
41	20.03	β-Terpinol	0.01	0.01	–
42	20.30	*Cis-p*-2,8-menthadien	–	0.02	0.08
43	21.35	Estragole	5.95	1.95	6.10
44	21.71	*Cis-p*-menth-2,8-dienol	–	0.07	–
45	22.47	Phenylmethyl-formic ester	–	–	0.12
46	22.92	2,3-Cyclohexen-1-methanol	0.02	0.03	0.10
47	23.13	*Epi*-bicyclosesquiphellardrene	0.19	–	–
48	24.06	2-Methyl-5-(1-methylethyl)-2-cyclohexen-1-one	0.01	0.14	0.07
49	24.30	1,4-Dimethoxy-benzene	0.02	0.02	0.03
50	25.12	1-Methoxy-4-(1-propenyl)-benzene	0.35	0.29	0.31
51	25.47	1,2,4a,5,8,8a-Hexadehyde-naphthalene	–	–	0.07
52	28.33	4-Methyl-bicyclo[3.1.1]hept-3-en-2-ol	–	–	0.69
53	28.54	*Trans*-anethole	73.20	73.27	66.71
54	29.10	2-Methyl-5-(1-methylethyl)-2-cyclohexen-1-ol	0.06	0.03	0.10
55	29.65	2-Methyl-5-(1-methylethyl)-phenol	0.02	0.08	–
56	30.32	Mannoheptulose	0.02	0.05	–
57	30.47	Allantonic acid	–	0.06	–
58	30.82	1-Undecanol	–	0.33	–
59	33.12	Benzothiazole	0.03	0.16	–
60	33.49	*E*-pinane	0.03	–	–
61	34.98	2-Cyclohexen-1-ol	–	0.34	–
62	36.60	2-Methyl-bezenemethanol	–	0.01	0.02

Table 1 (*Continued*)

No.	Retention time (min)	Compounds	RA%		
			SD-GC–MS	SPME-GC–MS	HSME-GC–MS
63	36.870	4-Methoxy-benzaldehyde	1.99	16.32	5.68
64	39.05	2,4-Dimethyl-benzenamine	0.13	–	–
65	39.33	2-Methoxycyclohexanone	–	0.08	–
66	40.23	β-Elemenone	–	0.02	–
67	41.17	Mephenesin	–	–	0.01
68	42.69	4′-Methoxy-acetophenone	–	0.07	0.02
69	43.04	Cathine	–	0.01	–
70	43.28	Folic acid	–	0.02	0.01
71	44.86	1-(Methoxyphenyl)-2-propanone	0.13	1.42	0.20
72	45.09	1,6-Hexanediol	–	0.13	–
73	46.47	4-Fluorohistamine	–	0.11	–
74	46.64	1,2-Dimethoxy-4-(1-propenyl)-benzene	0.05	0.01	0.01
75	46.77	(*E*)-2-Hydroxy-4′-cyano-stillbene	–	0.10	–
76	47.42	1-(3-Methoxyphenyl)-1-propanone	0.14	0.38	–

3.1.3. Extraction time

The extraction time was investigated at 3, 5, 7, 10, 15, 20 and 25 min using 120 mesh samples at 70 °C with a headspace volume of 10.9 ml, and the results are shown in Fig. 2. On the basis of Fig. 2, it can be found that the amount of analytes in the extracting solvent reached its maximum at 20 min. This might result from that before 20 min, the amount of analytes in the microdrop increases with the extraction time, but after that time, a longer extraction time could reduce the volume of microdrop, leading to the decrease of n value. Thus, the extraction time of 20 min was finally adopted for the analysis.

3.1.4. Headspace volume

Headspace volume was tested (14.0, 13.6, 12.9, 12.1, 10.9, 9.4 and 7.8 ml) at 70 °C for 20 min by using 120 mesh samples and the results are shown in Fig. 3. Fig. 3 shows that the peak areas of analytes increase from 14.0 to 12.1 ml and then decrease afterwards, exhibiting a maximum at the headspace volume of 12.1 ml. In a given vial for extraction, headspace volume is decreased with the increase of the sample mass. The decrease of the peak areas after 12.1 ml probably resulted from the poor transfer and convection of the analytes in the solid sample matrix, which prevent the analytes from getting into the headspace and the extraction solvent. Finally, a headspace volume of 12.1 ml (corresponding to 1.0 g sample mass) was chosen for the analysis.

3.1.5. Particle size of sample

For a solid sample, particle size plays an important part in the extraction. Particle size of the sample was tested from 60 to 120 mesh at 70 °C for 20 min with a headspace volume of 12.1 ml and the result are shown in Fig. 4. The results show that the amount of volatile compounds increased with the decrease of particle size, i.e., the finer the powdered sample, the larger the extraction amount of analytes. But if the particles become even smaller than 120 mesh, the static effects will become worse and thus cause trouble for sampling. Hence, the powdered sample of 120 mesh was finally used.

3.2. Repeatability

The repeatability was determined by performing six replicate experiments under the optimum extraction parameters. Relative standard deviations (R.S.D.) of the peak area ratios of the analytes of interest to the internal standard were less than 9.8%, indicating the satisfactory repeatability of the HSME-GC–MS method.

3.3. Analysis of the volatile compounds in Foeniculum vulgare Mill by HSME-GC–MS

Analysis of volatile compounds in *Foeniculum vulgare* Mill by HSME-GC–MS method was performed under the described conditions and 52 compounds were tentatively identified. The results are shown in Table 1 and Fig. 5. Based on Table 1 in which the percentage of relative amount (RA%) for each compound was given, the main compounds found by the HSME-GC–MS method were limonene (2.02%), γ-terpinene (0.82%), fenchone (5.49%), estragole (6.10%), *trans*-anethole (66.71%) and 4-methoxy-benzaldehyde (5.68%).

3.4. Comparison of HSME-GC–MS versus SPME-GC–MS and SD-GC–MS methods

The results for SPME-GC–MS and SD-GC–MS methods are shown in Table 1 and Fig. 5. It can be found that the chromatograms from the three methods were quite similar and the number of the compounds identified by SD-GC–MS and SPME-GC–MS methods were 55 and 47, respectively. To find if there were any differences of the three extraction methods, the relative amounts of the six aforementioned compounds are compared and the results are shown in Fig. 6. It is delightful to find that the relative amounts of the four major compounds (*trans*-anethole, estragole, fenchone and 4-methoxy-benzaldehyde) by HSME-GC–MS method are close to or higher than those of the corresponding compounds by SD-GC–MS method, indicating that HSME-GC–MS method can be used as an alternative

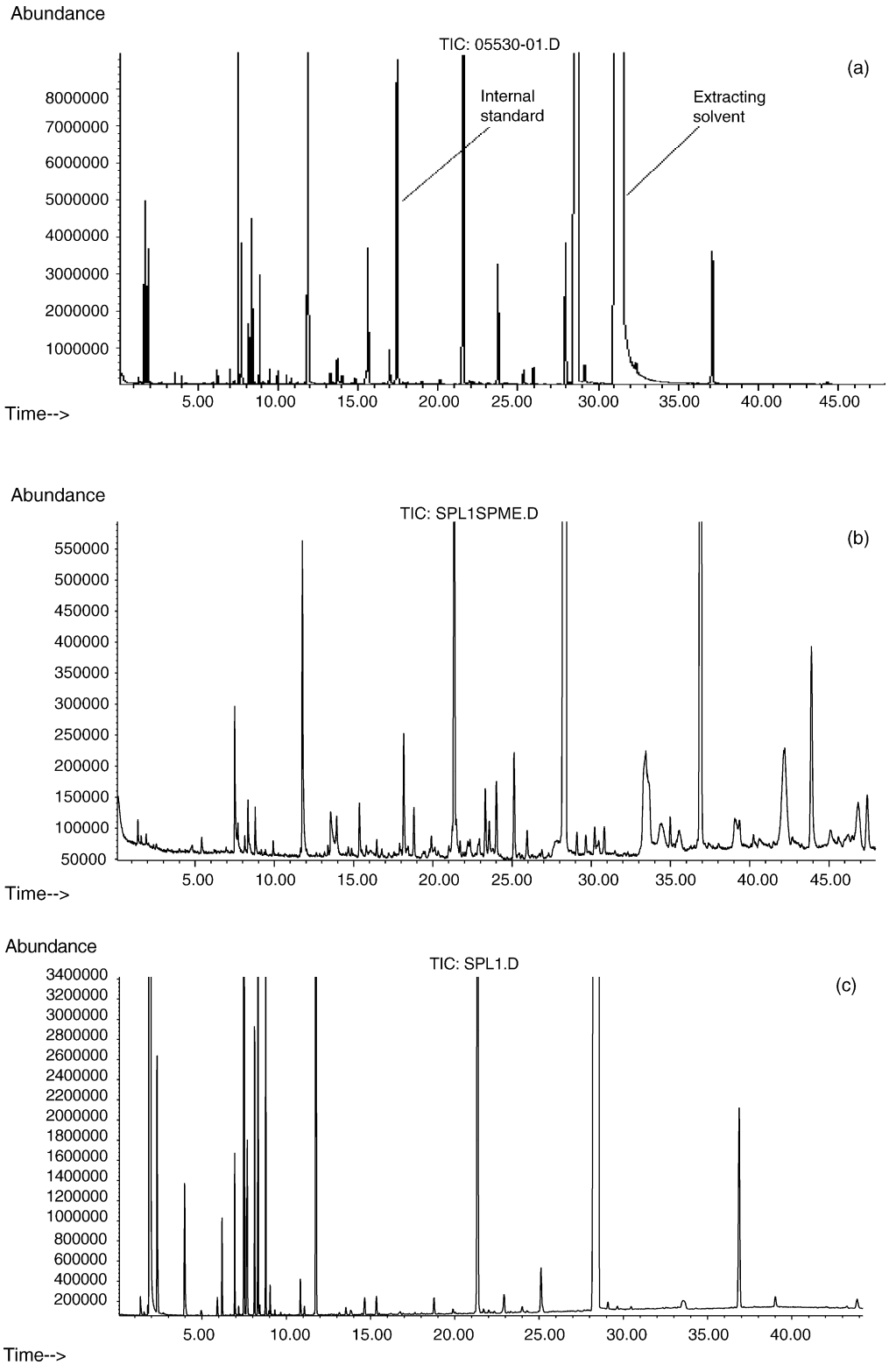

Fig. 5. Total ion chromatograms of the volatile compounds of *Foeniculum vulgare* Mill by: (a) HSME-GC–MS, (b) SPME-GC–MS and (c) SD-GC–MS methods.

method to SD-GC–MS method for the analysis of volatile compounds in TCMs.

But it can also be found that there are some differences between HSME-GC–MS and SPME-GC–MS methods in terms of the relative amounts of the main compounds. In comparison with SPME-GC–MS, HSME-GC–MS method gave higher relative amounts for most of the compounds prior to about 25 min but lower relative amounts after that time. It might result from the higher extraction efficiency of benzyl alcohol for the apolar or weakly polar compounds.

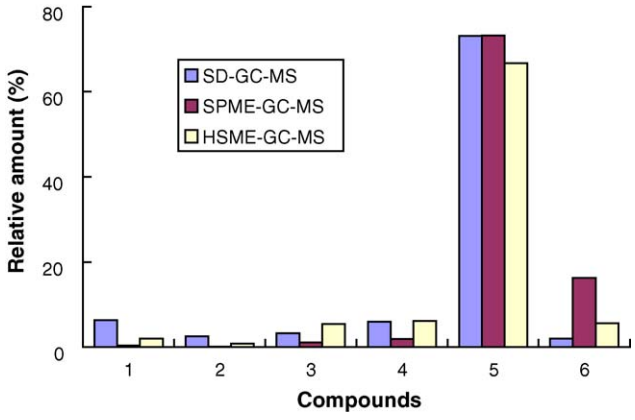

Fig. 6. Comparison of the relative amounts of the main compounds in *Foeniculum vulgare* Mill by HSME-GC–MS, SPME-GC–MS and SD-GC–MS methods. Compounds: 1, limonene; 2, γ-terpinene; 3, fenchone; 4, estragole; 5, *trans*-anethole; 6, 4-methoxy-benzaldehyde.

4. Conclusions

The present study describes a novel and simple HSME-GC–MS method for analysis of volatile compounds in *Foeniculum vulgare* Mill. The parameters possibly affecting the extraction efficiency (extracting solvent, extraction time and temperature, headspace volume and particle size) were optimized. Compared with SD-GC–MS method, HSME-GC–MS method requires a much smaller amount of a sample and a shorter time and can directly utilizes the ground powder of the TCM for the analysis. Compared with SPME-GC–MS, HSME-GC–MS is less expensive and wider applicability of numerous solvents. As a conclusion, HSME-GC–MS method is simple and effective and can be used for the analysis of volatile compounds in TCMs.

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References

[1] K.C. Wen, C.Y. Huang, F.L. Lu, J. Chromatogr. 631 (1993) 241–250.
[2] Q.G. Fang, Z.L. Yi, J.X. Lang, F.H. Lan, J. Chromatogr. A. 1016 (2003) 99–110.
[3] M.H. Wu, L.Y. Nie, L.P. Wei, Chin. J. Pharm. Anal. 21 (2001) 415–418.
[4] H. Peng, Z.D. Guo, J.C. Zhang, Chin. Pharm. J. 32 (1997) 337–339.
[5] J. Cao, M.L. Qi, L.H. Fang, A. Zhou, R.N. Fu, J. Pharm. Biomed. Anal., in press, available online 21 September 2005.
[6] M.M. Liang, M.L. Qi, C.B. Zhang, S. Zhou, R.N. Fu, J.X. Huang, Anal. Chim. Acta. 531 (2005) 97–104.
[7] A.L. Theis, A.J. Waldack, S.M. Hansen, M.A. Jeannot, Anal. Chem. 73 (2001) 5651–5654.
[8] A. Przyjazny, J.M. Kokosa, J. Chromatogr. A 977 (2002) 143–153.
[9] G. Shen, H.K. Lee, Anal. Chem. 75 (2003) 98–103.
[10] J.M. Kokosa, A. Przyjazny, J. Chromatogr. A. 983 (2003) 205–214.
[11] Y. Yamini, M.H. Hosseini, M. Hojaty, J. Arab, J. Chromatogr. Sci. 42 (2004) 32–36.
[12] N. Bahramifar, Y. Yamini, S. Shariati-Feizabadi, M. Shamsipur, J. Chromatogr. A. 1042 (2004) 211–217.
[13] Y. Yamini, M. Hojjati, M. Haji-Hosseini, M. Shamsipur, Talanta 62 (2004) 265–270.
[14] S. Shariati-Feizabadi, Y. Yamini, N. Bahramifar, Anal. Chim. Acta 489 (2003) 21–31.
[15] N. Li, C. Deng, X. Yin, N. Yao, X. Shen, X. Zhang, Anal. Biochem. 342 (2005) 318–326.
[16] C. Deng, N. Li, X. Wang, X. Zhang, J. Zeng, Rapid Commun. Mass Spectrom. 19 (2005) 647–653.
[17] P. Das, M. Gupta, A. Jain, K.K. Verma, J. Chromatogr. A 1023 (2004) 33–39.
[18] V. Clolombini, C. Bancon-Montigny, L. Yang, P. Maxwell, R.E. Sturgeon, Z. Mester, Talanta 63 (2004) 555–560.
[19] R. Zhao, W. Lao, X. Xu, Talanta 62 (2004) 751–756.
[20] A. Besharati-Seidani, A. Jabbari, Y. Yamini, Anal. Chim. Acta 530 (2005) 155–161.
[21] J. Cao, M.L. Qi, Y. Zhang, S. Zhou, Q.L. Shao, R.N. Fu, Anal. Chim. Acta, in press.