Advance Journal of Food Science and Technology 9(6): 398-405, 2015
DOI: 10.19026/ajfst.9.1893
ISSN: 2042-4868; e-ISSN: 2042-4876

Submitted: January 19, 2015 Accepted: February 27, 2015 Published: August 25, 2015

Research Article

Analysis of Volatile Flavor Compounds of Jujube Brandy by GC-MS and GC-O Combined with SPME

Ya-Nan Xia, Yanli Ma, Jianfeng Sun, Ying Shu and Jie Wang
College of Food Science and Technology, Agriculture University of Hebei, Baoding 071000, China

Abstract: To identify the unique flavor compounds in jujube brandy and changes in flavor compounds in the process of aging, Gas Chromatography-Mass Spectrometry (GC-MS) and GC-Olfactometry (GC-O) combined with solid-phase micro-extraction were used for the analysis of the volatile flavor compounds of fresh and aged jujube brandy. The equilibrium of the flavor compounds required divinylbenzene/carboxen/polydimethylsiloxane fiber for 40 min at 40°C. A total of 72 compounds were positively or tentatively identified by GC-MS, including 34 esters, 12 alcohols, 2 acids, 7 hydrocarbons, 3 aldehydes, 3 ketones and 8 terpenes in jujube brandy. Among them, ethyl laurate, ethyl caproate, ethylbenzoate and ethyl hexanoate were the main components. The flavor components of jujube brandy were identified by GC-O and 47 flavors were detected. Among them, orange-like (ethyl acetate), apple-like (butanoic acid, ethyl ester), fermented (hexanoic acid, ethyl ester), chocolate-like (nonanoic acid, ethyl ester) and red date-like (dodecanoic acid, ethyl ester) were strongly sensed. Changes in the flavor compounds in the process of aging were detected. During the period of aging, the contents of alcohols, aldehydes and ketones generally decreased, whereas those of esters and acids increased.

Keywords: Aging, flavor compounds, GC-O, HS-SPME, jujube brandy

INTRODUCTION

Brandy, one of the world's six distilled wines, mostly uses grape as a raw material. Jujube brandy, a unique brandy product in China, has a long history. Jujube brandy is produced by fermentation, distillation and aging using jujube as a raw material. Jujube brandy has strong healthcare functions because of the high nutritional value of jujube (Song and Zhao, 2011). The sensory characteristics of jujube brandy are heavily influenced by its volatile flavor components. Therefore, the volatile flavor components of jujube brandy are often subjected to analysis.

Currently, research progress on volatile compounds in jujube brandy is still very scarce. A previous study used the liquid-liquid extraction method to study the golden-silk jujube wine aroma and identified 35 compounds, of which alcohol had the highest content (Lv *et al*., 2011). Simultaneous distillation extraction was carried out to study the influence of ultra-high pressure treatment on dry red wine aroma components; 53 compounds were identified and the contents of senior alcohols, esters, organic acids, aldehydes and ketones changed after ultra-high pressure treatment (Zhang *et al*., 2007). Research about HS-SPME combined with Gas Chromatography-Mass Spectrometry (GC-MS) analysis of the aroma composition of jujube brandy is almost nonexistent at home and abroad.

Wine aroma, one of the most important characteristics of wine quality, represents a good balance of several hundred volatile compounds. The quality of wine is closely related to its aroma components, so flavor compounds can be used as one of the wine classification standards. Different groups of volatile compounds, such as alcohols, esters, aldehydes, lactones, terpenes and phenols, have been identified in wines in a wide concentration range. These groups affect wine aroma even at low concentrations. Among the volatiles, alcohols and esters have the highest contents in wines. Esters are important constituents of wine aroma and they possess high fruity nuances (Fan and Qian, 2005).

Qualitative and quantitative characterizations of volatile compounds in wine are usually performed by GC-MS, one of the most sensitive techniques for the analysis of aroma in different samples (Fan and Qian, 2006a; Zhu *et al*., 2007). By contrast, solid-phase micro-extraction (SPME is a relatively new and simple adsorption technique for the isolation of headspace flavor compounds (Arthur and Pawliszyn, 1990; Arthur *et al*., 1992; Zhang and Pawliszyn, 1993). Headspace SPME sampling requires neither solvent extraction and purification steps nor a complicated purge-and-trap apparatus. The SPME-GC method is simple to use,

Corresponding Author: Jie Wang, College of Food Science and Technology, Agricultural University of Hebei, Baoding 071000, China, Tel.: +86-13131262819

inexpensive and does not require solvent extraction. However, SPME analysis is quite sensitive to experimental conditions, such as heating temperature and time, sample volume, concentration and sample matrix and uniformity (Yang and Peppard, 1994; Fan and Qian, 2006b). The application of this technique to flavor analysis of foods and beverages still requires further modification to improve the reproducibility, sensitivity and resolution of the chromatogram. This technique shows high repeatability and possibility of carrying out simultaneous extractions, which is one of its advantages over other solvent-free techniques.

In this study, we evaluated the flavor components in jujube brandy using GC-MS and GC-Olfactometry (GC-O) combined with SPME to identify the compounds that contributed to the unique odor of jujube brandy and changes in aromatic compounds in the process of aging.

MATERIALS AND METHODS

Optimization of SPME analysis for headspace flavor compounds of jujube brandy: Fresh jujube brandies (Hebei, Fuping) were analyzed by GC with SPME using Divinylbenzene/Carboxen/Polydimethylsiloxane (DVB/CAR/PDMS), DVB/PDMS and PDMS. These three types of SPME fibers were compared for their adsorption capabilities on the volatile compounds of jujube brandy. Jujube brandy was diluted with distilled water (10% alcohol content). Sodium chloride (1 g) was added to 7.5 mL of sample solution in a 20 mL sealed glass vial.

To determine the effects of heating temperature and time on the equilibrium of flavor compounds between the SPME coating and headspace of the sample bottle, the sample bottles were maintained at 30, 40, 50 and 60°C for 30, 40, 50 and 60 min, respectively.

GC-MS analysis of volatile flavor compounds: Flavor compounds of jujube brandy were detected by GC-MS with semi-quantitative method. The contents of flavor compounds were quantified using an internal standard (3-octanol, 99%, Sigma-Aldrich). Wine volatile compounds were analyzed using an Agilent 5975 Mass Spectrometer coupled to an Agilent 7890A Gas Chromatograph (Agilent, Santa Clara, USA). A DB-WAX column (60 m×0.25 mm ID and 0.25 μm film thickness) was used for separation. The working parameters were as follows: injector temperature of 250°C, EI source of 230°C, MS Quad of 150°C and transfer line of 250°C. The initial temperature was 50°C for 3 min, which was increased to 80°C at a rate of 3°C/min. The temperature was further raised to 230°C at 5°C/min and maintained at 230°C for 6 min. The carrier gas had a flow rate of 1.0 mL/min. Samples were injected using the splitless mode. A mass range of 50-550 m/z was recorded at 1 scan/sec.

GC-O analysis of volatile flavor compounds: Characteristic flavor compounds of jujube brandy were specified by GC-O with aroma intensity method by 3 persons 3 times each. GC analysis of volatile compounds was carried out on a GC-7890A equipped with a Flame Ionization Detector (FID) and sniffing port. The column and temperature program was identical to GC-MS analysis. The effluent from the capillary column was split 1:1 between the FID and sniffing port using a "Y" splitter. Sniffing was carried out using OSS-9000 sniffer.

GC-MS analysis of volatile flavor compounds in different aging ages: Jujube brandies in different ages (1, 2, 4, 7, 8, 10 and 20 years, respectively) were detected by GC-MS to determine the changes in volatile flavor compounds during aging ages.

RESULTS AND DISCUSSION

Optimization of SPME analysis for headspace flavor compounds of jujube brandy: Three types of SPME fibers were compared for their adsorption capabilities (Fig. 1). DVB/CAR/PDMS, PDMS and PDMS/DVB extracted 118, 119 and 88 aroma compounds in the sample wine, respectively. Of the three types of SPME fibers, DVB/CAR/PDMS extracted the most flavor compounds (Table 1). The abilities of the three fibers in extracting aroma compounds differed. After comparison on compounds amounts and concentration, DVB/CAR/PDMS was more sensitive to absorbing alcohols, terpene, aldehyde and ketone; PDMS/DVB was more sensitive to esters and least sensitive to organic acids; and PDMS was more sensitive to organic acids and least sensitive to most aroma compounds. DVB/CAR/PDMS was sensitive to most aroma compounds, but the other two fibers both least sensitive to specific compounds. In consideration of the aforementioned factors, DVB/CAR/PDMS was the ideal fiber to extract more aroma compounds in wine for GC analysis among the three fibers.

The balance time of analytes into the stationary phase is related to the extraction temperature. An appropriate extraction temperature should be selected to obtain satisfactory sensitivity in GC analysis. Table 2 shows the results of jujube brandy aroma components at different extraction temperatures. Esters and alcohols contained the largest amounts at 40 and 30°C, with the highest contents at 60 and 40°C, respectively. Acids could only be detected at 40°C. Although hydrocarbons, aldehydes and ketones were best adsorbed at 50 and 60°C, the extraction contents demonstrated no differences at 40°C. Thus, 40°C was considered the most appropriate extraction temperature for jujube brandy.

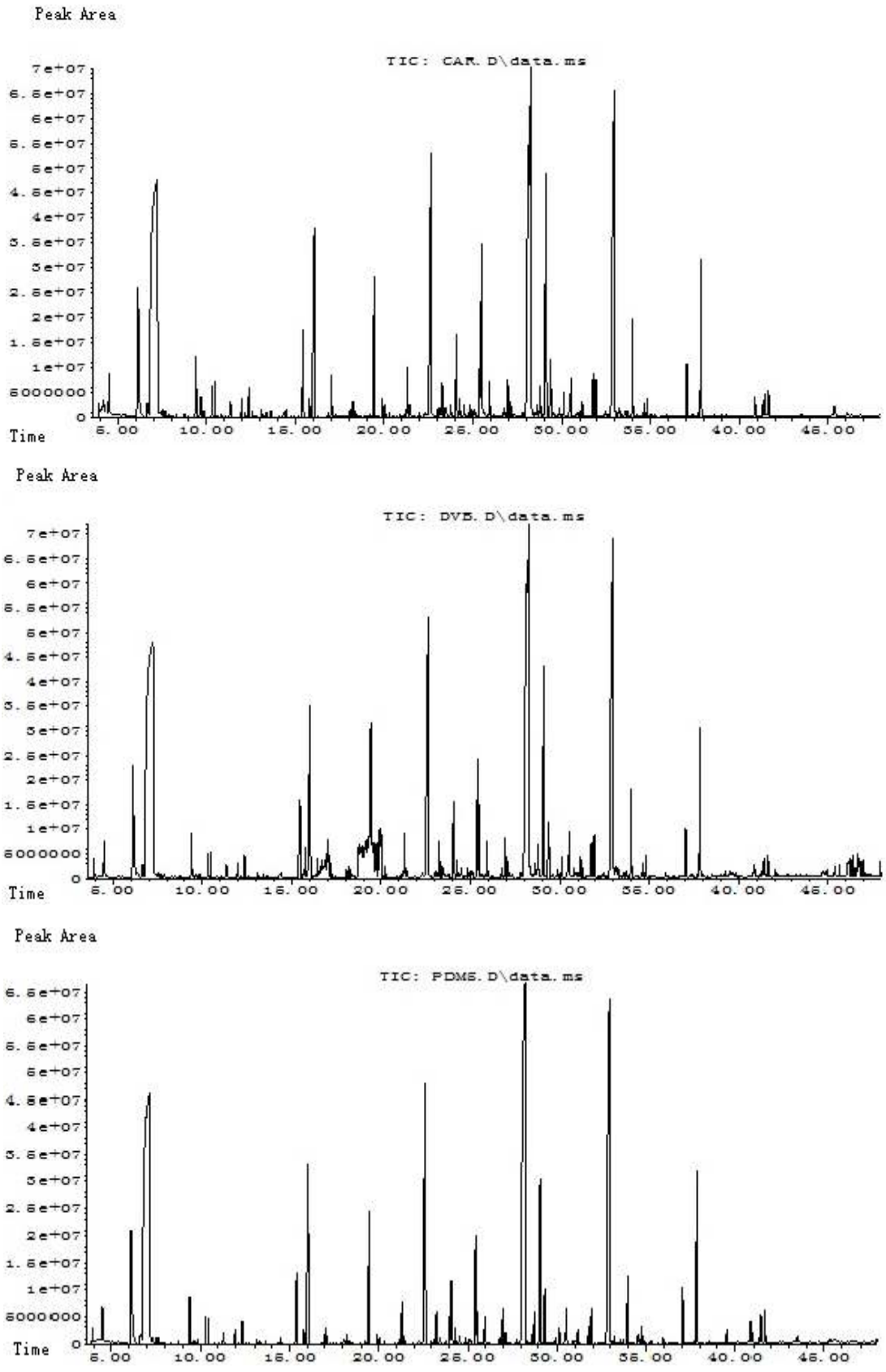

Fig. 1: Gas chromatogram of volatile compounds in different SPME fibers (DVB/CAR/PDMS, DVB/PDMS, PDMS, respectively)

Table 1: Comparison of SPME fibers on aroma component amount and content

	DVB/CAR/PDMS		PDMS/DVB		PDMS	
	Amount	Content (mg/L)	Amount	Content (mg/L)	Amount	Content (mg/L)
Esters	51	9.63	48	12.87	59	9.23
Alcohols	12	4.79	9	5.94	10	3.21
Acids	3	0.10	2	0.05	6	0.13
Terpenes	9	0.14	7	0.18	8	0.14
Aldoketones	22	1.07	14	0.57	15	0.56
Hydrocarbons	3	0.11	2	0.11	2	0.01
Acetals	5	0.11	0	0.12	1	0.14
Furans	5	0.07	3	0.00	8	0.40
Total	118	16.10	88	20.00	119	13.94

Table 2: Changes in volatile compounds amount and content at different equilibrium temperature

Temperature (°C)	Esters	Alcohols	Acids	Aldehydes and ketones	Hydrocarbons	Terpenes	Total peak area
30	2.77E+10	9.70E+08	0	7.41E+08	9.43E+08	4.00E+08	3.08E+10
40	2.69E+10	3.27E+09	5.60E+07	9.97E+08	1.30E+09	3.50E+08	3.29E+10
50	2.74E+10	9.89E+08	0	9.28E+08	1.42E+09	5.91E+08	3.13E+10
60	5.55E+10	8.35E+08	0.00E+00	9.70E+08	1.27E+09	1.38E+09	6.00E+10

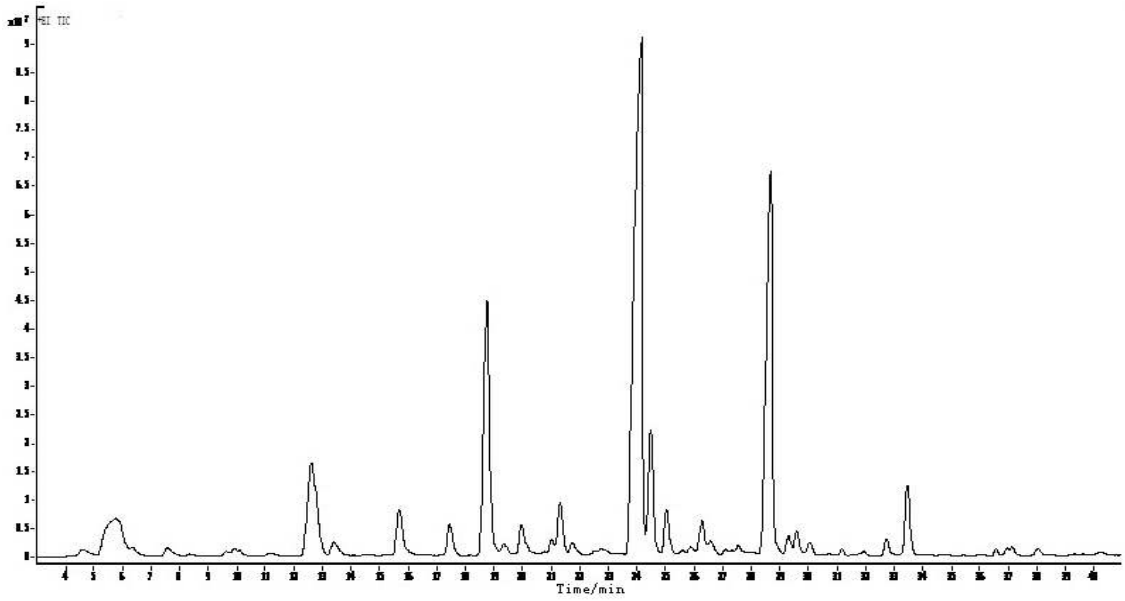

Fig. 2: Gas chromatogram of volatile compounds in fresh jujube brandy

SPME was used to measure analytes under a state of equilibrium. When volatile components obtained adsorption equilibrium between two phases, redundant extraction times were not beneficial on the extraction effect. By contrast, the excrescent time could increase the chances of components reacting chemically and reduce the lifetime of SPME fiber. As Table 3 shows, most of the compounds reached maximum extraction quantity in 40 min. Small molecular substances decreased when the time was extended. Therefore, 40 min was the optimal extraction time.

Flavor analysis of jujube brandy by GC-MS: Flavor compounds of jujube brandy were detected by GC-MS. A total of 72 compounds were positively or tentatively identified by GC-MS, including 34 esters, 12 alcohols, 2 acids, 7 hydrocarbons, 6 aldehydes and ketones and 8 terpenes in jujube brandy. With the most contents, ethyl laurate, ethyl decanoate, ethyl octanoate and ethyl hexanoate were the main components.

Flavor analysis of jujube brandy by GC-O: Characteristic flavor compounds were identified by GC-O. The gas chromatogram of volatile compounds in fresh jujube brandy is shown in Fig. 2. The identified volatile compounds in fresh jujube brandy are listed in Table 3 to 5. A total of 47 compounds were definitely or tentatively identified by GC-MS and 26 flavors were sensed in GC-O analysis. Among them, 27 esters were sensed, of which the contents of decanoic acid ethyl ester, dodecanoic acid ethyl ester, octanoic acid ethyl ester and hexanoic acid ethyl ester were the highest. Two alcohols, namely, ethanol (alcohol-like) and 1-dodecanol, 3, 7, 11-trimethyl- (green), were sensed.

Two terpenes, namely, ocimene (green) and π-Calacorene (green) were sensed. Dodecanoic acid (oil-like) and benzaldehyde (bitter almonds) were also sensed.

Among the 26 flavors sensed in GC-O analysis, esters with the fragrance of fruits and flowers were sensed most strongly, followed by alcohols and terpenes with the fragrance of green. Dodecanoic acid ethyl ester, benzenepropanoic acid ethyl ester andtetradecanoic acid ethyl ester gave this wine the scent of red dates, which constituted the unique feature of jujube brandy.

Based on the analysis of characteristic flavor and odor strength, ethyl acetate (orange); butanoic acid, ethyl ester (fruit/apple); butanoic acid, 3-methyl-, ethyl ester (apple); hexanoic acid, ethyl ester (fermented);

Table 3: Changes in volatile compounds peak area at different equilibrium time

Time (min)	Esters	Alcohols	Acids	Aldehydes and ketones	Hydrocarbons	Terpenes	Total peak area
30	1.87E+10	8.75E+08	0	7.45E+08	1.12E+09	4.52E+08	1.87E+10
40	2.69E+10	3.27E+09	5.60E+07	9.97E+08	1.30E+09	3.50E+08	2.69E+10
50	1.75E+10	7.99E+08	0	8.54E+08	1.05E+09	5.87E+08	1.75E+10
60	1.49E+10	7.23E+08	2.90E+07	7.70E+08	9.60E+08	4.80E+08	1.49E+10

Table 4: Identification of volatile compounds in jujube brandy by GC-O

Time (min)	RI	Content (mg/L)	Odor strength	Characteristic flavor	Compounds
4.63	891	0.12	3	Orange	Ethyl acetate
5.65	1018	0.87	3	Alcohol like	Ethanol
7.57	1129	0.10	3	Fruit/apple	Butanoic acid, ethyl ester
8.31	1103	0.04	3	Apple	Butanoic acid, 3-methyl-, ethyl ester
9.62	1055	0.05	2	Pear	1-butanol, 3-methyl-, acetate
9.92	1045	0.06	3	Fruit	Pentanoic acid, ethyl ester
11.25	1197	0.06	2	Green	Ocimene
12.81	1144	1.14	3	Fermented	Hexanoic acid, ethyl ester
13.41	1123	0.17			Styrene
14.45	1287	0.01			2-hexadecanol
14.68	1279	0.02			3-hexenoic acid, ethyl ester
15.73	1242	0.42	1	Flower/fruit	Heptanoic acid, ethyl ester
17.48	1379	0.26			3-octanol
18.17	1353	0.01			7-methyl-Z-tetradecen-1-ol acetate
18.82	1329	1.98	3	Cream	Octanoic acid, ethyl ester
19.36	1309	0.12	3	Chocolate	Isopentyl hexanoate
19.70	1496	0.01			4-octenoic acid, ethyl ether
19.97	1485	0.30			7-octenoic acid, ethyl ester
20.98	1446	0.10	2	Bitter almonds	Benzaldehyde
21.36	1431	0.39	3	Chocolate	Nonanoic acid, ethyl ester
21.75	1416	0.13	2	Ink like	Ethyl (E)-2-octenoate
22.49	1586	0.05	2	Sweet	3-nonenoic acid, ethyl ester
22.88	1570	0.10	4	Green	1-octen-3-ol
24.13	1518	5.29	3	Pineapple	Decanoic acid, ethyl ester
24.48	1504	0.85	2	Honey/flower	Benzoic acid, ethyl ester
25.03	1680	0.33			Ethyl trans-4-decenoate
25.59	1656	0.03	2	Green	1-dodecanol, 3, 7, 11-trimethyl-
25.87	1644	0.08			Epiglobulol
26.28	1626	0.27			Oxime-, methoxy-phenyl-_
26.58	1613	0.13			Naphthalene, 1, 2, 4a, 5, 8, 8a-hexahydro-4, 7-dimethyl-1-(1-methylethyl)-, [1S- (1π4aπ8aπ]-
27.10	1790	0.04	2	Rose	Benzeneacetic acid, ethyl ester
27.55	1769	0.10	3	Cucumber/ honey	Dodecanoic acid, methyl ester
27.97	1750	0.02			2-methyl-4-(2, 6, 6-trimethylcyclohex-1-enyl) but-2-en-1-ol
28.66	1719	2.96	5	Red dates	Dodecanoic acid, ethyl ester
29.31	1889	0.13	4	Red dates	Benzenepropanoic acid, ethyl ester
29.58	1876	0.17	1	Flower	E-11-hexadecenoic acid, ethyl ester
30.05	1854	0.11	2	Green	πCalacorene
30.71	1823	0.02			Hexadecanoic acid, ethyl ester
31.18	1800	0.04			Naphthalene, 1, 7-dimethyl-
32.73	1924	0.12	2	Red dates	Tetradecanoic acid, ethyl ester
33.46	1888	0.47			Ethyl 9-tetradecenoate
34.67	2025	0.01			Murolan-3, 9 (11)-diene-10-peroxy
34.90	2013	0.01			3-(2-methyl-propenyl)-1H-indene
35.68	1972	0.01			5, 8, 11, 14-eicosatetraynoic acid
36.02	2148	0.02			Azulene, 1, 4-dimethyl-7-(1-methylethyl)-
36.54	2118	0.04			Hexadecanoic acid, ethyl ester
39.61	2493	0.03	2	Oil like	Dodecanoic acid

Table 5: Changes in flavor content during aging process

Compounds	RI	Fresh (mg/L)	1 year (mg/L)	2 year (mg/L)	4 year (mg/L)	7 year (mg/L)	8 year (mg/L)	10 year (mg/L)	20 year (mg/L)
Ethyl acetate		0.015	0.025		0.068	0.294			0.308
Propanoic acid, ethyl ester	877	0.004	0.006	0.013	0.010	0.019	0.014	0.012	0.036
Butanoic acid, ethyl ester	928	0.034	0.078	0.233	0.169	0.193	0.108	0.098	0.564
Pentanoic acid, ethyl ester	1037	0.019	0.041	0.080	0.075	0.092	0.060	0.059	0.178
Hexanoic acid, ethyl ester	1177	0.405	0.798	1.386	1.265	1.510	0.878	0.909	2.550
Heptanoic acid, ethyl ester	1268	0.237	0.448	0.988	0.974	0.864	0.510	0.480	1.147
Octanoic acid, ethyl ester	1358		1.157	2.158	2.067	2.169	2.250	2.218	
Isopentyl hexanoate	1374	0.054	0.048	0.088	0.084	0.079	0.041	0.045	0.071
Nonanoic acid, ethyl ester	1439	0.284	0.218	0.566	0.518	0.578	0.009	0.340	0.349
n-caprylic acid isobutyl ester	1450	0.006				0.004			
2-furancarboxylic acid, ethyl ester	1519	0.006	0.015	0.024	0.028	0.036	0.037	0.031	0.088
Decanoic acid, ethyl ester	1527	3.482	2.569	2.385	2.297	2.810	2.386	2.649	2.674
Benzoic acid, ethyl ester	1574	0.824	1.559	2.114	1.706	2.198	2.535	2.485	2.669
n-capric acid isobutyl ester	1641	0.010							
n-propyl benzoate	1652								0.067
Benzeneacetic acid, ethyl ester	1678	0.090	0.048	0.059		0.311	0.129	0.139	0.281
Benzoic acid, 2-hydroxy-, ethyl ester	1711	0.022	0.037			0.075	0.082	0.043	0.099
Dodecanoic acid, ethyl ester	1740	3.593	2.297	1.080	2.285	2.001	2.235	2.216	1.917
Benzenepropanoic acid, ethyl ester	1780	0.221	0.273	0.334			0.261	0.314	0.698
Ethyl tridecanoate	1824	0.004	0.009	0.013	0.008	0.017		0.010	
Isobutyl laurate	1837	0.003	0.003	0.005	0.003	0.005	0.003	0.005	
Tetradecanoic acid, ethyl ester	2023	0.106	0.167	0.253	0.167	0.383	0.142	0.218	0.209
Diethyl suberate	2080	0.001	0.002	0.002		0.004	0.001	0.002	0.006
Pentadecanoic acid, ethyl ester		0.006	0.008	0.010	0.006	0.017		0.009	
Hexadecanoic acid, ethyl ester		0.047	0.042	0.075	0.065	0.086	0.049	0.072	0.093
Octadecanoic acid, ethyl ester						0.001		0.000	
Ethyl oleate		0.003	0.002	0.004	0.004	0.001	0.006	0.004	0.005
Linoleic acid ethyl ester		0.002		0.002	0.002	0.004		0.001	0.004
1-Butanol, 2-methyl-, (.+/-.)-	1160	0.142	0.134	0.021	0.016				
1-hexanol	1286	0.007	0.013		0.015				0.010
1-undecanol	1298	0.007							
2-octanol	1321	0.003							
1-octen-3-ol	1365	0.015	0.040	0.035	0.035	0.028	0.032	0.028	0.026
1-heptanol	1370							0.010	0.010
1-nonanol	1548	0.028							
Borneol	1595	0.020	0.021	0.016		0.012	0.017		
1-dodecanol	1643	0.031							
Benzyl alcohol	1766	0.008	0.013						0.018
Phenylethyl alcohol	1801		0.009	0.010	0.004	0.006	0.002	0.005	0.005
1-tetradecanol	1840	0.008	0.010					0.005	
3-dodecen-1-ol		0.008							
2-methyl-propionic acid		0.084							
Butanoic acid				0.006		0.021	0.012	0.021	0.016
Pentanoic acid	1344	0.008					0.011	0.005	0.002
Hextanoic acid						0.010	0.007	0.011	
Heptanoic acid	1844					0.004		0.004	
Octanoic acid						0.022	0.016	0.025	0.021
Detanoic acid		0.041	0.033	0.040	0.014	0.027	0.020	0.027	0.096
9, 12-octadecadienoic acid (Z, Z)-						0.002	0.001	0.002	0.001
Dodecanoic acid		0.036	0.038	0.039	0.049	0.047	0.027	0.031	0.047
Hexanal	976		0.071					0.004	
3-octanone	1200	0.008	0.007	0.011	0.010	0.008	0.008	0.008	0.006
2-nonanone	1315	0.022		0.053	0.048	0.034	0.037	0.028	0.025
Furfural	1387	0.029	0.045	0.070	0.045	0.061		0.061	0.051
3-furaldehyde	1387						0.051		
Decanal	1410	0.091	0.026	0.060		0.040		0.042	0.022
Benzaldehyde	1441	0.559	0.210	0.429	0.441	0.453	0.438	0.438	0.309
2-undecanone	1497	0.056	0.020		0.079	0.062	0.079	0.073	0.034
Benzaldehyde, 2-hydroxy-	1587	0.032	0.014			0.007	0.006		0.011
2-tridecanone	1696		0.016	0.014	0.011	0.007	0.004	0.013	0.007
2-buten-1-one, 1-(2, 6, 6-trimethyl-1, 3-cyclohexadien-1-yl)-, (E)-	1716	0.024	0.017	0.018	0.014	0.017	0.012	0.020	0.019
Benzeneacetaldehyde, alpha.-ethylidene-	1828	0.013			0.004	0.008	0.007	0.008	
2-pentadecanone, 6, 10, 14-trimethyl-	2097	0.014	0.011	0.010	0.008	0.009	0.006	0.013	0.009
D-limonene	1119	0.039	0.034		0.013	0.030		0.030	
Eucalyptol	1140		0.472					0.001	
(+)-4-carene	1218	0.003							

Table 5: Continue

Compounds	RI	Fresh (mg/L)	1 year (mg/L)	2 year (mg/L)	4 year (mg/L)	7 year (mg/L)	8 year (mg/L)	10 year (mg/L)	20 year (mg/L)
Naphthalene, 1, 2, 3, 4, 4a, 5, 6, 8a-octahydro-7-methyl-4-methylene-1-(1-methylethyl)-, (1.alpha., 4a.alpha., 8a.alpha.)-b-selinene	1591	0.030	0.017	0.020	0.017	0.009	0.009	0.015	
Naphthalene, 1, 2, 3, 5, 6, 8a-hexahydro-4, 7-dimethyl-1-(1-methylethyl)-, (1S-cis)-	1623			0.045	0.036	0.056	0.041		
Naphthalene, 1, 2, 3, 4, 4a, 5, 6, 8a-octahydro-7-methyl-4-methylene-1-(1-methylethyl)-, (1.alpha., 4a.beta., 8a.alpha.)-.alpha.-calacorene	1653		0.044	0.085	0.052	0.034	0.028	0.037	
Butane, 1, 1-diethoxy-3-methyl-	1658			0.010					
Hexane, 1, 1-diethoxy-	1816		0.066	0.107	0.060	0.071	0.055	0.002	
Heptane, 1, 1-diethoxy-	964	0.044	0.010	0.022	0.002			0.025	0.018
Nonane, 1, 1-diethoxy-	1156				0.006				0.015
Thiazole, 5-methyl-	1260	0.008							0.004
Furan, 2-pentyl-	1426	0.019	0.015			0.016	0.008	0.024	0.011
1H-Indene, 2, 3-dihydro-4, 7-dimethyl-	1157	0.034		0.015	0.009		0.000		
Benzoic acid, hydrazide	1503				0.029				
Oxime-, methoxy-phenyl-_	1524		0.040						
2-ethyl-phenol	1626	0.550	0.366	0.442	0.376	0.277	0.242	0.248	0.138
		0.006							

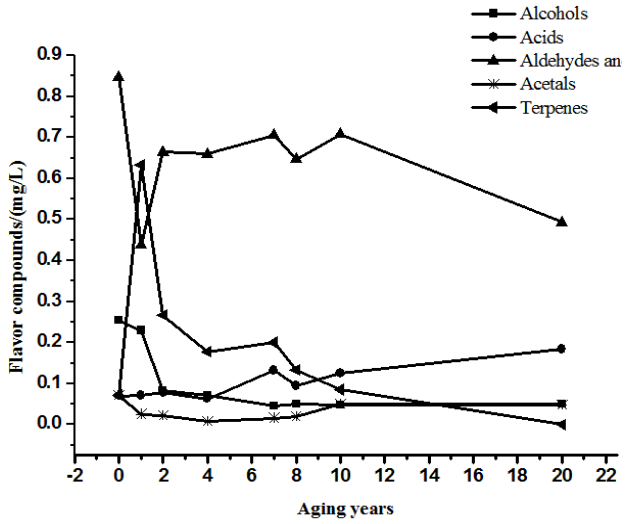

Fig. 3: Changes in content of every type of flavor during aging process

nonanoic acid, ethyl ester (chocolate); dodecanoic acid, methyl ester (cucumber/honey); dodecanoic acid, ethyl ester (red dates); benzenepropanoic acid, ethyl ester (red dates); and tetradecanoic acid and ethyl ester (red dates) mainly contributed to the fragrance of jujube brandy.

The Odor Activity Values (OAVs) of butanoic acid, 3-methyl-, ethyl ester; pentanoic acid, ethyl ester; hexanoic acid, ethyl ester; heptanoic acid, ethyl ester; octanoic acid, ethyl ester; decanoic acid, ethyl ester; dodecanoic acid, ethyl ester; and 1-octen-3-ol were greater than 1. Octanoic acid, decanoic acid and ethyl ester were the most important flavor compounds in jujube brandy and they attained the maximum OAVs (Fig. 3).

Flavor analysis of jujube brandy in different ages by GC-MS: Several differences between the fragrance of fresh and aged jujube brandies were observed, especially in terms of the contents of alcohols, acids and terpenes. Most aroma compounds in fresh jujube brandy could be detected in aged wine, whereas n-capric acid isobutyl ester, (+)-4-carene, 1-undecanol, 2-octanol, 1-nontanol, 1-dodecanol and 2-methyl-propionic acid could only be detected in fresh wine. 2-tridecanone was not detected in fresh wine, but it was detected in all aged wines. Nine, 12-Octadecadienoic acid started to appear in wine aged after 7 years. Three-Furaldehyde could only be detected in wine aged for 8 years and 1-heptanol began to appear in wine aged after 10 years. Benzoic acid propylester, 3-furaldehyde and 1-heptanol form late in the aging process. Therefore, jujube brandies at different ages showed varying aromatic characteristics because of dynamicchanges, such as production, replacement and disappearance of aromatic compounds, in aging years.

Among esters, except n-caprylic acid isobutyl ester, decanoic acid, dodecanoic acid and ethyl ester decreased in the process of aging, whereas the contents of other esters demonstrated an upward trend. 1-Butanol, 2-methyl- and 1-octen-3-ol were the main alcohols and the contents of alcohols demonstrated an overall reducing trend. Among the acids, the levels of decanoic acid and dodecanoic acid were the highest, whereas the contents of acids and aldehydes only slightly increased. The decrease in the alcohols and an increase in the esters would be expected due to slow acid catalyzed esterification reactions. Terpenes initially decreased and then increased with the aging year, but could not be detected in 20-year-old jujube brandy.

CONCLUSION

DVB/CAR/PDMS fiber was the optimal choice to extract aroma compounds of jujube brandy. The vial containing the sample was incubated at 40°C for 10 min. The flavor compounds of jujube brandy were detected by GC-MS. A total of 72 compounds were positively or tentatively identified by GC-MS, including 34 esters, 12 alcohols, 2 acids, 7 hydrocarbons, 3 aldehyde, 3 ketones and 8 terpenes, in jujube brandy. Among them, ethyl laurate, ethyl caproate, ethyl benzoate and ethyl hexanoate were the main components.

In GC-O analysis, ethyl acetate (orange); butanoic acid, ethyl ester (fruit/apple); butanoic acid, 3-methyl-, ethyl ester (apple); hexanoic acid, ethyl ester (fermented); nonanoic acid, ethyl ester (chocolate); dodecanoic acid, methyl ester (cucumber/honey); dodecanoic acid, ethyl ester (red dates); benzenepropanoic acid, ethyl ester (red dates); and tetradecanoic acid and ethyl ester (red dates) mainly contributed to the fragrance of jujube brandy. Dodecanoic acid, benzenepropanoic acid, tetradecanoic acid and ethyl ester gave this wine the scent of red dates, which constituted the unique feature of jujube brandy.

During the period of aging, 81 aroma components were detected. The contents of 11 types of common components (e.g., hexanoic acid, ethyl ester, octanoic acid, decanoic acid, dodecanoic acid and benzaldehyde) were the highest. At each stage of aging, esters had the most content, followed by alcohols, terpene, aldehydes and ketones. Acids had the least content by this fiber. However, the main aroma composition types and their contents differed. The contents of alcohols, aldehydes and ketones generally decreased, whereas those of esters and acids increased during the process of aging.

ACKNOWLEDGMENT

This research was supported by the National Natural Science Foundation of China:

- The Research of Methanol and Fusel Oil Formation Mechanism and Control Measures in Traditional Chinese Jujube Brandy (Founding No. 31171725/2011).
- Study on the flavor character and its formation mechanism of Chinese date brandy (Founding No. 31371815).

REFERENCES

Arthur, C.L. and J. Pawliszyn, 1990. Solid-phase micro-extraction with thermal desorption using fused silica optical fibers. Anal. Chem., 62: 2145-2148.

Arthur, C.L., L.M. Killam, K.D. Buchholz, J. Pawliszyn and J.R. Berg, 1992. Automation and optimization of solid-phase microextraction. Anal. Chem., 64: 1960-1966.

Fan, W. and M.C. Qian, 2005. Headspace solid phase microextraction (HS-SPME) and gas chromatography-olfactometry dilution analysis of young and aged Chinese 'Yanghe Daqu' liquors. J. Agr. Food Chem., 53(20): 7931-7938.

Fan, W. and M.C. Qian, 2006a. Characterization of aroma compounds of Chinese 'Wuliangye' and 'Jiannanchun' liquors by aroma extraction dilution analysis. J. Agr. Food Chem., 54(7): 2695-2704.

Fan, W.L. and M.C. Qian, 2006b. Identification of aroma compounds in Chinese 'Yanghe Daqu' liquor by normal phase chromatography fractionation followed by gas chromatography-olfactometry. Flavour Frag. J., 21(2): 333-342.

Lv, Z.X., P. Liu *et al*., 2011. Research progress of jujube processing products. Farm Prod. Process., 12: 58-59.

Song, W. and B.H. Zhao, 2011. Analysis of the present situation and countermeasures of the jujube industry in fuping county. J. Anhui Agr. Sci., 39: 21475-21477.

Yang, X. and T. Peppard, 1994. Solid-phase microextraction for flavor analysis. Agric. Food Chem., 42: 1925-1930.

Zhang, Z. and J. Pawliszyn, 1993. Headspace solid-phase microextraction. Anal. Chem., 65: 1843-1852.

Zhang, W., J. Zhang, G. Zhao, D. Mao and G. Yang, 2007. Effect of flavor compounds in ultra high pressure treated dry date wine. Chinese Agr. Sci. Bull., 23(5): 120-120.

Zhu, S., X. Lu, K. Ji, K. Guo, Y. Li, C. Wu and G. Xu, 2007. Characterization of flavor compounds in Chinese liquor Moutai by comprehensive two-dimensional gas chromatography/time-of-flight mass spectrometry. Anal. Chim. Acta, 597(2): 340-348.