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ORIGINAL PAPER

Comparison on aroma compounds in Chinese soy sauce and strong aroma type liquors by gas chromatography–olfactometry, chemical quantitative and odor activity values analysis

Xiaoxin Wang · Wenlai Fan · Yan Xu

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Abstract In order to elucidate the differences on aroma compounds in Chinese liquors with different aroma styles and the reasons, aroma compounds of *Xijiu* in soy sauce aroma and strong aroma type were investigated in the research. By gas chromatography–olfactometry (GC–O), aroma compounds in Chinese liquor were chosen for quantitative and odor activity value (OAV) analysis. Ethyl hexanoate, butanoic acid, 3-methylbutanoic acid, hexanoic acid and dimethyl trisulfide were considered to be the most powerful odorants in both liquor samples (aroma intensity ≥3.5) by GC–O. As important aroma compounds (OAV ≥10) in the liquors, ethyl propanoate, ethyl 2-methylpropanoate and 1-propanol were considered with much higher OAVs in soy sauce aroma type liquor, while OAVs of ethyl pentanoate, ethyl hexanoate, ethyl heptanoate, ethyl octanoate, ethyl lactate, hexyl acetate, butyl hexanoate, hexyl hexanoate and hexanoic acid were far lower in strong aroma type liquor. The OAV of ethyl hexanoate in strong aroma type liquor exceeded 50,000, which explained the reason why strong aroma liquor was considered with prominent fruity aroma. The odor differences between the liquors were mainly caused by the manufacturing practices.

Keywords Chinese liquor · Aroma compounds · Gas chromatography–mass spectrometer · Gas chromatography–olfactometry · Odor activity value

X. Wang · W. Fan (✉) · Y. Xu
Synergetic Innovation Center of Food Safety and Nutrition, Key Laboratory of Industrial Biotechnology, Ministry of Education, Laboratory of Brewing Microbiology and Applied Enzymology, School of Biotechnology, Jiangnan University, Wuxi 214122, Jiangsu, China
e-mail: Wenlai.Fan@gmail.com

X. Wang
e-mail: 15031960183@126.com

Introduction

Chinese liquor, with production of approximate 12 million kiloliters in 2012, is one of the oldest distillates in the world. It is typically obtained from grains by traditional solid or semi-solid fermentation using natural culture starters, *daqu* or *xiaoqu* [1, 2]. According to aroma and flavor characteristics, Chinese liquor can be classified into five types: strong, light, soy sauce, sweet honey and miscellaneous aroma type liquor [3]. Because of the particular manufacturing practice, involving the high temperature of *daqu*-making (around 70 °C during 10 days), stacking of fermenting grains for 3–5 days, fermentation for 30 days, distillation and long aging (more than 5 years), soy sauce aroma type liquor provides a distinct different aroma and flavor from the others [2].

The volatile aroma composition of Chinese liquor is quite complex, especially for Chinese soy sauce aroma type liquor. Researchers had done some work in flavor analysis to Chinese liquor, and many traditional aroma compounds were identified [4, 5]. In 2010, Fan et al. [2] identified 76 volatile compounds in 14 soy sauce type liquors by stir bar sorptive extraction (SBSE) coupled with gas chromatography–mass spectrometry (GC–MS), including esters, alcohols, aldehydes ketones, aromatic compounds, furans, nitrogen-containing compounds, fatty acids, phenols, terpenes, sulfide-containing compounds and lactones. At the same year, Fan et al. [3] identified 186 aroma-active compounds by gas chromatography–olfactometry (GC–O) and GC–MS in *Moutai* and *Langjiu* liquors, belonging to soy sauce aroma style liquor. Among these compounds, ethyl hexanoate, hexanoic acid, 3-methylbutanoic acid, 3-methylbutanol, 2,3,5,6-tetramethylpyrazine, ethyl 2-phenylacetate, 2-phenylethyl acetate, ethyl 3-phenylpropanoate, 4-methylguaiacol and γ-decalactone had the highest aroma intensities. However, all studies were only for one type liquor or a class of compounds in Chinese liquors, and there was no comprehensive comparison on the aroma differences among different types of Chinese liquor. The differences on aroma compounds in Chinese liquors with different odor styles and the reasons for these differences were unclear.

Now, headspace solid–phase microextraction (HS–SPME) has been widely used in the quantification of volatile aroma compounds in Chinese liquor [6], wine [7], rice wine [8, 9] and grapes [10]. Based on the quantitation, calculation of odor activity values (OAVs) enable a more reliable evaluation of important odorants in Chinese liquor. OAV is calculated as the ratio of the concentration of the odorant in the matrix to its odor threshold in the similar matrix. Generally, the higher the OAV of an odorant is, the more significantly it contributes to the aroma [11].

Many factors could affect aroma profile and quality of liquor, such as raw materials, climate, environment and manufacturing practices. So we chose soy sauce and strong aroma type liquors produced in the same factory, *Xijiu* Distillery in Guizhou province for this study. The aims of the present study were (1) to identify important odorants in the two type liquors clearly in their overall aroma profile by GC–O; (2) to quantitate these compounds by HS–SPME followed by GC–mass spectrometry (MS), complement with liquid–liquid microextraction (LLME)/GC–MS and GC–flame ionization detector (FID) to find out the aroma differences and reasons in these aroma styles.

Materials and methods

Chemicals

All of the reagents used were of analytical quality, obtained from Sigma-Aldrich China Co. (Shanghai, China) with at least 980 mg/L purity. Ethanol (≥99.80 %) was obtained from CNW Technologies GmbH (Shanghai, China). Analytical-grade sodium chloride, anhydrous sodium sulfate, pentane and diethyl ether were purchased from China National Pharmaceutical Group Corp. (Shanghai, China). Pure water was obtained from a Milli-Q purification system (Millipore, Bedford, MA).

Chinese liquor samples

All liquor samples were supplied by *Xijiu* Distillery Co. Ltd. in Zunyi city, Guizhou province of China. In the study, J-1 and J-2 liquors were bottled in 2012, J-3 to J-10 liquors were produced in 2005–2012, and were soy sauce aroma type liquors (53 % ethanol by volume). While N-1 and N-2 liquors were bottled in 2012 (53 % ethanol by volume), N-3 to N-10 liquors were produced in 2005–2012 (63–67 % ethanol by volume), belonging to strong aroma type liquor. J-1 and N-1 liquors were used for odor profiles and GC–O analysis, while all the samples, including J-1 and N-1, were used for quantitative analysis. The final concentration of a compound in one aroma type liquor was the mean value of it in all liquors with the same aroma type (Table 3).

Aroma profile analysis

As the method reported [12], the sensory evaluation of the *Xijiu* liquor samples was performed by 10 trained panelists (eight students and two teachers with more than 10 years of sensory analysis experience in Chinese liquor) recruited from the Laboratory of Brewing Microbiology and Applied Enzymology in Jiangnan University. The assessors were regularly trained to recognize the 10 aromas [13], and they were subjected to a triangular test with a series of reference solutions of ethyl butanoate (fruity), 2-phenylethanol (floral), γ-nonalactone (sweet), 1-butanol (alcoholic), 3-methylbutanal (green), furfuryl acetate (caramel-like), 2,3,5-trimethylpyrazine (roasted/nutty), phenol (phenolic) and hexanoic acid (rancid/cheesy). The sauce-like aroma was represented with the separated soy sauce aroma type liquor which had been dislodged other aromas. Triangular series were prepared by presenting one odorant solution, and two vessels contained pure water (15 mL) as blank. The panelists were asked to mark the differing samples in the series. Then, the series were presented in decreasing concentrations with alternating the sequence of each triangular series [14]. At last, the assessors were asked to evaluate the intensities of the 10 odor attributes above in the liquor samples from 0 (not perceivable) to 5 (strongly perceivable). Samples (15 mL) were presented in covered glass vessels (total volume = 47 mL) at room temperature (20 ± 1 °C), and the aroma intensities smelled were averaged by arithmetic mean method and plotted in a spiderweb diagram.

GC–O analysis

According to the literature reported [15, 16], 100 mL liquor sample was diluted to 10 % ethanol by volume with boiled ultrapure water, saturated with sodium chloride and then extracted 3 times with 60 mL freshly distilled diethyl ether. Then, the aroma extract of each liquor sample was separated into acidic/water-soluble, neutral and basic fractions. The extracts were dried with anhydrous sodium sulfate overnight and then concentrated to a final volume of 200 μL under a gentle stream of nitrogen. Each concentrated fraction (1 μL) was injected into GC–MS with an olfactory detection port for GC–O analysis.

Two panelists (one male and one female) were selected for the GC–O, and both panelists were familiar with the technique and well trained with extract of Chinese liquor for more than 100 h. Panelists were asked to evaluate the intensity of the odor attributes from 0 (not perceivable) to 5 (strongly perceivable). Each fraction was replicated three times by each panelist, when a volatile compound was sniffed every time; this analyte was determined to be a declared aroma compound. The aroma intensities smelled were averaged by arithmetic mean method.

GC–MS method

GC–MS analysis was carried out using an Agilent 6890 GC equipped with an Agilent 5975 mass selective detector (MSD). The separations were performed using a DB-FFAP column (60 m length, 0.25 mm i.d., 0.25 μm film thickness; J & W Scientific) with an oven temperature programmer of 50 °C (2 min), ramped at 6 °C/min to 230 °C (15 min). The column carrier gas was helium at a constant flow rate of 2 mL/min. The electron impact energy was 70 eV, and the ion source temperature was set at 230 °C. Electron impact (EI) mass spectra were recorded in the 35–350 amu range. The identification to aroma compounds was same with the Ref. [1], which was based on aroma description, mass spectra and retention indices (RIs) relative to that of pure reference compound.

Quantification methods

HS–SPME for quantification of micro aroma compounds

As the methods reported [6], each liquor sample was diluted with boiled pure water to a final concentration of 10 % ethanol by volume, and total 8 mL solution with 10 μL internal standards (ISs) solution [95.57 μg/L final concentration of methyl hexanoate (IS1), and 55.55 μg/L octyl propanoate (IS2)] was put into a 20 mL vial, saturated with sodium chloride. An autosampler system (MultiPurposeSample MPS 2 with a SPME adapter, Gerstel Inc., Baltimore, MD) with a 50/30 μm divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) fiber (2 cm, Supelco, Inc., Bellefonte, PA, USA) was used for aroma compounds extraction. The conditions of HS–SPME remained unchanged with the reference, and the sample was equilibrated at 50 °C in a thermostatic bath for 5 min and extracted for 45 min at the same temperature under stirring. After extraction, the fiber was inserted into the injection port of GC (250 °C) to desorb the analytes for 5 min. The GC–MS conditions were set as described above.

LLME for quantification of fatty acids

According to the method described by Wang et al. [17], 18 mL diluted liquor sample with 6 μL 2,2-dimethyl propanoic acid solution (3.41 mg/L final concentration, IS3) was saturated with sodium chloride and then extracted for 3 min with 1 mL redistilled diethyl ether. After extraction, 1 μL extract was injected into the GC–MS. The GC–MS conditions were also set as described above.

GC–FID quantification of some compounds with high concentrations

GC–FID was employed for quantification of several compounds with high concentrations, including ethyl acetate, ethyl butanoate, ethyl pentanoate, ethyl hexanoate, ethyl lactate, 1-propanol, 1-butanol, 2-methylpropanol and 3-methylbutanol. It was carried out using an Agilent 6890 GC equipped with a FID, modified method from Ref. [18]. The column carrier gas was nitrogen at a constant flow rate of 1 mL/min. The separations were performed using a DB-Wax column (30 m length, 0.25 mm i.d., 0.25 μm film thickness; J & W Scientific) with an oven temperature programmer of 60 °C (3 min), ramped at 5 °C/min to 150 °C (15 min) and then ramped at 10 °C/min to 230 °C (5 min). One microliter of diluted liquor sample (40 % ethanol by volume) with 176.00 mg/L final concentration of pentyl acetate (IS4) solution was injected into the GC. The correction factors calculated in 40 % ethanol by volume were showed in Table 1.

Table 1 Correction factors of volatile aroma compounds with GC–FID[a]

No.[b]	Compounds	Density[c] (25 °C)	Ret time	Correction factor (F)[a]
1	Ethyl acetate	0.90	1.90	1.47
19	1-Propanol	0.80	2.81	0.83
4	Ethyl butanoate	0.88	2.98	1.05
20	2-Methyl-1-propanol	0.80	3.81	0.72
5	Ethyl pentanoate	0.88	4.21	0.96
21	1-Butanol	0.81	4.67	0.75
23	3-Methylbutanol	0.81	5.90	0.54
6	Ethyl hexanoate	0.87	6.17	1.16
11	Ethyl lactate	1.03	8.90	1.54

[a] Pentyl acetate was used as IS

[b] Numbers represented the aroma compounds in Table 3

[c] Density (g/mL)

Table 2 The standard curve of volatile aroma compounds in Chinese *Xijiu* liquor with GC–MS

No.[a]	Compounds	Quantify ions	Slope	Intercept	*n*	R^2	LOD (μg/L)	Recovery (%)	Range concentration (μg/L)
Esters									
2	Ethyl propanoate[b]	57	63.20	2.98	7	0.9900	75.69	78.67	196.79–12,594.54
3	Ethyl 2-methylpropanoate[b]	71	582.30	21.22	9	0.9916	72.30	89.45	250.63–64,160.00
7	Isopentyl butanoate[b]	71	3.57	0.13	10	0.9990	2.24	109.39	4.18–2,139.89
8	Hexyl acetate[b]	84	279.89	2.75	6	0.9981	63.05	118.29	330.02–221,121.49
9	Propyl hexanoate[b]	99	2.24	0.97	12	0.9950	5.25	119.31	12.24–25,068.98
10	Ethyl heptanoate[b]	88	5.07	0.69	11	0.9995	20.65	105.38	27.54–112,800.00
12	Butyl hexanoate[b]	56	2.41	0.09	6	0.9940	2.15	102.19	20.10–10,294.71
13	Ethyl octanoate[b]	88	2.14	0.05	9	0.9968	39.09	100.34	338.74–43,359.18
14	Ethyl 2-hydroxyhexanoate[d]	69	1.60	0.26	8	0.9988	52.64	90.58	147.80–18,918.92
15	Hexyl hexanoate[c]	117	0.97	0.50	11	0.9977	2.59	100.03	4.49–2,298.12
16	Ethyl decanoate[c]	88	0.94	0.10	9	0.9997	1.01	101.60	1.15–1,172.50
17	Diethyl butanedioate[c]	101	54.46	0.06	5	0.9983	4.95	110.69	95.07–6,084.40
Alcohols									
18	2-Butanol[b]	59	5,649.40	2.98	6	0.9900	405.38	79.45	459.43–58,807.10
22	2-Pentanol[b]	45	130.91	2.29	8	0.9918	10.56	101.26	56.34–7,212.00
24	1-Pentanol[d]	42	2.24	0.31	8	0.9994	51.86	98.49	147.80–18,918.92
25	2-Heptanol[b]	45	0.40	−0.03	5	0.9961	3.46	108.39	5.54–44.31
26	1-Hexanol[b]	69	205.99	1.49	11	0.9910	25.52	100.16	59.55–60,980.09
27	3-Octanol[b]	59	9.25	−0.04	7	0.9969	2.32	101.22	2.63–336.98
28	1-Octanol[c]	56	30.80	−0.99	5	0.9953	4.13	108.26	95.56–764.45
29	1-Nonanol[c]	56	6.73	−0.18	6	0.9907	1.77	89.37	4.25–272.17
Acids									
30	Acetic acid[d]	60	52.16	2.39	6	0.9933	2,276.83	79.21	3,462.93–233,147.34
31	Propanoic acid[d]	74	9.06	0.46	6	0.9968	214.24	89.19	314.22–80,440.56
32	2-Methylpropanoic acid[d]	43	2.37	0.06	5	0.9994	159.18	94.81	181.62–11,623.50
33	Butanoic acid[d]	60	3.00	0.13	7	0.9957	537.51	82.67	5,759.01–3,685,76.56
34	3-Methylbutanoic acid[d]	60	1.21	0.04	5	0.9997	362.65	90.12	580.23–9,283.74
35	Pentanoic acid[d]	60	1.87	1.69	5	0.9992	658.07	96.24	6,350.78–101,612.51
36	4-Methylpentanoic acid[d]	57	2.20	0.02	8	0.999	144.44	102.12	269.62–34,511.24
37	Hexanoic acid[d]	60	3.33	−5.98	6	0.9965	727.58	84.06	3,150.59–806,550.00
38	Heptanoic acid[d]	60	1.77	0.53	7	0.998	643.45	99.01	386.07–98,834.27
39	Octanoic acid[d]	60	1.89	0.09	6	0.996	197.21	96.37	236.66–15,146.00
40	Nonanoic acid[d]	60	2.08	0.05	7	0.9994	171.10	111.62	262.36–16,791.04
41	Decanoic acid[d]	60	2.80	0.03	7	0.999	247.09	107.28	296.50–18,976.26
Aldehydes and ketones									
42	Acetaldehyde[b]	43	790.20	76.19	8	0.9909	101.39	101.39	2,430.30–311,073.00
43	2-Methylpropanal[b]	72	54.43	0.02	7	0.9986	20.50	102.50	21.87–1,399.66
44	3-Methylbutanal[b]	58	212.28	5.12	7	0.9942	65.48	110.97	240.08–30,729.93
45	2-Nonanone[b]	58	2.05	−0.10	12	0.9927	0.37	100.18	0.37–757.96
Aromatic compounds									
46	Benzaldehyde[b]	106	9.32	−0.04	10	0.9941	4.38	95.29	3.38–1,728.75
47	Acetophenone[c]	105	7.06	0.01	6	0.9947	1.08	90.37	32.32–517.09
48	Phenylacetaldehyde[c]	91	75.72	−2.06	6	0.9926	12.86	98.53	106.00–3,392.12
49	Ethyl 2-phenylacetate[c]	91	0.57	0.04	5	0.9981	0.24	109.36	2.04–32.58
50	2-Phenylethyl acetate[c]	104	2.24	0.04	7	0.9934	1.79	96.39	3.10–396.76
51	2-Phenylethanol[c]	91	28.08	−0.03	6	0.9961	11.12	104.45	41.53–10,631.44
52	2-Phenylethyl butanoate[c]	104	0.68	−0.03	8	0.9979	2.28	109.36	2.28–583.99
53	2-Phenylethyl hexanoate[c]	104	0.95	0.04	7	0.9968	1.85	110.94	3.45–888.40

Table 2 continued

No.[a]	Compounds	Quantify ions	Slope	Intercept	n	R^2	LOD (μg/L)	Recovery (%)	Range concentration (μg/L)
Phenols									
54	4-Methylguaiacol[c]	123	96.39	−0.26	5	0.992	7.24	89.37	15.44–494.00
55	Phenol[c]	94	120.67	−0.16	8	0.9971	1.10	90.29	1.30–284.20
56	4-Ethylguaiacol[c]	137	1.52	0.03	5	0.9915	7.72	95.76	20.90–334.45
57	4-Methylphenol[c]	107	15.43	0.34	7	0.9923	4.26	94.07	14.19–29,056.10
58	4-Ethylphenol[c]	107	25.32	−0.21	6	0.9952	3.59	96.41	57.44–1,838.00
Furans									
59	Furfural[b]	96	56.71	−9.61	6	0.9912	21.17	98.52	338.77–86,724.00
60	5-Methyl-2-furfural[c]	110	127.26	−0.90	5	0.9996	8.16	101.83	16.32–522.37
61	2-Acetyl-5-methylfuran[c]	109	34.90	0.01	6	0.9899	16.3	103.64	23.30–261.20
62	2-Furanmethanol[d]	98	9.05	0.30	7	0.9989	138.24	95.17	295.60–18,918.92
Pyrazines									
63	2,6-Dimethylpyrazine[b]	108	111.56	1.29	7	0.9985	24.12	91.72	53.33–3,413.31
64	2,3,5-Trimethylpyrazine[b]	122	66.86	−0.21	10	0.9993	3.30	93.45	9.24–4,733.00
65	2,3-Diethyl pyrazine[b]	136	6.97	0.16	8	0.9979	4.33	89.38	6.75–480.31
66	2,3,5,6-Tetramethylpyrazine[b]	136	5.59	1.36	10	0.9906	3.17	90.54	6.76–3,461.95
Sulfide									
67	Dimethyl trisulfide[b]	126	7.16	1.60	5	0.9935	6.89	97.91	23.88–2,444.80
Acetal									
68	1,1-diethoxyethane[b]	103	8,705.00	166.40	6	0.9970	568.10	114.27	13,331.30–426,600.00

LOD limit of detection

[a] Numbers represented the aroma compounds in Table 3

[b] Compounds were quantified by HS–SPME/GC–MS; methyl hexanoate was used as IS

[c] Compounds were quantified by HS–SPME/GC–MS; octyl propanoate was used as IS

[d] Compounds were quantified by LLME/GC–MS; 2,2-dimethyl propanoic acid was used as IS

Calibration of standard curves

HS–SPME/GC–MS

In the total of 8 mL 10 % ethanol/water solution (by volume) containing different concentrations of volatile standards, 3 g NaCl and 10 μL ISs solution, a mixture of methyl hexanoate (IS1, 95.57 μg/L of final concentration) and octyl propanoate (IS2, 55.55 μg/L of final concentration) were placed in the 20 mL vials. Assays were performed with the same type of fiber, while the HS–SPME/GC–MS conditions were set as described above.

LLME/GC–MS

A total of 18 mL 10 % ethanol/water solution (by volume) containing different concentrations of volatile standards, 6 g NaCl and 6 μL IS3 solution, 2,2-dimethyl propanoic acid (3.41 mg/L), was extracted for 3 min with 1 mL redistilled diethyl ether. The LLME/GC–MS conditions were set as mentioned above.

Selective ion monitoring (SIM) mass spectrometry was used to quantify the aroma compounds by HS–SPME/GC–MS and LLME/GC–MS methods. And the ions monitored of IS1, IS2 and IS3 in the SIM run were *m/z* 74, 75 and 57, respectively. The standard curve for individual volatile aroma compound was built up by plotting the response ratio of target compounds and corresponding ISs against the concentration ratio (Table 2).

Determination of odor thresholds

For the calculation of OAVs, odor thresholds were determined in 46 % ethanol/water solution (ethanol content of Chinese liquor is normally 38–55 % by volume) as method reported [14].

Results and discussion

Odor profiles analysis to two types of Chinese liquor

As it was known to all, soy sauce and strong aroma type liquors have distinctly different aroma characteristics. However, there was still not an accurate and comprehensive description to the flavor differences between the two

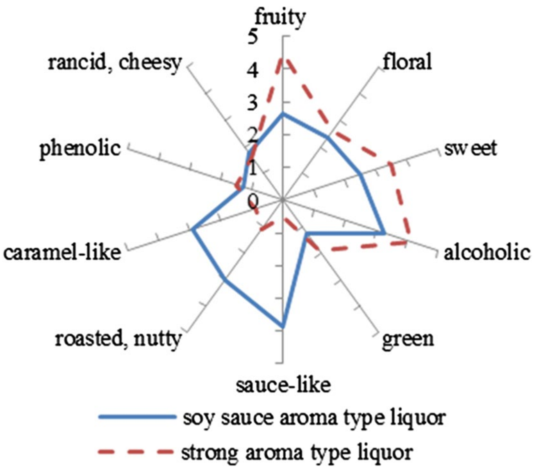

Fig. 1 Odor profiles of Chinese soy sauce and strong aroma type liquors

types of Chinese liquor. So the two liquors with different typical aromas (J-1 and N-1) were chosen for odor profiles analysis to have a comprehensive overall aroma perception (Fig. 1). The aroma outlines of the two liquor samples were obviously different. The strong aroma type liquor (N-1) was mainly characterized by fruity, sweet, alcoholic and floral aromas. Although soy sauce aroma type liquor (J-1) was also with the corresponding aroma, the strengths of these odors were much lower. Otherwise, it had obvious differences in soy sauce-like, baked and caramel-like aromas compared with N-1 (Fig. 1).

GC–O analysis

The aroma extract (J-1 and N-1 liquors) was fractionated into acidic/water-soluble, neutral and basic fractions (Fig. 2). A total of 61 volatile compounds were identified (Table 3), including esters, alcohols, fatty acids, aldehydes and ketones, phenols, aromatic compounds, furans, pyrazines and sulfide.

Esters represented one of the most important aroma classes, such as ethyl butanoate, ethyl pentanoate, ethyl hexanoate, 3-methylbutanol butanoate, hexyl acetate and ethyl decanoate (intensity $\geq$3.0), could be important due to their high odor intensities in J-1 liquor. In N-1 liquor, ethyl butanoate, ethyl hexanoate, ethyl octanoate, ethyl 2-hydroxyhexanoate and ethyl decanoate were important. Ethyl hexanoate was considered with the highest aroma intensity in both J-1 and N-1 liquors, contributed fruity and sweet aroma to the liquor. Overall, most ester compounds were esterified formed by the alcohol and acid during the fermentation and storage [1].

Twelve alcohols were detected in this study. Alcohols mainly gave fruity, green and alcoholic aromas. In J-1 liquor, 2-butanol, 1-propanol, 2-methyl propanol, 1-butanol and 3-methylbutanol were detected with high intensities ($\geq$3.0), while 1-butanol, 3-methylbutanol, 1-hexanol and 1-octanol were detected with high intensities in N-1. During fermentation of Chinese liquor, most of them were formed from sugars under aerobic conditions and from amino acids under anaerobic conditions [19].

A total of 12 fatty acids were detected in the acidic/water-soluble fraction. Acetic, propanoic, 2-methyl propanoic, butanoic, 3-methylbutanoic and hexanoic acids could be important in J-1 liquor, while 2-methyl propanoic, butanoic, 3-methylbutanoic and hexanoic acids were important in N-1. Acetic acid and propanoic acid gave acidic and vinegar aromas, while others contributed rancid, cheesy and sweaty aromas. 4-Methylpentanoic acid showed sweaty and sour aroma, which was firstly detected in *Yanghe Daqu* liquor [1].

In the study, 8 aromatic compounds were identified in J-1 liquor, while 7 aromatic compounds were identified in N-1. 2-Phenylethanol was detected in all the three fractions with the greatest aroma intensity (3.2–3.5). The aromatic compounds mainly contributed floral, fruity and sweet aromas. Little intensity differences were determined between the two samples in aromatic compounds.

Only 3 phenols were found in soy sauce aroma type sample, while 5 phenols were detected in strong aroma type sample. The intensities of all phenols were smaller than 2.5. In these compounds, 4-methylphenol was identified with highest aroma intensity, which was the main by-product from fermentation of tyrosine, showing animal and phenol aroma [20]. 4-Ethylguaiacol and 4-ethylphenol were not detected in J-1 liquor, 4-ethylguaiacol contributed cloves aroma, while 4-ethylphenol was considered with herbal aroma. Maybe most phenols were derived from lignin degradation during the fermentation of Chinese liquor [21].

There were obvious aroma intensity differences between two liquors in furans. In J-1 liquor, 4 furan compounds could be detected, while only furfural was detected in N-1 with lower aroma intensity. Furfural gave sweet and almond odors. In addition to furfural, the aroma intensities of 5-methyl-2-furfural, 2-acetyl-5-methyl furan and 2-furanmethanol were 2.0 or above, mainly contributed caramel and roasted aromas. In the odor profiles, J-1 liquor was considered with much stronger caramel and bake aromas than N-1 (Fig. 1). Furfural was formed in the distillation process [22].

Four pyrazine compounds were detected in J-1 liquor, while 3 pyrazines detected in N-1, and the aroma intensities were much lower than J-1. In J-1, the intensities of pyrazines were exceeding 2.0, with roasted and bake aromas.

Only 2-nonanone was detected in the neutral extraction of two liquor samples, contributed fruity aroma. Its intensity was slightly greater in J-1 liquor. Dimethyl trisulfide was the only one sulfur-containing compound detected in this experiment, and in both samples, it was detected with great intensity (aroma intensity = 3.5), contributed to rotten cabbage aroma.

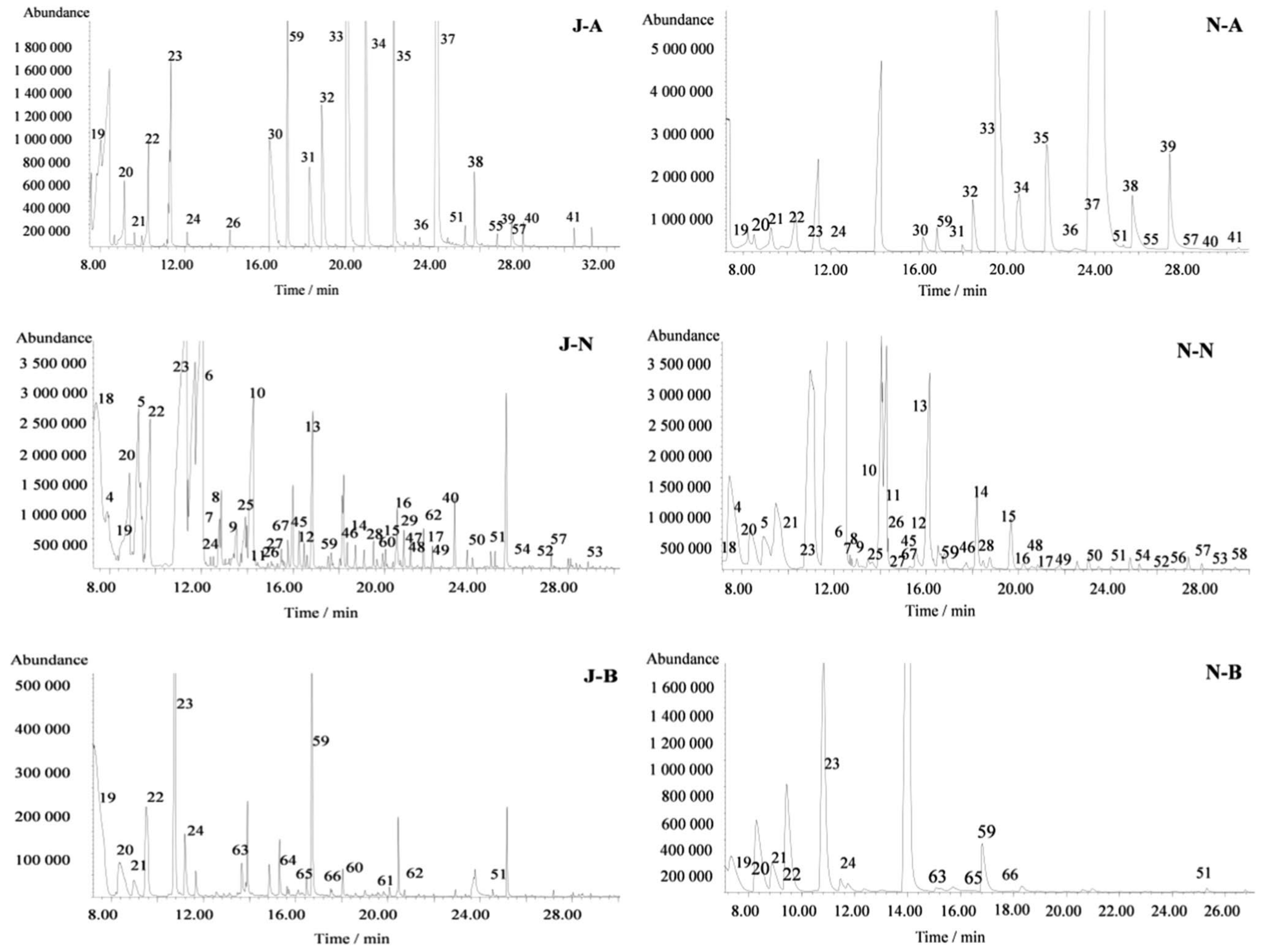

Fig. 2 The total ionic chromatography of the volatile aroma compounds in the soy sauce and strong aroma type *Xijiu* liquors (J-A, J-N, J-B: acidic/water-soluble, neutral and basic fractions in soy sauce aroma type liquor; N-A, N-N, N-B: acidic/water-soluble, neutral and basic fractions in strong aroma type liquor; Numbers represented the aroma compounds in Table 3)

Quantitative analysis

Because of solvent delay, some important aroma compounds, such as ethyl acetate, ethyl propanoate, ethyl 2-methylpropanoate, acetaldehyde, 2-methylpropanal, 3-methylbutanal and 1,1-diethoxyethane could not be detected in GC–O and GC–MS. These compounds were quantified in this study.

According to quantitative data (Table 3), the contents of ethyl acetate, ethyl hexanoate, ethyl lactate, 1-propanol and acetic acid were more than 1,000 mg/L. Ethyl hexanoate was the most abundant aroma compound in strong aroma type liquor with concentrations exceeding 4,000 mg/L, but the content was only about 300 mg/L in soy sauce aroma type liquor. Besides, the concentration of ethyl lactate in soy sauce aroma type liquor was a quarter of that in strong aroma type liquor. On the contrary, 1-propanol and acetic acid were detected with far higher contents in soy sauce aroma type liquor, especially for 1-propanol, which was about 1,800 mg/L and 30 times of the content in strong aroma type liquor.

Ethyl propanoate, ethyl butanoate, ethyl pentanoate, ethyl heptanoate, ethyl octanoate, hexyl acetate, ethyl 2-methylpropanoate, 2-butanol, 1-butanol, 2-methylpropanol, 3-methylbutanol, butanoic acid, hexanoic acid, acetaldehyde and 1,1-diethoxyethane were between 100 and 1,000 mg/L in the liquors. Compared to strong aroma type liquor, the contents of ethyl propanoate and 2-butanol exceeded a lot, while ethyl pentanoate, ethyl heptanoate, ethyl octanoate and hexyl acetate were detected with far less concentrations in soy sauce aroma type liquor.

Ethyl 2-hydroxyhexanoate, butyl hexanoate, hexyl hexanoate, 1-pentanol, 1-hexanol, propanoic acid, pentanoic acid, heptanoic acid, octanoic acid, 2-methylpropanoic acid, 3-methylbutanoic acid, 3-methylbutanal, furfural and 2-furanmethanol ranged from 10 to 100 mg/L. Compared

Table 3 Osme intensities, concentrations (µg/L) and OAVs of aroma compounds in two type Chinese liquors

No.	Compounds[a]	RI	Descriptor	Frac[c]	Intensities		Ions (*m/z*)	Odor threshold	Mean concentration ± SD[f]		P[g]	OAVs	
					J-1	N-1			J liquor	N liquor		J liquor	N liquor
Esters													
1	Ethyl acetate[b]	890					FID[d]	32,600[e]	2,636.49 ± 452.47	1,903.28 ± 162.53	*	81	58
2	Ethyl propanoate[b]	953					57	19,000[e]	275.89 ± 55.35	51.68 ± 14.92	**	15	3
3	Ethyl 2-methylpropanoate[b]	956					71	57.5[e]	287.64 ± 54.61	115.42 ± 31.69	***	5,002	2,007
4	Ethyl butanoate[b]	1,033	Pineapple	N	4.0	3.0	FID	81.5[e]	492.66 ± 154.55	737.69 ± 100.16	*	6,045	9,051
5	Ethyl pentanoate[b]	1,128	Apple	N	3.3	2.4	FID	26.8[e]	71.68 ± 27.75	190.55 ± 57.90	**	2,675	7,110
6	Ethyl hexanoate[b]	1,231	Fruity, floral	N	4.8	5.0	FID	55.3[e]	328.57 ± 155.12	4,500.01 ± 1,002.19	***	5,942	59,594
7	Isopentyl butanoate	1,252	Floral, fruity	N	3.0	2.5	71	915	1,314.88 ± 302.87	1,388.06 ± 351.53	NS	1	2
8	Hexyl acetate[b]	1,267	Fruity, floral	N	3.0	2.4	84	5,560	15.24 ± 3.96	148.02 ± 46.06	***	3	27
9	Propyl hexanoate[b]	1,289	Pineapple	N	1.6	2.0	99	12,800	9.03 ± 3.65	6.53 ± 2.26	NS	<1	<1
10	Ethyl heptanoate[b]	1,313	Fruity	N	2.5	2.5	88	13,200[e]	32.27 ± 12.12	192.13 ± 44.84	***	2	15
11	Ethyl lactate[b]	1,335	Fruity	N	1.0	1.2	FID	128,000[e]	671.69 ± 126.52	2,133.33 ± 332.49	***	5	17
12	Butyl hexanoate[b]	1,394	Pineapple	N	1.3	2.0	56	678	4.18 ± 2.16	17.97 ± 6.03	**	6	27
13	Ethyl octanoate[b]	1,427	Fruity	N	2.3	3.5	88	12.9[e]	15.50 ± 3.38	121.82 ± 28.71	***	1,202	9,443
14	Ethyl 2-hydroxyhexanoate[b]	1,525	Floral	N	2.8	3.2	69	51,400	19.22 ± 1.59	42.26 ± 7.47	***	<1	<1
15	Hexyl hexanoate[b]	1,590	Fruity, apple	N	1.2	2.5	117	1,890	2.68 ± 1.26	19.89 ± 7.12	**	1	11
16	Ethyl decanoate	1,612	Fruity, grape	N	3.2	3.0	88	1,120[e]	1,675.77 ± 301.52	2,989.25 ± 483.65	**	1	3
17	Diethyl butanedioate	1,667	Fruity, sweet	N	2.0	2.5	101	353,000[e]	2,398.29 ± 504.58	338.80 ± 63.71	***	<1	<1
Alcohols													
18	2-Butanol[b]	1,021	Fruity	N	3.0	2.0	59	50,000	360.22 ± 111.54	92.81 ± 36.81	*	7	2
19	1-Propanol[b]	1,037	Fruity, alcoholic	N + A + B	3.5	2.5	FID	54,000	1,886.77 ± 682.11	55.66 ± 11.49	***	35	1
20	2-Methylpropanol[b]	1,083	Wine	N + A + B	3.0	2.0	FID	28,300[e]	147.70 ± 15.77	111.67 ± 9.24	**	5	4
21	2-Pentanol	1,117	Alcoholic	N + A + B	3.2	3.0	45	194,000	7,392.63 ± 3,827.76	6,592.6 ± 1,886.6	NS	<1	<1
22	1-Butanol[b]	1,134	Fruity	N + A + B	2.7	2.5	FID	2,730[e]	157.97 ± 36.05	177.34 ± 40.25	NS	58	65
23	3-Methylbutanol[b]	1,236	Fruity, nail polish	N + A + B	3.0	3.2	FID[a]	179,000[e]	312.05 ± 20.06	272.44 ± 23.5	NS	2	2
24	1-Pentanol[b]	1,252	Fruity	N + A + B	2.5	1.8	42	37,400	42.54 ± 12.54	10.21 ± 2.02	***	1	<1
25	2-Heptanol	1,304	Fruity	N	1.3	2.8	45	1,430[e]	16.15 ± 6.95	88.97 ± 32.99	**	<1	<1
26	1-Hexanol[b]	1,356	Floral, green	N	2.7	3.0	69	5,370[e]	60.29 ± 16.67	72.64 ± 30.63	NS	11	14
27	3-Octanol	1,370	Green, mushroom	N	2.0	2.5	59	393	534.69 ± 209.89	125.26 ± 48.39	**	1	<1
28	1-Octanol	1,549	Fruity	N	2.5	3.0	56	1,100	2,280.95 ± 656.19	6,255.70 ± 3,267.48	NS	2	6
29	1-Nonanol	1,618	Green	N	2.0		56	806	262.39 ± 37.42	164.92 ± 59.65	*	<1	<1
Acids													
30	Acetic acid[b]	1,455	Acidic, vinegar	A	4.3	2.8	60	160,000[e]	1,110.48 ± 183.17	409.46 ± 100.22	***	7	3
31	Propanoic acid[b]	1,532	Vinegar	A	3.0	2.5	74	18,200	63.70 ± 20.54	17.10 ± 2.07	**	4	<1
32	2-Methylpropanoic acid[b]	1,557	Acidic, rancid	A	3.2	3.0	43	1,580[e]	27.13 ± 6.92	18.10 ± 7.38	NS	17	11

Table 3 continued

No.	Compounds^{a}	RI	Descriptor	Frac^{c}	Intensities		Ions (*m/z*)	Odor threshold	Mean concentration ± SD^{f}		P^{g}	OAVs	
					J-1	N-1			J liquor	N liquor		J liquor	N liquor
33	Butanoic acid^{b}	1,603	Rancid, cheesy	A	3.5	4.2	60	964^{e}	128.13 ± 50.77	148.97 ± 27.47	NS	133	155
34	3-Methylbutanoic acid^{b}	1,630	Rancid, acidic	A	4.0	3.5	60	1,050^{e}	14.95 ± 3.77	8.94 ± 1.88	*	14	9
35	Pentanoic acid^{b}	1,731	Rancid, sweet	A	2.5	1.5	60	389^{e}	57.89 ± 14.71	60.51 ± 5.15	NS	149	156
36	4-Methylpentanoic acid	1,822	Sweaty, sour	A	1.8	2.2	57	144	798.35 ± 164.44	1,438.49 ± 431.31	*	6	10
37	Hexanoic acid^{b}	1,829	Sweaty, cheesy	A	3.5	4.5	60	2,520^{e}	126.16 ± 66.58	734.00 ± 110.95	***	50	291
38	Heptanoic acid^{b}	1,963	Sweaty	A	2.0	2.5	60	13,300	11.11 ± 0.86	25.32 ± 6.87	*	<1	2
39	Octanoic acid^{b}	2,067	Sweaty, cheesy	A	2.3	2.0	60	2,700	2.29 ± 0.20	25.11 ± 1.50	*	<1	9
40	Nonanoic acid	2,173	Fatty	A	0.8	1.0	60	3,560	1,116.12 ± 32.88	3,327.93 ± 992.64	*	<1	<1
41	Decanoic acid	2,285	Fatty	A	1.0	1.5	60	13,700	1,001.86 ± 98.71	3,349.04 ± 2,085.68	*	<1	<1
Aldehydes and ketones													
42	Acetaldehyde^{b}	659					44	1,200	155.25 ± 15.77	265.09 ± 27.46	***	129	221
43	2-Methylpropanal	748					72	1,300	2,221.61 ± 553.44	1,048.46 ± 227.21	**	2	<1
44	3-Methylbutanal^{b}	921					58	17	72.64 ± 17.80	83.50 ± 28.03	NS	4,273	4,912
45	2-Nonanone	1,371	Sweet, fruity	N	3.4	2.3	58	483	176.50 ± 32.85	832.62 ± 277.08	**	<1	2
Aromatic compounds													
46	Benzaldehyde	1,513	Fruity	N	2.0	2.2	106	4,200^{e}	2,982.02 ± 874.73	4,684.45 ± 1,091.50	NS	<1	1
47	Acetophenone	1,625	Floral, fruity	N	2.0		105	256	166.77 ± 37.94	38.51 ± 10.66	***	<1	<1
48	Phenylacetaldehyde^{b}	1,637	Fruity	N	2.2	1.7	91	262^{e}	6.18 ± 2.13	1.21 ± 0.67	***	24	5
49	Ethyl 2-phenylacetate	1,782	Rosy, honey	N	2.7	2.0	104	407^{e}	916.99 ± 184.35	540.14 ± 193.15	*	2	1
50	2-Phenylethyl acetate	1,810	Floral	N	2.5	2.5	104	909^{e}	612.25 ± 181.39	162.03 ± 129.29	**	<1	<1
51	2-Phenylethanol	1,900	Rosy, honey	N + A + B	3.5	3.2	104	28,900^{e}	4,849.08 ± 922.67	443.7 ± 108.99	***	<1	<1
52	2-Phenylethyl butyrate	1,956	Fruity	N	2.0	1.5	104	961	134.61 ± 53.60	26.24 ± 11.79	**	<1	<1
53	2-Phenylethyl hexanoate	2,173	Fruity	N	2.8	1.2	106	94	418.72 ± 182.79	782.83 ± 214.31	NS	4	8
Phenols													
54	4-Methylguaiacol	1,943	Smoky	N	1.8	0.8	123	315^{e}	261.07 ± 90.28	372.09 ± 214.20	NS	<1	1
55	Phenol	2,002	Phenol, medicinal	A	1.2	1.5	94	18,900^{e}	731.78 ± 240.33	851.36 ± 368.11	NS	<1	<1
56	4-Ethylguaiacol	2,008	Clove, spicy	N		2.0	137	123^{e}	8.32 ± 2.18	99.11 ± 52.84	*	<1	<1
57	4-Methylphenol	2,075	Animal, phenol	N + A	2.2	2.5	107	167^{e}	846.75 ± 408.97	777.13 ± 203.00	NS	5	5
58	4-Ethylphenol	2,189	Smoky	N		1.5	107	123	53.02 ± 19.73	513.5 ± 304.47	*	<1	4
Furans													
59	Furfural^{b}	1,470	Sweet, almond	N + A + B	3.0	2.5	96	44,000^{e}	52.78 ± 11.30	27.23 ± 8.24	*	1	<1
60	5-Methyl-2-furfural	1,553	Green, roasted	N + B	3.0		110	466,000	2,559.27 ± 549.51	292.00 ± 78.12	***	<1	<1
61	2-Acetyl-5-methylfuran	1,590	Roasted	B	2.4		109	40,900^{e}	451.30 ± 105.09	113.12 ± 35.32	***	<1	<1
62	2-Furanmethanol^{b}	1,645	Baked	N + B	3.0		98	54,700	30.31 ± 4.81	10.16 ± 1.96	***	<1	<1

Table 3 continued

No.	Compounds[a]	RI	Descriptor	Frac[c]	Intensities		Ions (m/z)	Odor threshold	Mean concentration ± SD[f]		P[g]	OAVs	
					J-1	N-1			J liquor	N liquor		J liquor	N liquor
Pyrazines													
63	2,6-Dimethylpyrazine	1,320	Nutty	B	2.7	1.2	108	791	2,186.28 ± 396.57	1,131.26 ± 317.64	**	3	1
64	2,3,5-Trimethylpyrazine	1,393	Nutty, roasted	B	3.5		122	730	524.64 ± 142.28	n.d.[h]	***	<1	n.d.
65	2,3-Diethylpyrazine	1,450	Baked	B	2.5	2.0	136	172	100.47 ± 8.64	107.33 ± 7.56	*	<1	<1
66	2,3,5,6-Tetramethylpyrazine	1,458	Baked	B	4.0	2.0	136	80,100	705.63 ± 9.72	191.47 ± 174.89	***	<1	<1
Sulfide													
67	Dimethyl trisulfide	1,351	Rotten cabbage	N	3.5	3.5	126	0.36	1,270.03 ± 124.69	2,140.19 ± 410.79	**	3,528	5,945
Acetal													
68	1,1-diethoxyethane[b]	901					103	2,090[e]	242.40 ± 53.34	216.44 ± 52.70	NS	116	104

[a] All compounds detected by GC–O were indentified by MS spectra, aroma descriptors and retention index (RI) comparisons to pure standards

[b] Concentration (mg/L)

[c] Odorants were detected in the fraction: A, acidic/water-soluble fraction; N, neutral fraction; B, basic fraction

[d] FID, quantified by GC–FID

[e] Odor thresholds were from the literature [16]

[f] Mean concentration of 10 liquors (J-1 to J-10 or N-1 to N-10) in the same aroma type, at 53 % ethanol by volume; SD, standard deviation; J liquor, soy sauce aroma type liquor (J-1 to J-10); N liquor, strong aroma type liquor (N-1 to N-10)

[g] Probability that there was a difference between soy sauce and strong aroma type liquors; NS, no significant difference between means ($P > 0.05$); * significant at the 5 % level; ** significant at the 1 % level; *** significant at the 0.1 % level

[h] Not detected

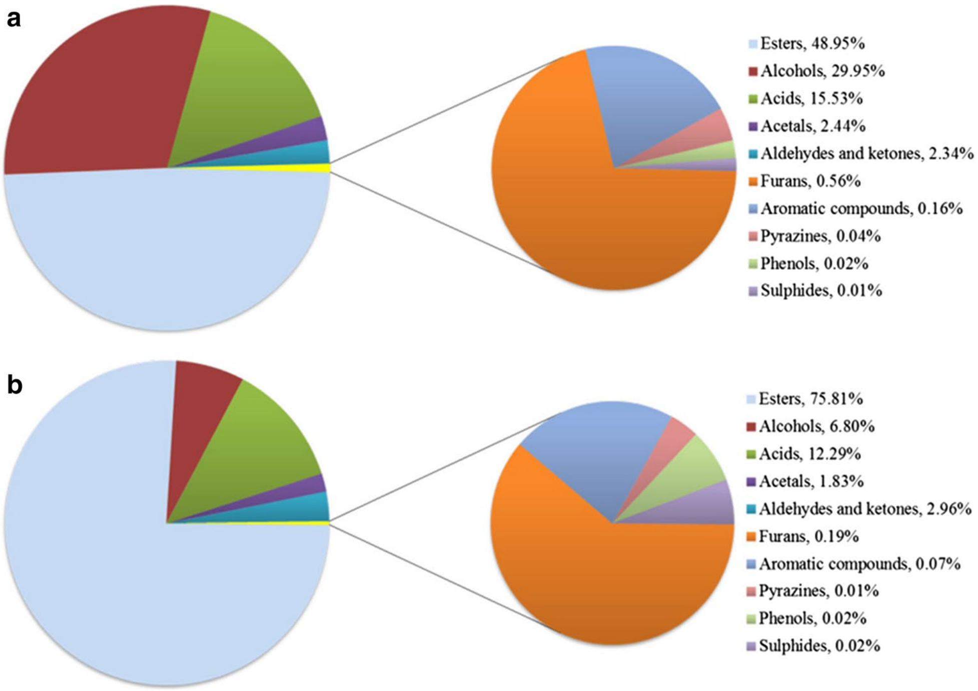

Fig. 3 Concentrations of aroma compounds in Chinese soy sauce aroma type liquor (**a**) and strong aroma type liquor (**b**)

to soy sauce aroma type liquor, the concentrations of butyl hexanoate, hexyl hexanoate and octanoic acid in strong aroma type liquor were much higher, whereas the concentrations of propanoic acid, furfural and 2-furanmethanol were far lower.

The concentrations of the other aroma compounds were below 10 mg/L, including diethyl butanedioate, 2-phenylethanol, 2-phenylethyl butanoate, 4-ethylguaiacol, 4-ethylphenol, 2,3,5-trimethylpyrazine and 2,3,5,6-tetramethylpyrazine were detected with significantly different contents in these two types of liquors. Except 4-ethylguaiacol and 4-ethylphenol, the concentrations of other compounds were higher in soy sauce aroma type liquors than in strong aroma type liquors.

Generally speaking, esters were detected with the highest concentration in the two liquor samples. Esters, alcohols and fatty acids accounted for 95 percent of the total concentration of aroma compounds (Fig. 3). The concentrations of fatty acids, esters and alcohols with carbon atoms less than 4 in soy sauce aroma type liquor were much higher than the ones in strong aroma type liquor, while those with carbon atoms more than 4 were just on the contrary. For instance, the concentration of ethyl acetate was much more in soy sauce aroma liquor, whereas ethyl hexanoate was detected with higher concentration in strong aroma type liquor. Presumably, the differences were caused by the different fermenter, which was coated inside with a layer of fermentation mud made of clay, spent grain, bean cake powder and fermentation bacteria (*Clostridium* sp.) [23]. *Clostridium* sp. could convert ethanol to hexanoic acid, acetic acid and butanoic acid, the intermediate product in the process [23]. Different from the strong aroma type fermenter coated inside with mud, the fermenter used for soy sauce aroma type liquor was a vessel made of stones [3]. So *Clostridium* sp. would be sparsely populated in soy sauce aroma type fermenter compared with strong aroma type fermenter. Otherwise, the production cycle of soy sauce aroma type liquor was 30 days, while strong aroma type liquor needs about 50 days to be removed from the fermenter, much longer than soy sauce aroma type liquor. Then, acids with carbon atoms more than 4, such as hexanoic acid, were detected with lower concentrations in soy sauce aroma type liquor, while those with less carbon atoms would accumulate in the liquor.

In addition to esters, alcohols and fatty acids, the concentrations of furans and pyrazines in soy sauce aroma type liquor were at distinctively different levels with strong aroma type liquor, and these phenomenon could also be seen in the GC–O analysis. As pyrazines were formed through the action of microorganisms [24], not only the process of fermentation with high temperature, but also high temperature *daqu*-making, and the unique stacking procedure of grains before fermentation in soy sauce aroma type liquor would promote the generation of this kind of compounds. Meanwhile, the distillation to the acidic fermented grains in high temperature would cause a high furans level, especially for furfural [2].

Determination of odor thresholds

Triangular tests were performed for odor thresholds determination as mentioned above. As shown in Table 3, odor thresholds of 34 aroma compounds were determined, and the odor thresholds in Chinese liquor ranged from 0.36 (dimethyl trisulfide) to 466,000 μg/L (5-methyl-2-furfural). So contribution to the liquor would depend not only on the concentration of one aroma compound, but also its odor threshold.

OAVs analysis

Combining with the thresholds (Table 3), 42 aroma components in soy sauce aroma type liquor and 43 aroma components in strong aroma type liquor were at concentrations higher than their corresponding odor thresholds in Chinese liquors.

In soy sauce aroma type liquor, the OAVs of ethyl butanoate, ethyl hexanoate, ethyl 2-methylpropanoate, 3-methylbutanal, dimethyl trisulfide, ethyl pentanoate and ethyl octanoate were higher than 1,000, and they contributed obvious aromas to the liquor. Second group compounds were considered with OAVs from 100 to 1,000, consisted of pentanoic acid, butanoic acid, acetaldehyde and 1,1-diethoxyethane. Ethyl acetate, hexanoic acid, 1-propanol, phenylacetaldehyde, 2-methylpropanoic acid, ethyl propanoate, 3-methylbutanoic acid and 1-hexanol ranked the third group, whose OAVs were between 10 and 100. The others were considered with lower importance, even no contribution to the liquor.

In strong aroma type liquor, ethyl hexanoate had the highest OAVs nearly 60,000, while OAVs of others were far less. It was a key aroma compound in strong aroma type liquor with fruity, floral and sweet aromas. However, in soy sauce aroma type liquor, the OAV of this compound was about 6,000, lower than ethyl butanoate. Ethyl octanoate, ethyl butanoate, ethyl pentanoate, dimethyl trisulfide, 3-methylbutanal and ethyl 2-methylpropanoate were also important compounds with OAVs higher than 1,000 in strong aroma liquor. Compared to soy sauce aroma type liquor, OAVs of ethyl pentanoate and ethyl octanoate were much higher in strong aroma type liquor. OAVs of hexanoic acid, acetaldehyde, pentanoic acid, butanoic acid and 1,1-diethoxyethane were from 100 to 1,000, followed by 1-butanol, ethyl acetate, hexyl acetate, butyl hexanoate, ethyl lactate, ethyl heptanoate, 1-hexanol, 2-methylpropanoic acid, hexyl hexanoate and 4-methylpentanoic acid with OAVs between 10 and 100. OAV of hexanoic acid was 291 in strong aroma type liquor, while it was only 50 in soy sauce aroma type liquor. Ethyl lactate, ethyl heptanoate, hexyl acetate, butyl hexanoate and hexyl hexanoate were calculated with significantly different OAVs in the two types of liquor, and they were a lot higher in strong aroma type than them in soy sauce aroma type liquor. Nevertheless, 1-propanol, phenylacetaldehyde and ethyl propanoate were just on the contrary, whose OAVs were below 10 in strong aroma type liquor. It was supposed to be caused by the fermenter with different structure as mentioned above.

Conclusions

Significantly flavor differences were detected in the Chinese liquors with different aroma styles. According to the results obtained, the aroma compounds in soy sauce and strong aroma type liquors produced in the same factory were detected with distinct differences, such as furans and pyrazines. Otherwise, concentrations of fatty acids, esters and alcohols with carbon atoms less than 4 in soy sauce aroma type liquor were much higher than the ones in strong aroma type liquor, while those with carbon atoms more than 4 were just on the contrary. Ethyl hexanoate was one of the typical representative compounds. It was supposed that the aroma differences were mainly from the manufacturing process and had little to do with the environment and raw material.

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Conflict of interest None.

Compliance with Ethics Requirement This article does not contain any studies with human or animal subjects.

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