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Characterization of the Key Odorants in Light Aroma Type Chinese Liquor by Gas Chromatography−Olfactometry, Quantitative Measurements, Aroma Recombination, and Omission Studies

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ABSTRACT: The light aroma type liquor is widely welcomed by consumers due to its pleasant fruity and floral aroma, particularly in northern China. To answer the puzzling question of which key aroma compounds are responsible for the typical aroma, three typical liquors were studied in this paper. A total of 66 aroma compounds were identified in three liquors by means of gas chromatography−olfactometry (GC-O) coupled with mass spectrometry (MS), and 27 odorants were further screened out as the important odorants according to quantitative study and odor activity values (OAVs). For OAV calculation, odor thresholds of the odorants were determined in a hydroalcoholic solution at 46% ethanol by volume. The typical light type aroma dominated by fruity and floral notes was successfully simulated by dissolving these important odorants in the 46% vol hydroalcoholic solution in their natural concentrations. Omission experiments further confirmed β-damascenone and ethyl acetate as the key odorants and revealed the significance of the entire group of esters, particularly ethyl lactate, geosmin, acetic acid, and 2-methylpropanoic acid, for the overall aroma of the light aroma type Chinese liquor.

KEYWORDS: *Chinese light aroma type liquor, gas chromatography−olfactometry, gas chromatography−mass spectrometry, odor activity value, aroma recombination and omission, β-damascenone*

■ INTRODUCTION

Chinese liquor, also called *baijiu* or *shaojiu*, is a worldwide consumed distilled alcoholic beverage of great reputation, especially in China. It commonly has an ethanol content of 40−55% by volume.[1] Due to the great varieties of production processes, Chinese liquors from different manufacturers have significant differences in aroma profile. On the basis of the aroma characteristics, they are generally classified into the following categories: light aroma type, strong aroma type, soy sauce aroma type, sweet and honey aroma type, and miscellaneous aroma type liquors.[2] Among them, light aroma type liquor is widely welcomed by consumers due to its pleasant fruity and floral aroma, particularly in northern China.

As known to all, the quality of a beverage is influenced by many factors, such as raw materials and the fermentation process. In general, the main raw materials used for light aroma type liquor production are sorghum, barley, and pea: the former is used for making liquor, and the latter two are used for making *qu*.[3] In addition, rice husks are used as a fermentation accessory. *Qu*, which is made of pulverized barley and pea, is usually used as a fermentation starter to initiate the fermentation process. The various microorganisms and complex enzyme system in *qu* can generate abundant aroma compounds during the fermentation process.[4] The major producing steps of light aroma type liquor are as follows: mixing raw materials with *qu*, solid-state saccharification and fermentation in a pottery jar (350−400 L) under anaerobic conditions, and distillation.[2] Subsequently, the freshly distilled liquors are aged in sealed ceramic jars to develop balanced aroma and taste. Finally, the aged liquors are adjusted to a target ethanol concentration and blended for a constant quality of the final product.[5]

The aroma of Chinese liquor is an important factor in product quality, and it is mostly influenced by the complex aroma active compounds. Some studies have been made previously, and various techniques have been applied to investigate these aroma compounds. Fan and co-workers[5−7] have identified 126 odorants in *Wuliangye* and *Jiannanchun* liquor by gas chromatography−olfactometry (GC-O) and gas chromatography−mass spectrometry (GC-MS) techniques in 2006; afterward, they studied 27 pyrazines in Chinese liquors using GC-MS and headspace solid phase microextraction (HS-SPME) coupled with gas chromatograpy−flame thermionic detector (GC-FTD) in 2007, and later in 2011, they quantitated 76 volatile compounds in *Langjiu* through stir bar sorptive extraction (SBSE) coupled with GC-MS. Moreover, Zhu et al.[8] have shown the great complexity of the composition in *Maotai* liquor with 528 volatiles identified by means of comprehensive two-dimensional GC−time-of-flight MS. However, most of these studies were focused on the identification and quantitation of aroma compounds, and none comprehensively explored the contribution of key odorants from numerous constituents to the overall aroma.

Recently, techniques including not only GC-O and quantitation analysis but also odor activity value (OAV) analysis, descriptive profile test, aroma recombination, and

omission experiments are being extensively and successfully used to investigate the key aroma compounds of alcoholic beverages, such as whiskey,[9,10] beer,[11] brandy,[12] and Chinese rice wine,[13] as well as other foods.[14−17]

Therefore, to answer the puzzling question of which key aroma compounds are responsible for the typical aroma of light aroma type Chinese liquor, our study investigated three representative liquors in the following ways: identify and quantitate their potent aroma compounds in common, rate these compounds on the basis of OAVs and find the important odorants, and, finally, confirm the aroma contribution of selected important odorants by means of aroma recombination and omission experiments performed in the *Fenjiu* liquor. These data can be used for the optimization of the aroma and flavor of Chinese liquors during their production.

■ MATERIALS AND METHODS

Liquors. Three premium Chinese light aroma type liquors from different origins were under investigation: *Fenjiu* liquor (FJ, 45% ethanol by volume, from Shanxi province in north-central China), *Baofeng* liquor (BFJ, 46% ethanol by volume, from Henan province in central China), and *Qingke* liquor (QKJ, 52% ethanol by volume, from Qinghai province in northwestern China). All liquors (500 mL for each) were supplied by corresponding cooperant distilleries and stored at 4 °C until analysis.

Chemicals. Authentic standards were obtained from commercial sources: 1-Propanol, 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, 2-methylpropanol, 3-methylbutanol, 1-octen-3-ol, 2-butanol, 2-heptanol, ethyl acetate, ethyl propanoate, ethyl 2-methylpropanoate, 2-methylpropyl acetate, ethyl butanoate, ethyl 3-methylbutanoate, 3-methylbutyl acetate, ethyl pentanoate, ethyl hexanoate, hexyl acetate, ethyl lactate, ethyl heptanoate, ethyl octanoate, ethyl nonanoate, ethyl decanoate, diethylbutanedioate, 3-methylbutyl hexanoate, ethyl undecanoate, ethyl dodecanoate, ethyl 2-hydroxyhexanoate, propanoic acid, 3-methylbutanoic acid, pentanoic acid, hexanoic acid, decanoic acid, 3-methylbutanal, hexanal, nonanal, decanal, 2-nonanone, (E,Z)-2,6-nonadienal, benzaldehyde, phenylacetaldehyde, ethyl benzoate, ethyl 2-phenylacetate, 2-phenylethyl acetate, ethyl 3-phenylpropanoate, benzenemethanol, 2-phenylethanol, phenol, 4-methylphenol, 4-methylguaiacol, 4-ethylguaiacol, furfural, 2-acetyl-5-methylfuran, β-damascenone, γ-hexalactone, γ-nonalactone, 1,1-diethoxyethane, 1,1,3-triethoxypropane, and geosmin were purchased from Sigma-Aldrich (Shanghai, China). Acetic acid, 2-methylpropanoic acid, butanoic acid, and naphthalene were obtained from Alfa Aesar (Tianjin, China). Octyl propanoate (internal standard, IS), 2,2-dimethylpropanoic acid (IS), pentyl acetate (IS), and L-menthol (IS) (Sigma-Aldrich, Shanghai, China) were used as internal standards. A $C_5−C_{30}$ n-alkane mixture (Sigma-Aldrich, Shanghai, China) was employed for determination of linear retention indices (RIs). All of the substances used above were of GC quality, with at least 97% purity.

Sodium chloride (NaCl), anhydrous sodium sulfate (Na_2SO_4), sodium bicarbonate ($NaHCO_3$), sulfuric acid (H_2SO_4), and absolute ethanol were from China National Pharmaceutical Group Corp. (Shanghai, China). Diethyl ether and pentane from ANPEL Scientific Instrument Co., Ltd. (Shanghai, China) were freshly distilled before use.

Aroma Extraction and Fractionation. Following ref 5, liquors (50 mL) were diluted to 10% ethanol by volume with boiled ultrapure water, saturated with NaCl, and then extracted with diethyl ether (3 × 20 mL). The combined extracts were further separated into acidic/water-soluble, neutral, and basic fractions, using a mixture of pentane/diethyl ether (1:1 by volume) as extraction solvent. Afterward, each fraction was dried with anhydrous Na_2SO_4 overnight and concentrated under a gentle stream of nitrogen to a final volume of 200 µL. These concentrated fractions were stored at −20 °C prior to the GC-O analysis.

Identification by GC-O and GC-MS Analysis. GC-O and GC-MS analysis were performed on an Agilent 6890N GC coupled to an Agilent 5975 mass selective detector (MSD) and an olfactometer.

GC-MS Analysis. The concentrated fraction (1 µL) was injected in splitless mode. Samples were analyzed on both a DB-Wax column (30 m × 0.32 mm i.d. × 0.25 µm, J&W Scientific) and a DB-5 column (30 m × 0.32 mm i.d. × 1 µm, J&W Scientific). Helium at a constant flow rate of 2 mL/min was used as carrier gas. The injector was held at 250 °C. The oven temperature was held at 50 °C for 2 min, then programmed to 230 °C at a rate of 6 °C/min, and finally kept at 230 °C for 20 min. The column flow was split at the end of the capillary; one was directed to a heated olfactometer (Olfactory Detector Port ODP 2, Gerstel Inc., Mülheim, Ruhr, Germany), whereas the other one was directed to the MSD. The temperature of the olfactory port was 280 °C. Mass spectra in the electron ionization mode (MS-EI) were recorded at 70 eV ionization energy, and the ion source temperature was set at 230 °C. Full-scan acquisition was used in the 30−350 amu range of masses.

GC-O Analysis. Six trained panelists (three males and three females, 26 years old on average) from the Laboratory of Brewing Microbiology and Applied Enzymology at Jiangnan University were recruited to perform GC-O analysis. The panelists were trained for 3 months in GC-O using at least 30 odor-active reference compounds in a concentration 10 times above their odor thresholds in air. During a GC run described above, a panelist placed his/her nose close to the sniffing port, responded to the aroma intensity of the stimulus, and recorded the aroma descriptor and intensity value as well as retention time. The sniffing time of each run was not more than 30 min. The aroma descriptors were determined by an evaluation of the odor quality of reference odorants previously. A six-point scale ranging from 0 to 5 was used for intensity judgment: 0 = none, 1 = very weak, 2 = weak, 3 = moderate, 4 = strong, and 5 = very strong. The Osme value for aroma intensity was an average result of the six panelists.[18]

Identification of Aroma Compounds. Peak identifications of the odorants were performed by comparison of mass spectra with those of the NIST 05 a.L database (Agilent Technologies Inc., Santa Clara, CA, USA). Positive identification was achieved by comparison of their odors, retention indices (RIs), and mass spectra with those of pure standards. RIs of the odorants were calculated from the retention times of n-alkanes ($C_5−C_{30}$), according to a modified Kovats method.[19]

Quantitation by HS-SPME-GC-MS. An automatic headspace sampling system (MultiPurposeSample MPS 2 with a SPME adapter, from Gerstel Inc., Mülheim, Ruhr, Germany) with a 50/30 µm divinylbenzene/carboxen/poly(dimethylsiloxane) (DVB/CAR/PDMS) fiber (2 cm, Supelco Inc., Bellefonte, PA, USA) was used for extraction of volatile aroma compounds. The liquors were diluted with boiled ultrapure water to a final concentration of 10% ethanol by volume. A total of 8 mL of this diluted sample was transferred into a screw-capped vial, saturated with NaCl, and spiked with 10 µL of a mixed internal standard (octyl propanoate and L-menthol, with a final concentration of 66.7 or 125.2 µg/L, respectively). Tightly capped with a Teflon-faced silicone septum, the sample was equilibrated at 50 °C for 5 min and extracted for 45 min at the same temperature under stirring at the rotation speed of 250g. After extraction, the fiber was inserted into the injection port of GC for a 5 min desorption. The injector and oven temperatures were identical to those used for GC-MS analysis described previously, and a DB-Wax column was used. All samples were performed in triplicate

Selective ion monitoring (SIM) mass spectrometry was used to quantitate the aroma compounds. The ions monitored of octyl propanoate and L-menthol in the SIM run were m/z 75 and 138, 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 as reported (Table 2).[20]

Liquid−Liquid Microextraction (LLME) for Quantitation of Fatty Acids. Due to the poor adsorption of the DVB/CAR/PDMS fiber to strong polar fatty acids, LLME was used as a separate extraction of these acids. According to the method described by Wang and co-workers,[21] each liquor sample was diluted with boiled ultrapure water

Table 1. Aroma Compounds Identified by GC-O in Three Light Aroma Type Chinese Liquors

no.	aroma compound[a]	descriptor	RI DB-Wax	RI DB-5	fraction[b]	Osme values[c] FJ	BFJ	QKJ
1	ethyl acetate	pineapple	895	589	N	3.83	4.00	2.67
2	1,1-diethoxyethane	fruity	897	721	N	2.17	2.33	3.33
3	3-methylbutanal	green, malty	923	624	N	1.67	1.67	1.83
4	ethyl propanoate	banana	950	697	N	2.67	2.33	2.33
5	ethyl 2-methylpropanoate	fruity	958	750	N	2.83	2.50	2.83
6	2-methylpropyl acetate	fruity	978	776	N	2.33	2.17	2.67
7	2-butanol	fruity	1008		A	1.83	0.33	1.50
8	1-propanol	alcoholic	1027		A	1.83	1.83	1.67
9	ethyl butanoate	pineapple	1028	817	N	2.17	2.83	3.50
10	ethyl 3-methylbutanoate	apple	1064	856	N	2.50	2.33	2.83
11	hexanal	grassy, green	1080	803	N	2.83	2.17	2.50
12	2-methylpropanol	malty	1092	620	A	4.17	3.67	4.00
13	3-methylbutyl acetate	fruity	1112	868	N	2.50	2.83	2.83
14	ethyl pentanoate	apple	1126	913	N	2.17	2.00	2.50
15	1-butanol	alcoholic, solvent	1142	669	N+A	3.00	2.33	2.17
16	3-methylbutanol	malty	1197	789	B+A	3.33	4.00	2.50
17	ethyl hexanoate	fruity	1239	1028	N	2.67	2.83	2.83
18	hexyl acetate	fruity	1248	1021	N	1.83	1.33	1.50
19	1-pentanol	balsamic	1259	763	A	1.83	0.82	0.67
20	1,1,3-triethoxypropane	vegetal	1288	1128	N	1.50	1.33	1.17
21	2-heptanol	fruity	1299	902	A	2.67	2.17	2.00
22	ethyl heptanoate	fruity	1304	1115	N	2.83	2.33	2.83
23	ethyl lactate	fruity	1328	823	N	2.83	2.33	2.17
24	1-hexanol	floral	1350	892	A	2.83	2.50	2.67
25	nonanal	soapy	1361	1121	N	2.17	2.17	2.33
26	2-nonanone	floral	1376		N		1.17	1.33
27	ethyl octanoate	fruity	1413	1203	N	4.17	4.00	4.33
28	3-methylbutyl hexanoate	fruity	1419	1269	N	1.83	1.50	1.33
29	acetic acid	acidic, vinegar	1420	601	A	3.17	2.33	2.33
30	1-heptanol	alcoholic	1448	978	A	1.67	1.17	1.17
31	decanal	oily	1453	1214	N	2.33	2.17	2.17
32	furfural	sweet, almond	1459	840	N+A	2.17	2.50	2.33
33	1-octen-3-ol	mushroom	1469	994	N	2.83	2.67	3.67
34	benzaldehyde	fruity, floral	1497	978	N	2.17	2.33	2.33
35	ethyl nonanoate	fruity	1512	1289	N	2.83	2.33	2.50
36	propanoic acid	vinegar	1520		A	1.67	1.33	1.50
37	ethyl 2-hydroxyhexanoate	floral	1529	1068	N	1.67	1.50	1.50
38	1-octanol	fruity	1530	1090	A	1.83	1.00	1.33
39	2-methylpropanoic acid	sweaty, acidic	1551	792	A	3.67	2.33	3.17
40	2-acetyl-5-methylfuran	nutty, sweet	1587		N	3.50	2.33	2.17
41	butanoic acid	sweaty, acidic	1594	802	A	2.83	2.67	3.33
42	ethyl decanoate	fruity	1602	1398	N	2.67	2.17	2.17
43	phenylacetaldehyde	floral	1617	1052	N	3.83	2.67	3.17
44	ethyl benzoate	fruity	1639	1165	N	3.33	2.67	2.17
45	diethyl butanedioate	fruity	1657	1170	N	2.17	2.17	2.17
46	3-methylbutanoic acid	sweaty, acidic	1660	837	A	3.67	2.50	2.17
47	γ-hexalactone	sweet, coconut	1688		N	1.50		1.67
48	(E,Z)-2,6-nonadienal	green, cucumber	1694	1228	N	1.67	1.33	1.17
49	naphthalene	mothball-like	1715		N	1.67		1.67
50	pentanoic acid	sweaty, rancid	1718		A	2.83	2.17	2.00
51	ethyl undecanoate	fruity	1730		N	1.33	1.33	1.17
52	ethyl phenylacetate	rosy, honey	1772	1254	N	4.50	3.00	2.17
53	2-phenylethyl acetate	floral	1810	1271	N	4.50	2.17	2.50
54	ethyl dodecanoate	fruity	1819	1589	N	1.17	1.33	1.33
55	geosmin	earthy	1820	1450	N	2.33	2.50	2.17
56	β-damascenone	floral, honey	1837	1379	N	4.33	4.67	4.17
57	hexanoic acid	sweaty	1840	971	A	2.50	2.17	2.00
58	benzenemethanol	floral	1864		A	1.83	1.67	1.83
59	ethyl 3-phenylpropanoate	floral	1868	1348	N	3.33	3.67	3.17

Table 1. continued

no.	aroma compound[a]	descriptor	RI		fraction[b]	Osme values[c]		
			DB-Wax	DB-5		FJ	BFJ	QKJ
60	2-phenylethanol	rosy, honey	1902	1132	N+A	4.50	4.67	4.00
61	4-methylguaiacol	smoky	1962	1199	N	2.17	2.50	2.17
62	phenol	phenol, medicinal	2014	991	N+A	2.17	2.17	2.00
63	γ-nonalactone	coconut	2014	1359	N	3.33	3.67	2.67
64	4-ethylguaiacol	clove	2041	1297	A	2.50	2.17	2.17
65	4-methylphenol	animal, horse stable-like	2098		A	2.33	2.33	2.00
66	decanoic acid	sweaty	2274		A	1.67	1.17	1.33

[a]The odorants were identified by comparing their RIs, mass spectra, and aroma attributes with those of standards. [b]The odorants were detected in fraction A, acidic/water-soluble fraction; N, neutral fraction; or B, basic fraction. [c]FJ, *Fenjiu* liquor; BFJ, *Baofeng* liquor; QKJ, *Qingke* liquor.

to a final concentration of 10% ethanol by volume. Eighteen milliliters of diluted liquor sample with 6 μL of IS solution (3.40 mg/L final concentration of 2,2-dimethylpropanoic acid (IS)) was saturated with NaCl and then mixed for 3 min with 1 mL of redistilled diethyl ether. After extraction, 1 μL of extract was injected into the injection port of the GC (250 °C) for analysis. The SIM method was used to quantitate the fatty acids (Table 2). The ion monitored of 2,2-dimethylpropanoic acid was m/z 57. The standard curves for fatty acids were built up as mentioned above.

GC-FID for Quantitation of Some Compounds with High Concentrations. GC-FID was employed for quantitation of ethyl acetate and ethyl lactate, because these two compounds have a high concentration of >1 g/L (Table 2). It was carried out using an Agilent 6890 GC equipped with a FID, modified from the method of ref 22. 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 program 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 mg/L final concentration of pentyl acetate was injected into the GC. The split ratio was 37:1. Injector and detector temperatures were 250 °C. The identification of compounds and the correction factors calculated in 40% ethanol by volume were performed according to ref 22.

Determination of Odor Thresholds. On the basis of the method previously described,[23] the orthonasal thresholds of the odorants were determined by a forced-choice test at seven concentration steps. A certain amount of the odorant in ethanol was pipetted into a Teflon vessel containing 50 mL of hydroalcoholic solution at 46% ethanol by volume, stirred for 2 min, and stepwise diluted (1:3 by volume, with the hydroalcoholic solution). Triangular series including one glass of the dilution and two glasses of hydroalcoholic solution were prepared. All of the series were labeled with random four-digit numbers and presented in decreasing concentrations. A sensory panel consisting of 32 panelists was asked to sniff each triangular series and select the differing one. The minimum concentration that the assessors correctly selected and the maximum concentration incorrectly selected were recorded. The odor threshold of each odorant was calculated by using the formulas described in ref 23. Sensory tests were performed at 21 ± 1 °C in a sensory room, and all of the panelists were national liquor tasters and had prior sensory training in Chinese liquor evaluation.

Aroma Recombination of FJ. A hydroalcoholic solution at 46% ethanol by volume was used as the matrix for recombination. All 27 odorants with OAVs ≥ 1 simultaneously in three liquors were dissolved in the matrix in their natural concentrations (Table 2) and then equilibrated for 10 min at ambient temperature; thus, a complete recombinate was obtained. This recombinate of 20 mL was finally presented in a glass covered with aluminum foil. Besides, a glass of FJ liquor was also prepared for the following sensory evaluation.

Descriptive profile tests were performed by 10 assessors (5 males and 5 females, 32 years old on average), 6 of whom were from the GC-O analysis and the other 4 were laboratory staff members familiar with the sensory attributes of Chinese liquors. All of the assessors were previously trained in orthonasal odor perception and participated

regularly in sensory evaluation. Eight attributes were chosen as the most relevant odor to describe the overall aroma: fruity, floral, acid, earthy, alcoholic, grassy, mushroom, and coconut. The assessors were asked to evaluate the odor intensity of these attributes on a six-point scale from 0 to 5 (same as that described for GC-O analysis). The results obtained from 10 assessors were averaged and finally plotted in a spider web diagram. All of the tests were conducted in a sensory panel room at 20 ± 1 °C.

Omission Experiments. Triangle tests were performed to determine the significance of certain compounds according to the method previously reported.[24] For this purpose, 15 aroma omission models were prepared in the same way as complete recombinate but omitting one or a group of selected components, shown in Table 4. Three samples, including one omission model and two complete recombinates, were presented simultaneously to the assessors. All of the samples (20 mL) were randomly coded, and the assessors were the same people from the descriptive profile tests. The assessors were asked to sniff the samples and determine the differing one. The significance of difference between omission model and complete recombinates was determined according to the method described.[24]

■ RESULTS AND DISCUSSION

Identification of Odor-Active Constituents. By extraction with diethyl ether, an organic phase was obtained, which exactly elicited the typical light type aroma when sniffed by the panelists on a fragrance blotter. Thus, the isolation method used in this study turned out to be appropriate and reliable. For the purpose of facilitating GC-O analysis and compound identification, the extract obtained was further separated into acidic/water-soluble, neutral, and basic fractions to reduce complexity as previously described by Fan and Qian.[5] To identify the constituents responsible for the odors, odor-active areas were first located by GC-O and their RIs on both DB-Wax and DB-5 columns were determined. Besides, mass spectra in EI mode were recorded in the meantime, which were then compared with those available in NIST05a.L (Agilent Technologies, Inc.). To confirm these compounds further, their RIs, mass spectra, and aroma attributes were finally compared to the data obtained from the respective reference compounds.

Following this procedure, a total of 66 aroma compounds were identified in three light aroma type liquors in this study (Table 1). Among them, the highest Osme value of 4.67 was determined for β-damascenone and 2-phenylethanol. 2-Phenylethanol exhibited rosy and honey odors and β-damascenone presented honey and floral aromas. Both of these two compounds were previously reported as important odorants in whiskey, rum, and brandy.[9,12,25] One further compound with an Osme value above 4.00 simultaneously in three liquors was identified as ethyl octanoate, which showed an intense fruity odor. In addition, odorants with somewhat lower Osme values

Table 2. Standard Curves and Concentrations of 47 Odorants in Three Light Aroma Type Chinese Liquors

			standard curve		FJ[a]		BFJ[b]		QKJ[c]	
no.	aroma compound	quantitate ion	slope	intercept	av (µg/L)[d]	RSD[e] (%)	av (µg/L)	RSD (%)	av (µg/L)	RSD (%)
23	ethyl lactate[f,g]				4910	2	1060	2	1020	2
1	ethyl acetate[f,g]				2120	2	2760	8	3230	3
16	3-methylbutanol[g]	70	137	−16.4	514	2	886	9	454	4
2	1,1-diethoxyethane[g]	103	173	−2.38	419	4	214	7	558	4
29	acetic acid[h,g]	60	166	5.13	397	1	415	6	770	3
12	2-methylpropanol[g]	43	1870	−21.1	194	2	392	10	291	5
45	diethyl butanedioate[g]	101	13.1	−2.12	48.7	6	10.4	5	11.8	3
60	2-phenylethanol[g]	91	13.1	−0.79	11.1	2	20.3	9	42.7	3
4	ethyl propanoate	57	46.3	−0.80	9070	5	3070	4	4580	2
39	2-methylpropanoic acid[h]	73	5.27	0.366	7840	6	2030	4	2120	6
42	ethyl decanoate	88	1.06	−0.29	6570	9	7340	7	6820	4
24	1-hexanol	56	28.8	0.192	6300	2	7290	8	6710	2
15	1-butanol	56	29.4	0.624	6160	2	5520	10	10100	2
13	3-methylbutyl acetate	70	56.1	2.58	5870	4	13700	10	14100	3
27	ethyl octanoate	88	15.3	24.9	5040	2	6390	9	19300	3
17	ethyl hexanoate	88	8.24	−0.352	3090	4	5390	9	7680	1
32	furfural	96	109	31.8	2890	7	4370	3	27900	9
57	hexanoic acid[h]	60	27.2	1.89	2610	7	1670	5	1410	4
6	2-methylpropyl acetate	56	34.3	−0.162	2140	4	3500	7	1010	2
9	ethyl butanoate	71	37.9	−0.619	1820	7	3810	2	42800	2
43	phenylacetaldehyde	91	12	2.49	1780	7	535	4	784	2
46	3-methylbutanoic acid[h]	60	29.9	−0.211	1250	4	899	8	496	3
41	butanoic acid[h]	60	46	1.88	969	5	483	5	3320	3
31	decanal	57	5.3	0.036	798	2	253	8	587	3
53	2-phenylethyl acetate	104	0.218	−0.012	793	8	883	4	641	2
5	ethyl 2-methylpropanoate	71	316	−1.40	642	4	2100	7	8580	6
11	hexanal	56	37.1	−0.269	484	2	208	9	813	2
50	pentanoic acid[h]	60	46.5	1.33	416	2	313	2	292	3
35	ethyl nonanoate	88	3.93	−0.16	408	10	267	10	635	2
34	benzaldehyde	106	121	−3.47	354	1	222	8	21600	2
63	γ-nonalactone	85	8.32	0.033	275	6	169	7	324	2
14	ethyl pentanoate	57	73.1	13.6	256	3	498	5	8620	1
52	ethyl phenylacetate	91	0.312	−0.039	222	5	189	4	394	3
61	4-methylguaiacol	123	87.3	0.81	195	9	294	8	nd[i]	
44	ethyl benzoate	105 + 122	8.18	−0.01	190	1	602	7	408	4
59	ethyl 3-phenylpropanoate	104	9.09	−0.198	145	4	201	3	2780	4
62	phenol	94	6.91	0.022	122	3	263	6	103	6
10	ethyl 3-methylbutanoate	88	26.6	7.87	119	9	49.8	9	2870	3
25	nonanal	57	1.33	−0.032	117	2	160	9	287	1
22	ethyl heptanoate	88	13.6	0.021	110	3	53.9	8	245	1
64	4-ethylguaiacol	137	1.03	0.299	104	5	101	2	nd	
33	1-octen-3-ol	57	95.8	−0.129	48.2	5	23.3	5	52.4	5
21	2-heptanol	45	3.29	1.77	42.9	3	5.66	4	56.2	4
65	4-methylphenol	107	3.19	0.052	33.5	4	138	2	nd	
56	β-damascenone	69 + 121	0.192	0.018	19.1	2	28.6	4	11.5	1
40	2-acetyl-5-methylfuran	109	2.79	0.01	16.1	2	39.0	3	nd	
55	geosmin	112	1.29	−0.08	1.10	7	1.22	4	1.17	4

[a]FJ, *Fenjiu* liquor. [b]BFJ, *Baofeng* liquor. [c]QKJ, *Qingke* liquor. [d]av, average concentration of triplicates. [e]RSD, relative standard deviation of the average concentration. [f]These compounds were quantitated by GC-FID method. Correction factors of ethyl acetate and ethyl lactate were 1.47 and 1.54, respectively. [g]The concentration was mg/L. [h]These compounds were quantitated by LLME coupled with GC-MS method. [i]nd, not detected.

were identified as ethyl acetate (pineapple), 2-methylpropanol (malty), 3-methylbutanol (malty), ethyl phenylacetate (rosy and honey), and 2-phenylethyl acetate (floral). With their high Osme values, which were above 4.00 in at least one of the three liquors, these compounds were likely to contribute a lot to the overall light type aroma. However, other odorants, such as 3-methylbutanal (green and malty), 2-butanol (fruity), hexyl acetate (fruity), propanoic acid (vinegar), γ-hexalactone (sweet

and coconut), naphthalene (mothball-like), and benzenemethanol (floral), appeared with lower Osme values below 2.00 in all three liquors. Most of these compounds have been earlier identified as aroma compounds in FJ, as well as in other aroma types of Chinese liquor.[5,8,26] Among them, β-damascenone was detected for the first time in BFJ and QKJ.

Quantitation of Odor-Active Compounds and OAV Analysis. Although GC-O analysis is an effective means for

odorant identification, it could not indicate a final importance of the odorant to the overall aroma. One main reason is the fact that compounds in GC-O analysis were significantly separated and concentrated before sniffing, but in authentic liquors only the odorant present at a concentration above its odor threshold contributes to the overall aroma. Besides, as Grosch[27] reported, the influence of ethanol concentration on the volatility of an odorant should not be ignored. Taking these cases into consideration, the odor activity value (OAV) concept,[28] which correlated quantitative data to odor thresholds in a matrix, was applied to get closer to the liquors themselves.

For this reason, a total of 47 odorants with Osme values of ≥2.00 simultaneously in three liquors were quantitated (Table 2). Among these odorants, ethyl acetate and ethyl lactate, which had been reported as the most abundant odorants in light aroma type liquor,[29] appeared with the highest concentrations as expected. Both of them were >1.00 g/L. Besides, odorants 1,1-diethoxyethane, 2-methylpropanol, 3-methylbutanol, and acetic acid had higher concentrations of 0.1−0.9 g/L. However, two notable odorants, namely, β-damascenone (12−29 μg/L) and geosmin (1.0−1.2 μg/L), were present only in trace amounts, far lower than any other compounds.

To get as close as possible to the authentic liquor, the thresholds of single compounds were determined in a hydroalcoholic solution at 46% ethanol by volume, the typical ethanol content in Chinese liquor. Except that of geosmin, all of these thresholds were determined for the first time. As shown in Table 3, odorants such as ethyl acetate had a fairly high threshold of 32.6 mg/L in 46% vol hydroalcoholic solution. However, thresholds of some compounds present at trace amounts in Chinese liquors were extremely low, such as β-damascenone and geosmin. In this study, β-damascenone was determined with a threshold value of 0.12 μg/L, 10 times higher than that in water.[23] The threshold value of geosmin in 46% vol hydroalcoholic solution was determined at 0.11 μg/L according to the previous study, also 10 times higher than that in water.[1] These data revealed that the higher ethanol concentration in Chinese liquor might lead to a higher threshold than that in water.

Subsequently, OAVs of the odorants in light aroma type liquors were calculated and are summarized in Table 3. The results indicated that altogether 27 odorants were calculated with OAVs > 1 simultaneously in three liquors. These odorants should be the important contributors to the characteristic aroma of light aroma type Chinese liquor. Among these odorants, ethyl octanoate had the highest OAV value, which exhibited an intense fruity aroma. Two odorants, β-damascenone (floral and honey) and 1,1-diethoxyethane (fruity), could also be significant according to their higher OAVs (>100). Other odorants with high OAVs (>10) were 3-methylbutyl acetate, ethyl acetate, ethyl hexanoate, ethyl butanoate, ethyl 2-methylpropanoate, and geosmin. They could also contribute to the overall aroma but to a lesser degree.

Aroma Recombination and Omission Experiments. To confirm that the odorants showing high OAVs were actually the important odorants of light aroma type liquor, aroma recombination and omission experiments based on FJ (the most representative light aroma type liquor in China) were undertaken. For this purpose, an aroma recombinate, consisting of 27 odorants with OAVs ≥ 1 simultaneously in the three liquors in their natural concentrations (Table 2), was prepared.

Table 3. Orthonasal Thresholds and OAVs of 47 Odorants in Three Light Aroma Type Chinese Liquors

			OAV[b]		
no.	aroma compound	odor threshold[a]	FJ	BFJ	QKJ
27	ethyl octanoate	12.9	391	495	1500
2	1,1-diethoxyethane	2090	200	102	267
56	β-damascenone	0.12	159	238	96
1	ethyl acetate	32600	65	85	99
13	3-methylbutyl acetate	93.9	63	146	150
17	ethyl hexanoate	55.3	56	97	139
23	ethyl lactate	128000	38	8	8
9	ethyl butanoate	81.5	22	47	525
11	hexanal	25.5	19	8	32
10	ethyl 3-methylbutanoate	6.89	17	7	417
31	decanal	70.8	11	4	8
5	ethyl 2-methylpropanoate	57.5	11	37	149
55	geosmin	0.11[c]	10	11	11
14	ethyl pentanoate	26.8	10	19	322
33	1-octen-3-ol	6.12	8	4	9
12	2-methylpropanol	28300	7	14	10
43	phenylacetaldehyde	262	7	2	3
42	ethyl decanoate	1120	6	7	6
39	2-methylpropanoic acid	1580	5	1	1
63	γ-nonalactone	90.7	3	2	4
16	3-methylbutanol	179000	3	5	3
29	acetic acid	160000	2	3	5
6	2-methylpropyl acetate	922	2	4	1
15	1-butanol	2730	2	2	4
59	ethyl 3-phenylpropanoate	125	1	2	22
25	nonanal	122	1	1	2
24	1-hexanol	5370	1	1	1
46	3-methylbutanoic acid	1050	1	<1	<1
57	hexanoic acid	2520	1	<1	<1
41	butanoic acid	964	1	<1	3
50	pentanoic acid	389	1	<1	<1
60	2-phenylethanol	28900	<1	<1	1
32	furfural	44000	<1	<1	<1
53	2-phenylethyl acetate	909	<1	<1	<1
64	4-ethylguaiacol	123	<1	<1	
61	4-methylguaiacol	315	<1	<1	
52	ethyl phenylacetate	407	<1	<1	<1
4	ethyl propanoate	19000	<1	<1	<1
65	4-methylphenol	167	<1	<1	
45	diethyl butanedioate	353000	<1	<1	<1
44	ethyl benzoate	1430	<1	<1	<1
35	ethyl nonanoate	3150	<1	<1	<1
34	benzaldehyde	4200	<1	<1	5
21	2-heptanol	1430	<1	<1	<1
22	ethyl heptanoate	13200	<1	<1	<1
62	phenol	18900	<1	<1	<1
40	2-acetyl-5-methylfuran	40900	<1	<1	

[a]Thresholds in 46% volume hydroalcoholic solution detected in this study, μg/L. [b]FJ, *Fenjiu* liquor; BFJ, *Baofeng* liquor; QKJ, *Qingke* liquor. [c]Odor thresholds were taken from ref 1.

Descriptive profile tests were then conducted by a sensory panel consisting of 10 trained assessors, and odor attributes of the recombinate and original liquor were compared. As shown in Figure 1, the aroma profile of the recombinate was in good similarity to that of the original liquor. Consequently, this result indicated the success in simulating the typical aroma of the
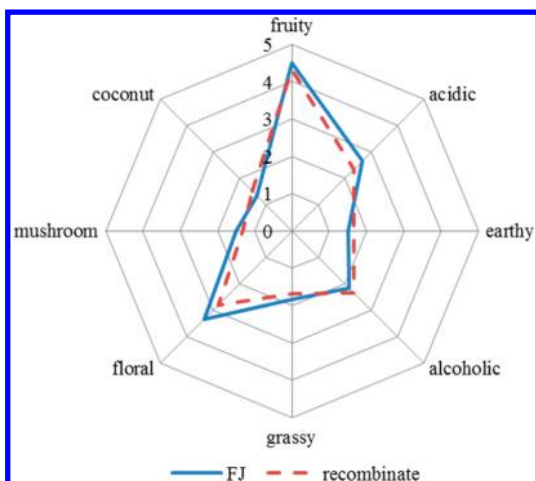
Figure 1. Aroma profile of FJ and the complete aroma recombinate.

investigated liquor by combining 27 odorants in their natural concentrations, using a 46% vol hydroalcoholic solution as the matrix.

To achieve a deeper investigation of the aroma contribution of certain compounds, 15 aroma omission models were prepared by omitting either a single odorant or a group of odorants from the complete recombinate (Table 4). Each of the omission models was presented to the assessors in comparison with the complete recombinate, using a triangle test. The results are shown in Table 4.

Table 4. Omission Experiments from the Complete Recombinate

no.	odorants omitted from the complete recombinate	n^a	significance^b
1	all esters	10	***
1A	ethyl octanoate	4	
1B	ethyl acetate	8	**
1C	ethyl lactate	7	*
1D	ethyl acetate and ethyl lactate	8	**
1E	all esters except ethyl acetate and ethyl lactate	6	
2	1,1-diethoxyethane	5	
3	β-damascenone	9	***
4	aromatic compounds	5	
5	acetic acid and 2-methylpropanoic acid	8	**
6	all alcohols	6	
7	all aldehydes	3	
8	geosmin	8	**
9	γ-nonalactone	3	
10	1-octen-3-ol	2	

^{a}Number of correct judgments from 10 assessors evaluating the aroma difference by means of a triangle test. ^{b}Significance: ***, very highly significant ($\alpha \leq 0.001$); **, highly significant ($\alpha \leq 0.01$); *, significant ($\alpha \leq 0.05$).

In the tests, all assessors were able to detect the omission model lacking the entire group of esters (model 1), thus leading to a very highly significant difference between the omission model and complete recombinate. This result revealed the fairly important role of these fruity note odorants to the overall aroma. Among them, ethyl octanoate was calculated for extremely high OAVs (Table 3), but as omission model 1A revealed, the absence of this compound was correctly detected by only 4 of 10 assessors in triangle tests. Therefore, no

significant difference was determined for its omission compared with the complete recombinate. Thus, this compound was excluded as the most important aroma contributor. Ethyl acetate and ethyl lactate were traditionally regarded as the most potent aroma compounds because of their particularly high concentrations,[29,30] but in our study their OAVs were not so much high. Therefore, several omission models were set up for a deeper investigation. When ethyl acetate and ethyl lactate were omitted together (model 1D), a high significance was evaluated. However, no significant difference was observed when all esters except these two compounds (model 1E) were omitted. This indicated the important role of these two fruity note odorants. Furthermore, when solely lacking ethyl acetate (model 1B), the assessors could detect a highly significant difference, whereas the omission of single ethyl lactate (model 1C) was determined as only significantly different by the assessors. This revealed a slightly more important role of ethyl acetate compared with ethyl lactate. In conclusion, these data indicated that ethyl acetate and ethyl lactate together rather than ethyl octanoate were responsible for the typical fruity note of light aroma type liquor, probably due to their high concentrations, and this finding fitted well with the conclusion previously drawn.[30] As reported previously, esters were formed mainly through esterification of alcohols and fatty acids during the fermentation, distillation, and aging processes.[31,32]

However, another fruity-smelling odorant, 1,1-diethoxy-ethane, should be mentioned, just as the case of ethyl octanoate. Despite its relatively high OAV calculated in Table 3, omission of this compound was detected with no significant difference by the assessors (model 2). This might be due to the very intense fruity note of the esters, which made up for the absence of the single 1,1-diethoxyethane.

An omission model without β-damascenone was evaluated with a very highly significant difference compared to the complete recombinate (model 3), thereby pinpointing the crucial role of this floral- or honey-like-smelling compound for the typical aroma of light aroma type liquor. This result was in accordance with the high OAVs determined for β-damascenone (Table 3). However, no difference of the model lacking in aromatic compounds, which exhibited a floral odor as well, was detected by the assessors (model 4). Consequently, the floral note present in the profile of overall aroma could be greatly linked to β-damascenone rather than the aromatic compounds. β-Damascenone has already been detected in many alcoholic beverages, such as whiskey, wine, and beer.[9,33,34] Researchers have suggested that 3-hydroxy-7,8-dihydro-β-ionol was the key precursor for the formation of β-damascenone through an acid-catalyzed pathway.[35] On the basis of these findings, Poisson and Schieberle[10] assumed that cereals could contain similar precursors leading to the generation of β-damascenone during fermentation and/or distillation.

As shown in Table 4, the omission of acetic acid and 2-methylpropanoic acid (model 5) was rated with a highly significant difference. This elucidated the important role of these two acidic- or vinegar-smelling odorants to the overall aroma. In addition, the omission of the earthy-smelling odorant geosmin (model 8) also resulted in a highly significant difference from the complete recombinate. This compound was previously detected in Chinese liquors by Du and co-workers.[1] However, the model lacking in alcohols (model 6) was not determined as significantly different when compared with the complete recombinate; thus, the alcoholic note from the aroma profile could not be correlated to certain odorants in

this study. Aldehydes mostly showed a grassy or green note; omission of this group of compounds was also determined with no significant difference by the assessors (model 7). The same results also occurred with γ-nonalactone (coconut smelling) and 1-octen-3-ol (mushroom smelling), as shown in models 9 and 10.

To sum up, with all of the findings above taken into account, conclusions can be drawn: (i) Aroma-active compounds in three representative Chinese light aroma type liquors have been successfully identified through GC-O analysis, and 27 odorants were further screened out as the important odorants according to quantitative study and OAV data. (ii) By means of aroma recombination and omission experiments, the typical light type aroma dominated by fruity and floral notes was successfully simulated using these 27 important odorants, and, additionally, ethyl acetate and β-damascenone were demonstrated as the key aroma contributors among them.

A careful literature inspection showed that this study is the first to investigate the key odorants of Chinese light aroma type liquor and to mimic its overall aroma through recombination and omission studies. Although limitations still exist, such as the simplified aroma model matrix that ignores the influence of nonvolatile compositions, our investigation could contribute to a better understanding of Chinese liquor.

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Notes
The authors declare no competing financial interest.

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