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Characterization of Aroma Compounds of Chinese "Wuliangye" and "Jiannanchun" Liquors by Aroma Extract Dilution Analysis

WENLAI FAN AND MICHAEL C. QIAN*

Department of Food Science and Technology, Oregon State University, Corvallis, Oregon 97331

Aroma compounds in Chinese "Wuliangye" liquor were identified by gas chromatography−olfactometry (GC−O) after fractionation. A total of 132 odorants were detected by GC−O in Wuliangye liquor on DB-wax and DB-5 columns. Of these, 126 aromas were identified by GC−mass spectrometry (MS). Aroma extract dilution analysis (AEDA) was further employed to identify the most important aroma compounds in "Wuliangye" and "Jiannanchun" liquors. The results showed that esters could be the most important class, especially ethyl esters. Various alcohols, aldehydes, acetals, alkylpyrazines, furan derivatives, lactones, and sulfur-containing and phenolic compounds were also found to be important. On the basis of flavor dilution (FD) values, the most important aroma compounds in Wuliangye and Jiannanchun liquors could be ethyl butanoate, ethyl pentanoate, ethyl hexanoate, ethyl octanoate, butyl hexanoate, ethyl 3-methylbutanoate, hexanoic acid, and 1,1-diethoxy-3-methylbutane (FD ≥ 1024). These compounds contributed to fruity, floral, and apple- and pineapple-like aromas with the exception of hexanoic acid, which imparts a sweaty note. Several pyrazines, including 2,5-dimethyl-3-ethylpyrazine, 2-ethyl-6-methylpyrazine, 2,6-dimethylpyrazine, 2,3,5-trimethylpyrazine, and 3,5-dimethyl-2-pentylpyrazine, were identified in these two liquors. Although further quantitative analysis is required, it seems that most of these pyrazine compounds had higher FD values in Wuliangye than in Jiannanchun liquor, thus imparting stronger nutty, baked, and roasted notes in Wuliangye liquor.

KEYWORDS: GC−olfactometry; AEDA; Wuliangye; Jiannanchun; Chinese liquors; distillate; aroma compounds; pyrazines

INTRODUCTION

Chinese liquor is a traditional distillate fermented from grains. After the fermentation, the fresh spirit is distilled out and then aged under controlled conditions. The aged distillate is adjusted to the designated ethanol concentration and blended to ensure the quality of finished product (*1*). Chinese liquor has an annual consumption of approximately 4 million kiloliters, creating a sales revenue of 500 billion Chinese Yuan. There is no standard procedure to make Chinese liquor. The traditional manufacturing is more of an art than a science. The raw materials for making Chinese liquor can be quite different depending upon availability and the economics of the raw materials. In general, Chinese liquor is made from sorghum or a mixture of sorghum, wheat, corn, rice, and sticky rice. Rice hull is typically used as the fermentation aide (*1*, *2*).

The saccharifying and fermentation cultures used for Chinese liquor are Daqu, Xiaoqu, or other enzyme preparations. Daqu is the most widely used culture and is made from wheat or a mixture of wheat, barley, and pea. The raw materials of Daqu are typically milled and pressed into a mould of different sizes depending upon the manufacturer. The Daqu is then incubated under controlled conditions. On the basis of the maximum temperature at which the Daqu is incubated, the types of Daqu can be classified into low-temperature Daqu (<45 °C), moderate-temperature Daqu (45−60 °C), and high-temperature Daqu (>60 °C). Daqu is rich in various microorganisms including bacteria, yeast, and fungi (*1*). In addition, complex enzyme systems are accumulated in the finished Daqu (*3*).

The grains used for liquor fermentation are first cooked and then mixed with Daqu powder. The fermentation is typically carried out at 28−32 °C for 60 days under anaerobic conditions in a solid state. After fermentation, the liquor is distilled out with steam and aged in sealed pottery jars to develop the balanced aroma. While most of the liquors are aged for about 1 year, some of them are aged for more than 3 years. The aged liquor is diluted with water and blended to yield an ethanol content of 40−55% (v/v) for constant quality in the finished product.

Because of differences in manufacturing practices, the aroma profiles of various Chinese Daqu liquors are quite different. On the basis of aroma characteristics, Chinese liquor can be classified into strong aroma style, light aroma style, soy sauce aroma style, sweet honey style, and miscellaneous style. Of

* To whom correspondence should be addressed: Department of Food Science and Technology, 100 Wiegand Hall, Oregon State University, Corvallis, OR 97331-6602. Telephone: 541-737-9114. Fax: 541-737-1877. E-mail: michael.qian@oregonstate.edu.

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these, the strong aroma style accounts for about 70% of total liquor production. Strong aroma style liquors typically have strong fruity, pineapple- and banana-like aromas (*4*). Within this category, "Wuliangye" and "Jiannanchun" are two of the most famous brands, followed by "Yanghe Daqu" and a few others.

The volatile composition of Chinese liquor has been studied extensively. Esters, alcohols, acids, aldehydes, ketones, acetals, and heterocyclic compounds are the major classes of compounds. These compounds are largely from the fermentation, distillation, and aging processes. Fan and Xu (*5*) quantified the volatile compounds of Wuliangye and Yanghe Daqu liquors. Among the compounds quantified, the content of ethyl hexanoate was the highest, with a concentration of more than 2 g/L. Several other esters such as ethyl acetate, ethyl butanoate and ethyl 2-methylpropanoate also had high concentrations. In addition to esters, acids such as hexanoic, acetic, butanoic, and 2-hydroxypropanoic acids were also found at high concentrations, along with 1,1-diethoxyethane. 3-Methylbutanol, 2-methylpropanol, 1-butanol, and propanol were the main alcohols. Aldehydes such as acetaldehyde, 1-propanal, 2-methylpropanal, 1-hexanal, and 3-methylbutanal were also detected, but their concentrations were relatively low in these liquors.

Very few studies have reported the aroma compounds in Chinese liquor that are odor-active or present at concentrations above the sensory threshold. Using the gas chromatography−olfactometry (GC−O) technique, Fan and Qian (*6*, *7*) have identified more than 70 odor-active compounds in Yanghe Daqu liquor. The results show that Yanghe Daqu liquor aroma is mainly contributed by esters and fatty acids. Ethyl butanoate, ethyl pentanoate, ethyl hexanoate, ethyl octanoate, and 3-methylethyl hexanoate are the most important aroma compounds in Yanghe Daqu liquor. In addition, methyl hexanoate, ethyl heptanoate, ethyl benzoate, and butyl hexanoate are also very important because of their high flavor dilution (FD) values.

Although Wuliangye and Jiannanchun are the two most popular liquors in China, the aroma compounds in these liquors have not been investigated yet. Compared to Yanghe Daqu liquor, Wuliangye and Jiannanchun liquors have more soy sauce and roasted characters. The flavor difference can be caused by many factors such as the raw ingredients used in the fermentation, fermentation conditions, distillation practices, and aging processes. Although Wuliangye, Jiannanchun, and Yanghe Daqu liquors are all made from sorghum, rice, sticky rice, wheat, and corn, the proportion of these raw materials will vary for each liquor. The key fermentation starter, Daqu, is also made differently. The Daqus of Wuliangye and Jiannanchun are produced from wheat, while the Daqu of Yanghe is made from a mixture of wheat, barley, and peas. Furthermore, differences in the environment, especially temperature and humidity, play an important role in the selection of microorganisms used for fermentation. As a result of these multiple variations, Wuliangye, Jiannanchun, and Yanghe Daqu all have unique aroma profiles (*1*, *5*). The objective of this study was to identify the odor-active compounds in Wuliangye liquor by normal-phase fractionation and GC−O and to examine the most important aroma compounds in both Wuliangye and Jiannanchun liquors using aroma extract dilution analysis (AEDA). It is expected that the findings of this research will help to better understand the aroma chemistry of these two famous Chinese liquors.

MATERIALS AND METHODS

Chemicals. Methyl hexanoate, ethyl octanoate, ethyl nonanoate, ethyl decanoate, heptanoic acid, and octanoic acid were from Eastman (Rochester, NY). Ethyl 2-methylpropanoate, propyl hexanoate, pentyl hexanoate, hexyl hexanoate, 2-methylpropyl acetate, 2-methylpropyl hexanoate, and 3-methylbutyl pentanoate were obtained from K and K Laboratories (Plainview, NY). 2-Pentanol and ethyl 2-hydroxypropanoate were from Matheson Coleman and Bell (East Rutherford, NJ). Ethyl benzoate was obtained from EKC, Inc. (Rosemont, IL). Phenol was purchased from EMD Chemical, Inc. (Gibbstown, NJ). The rest of the aroma standards were obtained from Sigma−Aldrich (St. Louis, MO). Pentane was from Mallinckrodt Baker, Inc. (Phillipsburg, NJ). Diethyl ether was obtained from Burdick and Jackson (Muskegon, MI). Sodium sulfate anhydrous was from EMD Chemicals, Inc. (Gibbstown, NJ). Sodium chloride, sodium bicarbonate, and sulfuric acid were obtained from Sigma−Aldrich (St. Louis, MO). Ethanol, absolute-200 proof, was purchased from AAPER Alcohol and Chemical Co. (Shelbyville, KY).

Synthesis of Esters. 3-Methylbutyl butanoate, 3-methylbutyl pentanoate, 3-methylbutyl octanoate, pentyl 3-methylbutanoate, heptyl hexanoate, 2-phenylethyl butanoate, and 2-phenylethyl hexanoate were individually synthesized by reacting their respective acids and alcohols (*6*). Each acid (600 μL) was mixed with 2 mL of alcohol in a 20 mL vial. The reactions were catalyzed by acid (1 N H_2SO_4, 500 μL) at 100 °C for 1 h, after which the mixture was cooled and mixed with 5 mL of saturated NaCl solution. The esters were extracted with 5 mL of Freon 11 in a separatory funnel, and 1 μL of extract was analyzed by GC−mass spectrometry (MS) (split ratio of 100:1) for confirmation of ester identity.

Synthesis of Acetals. 1,1-Diethoxy-2-methylpropane, 1,1-diethoxy-2-methylbutane, 1,1-diethoxy-3-methylbutane, 1,1-diethoxypropane, 1,1-diethoxyhexane, 1,1-diethoxynonane, and 1,1-diethoxy-2-phenylethane were synthesized by reacting 2-methylpropanal, 2-methylbutanal, 3-methylbutanal, propanal, hexanal, nonanal, and phenylacetaldehyde, respectively, with ethanol under acidic conditions (*6*, *8*). Each aldehyde (600 μL) was mixed with 2 mL of ethanol plus 2 mL of 1 N H_2SO_4. The mixture was stirred at 58 °C for 1 h. After cooling, 50 mL of saturated NaCl solution was added to the reaction mixture, and the product was extracted with 10 mL of Freon 11 in a separatory funnel. Each acetal solution (1 μL) was analyzed by GC−MS (split ratio of 100:1) for identification.

Liquors. Wuliangye liquor (500 mL, 52% ethanol by volume) was bottled on September 7, 2004, at Wuliangye Co. Ltd. in Yibin City, Sichuan Province, China. Jiannanchun liquor (500 mL, 52% ethanol by volume) was bottled on October 26, 2004, at Jiannanchun Chiew Distillery Co. Ltd. in Mianzhu City, Sichuan Province, China. Both samples were procured commercially in China and shipped to the US, where the samples were stored at −15 °C until analysis.

Identification of Aroma Compounds in Wuliangye Liquor by Fractionation and GC−O Analysis. *Aroma Extraction.* Wuliangye liquor was extracted using the same procedure as described previously (*6*). A total of 100 mL of liquor sample was diluted to 14% ethanol by volume with deodorized water (deionized water was boiled for 5 min and then cooled to room temperature). The diluted liquor sample was saturated with analytical-grade sodium chloride and extracted 3 times with 100 mL aliquots of freshly distilled diethyl ether in a separatory funnel. All extracts were combined and slowly concentrated to 50 mL under a gentle stream of nitrogen. This was labeled as "extract 1".

Acidic/Water-Soluble Fractionation. To facilitate GC−O and GC−MS analysis, the aroma extract of liquor was separated into acidic/water-soluble, neutral, and basic fractions, using a modified method of Qian and Reineccius (*9*). Freshly distilled pentane and deodorized water, 50 mL each, were added to "extract 1". The aqueous phase was adjusted to pH 9.0 with sodium bicarbonate solution (10%, w/v), then separated in a separatory funnel, and saved. The organic phase was washed twice with 10 mL of deodorized water. The washings were combined with the aqueous phase. The organic phase was labeled "extract 2".

The aqueous phase was further adjusted to pH 2 with 2 N H_2SO_4, saturated with NaCl, and then extracted twice with 20 mL aliquots of freshly distilled diethyl ether. The extracts were combined and dried with 5 g of anhydrous sodium sulfate overnight. The dried solution was filtered and then slowly concentrated to a final volume of 200 μL under a gentle stream of nitrogen. This concentrate was labeled as the "acidic/water-soluble fraction" for further GC−O analysis.

Basic Fraction. A total of 50 mL of deodorized water was added to "extract 2". The aqueous phase was adjusted to pH 1.3 with 2 N H_2SO_4, saturated with NaCl, and then separated in a separatory funnel. The organic phase was labeled "extract 3" and saved. The aqueous phase was then adjusted to pH 10 with sodium bicarbonate solution (10%, w/v) and then extracted twice with 30 mL of freshly distilled diethyl ether. The organic phase was combined and dried with 5 g of anhydrous sodium sulfate overnight. The extract was filtered and slowly concentrated to 200 μL under a gentle stream of nitrogen. This extract was labeled as the "basic fraction".

Neutral Fraction. The "extract 3" was dried with 5 g of anhydrous sodium sulfate overnight. The extract was filtered and slowly concentrated to 200 μL under a gentle stream of nitrogen. This extract was labeled as the "neutral fraction".

GC−O Analysis. GC−O analysis was performed on a Hewlett−Packard 5890 GC equipped with a flame ionization detector (FID) and an olfactometer. The column carrier gas was nitrogen, at a constant pressure (2 mL/min, column flow measured at 25 °C). Half of the column flow was directed to the FID, while the other half was directed to the olfactometer. The samples were analyzed on a DB-wax column (30 m × 0.32 mm i.d., 0.25 μm film thickness; J&W Scientific, Folsom, CA) and on a DB-5 column (30 m × 0.32 mm i.d., 1 μm film thickness; J&W Scientific). Each concentrated fraction (1 μL) was injected with a split ratio of 1:1. The oven temperature was held at 40 °C for 2 min, then raised to 230 °C at a rate of 4 °C/min, and held at 230 °C for 15 min on the DB-wax column, while the final temperature was 250 °C for 15 min on the DB-5 column. Injector and detector temperatures were 250 °C.

All of the fractionations were analyzed in duplicate by a well-trained panelist. Both the aroma descriptor and intensity were recorded. The perceived aroma intensity was relatively scaled as "very strong", "strong", "moderate", "weak", and "very weak". Aroma intensity was reported as "strong" if one of the two analyses detected it as "strong".

AEDA of Wuliangye and Jiannanchun Liquors. A total of 40 mL of liquor sample of either Wuliangye or Jiannanchun was diluted to 14% ethanol by volume with deodorized water to reduce the extraction of ethanol. The diluted liquor sample was saturated with NaCl and extracted with diethyl ether as described previously. The aroma extract was fractionated into the acidic/water-soluble fraction and the neutral/basic fraction. Both fractions were dried with 5 g of anhydrous sodium sulfate overnight. The extract was filtered and then concentrated to a final volume of 200 μL under a gentle stream of nitrogen.

Each concentrated fraction was diluted stepwise with diethyl ether using a series of 1:1 dilution, and each dilution was then analyzed by AEDA using the same GC conditions as above. The FD factors were determined for the odor-active compounds in each sample (*10*). Two panelists (both male), were selected for the AEDA study. One panelist had more than 5 years of sensory analysis experience in Chinese liquor, and the other was a student in the Department of Food Science and Technology at Oregon State University. Both panelists had previous GC−O experience and completed more than 30 h of training for GC−O analysis of Chinese liquors prior to the AEDA analysis. Each sample was analyzed in duplicate where the aroma descriptors and corresponding retention times were recorded by each panelist for each GC column. When a volatile compound was detected at least twice, this analyte was determined to be an aroma compound. These aroma compounds were cross-referenced with fractionation results for confirmation.

GC−MS Analysis. Identification was carried out using an Agilent 6890 GC coupled to an Agilent 5973 mass selective detector (MSD). Each concentrated fraction (1 μL) was analyzed on a DB-wax column (30 m × 0.25 mm i.d., 0.25 μm film thickness; J&W Scientific) and on a DB-5 column (30 m × 0.32 mm i.d., 0.25 μm film thickness; J&W Scientific). The oven and injector temperatures were identical to those of GC−O and AEDA analysis, described above. 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. Mass spectra of unknown compounds were compared with those in the Wiley 275.L Database (Agilent Technologies, Inc.). Retention indices (RIs) of unknown compounds were calculated in accordance with a modified Kovats method (*11*). Positive identification was achieved by comparing mass spectra, aromas, and RIs of the standards. Tentative identification was achieved by comparing aroma or mass spectra only.

RESULTS AND DISCUSSION

Synthesis of Some Esters and Acetals. Several esters and acetals were not available commercially; therefore, they were synthesized to provide a reference for positive identification. Esters were synthesized from corresponding alcohols and acids under acidic condition. After the reaction, the excess alcohols were washed out with water and the esters were extracted with Freon 11. Similarly, the acetals were synthesized by reacting excess ethanol with corresponding aldehydes under acidic conditions and then extracted with Freon 11. The synthesized esters and acetals were analyzed by GC−MS. The retention index and mass spectra of synthesized compounds are listed in **Table 1**.

Aroma Fractionation and GC−O of Wuliangye Liquor. To facilitate the identification of aromas, the extract of Wuliangye liquor was separated into three fractions: acidic/water-soluble, basic, and neutral. GC−O and GC−MS were performed on each fractionation. Because only one person performed the GC−O analysis, this approach cannot provide accurate odor intensity results. However, it can provide information of the aroma quality of the compounds, as well as positive MS identification because the fractionation process greatly reduced the complexity of each fraction. A total of 126 aroma compounds from Wuliangye liquor (15 in the basic fraction, 77 in the neutral fraction, and 44 in the acidic/water-soluble fraction) were identified by GC−O and GC−MS (**Tables 2−4**). In addition, 6 aroma compounds, unknown, were detected by GC−O but could not be identified by GC−MS.

The acidic/water-soluble fraction mainly consisted of fatty acids, alcohols, and phenolic compounds (**Table 2**). Hexanoic acid could be an important aroma contributor in this fraction based on its GC−O intensity of very strong. Among the alcohols, 3-methylbutanol had the highest aroma intensity detected by GC−O on the DB-wax column and was also identified in the basic and neutral fractions (intensity of moderate and strong, respectively) because of its high concentration and incomplete fractionation. 1-Pentanol, 2-phenylethanol, butanoic acid, 3-methylbutanoic acid, phenol, and 2-furancarboxaldehyde (furfural) had moderate intensities. Several alcohols, acids, and phenolic compounds identified in the acidic/water-soluble fraction had weaker intensities, including 1-butanol and acetic, propanoic, pentanoic, 4-methylpentanoic, heptanoic, and nonanoic acids (all with weak intensities), along with 4-ethylguaiacol, 4-methylphenol, 4-ethylphenol, and benzoic, phenylacetic, and phenylpropanoic acids (all with very weak intensities). Phenol and 4-methylphenol were also identified in this fraction.

The basic fraction mainly consisted of alkylpyrazines. In this fraction, only one alkylpyrazine, 2-ethyl-6-methylpyrazine, had a moderate intensity (**Table 3**). 2,3,5-Trimethylpyrazine had a weak intensity. Others had very weak intensities, including 2,6-dimethylpyrazine, 2,6-diethylpyrazine, 2,5-dimethyl-3-ethylpyrazine, 2,3,5,6-tetramethylpyrazine, 2,3,5-trimethyl-6-ethylpyrazine, 5-ethyl-2,3-dimethylpyrazine (tentatively identified), 3,5-dimethyl-2-butylpyrazine (tentatively identified), and 3,5-dimethyl-2-pentylpyrazine (tentatively identified). 2-Furanmethanol, although not a basic compound, was identified in this fraction and had a moderate intensity. In addition, 2-acetyl-6-methylpyridine was detected in this fraction, which is the first report of this compound in Chinese liquor.

The neutral fraction had the most complexity among the three fractions. It consisted of esters, acetals, sulfur-containing

Table 1. Retention Indices and Mass Spectra of Synthesized Aroma Compounds

synthesized compounds	RI_{wax}	RI_{DB-5}	mass spectrum (*m*/*z* %)
1,1-diethoxy-2-methylpropane	969	859	103 (100), 47 (94), 73 (79), 75 (68), 101 (50), 57 (47), 29 (40), 43 (39), 55 (35), 27 (23), 28 (23), 31 (23), 41 (19), 45 (19), 72 (16), 100 (13)
1,1-diethoxy-2-methylbutane	1063	953	103 (100), 47 (72), 75 (60), 20 (47), 45 (44), 71 (43), 28 (40), 41 (37), 115 (37), 57 (30), 43 (25), 31 (20), 70 (19), 69 (17), 27 (16), 87 (16), 55 (14), 99 (12), 59 (12), 114 (10)
1,1-diethoxy-3-methylbutane	1068	955	47 (100), 103 (94), 75 (63), 69 (56), 115 (41), 43 (28), 71 (25), 41 (24), 29 (22), 87 (10)
1,1-diethoxypropane	950	812	59 (100), 29 (97), 31 (68), 47 (64), 87 (60), 27 (60), 103 (43), 75 (33), 28 (26), 45 (20), 57 (18), 41 (17), 58 (14), 26 (13), 43 (12)
1,1-diethoxyhexane	1238	1092	103 (100), 47 (44), 129 (42), 75 (38), 83 (37), 55 (28), 29 (21), 57 (13), 41 (10), 43 (10)
1,1-diethoxynonane	1498	1382	103 (100), 57 (34), 85 (27), 75 (25), 171 (23), 69 (21), 47 (21), 29 (19), 43 (13), 55 (13), 83 (13), 41 (12)
1,1-diethoxy-2-phenylethane	1690	1328	103 (100), 91 (59), 75 (54), 47 (52), 29 (28), 121 (20), 31 (16), 120 (15), 149 (15), 27 (13), 65 (13), 148 (12)
3-methylbutyl butanoate	1255	1056	57 (100), 85 (77), 56 (76), 43 (62), 41 (55), 29 (55), 103 (43), 27 (23), 60 (22), 39 (13), 87 (12), 42 (12), 55 (12), 28 (11), 15 (10), 61 (10)
3-methylbutyl pentanoate	1346	1152	70 (100), 85 (58), 43 (53), 57 (42), 55 (37), 41 (31), 29 (20), 71 (19), 42 (12), 103 (11)
pentyl 3-methylbutanoate	1350	1155	43 (100), 85 (92), 70 (89), 57 (76), 41 (75), 103 (75), 42 (49), 29 (41), 55 (33), 27 (30), 87 (24), 60 (22), 39 (21), 61 (18), 71 (16), 69 (12), 56 (10), 102 (10)
3-methylbutyl octanoate	1606	1446	70 (100), 99 (54), 43 (48), 71 (42), 55 (24), 117 (14), 41 (13), 42 (10)
heptyl hexanoate	1683	1482	43 (100), 117 (96), 56 (80), 99 (76), 57 (73), 70 (67), 41 (61), 98 (61), 55 (48), 29 (38), 69 (37), 28 (36), 71 (32), 61 (29), 42 (28), 27 (23), 73 (15), 60 (14), 39 (13), 68 (10)
2-phenylethyl butanoate	1958	1447	104 (100), 43 (15), 71 (11), 105 (8)
2-phenylethyl hexanoate	2160	1649	104 (100), 43 (47), 105 (40), 99 (27), 71 (22), 91 (5)

compounds, lactones, pyrrole derivatives, aldehydes, and ketones (**Table 3**). In this fraction, ethyl butanoate, ethyl pentanoate, ethyl hexanoate, and 1,1-diethoxy-3-methylbutane had very strong intensities by GC−O. Several other aroma compounds had strong intensities, including ethyl 2-methylpropanoate, ethyl 3-methylbutanoate, 3-methylbutanol, and butyl hexanoate. Ethyl acetate, ethyl heptanoate, ethyl octanoate, ethyl cyclohexanecarboxylate, ethyl 3-phenylpropanoate, methyl hexanoate, hexyl hexanoate, 2-methylpropyl acetate, 2-furancarboxaldehyde, 2-furanmethanol, 1,1-diethoxyethane, and 1,1-diethoxy-2-methylbutane had moderate aroma intensities. Three sulfur-containing compounds, which had weak intensities, were detected in this fraction: dimethyl sulfide (tentatively identified), dimethyl disulfide, and dimethyl trisulfide. A few aldehydes were detected in this fraction, but they had weak or very weak intensities. γ-Octalactone, γ-nonalactone, γ-decalactone, and γ-dodecalactone, along with 2-acetylpyrrole, were also identified and had very weak intensities.

AEDA Analysis of Wuliangye and Jiannanchun Liquors. The aroma extracts were fractionated into acidic/water-soluble and neutral/basic fractions for AEDA analysis. Because the basic fraction had only a few aroma compounds and they had been positively identified by both GC−O and GC−MS, it was combined with the neutral fraction. The two fractions were diluted stepwise with diethyl ether using a series of 1:1 dilution, and each dilution was analyzed by GC−O. The acidic/water-soluble fraction was analyzed on the DB-wax column, while the neutral/basic fraction was analyzed on both the DB-wax and DB-5 columns because of the complex composition of Chinese liquors. The FD factors were determined for the odor-active compounds in each sample as described by Grosch (*10*).

Many compounds were identified including various acids, alcohols, esters, acetals, pyrazines, and many others. Fatty acids were detected by AEDA in the acidic/water-soluble fraction on the DB-wax column (**Table 2**). Hexanoic acid was probably the most important compound among the fatty acids based on its very high FD value (FD ≥ 1024). Butanoic, 3-methylbutanoic, and pentanoic acids were very important (FD ≥ 128) while acetic, propanoic, 4-methylpentanoic, and heptanoic acids had moderate FD values (FD ≥ 16). Acetic and propanoic acids gave acidic and vinegar odors, while butanoic, 3-methylbutanoic, pentanoic, 4-methylpentanoic, hexanoic, and heptanoic acids contributed to cheesy, rancid, sweaty, and sour aromas. These acids also exist in Yanghe Daqu liquors (*6*, *7*). Wuliangye, Jiannanchun, and Yanghe liquors are produced through solid-state fermentation; the fermentor is made of clay, and the inside is usually coated with a layer of mud comprised of clay, spent grains, and bean cake powder. After repeated use, the fermentors gradually mature and will contain a diversity of microorganisms, including butanoic and hexanoic acid-producing bacteria, on the inside of the fermentor (*5*, *12*). These microorganisms will effectively produce organic acids. In addition, the cooked grains are fermented in an open system, allowing for extensive generation of short-chain free fatty acids (*4*, *6*).

As expected with any alcoholic beverage, alcohols were among the major volatile compounds. During fermentation, yeast can form alcohols from sugars under aerobic conditions and from amino acids under anaerobic conditions (*13*). A small amount of alcohols can also be made by yeast through the chemical reduction of corresponding aldehydes (*14*). Although alcohols are typically separated into the neutral fraction, their high concentrations in alcoholic beverages interfere with the identification of other neutral compounds. Therefore, it is desirable to separate them into the acidic/water-soluble fraction to be analyzed simultaneously with the acids (*9*) (**Table 2**). Most alcohols have high sensory thresholds and impart fruity, floral, and alcohol-like aromas. 3-Methylbutanol, with a fruity and nail-polish-like odor, could be the most important among alcohols because of its FD value (FD ≥ 128). However, because of its high concentration, 3-methylbutanol could not be completely fractionated into the acidic/water-soluble fraction and could be smelled in the neutral/basic fraction where its FD was greater

Table 2. Aroma Compounds in Acidic/Water-Soluble Fraction Detected by GC–O on a DB-Wax Column

RI	aroma compounds	descriptor	basic of identification[b]	GC–O intensity[c]	FD factor[a]	
					WLY	JNC
1020	2-butanol	fruity	MS, aroma, RI	VW	1	ND
1035	1-propanol	alcoholic, fruity	MS, aroma, RI	VW		
1087	2-methylpropanol	wine, solvent	MS, aroma, RI	VW	4	1
1114	2-pentanol	fruity, alcoholic	MS, aroma, RI	VW	8	ND
1137	1-butanol	pungent, alcoholic	MS, aroma, RI	W	64	128
1201	3-methylbutanol	fruity, nail polish	MS, aroma, RI	S	256	128
1210	2-hexanol	fruity	MS, aroma, RI	VW		
1268	1-pentanol	fruity, balsamic	MS, aroma, RI	M	128	128
1304	3-hydroxy-2-butanone	buttery	MS, aroma, RI	VW		
1318	2-heptanol	fruity	MS, aroma, RI	VW	2	2
1341	1-hexanol	floral, green	MS, aroma, RI	VW	8	32
1424	acetic acid	acidic, vinegar	MS, aroma, RI	W	32	8
1442	2-(diethoxymethyl)furan[d]	roasted	MS, aroma	VW		
1443	1-heptanol	fruity, alcoholic	MS, aroma, RI	VW		
1456	2-furancarboxaldehyde	sweet, almond	MS, aroma, RI	M	128	2
1474	2-ethyl-1-hexanol	rosy, green	MS, aroma, RI	VW	8	16
1525	propanoic acid	vinegar	MS, aroma, RI	W	16	8
1539	1-octanol	fruity	MS, aroma, RI	VW		
1555	2-methylpropanoic acid	acid, rancid	MS, aroma, RI	VW	2	2
1602	butanoic acid	rancid, cheesy	MS, aroma, RI	M	512	512
1647	2-furanmethanol	burnt sugar	MS, aroma, RIL	VW	8	ND
1655	3-methylbutanoic acid	rancid, acidic	MS, aroma, RI	M	256	128
1659	2-methylbutanoic acid	cheesy, rancid	MS, aroma, RI	VW		
1727	pentanoic acid	sweaty, rancid	MS, aroma, RI	W	64	128
1764	2-methylpentanoic acid	sweaty, rancid	MS, aroma, RIL	VW		
1820	4-methylpentanoic acid	sweat, sour	MS, aroma, RI	W	16	8
1846	hexanoic acid	sweaty, cheesy	MS, aroma, RI	VS	512	1024
1872	benzenemethanol	floral	MS, aroma, RI	VW		
1906	2-phenylethanol	rosy, honey	MS, aroma, RI	M	128	128
1914	5-methylhexanoic acid[d]	cheesy, sweaty	MS, aroma	VW		
1955	heptanoic acid	sweaty	MS, aroma, RI	W	64	8
2007	phenol	phenol, medicinal	MS, aroma, RI	M	128	32
2031	4-ethylguaiacol	clove, spicy	MS, aroma, RI	VW	1	64
2060	octanoic acid	sweaty, cheese	MS, aroma, RI	VW	2	8
2080	4-methylphenol	animal, phenol	MS, aroma, RI	VW	4	32
2168	nonanoic acid	fatty	MS, aroma, RI	VW		
2185	4-ethylphenol	smoky	MS, aroma, RI	VW	2	8
2282	decanoic acid	fatty	MS, aroma, RI	VW		
2449	benzoic acid	fruity, cherry	MS, aroma, RI	VW		
2550	phenylacetic acid	fruity, rosy	MS, aroma, RI	VW		
2603	phenylpropanoic acid[d]	floral, fruity	MS, aroma	VW		

[a] WLY, Wuliangye liquor; JNC, Jiannanchun liquor; and ND, not detected by GC–O. [b] MS, compounds were identified by MS spectra; aroma, compounds were identified by the aroma descriptors; RI, compounds were identified by a comparison to the pure standard; and RIL, compounds were identified by a comparison with the retention index from the literatures. [c] VS, very strong; S, strong; M, moderate; W, weak; and VW, very weak. [d] Tentatively identified.

than 128 (**Table 3**). 1-Butanol and 1-pentanol had very high FD values (FD ≥ 128), while 1-hexanol and 2-ethyl-1-hexanol also contributed to the overall aroma because of their moderate FD values (FD ≥ 16). 2-Ethyl-1-hexanol, with a rosy green odor, has also been detected in freshly distilled Calvados and Cognac (*8*). 2-Phenylethanol was detected in both liquors (FD ≥ 128). This compound gave rosy and honey aromas and can be produced by yeast (*13*, *15*). Benzenemethanol was also detected by GC−O, but it had a very low intensity.

Esters, which were found in the neutral/basic fraction, were the most abundant aroma compounds in the Wuliangye and Jiannanchun liquors, with ethyl esters dominating this class. On the basis of the FD values detected on the DB-wax and DB-5 columns (**Tables 3** and **4**), ethyl butanoate, ethyl pentanoate, ethyl hexanoate, ethyl octanoate, ethyl 3-methylbutanoate, and butyl hexanoate could be extremely important odorants (FD ≥ 1024) in both liquors. These esters have also been identified as the most potent aromas in Yanghe Daqu liquors (*6*, *7*). Ethyl acetate, ethyl heptanoate, ethyl 2-methylpropanoate, methyl hexanoate, propyl hexanoate, hexyl hexanoate, and 2-methylpropyl acetate were of high importance because of their high FD values (FD ≥ 128) in the Wuliangye and Jiannanchun liquors. Ethyl propanoate, ethyl decanoate, ethyl 2-methylbutanoate, hexyl acetate, 3-methylbutyl butanoate, 3-methylbutyl hexanoate, and 2-methylpropyl hexanoate could also contribute to the aroma of both liquors but to a lesser degree (FD ≥ 16). All of these esters have been detected in Yanghe Daqu liquors (*6*, *7*). In addition, some long-chain esters were identified by GC−MS in these liquors, including ethyl hexadecanoate, ethyl 9-octadecenoate, and ethyl 9,12-octadecadienoate, all of which had high concentrations but were not detected by GC−O. Esters seemed to be the most important aroma compounds for strong aroma style Chinese liquor and contributed to the pleasant fruity, floral, pineapple-, apple-, and banana-like aromas.

Some hydroxy fatty acid esters were identified in both liquors (**Tables 3** and **4**). Among these esters, ethyl 2-hydroxypropanoate, ethyl 2-hydroxyhexanoate, and ethyl 2-hydroxy-3-methylbutanoate gave fruity, floral, and jasmine aromas and could have some importance to the aroma because of their FD values (FD ≥ 16). These hydroxy esters have been detected in Chinese liquor (*6*, *7*) and freshly distilled Calvados and Cognac (*8*, *14*). Hydroxy esters are formed from the esterification of corresponding hydroxy fatty acids, which could be produced from the reduction of keto acids. 2-Hydroxypropanoic acid

Table 3. Aroma Compounds in Neutral/Basic Fraction Detected by GC–O on a DB-Wax Column

RI	aroma compounds	descriptor	basic of identification[b]	GC–O intensity[c]	FD factor[a]	
					WLY	JNC
892	ethyl acetate	pineapple	MS, aroma, RI	M(N)	256	256
892	1,1-diethoxylethane	fruity	MS, aroma, RI	M(N)	256	256
911	2-methylbutanal	green	MS, aroma, RI	VW(N)		
915	3-methylbutanal	green, malty	MS, aroma, RI	W(N)	16	8
929	dimethyl sulfide[d]	cooked onion, sulfur	aroma, RI	W(N)	32	2
950	1,1-diethoxypropane	fruity	MS, aroma, RIS	VW(N)		
953	ethyl propanoate	banana, fruity	MS, aroma, RI	W(N)	64	8
961	ethyl 2-methylpropanoate	fruity, sweet	MS, aroma, RI	S(N)	512	32
969	1,1-diethoxy-2-methylpropane	fruity	MS, aroma, RIS	VW(N)	2	32
972	2-pentanone	fruity	MS, aroma, RI	VW(N)		
988	2-methylpropyl acetate	floral, fruity	MS, aroma, RI	M(N)	256	8
1031	ethyl butanoate	pineapple	MS, aroma, RI	VS(N)	2048	2048
1045	ethyl 2-methylbutanoate	berry, fruity	MS, aroma, RI	W(N)	32	64
1060	ethyl 3-methylbutanoate	apple	MS, aroma, RI	S(N)	512	1024
1061	dimethyl disulfide	onion, cabbage	MS, aroma, RI	W(N)	16	8
1063	1,1-diethoxy-2-methylbutane	fruity	MS, aroma, RIS	M(N)	32	8
1068	1,1-diethoxy-3-methylbutane	fruity	MS, aroma, RIS	VS(N)	4096	1024
1073	1-hexanal	apple, green grass	MS, aroma, RI	VW(N)		
1128	ethyl pentanoate	apple	MS, aroma, RI	VS(N)	2048	512
1102	3-methylbutyl acetate	fruity	MS, aroma, RI	VW(N)		
1137	1-butanol	pungent, alcoholic	MS, aroma, RI	VW(N)		
1178	methyl hexanoate	floral, fruity	MS, aroma, RI	M(N)	128	32
1182	unknown	fruity, floral		W(N)	64	64
1201	3-methylbutanol	fruity, nail polish	MS, aroma, RI	S(N), M(B)	128	32
1235	ethyl hexanoate	fruity, floral, sweet	MS, aroma, RI	VS(N)	8192	4096
1254	hexyl acetate	fruity, floral	MS, aroma, RI	VW(N)	4	32
1255	3-methylbutyl butanoate	floral, fruity	MS, aroma, RIS	W(N)	16	16
1288	unknown	fruity		W(N)	32	32
1291	1,1,3-triethoxypropane	fruity, vegetal	MS, aroma, RIL	W(N)	16	2
1293	propyl hexanoate	pineapple, sweet	MS, aroma, RI	W(N)	32	128
1310	ethyl heptanoate	fruity	MS, aroma, RI	M(N)	32	256
1330	2,6-dimethylpyrazine	nutty	MS, aroma, RI	VW(B)	2	32
1334	ethyl 2-hydroxypropanoate	fruity	MS, aroma, RI	W(N)	32	16
1341	1-hexanol	floral, green	MS, aroma, RI	VW(N)		
1360	dimethyl trisulfide	sulfur, rotten cabbage	MS, aroma, RI	W(N)	64	64
1368	2-hydroxy-3-pentanone	floral, fruity	MS, aroma, RIL	VW(N)		
1373	2-methylpropyl hexanoate	apple, sweet	MS, aroma, RI	W(N)	32	64
1375	2-ethyl-6-methylpyrazine	nutty, roasted	MS, aroma, RI	M(B)	128	4
1384	butyl hexanoate	pineapple, fruity	MS, aroma, RI	S(N)	1024	2048
1388	hexyl butanoate	fruity	MS, aroma, RI	VW(N)		
1397	2,3,5-trimethylpyrazine	roasted, nutty	MS, aroma, RI	W(B)	64	8
1399	ethyl 2-hydroxy-3-methylbutanoate	floral	MS, aroma, RIL	W(N)	32	8
1400	ethyl 2-hydroxybutanoate	fruity, floral	MS, aroma, RIL	VW(N)		
1404	ethyl cyclohexanecarboxylate	fruity, floral	MS, aroma, RIL	M(N)	256	256
1409	ethyl octanoate	fruity	MS, aroma, RI	M(N)	512	1024
1415	2,6-diethylpyrazine	nutty, baked	MS, aroma, RI	VW(B)		
1429	3-methylbutyl hexanoate	fruity, apple, green	MS, aroma, RI	VW(N)	1	16
1430	2,5-dimethyl-3-ethylpyrazine	roasted, baked	MS, aroma, RIL	M(B)	256	8
1445	5-ethyl-2,3-dimethylpyrazine[d]	baked	MS, aroma	VW(B)		
1456	2-furancarboxaldehyde	sweet, almond	MS, aroma, RI	M(N)	128	32
1460	2,3,5,6-tetramethylpyrazine	baked	MS, aroma, RI	VW(B)		
1489	2-acetylfuran	sweet, caramel	MS, aroma, RI	VW(N)	2	32
1491	2,3,5-trimethyl-6-ethylpyrazine	baked	MS, aroma, RI	VW(B)	2	1
1498	1,1-diethoxynonane	fruity	MS, aroma, RIS	VW(N)		
1501	benzaldehyde	fruity, berry	MS, aroma, RI	W(N)	16	2
1509	ethyl nonanoate	floral, fruity	MS, aroma, RI	VW(N)		
1523	furfuryl acetate	caramel, sweet	MS, aroma, RIL	W(N)	16	8
1527	ethyl 2-hydroxyhexanoate	floral, jasmine	MS, aroma, RIL	W(N)	16	16
1555	5-methyl-2-furfural	green, roasted	MS, aroma, RI	VW(N)	1	8
1583	hexyl hexanoate	apple, peach	MS, aroma, RI	M(N)	256	64
1583	3,5-dimethyl-2-butylpyrazine[d]	baked, roasted	MS, aroma	VW(B)	8	1
1593	2-acetyl-5-methylfuran	roasted	MS, aroma, RI	VW(N)	2	16
1603	ethyl 2-furoate	balsamic	MS, aroma, RI	VW(N)	8	8
1603	2-acetyl-6-methylpyridine[d]	roasted, baked	MS, aroma	VW(B)		
1610	ethyl decanoate	fruity, grape	MS, aroma, RI	VW(N)	8	16
1620	phenylacetaldehyde	floral, rose	MS, aroma, RI	W(N)	32	16
1640	ethyl benzoate	fruity	MS, aroma, RI	W(N)	64	32
1647	2-furanmethanol	burnt sugar	MS, aroma, RIL	M(B), N(W)	64	32
1649	furfuryl butanoate	sweet, caramel, fruity	MS, aroma, RI	W(N)	64	8
1655	diethyl butanedioate	fruity, sweet	MS, aroma, RI	VW(N)	1	8
1676	3,5-dimethyl-2-pentylpyrazine[d]	nutty, baked	MS, aroma	VW(B)	1	16
1683	heptyl hexanoate	sweet, fruity	MS, aroma, RIS	VW(N)		
1690	1,1-diethoxy-2-phenylethane	fruity	MS, aroma, RIS	VW(N)	8	64
1768	ethyl phenylacetate	rosy, honey	MS, aroma, RI	W(N)	64	128

Table 3. (Continued)

RI	aroma compounds	descriptor	basic of identification[b]	GC–O intensity[c]	FD factor[a] WLY	FD factor[a] JNC
1801	2-phenylethyl acetate	rosy, floral	MS, aroma, RI	W(N)	32	64
1828	ethyl dodecanoate	sweet, fruity	MS, aroma, RI	VW(N)	8	8
1857	furfuryl hexanoate	caramel, fruity	MS, aroma, RI	VW(N)	1	8
1872	ethyl 3-phenylpropanoate	fruity, floral	MS, aroma, RI	M(N)	128	32
1886	γ-octalactone	coconut, fruity	MS, aroma, RI	W(N)	32	2
1906	2-phenylethanol	rosy, honey	MS, aroma, RI	VW(N)		
1958	2-phenylethyl butanoate	fruity	MS, aroma, RIS	VW(N)	1	2
1972	2-acetylpyrrole	herbal, medicine	MS, aroma, RI	VW(N)	8	ND
2007	phenol	phenol, medicinal	MS, aroma, RI	VW(N)		
2018	γ-nonalactone	sweet, coconut	MS, aroma, RI	VW(N)	8	64
2110	γ-decalactone	coconut	MS, aroma, RI	VW(N)		
2160	2-phenylethyl hexanoate	fruity	MS, aroma, RIS	VW(N)		
2273	ethyl 2-hydroxy-3-phenylpropanoate	smoky	MS, aroma, RIL	VW(N)		
2365	γ-dodecalactone	sweet, coconut	MS, aroma, RI	VW(N)		

[a] WLY, Wuliangye liquor; JNC, Jiannanchun liquor; and ND, not detected by GC–O. [b] MS, compounds were identified by MS spectra; aroma, compounds were identified by the aroma descriptors; RI, compounds were identified by a comparison to the pure standard; RIL, compounds were identified by a comparison with the retention index from the literatures; and RIS, compounds were identified by a comparison with the retention index from the synthesized compounds. [c] VS, very strong; S, strong; M, moderate; W, weak; and VW, very weak. In the parenthesis, N, neutral fraction; B, basic fraction. [d] Tentatively identified.

(lactic acid) is formed by lactic acid bacteria, which is found to be the dominant species in the fermentation culture (*5*). One cyclic ester, ethyl cyclohexanecarboxylate, was detected in both liquors in this work. It had a high FD value (FD $\geq$ 128) and gave fruity and floral aromas. This compound has been identified in Yanghe Daqu liquor (*7*). Several aromatic esters were also detected in this study. Ethyl 3-phenylpropanoate and ethyl 2-phenylacetate had high FD values (FD $\geq$ 128), while ethyl benzoate and 2-phenylethyl acetate had moderate FD values (FD $\geq$ 16). These esters contributed rosy, honey, floral, and fruity odors and have been identified in Chinese liquors previously (*6*, *7*). One binary acid ester, diethyl butanedioate, was detected in the liquors, but it had a relative low FD value (FD $\leq$ 8); therefore, it is probably not important to the aroma.

Esters are formed mostly through esterification of alcohols with fatty acids during the fermentation, distillation, and aging processes (*6*, *7*, *14*). Yeast and other microorganisms can synthesize esters during fermentation. Strong aroma style Chinese liquors use Daqu powder as the saccharifying and fermentation agent. Daqu has high esterase activities (*16*) and can catalyze ester synthesis during the fermentation. Ester formation can be influenced by many factors such as fermentation temperature, oxygen availability, and fermentation strains. A higher temperature leads to a greater loss of esters because of the increased rates of hydrolysis and volatilization. In the fermentation processes of the Chinese liquors in this study, a relatively low temperature was maintained, thus favoring the formation of short-chained esters (*17*). Esters can also be formed during the aging process (*2*). A comparison of aged and young Yanghe Daqu liquors has shown that some esters in the aged liquor had higher FD values than in the young liquor, possibly because of higher concentrations in the aged liquor (*7*). However, their formation during the aging process is probably limited because the ester content was also relatively high in the young liquor.

Aldehydes had relatively low FD values (**Tables 3** and **4**) and contributed to green, grass, and malt aromas. 3-Methylbutanal and 2-methylpropanal both had moderate FD values (FD $\geq$ 16), where the latter was only detected on the DB-5 column. Aromatic aldehydes seemed to be important in these liquors, where phenylacetaldehyde had a high FD value (FD $\geq$ 256 on DB-5) and gave a floral aroma, while benzaldehyde had a moderate FD value (FD $\geq$ 16) and contributed to fruity and cherry odors. Although acetaldehyde was determined to have a relatively high FD value in Yanghe Daqu liquor (*7*), it was not found in this work probably because of the methodology used in this study. Acetaldehyde has an extremely low boiling point and can be easily lost during aroma concentration. Most aldehydes are probably formed by yeast metabolism (*18*). Aldehydes can be converted into other compounds during the liquor-aging process (*19*, *20*).

Acetals were found to have high FD values in both liquors (**Tables 3** and **4**). 1,1-Diethoxy-3-methylbutane was one of the most important aroma compounds (FD $\geq$ 1024), while 1,1-diethoxyethane (FD $\geq$ 128) was also of high importance in both liquors. 1,1-Diethoxy-2-methylpropane, 1,1-diethoxy-2-methylbutane, 1,1-diethoxyhexane (detected only on a DB-5 column), 1,1,3-triethoxypropane, and 1,1-diethoxy-2-phenylethane were all detected by GC−O in this work (FD $\geq$ 16). Most of these acetals have been identified in Yanghe Daqu liquors (*6*, *7*) and in freshly distilled Calvados and Cognac (*8*, *14*, *21*). It seemed that Wuliangye liquor had much higher levels of acetals than Jiannanchun because of the higher FD values, although quantitative analysis is needed to confirm this. Acetals are formed from the condensation of aldehydes with alcohols.

The importance of pyrazines to the aroma of Chinese liquor is poorly understood (*1*, *3*). On the basis of the FD values, pyrazines could be very important for Wuliangye and Jiannanchun liquors. 2,5-Dimethyl-3-ethylpyrazine and 2-ethyl-6-methylpyrazine had high FD values (FD $\geq$ 128). 2,6-Dimethylpyrazine, 2,3,5-trimethylpyrazine, and 3,5-dimethyl-2-pentylpyrazine (tentatively identified) had moderate FD values (FD $\geq$ 16). These alkylpyrazines impart nutty, baked, and roasted notes. Although several pyrazines have been identified in Yanghe Daqu liquor, many more pyrazines were identified in the Wuliangye and Jiannanchun liquors in this study. While this could be due to different methodologies used for aroma isolation, it is likely that Wuliangye and Jiannanchun liquors may contain more pyrazines. This could be due to differences involved in liquor manufacturing. Daqu is not only the starter, but it is also the fermentation material because it typically accounts for 25% of the total amount of grains used in the fermentation. The Daqu used for making Wuliangye and Jiannanchun liquors was exposed to 58−60 °C for 10−12 days, while the Daqu used for Yanghe Daqu liquor was only exposed to 54−56 °C for 5−7 days (*3*). The fermentation temperature of Wuliangye and

Table 4. Aroma Compounds in Neutral/Basic Fraction Detected by GC–O on a DB-5 Column

RI	aroma compounds	descriptor	basic of identification[b]	FD factor[a] WLY	FD factor[a] JNC
534	2-methylpropanal	green	MS, aroma, RI	2	64
584	ethyl acetate	fruity, ester	MS, aroma, RI	64	128
629	3-methylbutanal	green, malt	MS, aroma, RI	4	ND
705	ethyl propanoate	sweet, fruity	MS, aroma, RI	16	8
726	1,1-diethoxyethane	fruity	MS, aroma, RI	256	256
754	ethyl 2-methylpropanoate	fruity, sweet	MS, aroma, RI	128	32
756	dimethyl disulfide	cooked onion	MS, aroma, RI	4	4
770	2-methylpropyl acetate	strawberry, fruity	MS, aroma, RI	64	8
783	3-methylbutanol	nail polish, rancid	MS, aroma, RI	128	32
797	1-hexanal	green, grass	MS, aroma, RI	ND	8
800	ethyl butanoate	sweet, fruity	MS, aroma, RI	1024	1024
815	ethyl 2-hydroxypropanoate	fruity	MS, aroma, RI	1	8
831	2-furancarboxaldehyde	sweet, fruity, floral	MS, aroma, RI	64	32
849	ethyl 2-methylbutanoate	berry, sweet	MS, aroma, RI	64	128
852	ethyl 3-methylbutanoate	apple	MS, aroma, RI	256	1024
854	2-furanmethanol	burnt sugar	MS, aroma, RIL	64	32
859	1,1-diethoxy-2-methylpropane	fruity	MS, aroma, RIS	16	16
875	3-methylbutyl acetate	fruity	MS, aroma, RI	8	4
900	ethyl pentanoate	fruity	MS, aroma, RI	1024	2048
924	methyl hexanoate	green, fruity	MS, aroma, RI	64	8
955	1,1-diethoxy-3-methylbutane	fruity	MS, aroma, RIS	2048	1024
963	benzaldehyde	fruity, green	MS, aroma, RI	64	16
976	dimethyl trisulfide	rotten cabbage	MS, aroma, RI	16	64
1010	ethyl hexanoate	ester, fruity	MS, aroma, RI	8192	4096
1015	hexyl acetate	floral, fruity	MS, aroma, RI	32	64
1047	phenylacetaldehyde	fruity	MS, aroma, RI	256	64
1056	3-methylbutyl butanoate	fruity	MS, aroma, RIS	8	32
1062	ethyl 2-hydroxyhexanoate	fruity, jasmine	MS, aroma, RIL	4	2
1076	1,1,3-triethoxypropane	vegetal, fruity	MS, aroma, RIL	64	8
1089	2,5-dimethyl-3-ethylpyrazine	roasted, baked	MS, aroma, RIL	128	128
1092	1,1-diethoxyhexane	floral	MS, aroma, RIS	64	8
1093	propyl hexanoate	fruity	MS, aroma, RI	16	256
1097	ethyl heptanoate	fruity	MS, aroma, RI	64	256
1136	ethyl cyclohexanecarboxylate	fruity	MS, aroma, RIL	256	128
1150	2-methylpropyl hexanoate	floral, fruity	MS, aroma, RI	16	64
1152	3-methylbutyl pentanoate	fruity, floral	MS, aroma, RIS	4	8
1155	pentyl 3-methylbutanoate	fruity	MS, aroma, RIS	16	8
1163	2,3,5-trimethyl-6-ethylpyrazine	baked, nut	MS, aroma, RI	4	16
1171	furfuryl butanoate	fruity, sweet	MS, aroma, RI	16	2
1175	ethyl benzoate	floral	MS, aroma, RI	64	16
1176	diethyl butanedioate	fruity, wine	MS, aroma, RI	2	32
1183	unknown	nut, roasted		2	8
1189	butyl hexanoate	fruity	MS, aroma, RI	32	256
1191	hexyl butanoate	floral, fruity	MS, aroma, RI	1	16
1196	ethyl octanoate	fruity	MS, aroma, RI	1024	1024
1215	γ-octalactone	sweet, coconut	MS, aroma, RI	ND	8
1247	ethyl phenylacetate	rosy, honey	MS, aroma, RI	32	128
1260	2-phenylethyl acetate	rosy, honey	MS, aroma, RI	16	64
1287	pentyl hexanoate	fruity	MS, aroma, RI	2	32
1294	ethyl nonanoate	fruity	MS, aroma, RI	4	16
1328	1,1-diethoxy-2-phenylethane	fruity	MS, aroma, RIS	1	4
1353	ethyl 3-phenylpropanoate	fruity	MS, aroma, RI	128	64
1357	3,5-dimethyl-2-pentylpyrazine	baked, roasted	MS, aroma, RIL	64	2
1368	furfuryl hexanoate	caramel, fruity	MS, aroma, RI	4	16
1385	hexyl hexanoate	apple, peach	MS, aroma, RI	256	128
1394	ethyl decanoate	green, fruity	MS, aroma, RI	16	32
1401	unknown	roasted, nut		4	32
1446	3-methylbutyl octanoate	fruity, pineapple	MS, aroma, RIS	4	8
1456	ethyl 2-hydroxy-3-phenylpropanoate	goaty, smoky	MS, aroma, RIL	16	4
1482	heptyl hexanoate	fruity	MS, aroma, RIS	2	8
1556	unknown	baked, roasted		1	32
1563	ethyl dodecanoate	fruity	MS, aroma, RI	2	8

[a] WLY, Wuliangye liquor; JNC, Jiannanchun liquor; and ND, not detected by GC–O. [b] MS, compounds were identified by MS spectra; aroma, compounds were identified by the aroma descriptors; RI, compounds were identified by a comparison to the pure standard; RIL, compounds were identified by a comparison with the retention index from the literatures; and RIS, compounds were identified by a comparison with the retention index from the synthesized compounds.

Jiannanchun liquors was also higher than Yanghe Daqu (*5*). Because pyrazines are mostly formed through the Maillard reaction between saccharides and amino residues (*22*, *23*), a high temperature would benefit the Maillard reaction, and produce more pyrazines. On the basis of the FD values, Wuliangye liquor could have more pyrazines with higher concentrations than Jiannanchun liquor.

Similar to pyrazines, a high temperature also facilitates furan formation through nonenzymic browning of sugars (*24*). Several furan derivatives were identified in this study. Among these,

2-furancarboxaldehyde (furfural), with its sweet and almond-like aroma, could be very important because of a high FD value (FD ≥ 128). 2-Acetylfuran (sweet, caramel odor), 2-acetyl-5-methylfuran (green, roasted odor), and 2-furanmethanol (burnt sugar odor) were also important based on their FD values (FD ≥ 16). 5-Methyl-2-furfural (green, roasted odor) had a low FD value (FD ≥ 8). 2-Furancarboxylic acid was found in the acidic/water-soluble fraction of both liquors, and although it could not be detected by GC−O, its ester form, ethyl 2-furancarboxylate, was detected by GC−O in both liquors on the DB-wax column (FD ≥ 8). Ethyl 2-furancarboxylate imparts a balsamic note and has been identified in Calvados (*8*) and tequila (*25*). 2-Furanmethanol fatty acid esters were also identified in these two liquors including furfuryl acetate (FD ≥ 16), furfuryl butanoate (FD ≥ 16), and furfuryl hexanoate (FD ≥ 8), all contributing to sweet, fruity, and caramel aromas. Furfuryl hexanoate has been found in Yanghe Daqu liquors (*7*). Similar to pyrazines, it seems that Wuliangye liquor had a much higher concentration of furan derivatives than Jiannanchun liquor.

Among the lactones identified in this study, γ-octalactone had the highest FD value (FD ≥ 16), while γ-nonalactone had a lower FD value (FD ≤ 8). γ-Decalactone and γ-dodecalactone were identified by GC−MS, but they had very weak or no aroma in this study. γ-Lactones contribute to sweet, nut, coconut, and fruity odors, and these lactones have also been detected in Calvados and Cognac (*8*).

Sulfur-containing compounds often have very low sensory thresholds (*26*), and it is usually difficult to detect and identify them. Dimethyl trisulfide, dimethyl disulfide, and dimethyl sulfide (tentatively identified) could contribute to the aroma based on their moderate FD values (FD ≥ 16). They contributed to cooked onion, sulfur, fresh cabbage, and rotten cabbage odors. These three sulfur compounds have been found by GC−O in Yanghe Daqu liquors (*6*, *7*). The presence of these sulfur compounds is from the degradation of sulfur-containing amino acids (*26*).

Several phenolic compounds were identified on the DB-wax column (**Table 2**). Among them, phenol could be very important (FD ≥ 128), providing phenolic and medicinal aromas. 4-Ethylguaiacol (4-ethyl-2-methoxyphenol) and 4-methylphenol had moderate FD values (FD ≥ 16). 4-Ethylguaiacol contributed to clove and spicy odors, while 4-methylphenol gave animal and medical aromas. 4-Ethylphenol had a very low FD value (FD ≤ 8) and gave a smoky odor. Phenolic compounds have been detected in Chinese liquor (*6*, *7*), Calvados and Cognac (*8*), and tequila (*25*). Phenolic compounds belong to the secondary plant constituents and can be formed from lignin degradation in Chinese liquors because high levels of rice hull or sorghum hull are often used as the fermentation aide (*27*, *28*).

In summary, fractionation is an effective technique to simplify composition for the identification of aroma compounds in a complex sample. Alcohols and acids can be separated into the acidic/water-soluble fraction to minimize their interference with other constituents during GC−O and GC−MS analysis. Similarly, the separation of alkylpyrazines to the basic fraction makes for easier identification. AEDA results showed that esters could be very important in Chinese liquors, especially ethyl esters. Pyrazines and furans were identified in Wuliangye and Jiannanchun liquors, and these two classes are probably responsible for the nutty, toasty, and soy-sauce-like aroma perceived in these liquors. Both GC−O and AEDA are useful techniques to identify the most important compounds that contribute to aroma, although quantitative analysis is often needed for a more direct comparison.

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