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# Unraveling variation on the profile aroma compounds of strong aroma type of Baijiu in different regions by molecular matrix analysis and olfactory analysis

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Among 12 aroma types of Baijiu, the strong aroma type of Baijiu (Nongxiangxing Baijiu) is well received by customers for its rich and full aroma profile. According to the aroma characteristics of different geographical locations, Nongxiangxing Baijiu can be divided into Jianghuai, Sichuan and North categories. However, the reasons for the differences in Nongxiangxing Baijiu flavor in different regions are still unclear. Hence, representative brands (*i.e.*, Gujinggong, Luzhou Laojiao and Banchengshaoguo) of Nongxiangxing Baijiu from three representative regions were chosen to explore their differences in profile aroma compounds. In this study, a total of 50, 41, 35 potential aroma compounds in Banchengshaoguo, Gujinggong, and Luzhou Laojiao samples were respectively identified by direct injection combined with gas chromatography-olfactometry/mass spectrometry (GC-O/MS). Among them, 18 aroma compounds were further recognized as important aroma compounds owing to their high flavor dilution (FD) value, Osme value, and odor activity value (OAV)  $\geq 1$ . Moreover, the relationship between the above potential aroma compounds and the aroma profile of the three representative samples was analyzed by molecular matrix analysis. The results showed that various aroma compounds contributed differently to the flavor characteristics of Nongxiangxing Baijiu. In particular, 13 aroma compounds were tentatively defined as crucial profile aroma compounds due to their high aroma expression intensity and remarkable contribution to the flavor characteristics of Nongxiangxing Baijiu in different regions, and these crucial profile aroma compounds may be the reason for the difference in aroma profile of Nongxiangxing Baijiu from distinct regions.

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## 1. Introduction

Baijiu is widely recognized as the national liquor of China due to its long-standing history of production and popular flavor. In terms of data from the China National Bureau of Statistics, the annual output of Baijiu exceeded 7.4 million kiloliters (kL) in 2020, sales revenues had reached 584 billion yuan (renminbi, RMB), and the profit exceeded 159 billion yuan, with a year-on-year growth of 12.9%. Thus, Baijiu occupies an important position in China's food industry. Moreover, research on Baijiu might adhere to the dual guidance about "flavor" and "health" in the future, and more and more studies on Baijiu have been carried out.<sup>1–11</sup>

Based on its aroma characteristics, Baijiu can be roughly divided into 12 aroma types. In particular, strong-aroma (*i.e.*, Nongxiangxing), sauce-aroma, light-aroma, and rice-aroma are deemed to be the four basic Baijiu aroma types. The remaining eight Baijiu aroma types are considered to be derived from the above four Baijiu aroma types. The relationship between different Baijiu aroma types is shown in Fig. 1.<sup>12</sup> Of note, Nongxiangxing Baijiu is well received by customers for its fully balanced perfume, and the sales revenues of Nongxiangxing Baijiu account for 60–70% of the market share of the Baijiu industry. Generally, as shown in Fig. 2, distilleries producing Nongxiangxing Baijiu are mainly located in Sichuan province and the Huaihe River basin, such as Luzhou Laojiao, Wuliangye, Gujinggong, and Yanghe. In addition, Banchengshaoguo, Niulanshan, and Hetao liquor are situated in the north of China. They are divided into three categories on the basis of their aroma characteristics and place of origin (*i.e.*, Chuan, Jianghuai, and North categories). Nongxiangxing Baijiu of the Chuan category represents a rich and powerful aroma, Nongxiangxing Baijiu of the Jianghuai category shows an elegant

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and delicate fragrance, while Nongxiangxing Baijiu of the North category exhibits mellow and clear aroma characteristics.

Based on previous studies, it has been found that the flavor quality of Baijiu is closely related to the trace components contained in Baijiu.<sup>13–17</sup> Up to now, according to statistics from our research group, more than two thousand trace components have been found in Baijiu, including 510 esters, 249 alcohols, 140 acids, 18 lactones, 102 aldehydes, 160 ketones, 48 acetals, 82 sulfur compounds, 155 nitrogen compounds, 138 heterocyclic compounds, 170 aromatic compounds, 84 hydrocarbons, 104 terpenes, and 60 others. However, it was confirmed that only some of the trace components contributed directly to the aroma of Baijiu and were deemed as aroma active compounds or aroma compounds. Besides, these aroma active compounds or aroma compounds also had a certain effect on the taste of Baijiu, and then affected the overall flavor quality of Baijiu. Thus, research on the aroma compounds of Baijiu has been gradually carried out. So far, relevant studies have mainly focused on the characterization of aroma compounds in Nongxiangxing, sauce-aroma,<sup>18</sup> light-aroma,<sup>19,20</sup> and sesame-aroma Baijiu,<sup>21–27</sup> especially for Nongxiangxing Baijiu. For example, in 2018,<sup>28</sup> a total of 60 aroma compounds of Gujinggong (a kind of Nongxiangxing Baijiu) were identified by GC-O and GC-MS and 35 of them were further recognized as important aroma compounds owing to their OAVs  $\geq 1$  and sensory evaluation, including 10 esters, 10 acids, 6 alcohols, and 4 phenols. In terms of these findings, esters, acids, aromatic compounds, and alcohols were considered to make an extremely large contribution to the aroma profile of Nongxiangxing Baijiu. Specifically, the contents of esters were highest in Nongxiangxing Baijiu. Among them, ethyl hexanoate had the highest content and a relatively low odor threshold value ( $0.76 \text{ mg L}^{-1}$ ) and exhibited a fruity aroma. Ethyl hexanoate, ethyl lactate, ethyl acetate and ethyl butanoate are commonly deemed to be the major esters of Nongxiangxing Baijiu because of their high concentrations ( $100\text{--}2000 \text{ mg L}^{-1}$ ) and great contribution to the main aroma profile of Nongxiangxing Baijiu. In 2020, Shi Ke *et al.*<sup>29</sup> applied headspace-solid phase microextraction (HS-SPME), combined with a direct-gas chromatography-olfaction (D-GC-O) method to study the volatile compounds of Nongxiangxing Baijiu, and 18 key aroma compounds were identified by aroma intensity value and OAV, including 11 esters, 3 acids, 1 alcohol, 1 aldehyde, 1



Fig. 2 Geographical distribution of three representative brands of Nongxiangxing Baijiu.

ketone, and 1 sulfur compound. However, the current research mainly focused on the Nongxiangxing Baijiu of the Chuan and Jianghuai categories. There is a lack of research on the aroma compounds of the North category. Meanwhile, although they all belong to Nongxiangxing Baijiu, their flavor characteristics differ from region to region. The aroma compounds causing the diversity in aroma and taste characteristics of Nongxiangxing Baijiu from different regions still need to be explored, which is of great significance to promoting the standardization and modern development of the Baijiu industry.

Banchengshaoguo is a famous Nongxiangxing Baijiu of the North category, which is produced in Hebei province, China. It has the characteristics of a long history, pure body and clear liquor, which is unique in the North category. However, at present, there is little research on the trace components in Banchengshaoguo and the influences of aroma compounds on the aroma profile of Banchengshaoguo are also lacking in-depth studies. Therefore, it is of great value to carry out an analysis of the profile aroma compounds of Banchengshaoguo in order to stabilize the quality and improve the production technology of Nongxiangxing Baijiu of the North category, and further refine the standard of Nongxiangxing Baijiu.

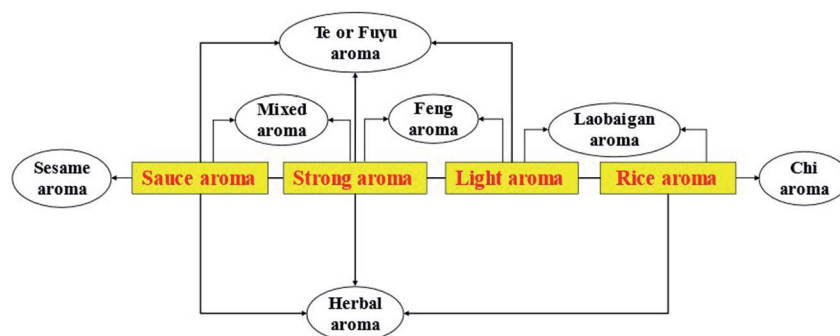


Fig. 1 The relationship between different Baijiu aroma types.



GC-O is a technique which combines the powerful separative capacity of a gas chromatograph with the acute sense of smell of a human, thereby contributing to identifying and analyzing the potential aroma compounds in Baijiu and preliminarily evaluating the aroma intensity.<sup>30,31</sup> For instance, AEDA and Osme have also been widely used to evaluate the aroma compounds in alcoholic beverages and other foods. Because the error caused by subjective factors is small and the results of research are relatively reliable, AEDA is widely used.<sup>32</sup> However, the matrix also has a certain effect on the expression of aroma compounds; thus, OAV calculation was conducted to evaluate the aroma expression of aroma compounds.<sup>33–38</sup> In 2019, a total of 12 key aroma compounds showing high FD factors were detected, including dimethyl disulfide, dimethyl trisulfide, and 2-propene-1-thiol.<sup>39</sup> In 2020, the sensory impacts of 2-methyl-3-furanthiol and 2-furfurylthiol, in sauce aroma-type Baijiu, Nongxiangxing Baijiu, and Light aroma-type Baijiu were evaluated by AEDA. The results showed that the OAVs of 2-methyl-3-furanthiol and 2-furfurylthiol were high (256–263); thus, they could be regarded as flavor markers for the sauce-aroma type of Baijiu.<sup>40</sup>

In this study, three representative brands of Jianghuai, Sichuan and North categories were selected as samples, which were Gujingong (GJG), Luzhou Laojiao (LZ) and Banchengshaoguo (BCSG), respectively. Based on the above, this study aims to characterize the profile aroma compounds of Banchengshaoguo by means of molecular sensory omics, and to analyze the variation in the profile aroma compounds of Nongxiangxing Baijiu from different categories by molecular matrix analysis. A molecular matrix was used to establish the correlation between aroma compounds and various aroma characteristics of Nongxiangxing Baijiu, and then to explore the profile aroma compounds that caused different sensory attributes (aroma and taste) of Nongxiangxing Baijiu in different regions.

## 2. Materials and methods

### 2.1 Chinese Baijiu samples

Three commercial liquor samples from BCSG, GJG, and LZ (50°, 50°, 50°), which belong to Nongxiangxing Baijiu, were used for the GC-O and GC-MS analyses. All samples were made from sorghum combined with wheat, corn, rice and sticky rice, and were stored at 4 °C until analysis. Herein, the mention of a brand name is only for research, rather than for advertising purposes.

### 2.2 Chemicals

Methyl lactate and 4-octanol were purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). 2-Ethylhexanoic acid, butyl benzoate, 2-butanol, 1-propanol, 2-pentanol, 2-methyl-1-butanol, 3-methyl-1-butanol, 2-hexanol, 1-pentanol, 2-heptanol, 1-hexanol, 1-heptanol, 2,3-butanediol, 2-methylpropanol, 1-octanol, 2-furan methanol, furfural, 2-butylfuran, phenylacetaldehyde diethyl acetal, ethyl 3-phenylpropionate, phenylethyl alcohol, 4-ethyl-2-methoxyphenol, ethyl benzoate, 4-methylphenol, acetic acid, propanoic acid, 2-methylpropionic

acid, butanoic acid, 3-methylbutanoic acid, 3-methylpentanoic acid, pentanoic acid, hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid, ethyl acetate, ethyl pentanoate, butyl formate, hexyl formate, butyl butanoate, ethyl hexanoate, propyl hexanoate, ethyl heptanoate, ethyl lactate, butyl hexanoate, hexyl butanoate, ethyl octanoate, isopentyl hexanoate, amyl hexanoate, ethyl nonanoate, isopentyl lactate, hexyl hexanoate, ethyl decanoate, diethyl butanedioate, ethyl tetradecanoate, ethyl pentadecanoate, ethyl hexadecanoate, ethyl 9-hexadecenoate, ethyl octadecenoate, ethyl oleate, ethyl butanoate, and ethyl 2-hydroxycaproate were purchased from J&K Science (Beijing, China).

### 2.3 Identification of aroma compounds

Identification of aroma compounds was performed on an Agilent 7890B gas chromatograph, equipped with an Agilent 5977A mass-selective detector (Agilent Technologies, USA) and an olfactometer (ODP C200, Gerstel, Germany).

Each 1 µL of sample was injected in a splitless mode and analyzed on a DB-WAX column (60 m × 0.25 mm i.d., 0.25 µm film thickness, J&W Scientific, USA) and a TG-5MS column (30 m × 0.25 mm i.d., 0.25 µm film thickness, Thermo Scientific, USA), respectively, for a cross-check of their RIs. Helium was used as the carrier gas at a constant flow rate of 1.5 mL min<sup>-1</sup>. The injector temperature was 250 °C. The temperature program of the oven was as follows: the oven temperature was held at 40 °C at first, then raised to 50 °C at a rate of 10 °C min<sup>-1</sup> and held for 20 min, then raised at 1 °C min<sup>-1</sup> up to 70 °C and held for 10 min, finally raised at 3 °C min<sup>-1</sup> up to 250 °C and held for 15 min. The MS was operated in an electron ionization (EI) mode at 70 eV. The temperature of the interface and the ion source were set at 250 and 230 °C, respectively. The identification of aroma compounds was conducted in a full scan mode. The mass range was set from 45 to 350 amu.

The temperature of the olfactory port was kept at 250 °C. Three trained panelists (one male and two female) were selected for the GC-O analysis. During a GC run, each panelist placed his or her nose close to and above the top of the sniffing port, and recorded the odor of the chromatographic effluent as well as retention time. All analyses were repeated in triplicate by each panelist. Before the GC-O analysis, panelists were trained by sniffing 50 reference compounds in concentrations 5 times above their odor thresholds in water or air.

The qualitative analysis methods of trace components in samples included mass spectrometry analysis, self-built library search, NIST 14 library search, retention index, standard comparison and aroma comparison.

### 2.4 Aroma expression evaluation

**2.4.1 Osme.** Osme was performed by GC-O on a DB-WAX column (60 m × 0.25 mm i.d., 0.25 µm film thickness, J&W Scientific, USA).

The panelists responded to the aroma intensity of the stimulus. The intensity value and aroma characteristics were recorded. Each fraction was replicated three times by each panelist.



**2.4.2 AEDA.** AEDA was performed by GC-O on a DB-WAX column (60 m × 0.25 mm i.d., 0.25 μm film thickness, J&W Scientific, USA).

Each sample was diluted 3, 9, 27, ..., 729 times and then subjected to GC-O analysis under the same GC-MS conditions described above until no aroma compound could be detected by the panelist. The flavor dilution (FD) value of each aroma compound represented the maximum dilution at which the aroma compound could still be perceived. All analyses were repeated in triplicate by each panelist.

## 2.5 Quantification of aroma compounds

**2.5.1 Direct injection combined with GC-MS.** The mixed standard was prepared with methyl lactate, 4-octanol, 2-ethylhexanoic acid and butyl benzoate in absolute ethanol. The final concentrations of methyl lactate, 4-octanol, 2-ethylhexanoic acid and butyl benzoate were 200 mg L<sup>-1</sup>, 100 mg L<sup>-1</sup>, 10 mg L<sup>-1</sup> and 5 mg L<sup>-1</sup>, respectively. Every sample (1 mL) was spiked with 10 μL of the mixed standard. Afterwards, 1 μL of each sample was injected in a splitless mode and analyzed under the same GC conditions described in Section 2.3, Identification of aroma compounds. The detector temperature was set at 250 °C. The above detected compounds were quantified and the OAVs of these compounds were calculated according to the quantitative results. The analytical limits of detection (LOD) of the aromas were obtained from the lowest concentrations of the analyte standard solutions based on a signal-to-noise ratio of 3. All analyses were repeated in triplicate. The analytical limits of quantitation (LOQ) of the aromas were obtained from the lowest concentrations of the analyte standard solutions based on a signal-to-noise ratio of 10.

## 2.6 Sensory evaluation

**2.6.1 Sensory panel.** The sensory evaluation was performed by 10 assessors (5 males and 5 females, aged 23–29), who belonged to the Beijing Key Laboratory of Flavor Chemistry, Beijing Technology and Business University. All of them had been previously trained by describing and recognizing the aroma characteristics of Baijiu through an oronasal route.

**2.6.2 Descriptive profile tests.** 6 aromatic attributes and 4 taste attributes were selected by the sensory panel as the most relevant contributors to describe the overall aroma profile of 3 Nongxiangxing Baijiu samples. The overall aroma profiles of the commercial BCSG, GJG, and LZ samples were evaluated by the sensory panel, who were asked to evaluate the odor and taste intensities of the ten aforementioned aromatic attributes using a six-point scale from 0 to 5 (0 = none, 1 = very weak, 2 = weak, 3 = moderate, 4 = strong, and 5 = very strong). The results obtained from the 3 assessors were averaged for each attribute.

## 2.7 Statistics analysis

All analyses were repeated in triplicate. The qualitative, quantitative and sensory evaluation results were statistically analyzed, and the deviation of the data was calculated (SPSS 16.0). The difference in aroma compounds in the three

representative Nongxiangxing Baijiu samples was visualized by a heat map (Origin 2019b). Meanwhile, the relationship between the aroma compounds and aroma characteristics of Nongxiangxing Baijiu was analyzed with a network diagram (Gephi).

# 3. Results and discussion

## 3.1 Identification and aroma expression evaluation of aroma compounds in Nongxiangxing Baijiu

Direct injection has the advantages of convenience and rapidity, which can directly reflect the distribution of aroma compounds in Baijiu. To identify the aroma compounds responsible for the overall aroma profile of Nongxiangxing Baijiu, BCSG, GJG and LZ were analyzed by direct injection combined with AEDA-GC-O and GC-MS. As shown in Fig. 3, a total of 50 aroma compounds were identified in BCSG, including 12 alcohols, 5 aromatic compounds, 1 aldehyde, 9 acids, and 23 esters. In total, there were 41 aroma compounds identified in GJG, including 7 alcohols, 4 aromatic compounds, 2 aldehydes, 9 acids, and 19 esters. In LZ, 35 aroma compounds were identified, including 7 alcohols, 4 aromatic compounds, 1 aldehyde, 9 acids, and 14 esters. Among them, the number of esters, alcohols and aromatic compounds in the three representative Nongxiangxing Baijiu samples were different. The number of alcohols and aromatic compounds in GJG and LZ were the same, while the kinds of esters were more abundant in BCSG. In summary, a total of 23 aroma compounds were detected in all three representative Nongxiangxing Baijiu samples, including 3 alcohols, 1 aromatic compound, 1 aldehyde, 7 acids, and 11 esters.

Based on the above qualitative results, AEDA and Osme were used to evaluate the aroma expression intensity of the identified potential aroma compounds. The results of GC-O showed that the aroma compounds from Nongxiangxing Baijiu presented a strong fruity aroma, with other odor characteristics such as sweet, acidic, floral, and alcoholic notes. These aroma characteristics were used as the basis of sensory evaluation in subsequent experiments. As presented in Table 1, it was found that the Osme values of acetic acid, butanoic acid and ethyl hexanoate were the top three. However, because of the subjectivity

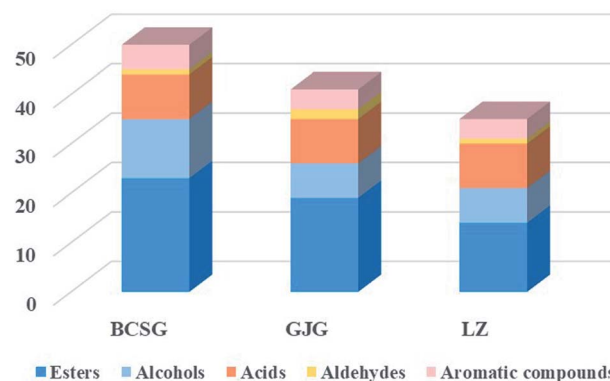


Fig. 3 Summary map of potential aroma compounds in three representative Nongxiangxing Baijiu samples.





Table 1 Analysis of three representative Nongxiangxing Baijiu samples by direct injection combined with AEDA

No.	Category	Aroma compounds	CAS number	Aroma characteristics <sup>a</sup>	Osme <sup>b</sup>			FD <sup>c</sup>		
					BCSG	GJG	LZ	BCSG	GJG	LZ
1	Alcohols	2-Butanol	78-92-2	Fruity	1 ± 0.47	— <sup>d</sup>	1 ± 0.00	27	—	9
2		1-Propanol	71-23-8	Fermented grain	1 ± 0.00	2 ± 0.00	1 ± 0.00	9	81	9
3		2-Methyl-1-propanol	78-83-1	Fruity, fermented grain	—	1 ± 0.47	—	—	9	—
4		3-Methyl-1-butanol	123-51-3	Banana	2 ± 0.47	2 ± 0.00	—	27	27	—
5		1-Pentanol	71-41-0	Fermented grain	1 ± 0.00	—	—	3	—	—
6		1-Hexanol	111-27-3	Ripe fruits	—	1 ± 0.47	—	—	3	—
7	Aromatic compounds	Ethyl 3-phenylpropionate	2021-28-5	Sweet	—	1 ± 0.47	—	—	9	—
8		<i>p</i> -Cresol	106-44-5	Animals	—	1 ± 0.47	1 ± 0.47	—	9	3
9		Phenylethyl alcohol	60-12-8	Fruity, flowers	1 ± 0.47	—	—	3	—	—
10		Furfural	98-01-1	Roasted	—	—	1 ± 0.00	—	—	3
11	Aldehyde	Acetaldehyde	75-07-7	Fruity	1 ± 0.47	—	1 ± 0.00	9	—	9
12	Acids	Acetic acid	64-19-7	Acidity	2 ± 0.47	2 ± 0.47	2 ± 0.47	27	27	27
13		Propanoic acid	79-09-4	Cheesy	1 ± 0.00	1 ± 0.47	—	3	3	—
14		Butanoic acid	107-92-6	Sludge, cheesy	3 ± 0.00	3 ± 0.47	3 ± 0.00	27	27	27
15		3-Methylbutanoic acid	503-74-2	Cheesy	—	2 ± 0.47	2 ± 0.47	—	9	9
16		Pentanoic acid	109-52-4	Sludge, cheesy	2 ± 0.47	2 ± 0.00	2 ± 0.47	81	9	9
17		Hexanoic acid	142-62-1	Cheesy	1 ± 0.47	2 ± 0.00	2 ± 0.47	9	27	81
18		Heptanoic acid	111-14-8	Grape, acidity	—	2 ± 0.47	—	—	3	—
19		Octanoic acid	124-07-2	Vegetables	—	2 ± 0.00	2 ± 0.00	—	9	9
20	Esters	Ethyl acetate	141-78-6	Ripe fruits	2 ± 0.47	1 ± 0.47	1 ± 0.47	243	243	243
21		Ethyl butanoate	105-54-4	Apple	2 ± 0.00	1 ± 0.47	1 ± 0.47	243	27	27
22		Ethyl pentanoate	539-82-2	Fruity	2 ± 0.00	2 ± 0.47	1 ± 0.47	27	27	3
23		Butyl formate	592-84-7	Ripe fruits	1 ± 0.47	—	1 ± 0.47	27	—	3
24		Butyl butanoate	109-21-7	Fruity, sweet	1 ± 0.47	—	—	3	—	—
25		Ethyl hexanoate	123-66-0	Pineapple, banana	3 ± 0.00	4 ± 0.47	3 ± 0.47	243	243	243
26		Ethyl heptanoate	106-30-9	Pineapple, sweet	2 ± 0.47	1 ± 0.47	2 ± 0.00	3	3	9
27		Ethyl lactate	97-64-3	Sweet, milky	1 ± 0.47	1 ± 0.00	1 ± 0.00	81	27	27
28		Propyl hexanoate	626-77-7	Sweet, fruity	—	1 ± 0.47	—	—	3	—
29		Butyl hexanoate	626-82-4	Pineapple, sweet	1 ± 0.00	1 ± 0.00	1 ± 0.47	3	3	3
30		Ethyl octanoate	106-32-1	Grape	2 ± 0.00	2 ± 0.00	1 ± 0.47	9	9	3
31		Hexyl butyrate	2639-63-6	Sweet	—	—	1 ± 0.47	—	—	3
32		Ethyl 2-hydroxycaproate	52 089-55-1	Sweet	—	1 ± 0.47	—	—	9	—
33		Hexyl hexanoate	6378-65-0	Green	—	1 ± 0.47	1 ± 0.82	—	3	3
34		Ethyl decanoate	110-38-3	Fruity, sweet	—	2 ± 0.47	—	—	3	—
35		Ethyl hexadecanoate	628-97-7	Sweet, milky	1 ± 0.47	—	—	9	—	—
36		Isopentyl hexanoate	2198-61-0	Sweet	1 ± 0.00	—	—	3	—	—
37	Hexyl formate	629-33-4	Apple	1 ± 0.94	—	—	3	—	—	

<sup>a</sup> Aroma characteristic, aroma characteristics of aroma compounds smelled by assessors. <sup>b</sup> Osme, the aroma intensity of each aroma compound was scored with 0–5 points, and they are represented as the mean value of triplicate samples ± standard deviation (mean ± SD). <sup>c</sup> FD, flavor dilution. <sup>d</sup> —, not detected.

of Osme, and it not being comprehensive using only one method, it is necessary to evaluate the aroma expression of aroma compounds in combination with another expression of aroma compounds in combination with another expression of aroma compounds. Considering its good stability and reliability, AEDA was chosen in the study. The FD values of those aroma compounds in the three representative samples were shown to be in the range between 3 and 243 based on the AEDA-GC-O analysis. In BCSG, three aroma compounds with FD values ≥ 243 were preliminarily and objectively considered as the profile aroma compounds, which were ethyl acetate, ethyl butanoate, and ethyl hexanoate. This result was basically consistent with the results of Osme. In GJG, there were 2 aroma compounds (ethyl acetate and ethyl hexanoate) confirmed with FD values ≥ 243. Similarly, the FD values of ethyl acetate and ethyl hexanoate in LZ were 243. Of note, compared with the other two kinds of Nongxiangxing Baijiu samples, ethyl butanoate with higher FD

values in BCSG had the characteristics of a clear and sweet fruit aroma, which may make the sweet aroma of BCSG more obvious. Furthermore, the FD values of ethyl lactate and pentanoic acid, which respectively had the aroma characteristics of over-ripe fruit and cheese, in BCSG were higher than those in the other two samples. The excessive aroma of over-ripe fruit and cheese was supposed to affect the harmony of the overall aroma profile of the BCSG samples. Meanwhile, the FD value of 1-propanol in the GJG sample was higher than that in the BCSG and LZ samples. 1-Propanol had the aroma of mature fermented grain, which might be one of the reasons why a grain aroma was more prominent in the GJG sample. In the LZ samples, the FD factor of hexanoic acid was higher than those of BCSG or GJG. Hexanoic acid had the aroma characteristics of fat and cheese and was devoted to the flavor characteristic of Baijiu. Meanwhile, hexanoic acid might affect the content of ethyl



Table 2 Concentration of aroma compounds in distinct Nongxiangxing Baijiu samples

No. <sup>a</sup>	Category	Compounds	CAS number	Concentration <sup>b</sup> (mg L <sup>-1</sup> )			Maximum	Minimum	Mean
				BCSG	GJG	LZ			
1	Alcohols	2-Butanol	78-92-2	71.11 ± 1.09	29.83 ± 0.56	20.70 ± 0.18	71.11	20.70	40.54
2		1-Propanol	71-23-8	107.03 ± 4.51	221.77 ± 2.81	52.74 ± 0.24	221.77	52.74	127.18
38		2-Pentanol	6032-29-7	23.04 ± 1.65	0.00	4.37 ± 0.17	23.04	0.00	9.14
39		2-Methyl-1-butanol	137-32-6	108.96 ± 2.19	136.09 ± 0.41	0.00	136.09	0.00	81.68
4		3-Methyl-1-butanol	123-51-3	314.59 ± 2.91	270.96 ± 0.43	220.07 ± 0.63	314.59	220.07	268.54
40		2-Hexanol	626-93-7	23.52 ± 0.33	0.00	0.00	23.52	0.00	7.84
5		1-Pentanol	71-41-0	13.59 ± 0.43	1.70 ± 0.03	0.00	13.59	0.00	5.10
41		2-Heptanol	543-49-7	3.12 ± 0.07	0.00	0.00	3.12	0.00	1.04
6		1-Hexanol	111-27-3	59.59 ± 0.28	0.00	25.58 ± 0.36	59.59	0.00	28.39
42		1-Heptanol	111-70-6	2.01 ± 0.05	0.86 ± 0.01	0.00	2.01	0.00	0.96
43	Aromatic compounds	2,3-Butanediol	513-85-9	4.05 ± 0.03	0.00	1.11 ± 0.01	4.05	0.00	1.72
3		2-Methylpropanol	78-83-1	0.00	31.81 ± 0.20	0.00	31.81	0.00	10.60
44		1-Octanol	111-87-5	0.00	0.00	0.27 ± 0.01	0.27	0.00	0.09
45		2-Furan methanol	98-00-0	4.66 ± 0.03	0.00	1.38 ± 0.02	4.66	0.00	2.01
10		Furfural	98-01-1	0.00	0.00	8.68 ± 0.09	8.68	0.00	2.89
46		2-Butylfuran	4466-24-4	5.78 ± 0.14	0.00	0.00	5.78	0.00	1.93
47		Phenylacetaldehyde diacetal	6314-97-2	1.26 ± 0.01	0.00	0.00	1.26	0.00	0.42
7		Ethyl 3-phenylpropionate	2021-28-5	4.99 ± 0.16	10.59 ± 0.17	0.00	10.59	0.00	5.20
9		Phenyl ethanol	60-12-8	4.55 ± 0.03	2.42 ± 0.01	1.36 ± 0.01	4.55	1.36	2.78
48		4-Ethyl-2-methoxyphenol	2785-89-9	2.00 ± 0.10	0.00	0.00	2.00	0.00	0.67
49	Acids	Ethyl benzoate	93-89-0	0.00	1.35 ± 0.01	0.00	1.35	0.00	0.45
8		4-Methylphenol	106-44-5	0.00	1.36 ± 0.01	1.24 ± 0.01	1.36	0.00	0.87
12		Acetic acid	64-19-7	317.50 ± 1.95	523.53 ± 0.24	553.57 ± 0.15	553.57	317.50	464.86
13		Propanoic acid	79-09-4	10.89 ± 0.57	2.52 ± 0.01	2.39 ± 0.03	8.87	2.39	4.59
50		2-Methylpropionic acid	79-31-2	6.14 ± 0.04	5.09 ± 0.15	4.40 ± 0.04	6.14	4.40	5.21
14		Butanoic acid	107-92-6	127.75 ± 0.56	186.84 ± 0.55	204.66 ± 0.28	204.66	127.75	173.08
15		3-Methylbutanoic acid	503-74-2	0.00	7.46 ± 0.09	8.92 ± 0.01	8.92	0.00	5.46
51		3-Methyl pentanoic acid	105-43-1	5.75 ± 0.60	0.00	0.00	5.75	0.00	1.92
16		Pentanoic acid	109-52-4	23.56 ± 0.27	7.95 ± 0.09	13.97 ± 0.02	23.56	7.95	15.16
17		Hexanoic acid	142-62-1	494.71 ± 1.60	321.41 ± 0.02	355.61 ± 4.80	494.71	321.41	390.58
18	Heptanoic acid	111-14-8	8.80 ± 0.04	8.34 ± 0.24	0.00	8.80	0.00	5.71	
19	Octanoic acid	124-07-2	5.15 ± 0.02	15.67 ± 0.34	6.49 ± 0.01	15.67	5.15	9.10	
52	Nonanoic acid	112-05-0	0.00	0.00	6.56 ± 0.05	6.56	0.00	2.19	
20	Esters	Ethyl acetate	141-78-6	2316.11 ± 14.39	1194.92 ± 0.68	1157.68 ± 0.53	2316.11	1157.68	1556.24
22		Ethyl pentanoate	539-82-2	72.20 ± 8.05	0.00	179.96 ± 0.86	179.96	0.00	84.05
23		Butyl formate	592-84-7	70.95 ± 0.87	51.19 ± 2.13	56.66 ± 0.28	70.95	51.19	59.60
37		Hexyl formate	629-33-4	0.00	99.17 ± 0.08	0.00	99.17	0.00	33.06
24		Butyl butanoate	109-21-7	34.06 ± 0.27	0.00	0.00	34.06	0.00	11.35
25		Ethyl hexanoate	123-66-0	2097.06 ± 4.11	2949.40 ± 7.09	2476.53 ± 9.56	2949.40	2097.06	2507.66
28		Propyl hexanoate	626-77-7	34.37 ± 0.12	15.84 ± 0.10	0.00	34.37	0.00	16.74
26		Ethyl heptanoate	106-30-9	379.17 ± 0.86	63.07 ± 0.30	110.23 ± 0.09	379.17	63.07	184.16
27		Ethyl lactate	97-64-3	882.58 ± 4.86	517.81 ± 0.51	638.26 ± 0.36	882.58	517.81	679.55
29		Butyl hexanoate	626-82-4	78.84 ± 0.14	14.97 ± 0.11	19.96 ± 0.12	78.84	14.97	37.92
31		Hexyl butanoate	2639-63-6	9.50 ± 0.25	0.00	0.00	9.50	0.00	3.17
30		Ethyl octanoate	106-32-1	274.30 ± 2.65	132.21 ± 1.01	72.40 ± 0.55	274.30	72.40	159.64
36		Isopentyl hexanoate	2198-61-0	98.78 ± 1.34	50.54 ± 0.05	0.00	98.78	0.00	49.77
53		Amyl hexanoate	540-07-8	8.82 ± 0.37	0.00	4.11 ± 0.08	8.82	0.00	4.31
54		Ethyl nonanoate	123-29-5	3.38 ± 0.06	0.00	0.00	3.38	0.00	1.13
55		Isopentyl lactate	19329-89-6	8.52 ± 0.25	3.52 ± 0.02	0.00	8.52	0.00	4.01
33		Hexyl hexanoate	6378-65-0	25.59 ± 0.15	50.49 ± 0.43	38.40 ± 0.17	50.49	25.59	38.16
34		Ethyl decanoate	110-38-3	15.13 ± 0.25	6.60 ± 0.25	0.00	15.13	0.00	7.24
56		Diethyl butanedioate	123-25-1	6.08 ± 0.05	15.17 ± 0.08	0.00	15.17	0.00	7.08
57		Ethyl tetradecanoate	124-06-1	0.00	4.94 ± 0.11	0.00	4.94	0.00	1.65
58	Ethylpentadecanoate	41114-00-5	4.98 ± 0.11	0.00	0.00	4.98	0.00	1.66	
35	Ethyl hexadecanoate	628-97-7	15.11 ± 1.14	79.51 ± 0.73	24.20 ± 0.23	79.51	15.11	39.61	
59	Ethyl 9-hexadecenoate	54 546-22-4	10.67 ± 0.09	0.00	0.00	10.67	0.00	3.56	
60	Ethyl octadecanoate	111-61-5	5.30 ± 0.14	0.00	0.00	5.30	0.00	1.77	
61	Ethyl oleate	111-62-6	11.06 ± 4.22	24.13 ± 0.12	19.22 ± 0.28	24.13	11.06	18.14	
21	Ethyl butanoate	105-54-4	149.94 ± 1.32	164.87 ± 0.98	209.73 ± 0.43	209.73	149.94	174.85	
32	Ethyl 2-hydroxycaproate	52089-55-1	0.00	57.30 ± 0.33	6.69 ± 0.04	57.30	0.00	21.33	

<sup>a</sup> The numbers are the same as the numbers listed in Table 1. <sup>b</sup> The concentrations of aroma compounds are represented as the mean value of triplicate samples ± standard deviation (mean ± SD).



hexanoate because of the formation of a chemical equilibrium with ethyl hexanoate. Ethyl hexanoate as a key aroma compound will further affect the aroma profile of Nongxiangxing Baijiu. The different FDs of the same compound in distinct samples may be one of the reasons for the diversity in the aroma characteristics of the three representative Nongxiangxing Baijiu samples.

### 3.2 Quantification of aroma compounds in Nongxiangxing Baijiu

On the basis of qualitative analysis, in order to further clarify the content distribution of aroma compounds, the aforementioned aroma compounds were further quantified by GC-MS after direct injection (DI). As shown in Table 2, esters showed the highest contents in the BCSG, GJG, and LZ samples, followed by short-chain organic acids and alcohols. Among them, the concentration of 3-methyl-1-butanol, acetic acid, butanoic acid, hexanoic acid, ethyl acetate, ethyl hexanoate, ethyl lactate and ethyl butanoate in the three representative Nongxiangxing Baijiu samples were all more than  $100 \text{ mg L}^{-1}$ , which were preliminarily believed to be the profile aroma compounds of Nongxiangxing Baijiu. Meanwhile, the contents of 1-propanol, 2-methyl-1-butanol and ethyl octanoate in BCSG and GJG were more than  $100 \text{ mg L}^{-1}$ , but less than  $100 \text{ mg L}^{-1}$  in LZ, which mainly presented the aroma of fermented grain, fruit and grape, respectively. The content of ethyl pentanoate in LZ was more than  $100 \text{ mg L}^{-1}$ , which mainly showed a fruit aroma, while the content of ethyl heptanoate with the aroma characteristics of pineapple and sweet only exceeded  $100 \text{ mg L}^{-1}$  in BCSG and LZ. Given their higher contents, these compounds may be the profile aroma compounds that caused the difference in aroma characteristics of the three representative Nongxiangxing Baijiu samples. Furthermore, as shown in Fig. 4, the distribution of some aroma compounds with low content in the three representative Nongxiangxing Baijiu samples was also quite different. For example, the contents of ethyl 3-phenylpropionate, 2-methylpropanol, and diethyl butanedioate were higher in GJG, which had the aroma characteristics of sweet, fermented grain and fruity, respectively, while the contents of 2-butanol, 2-pentanol, and propanoic acid in BCSG were relatively high. Of note, the proportions of several important aroma compounds were also different in the three representative samples. For example, the proportions of ethyl hexanoate and ethyl acetate in BCSG, GJG and LZ were 0.91, 2.47 and 2.14, respectively. The different proportions of the compounds in the three representative Nongxiangxing Baijiu samples may be one of the reasons for the difference in the aroma profile of Nongxiangxing Baijiu.

### 3.3 OAVs of aroma compounds

As described above, the contributions of aroma compounds in Baijiu were not just determined by their contents, but also by their FD values. Aside from the aforementioned factors, the matrix effect should also be considered. Hence, in order to gain a deep insight into the contribution of each aroma compound in the three representative Nongxiangxing Baijiu samples, their OAVs were also determined. Odor thresholds were taken from

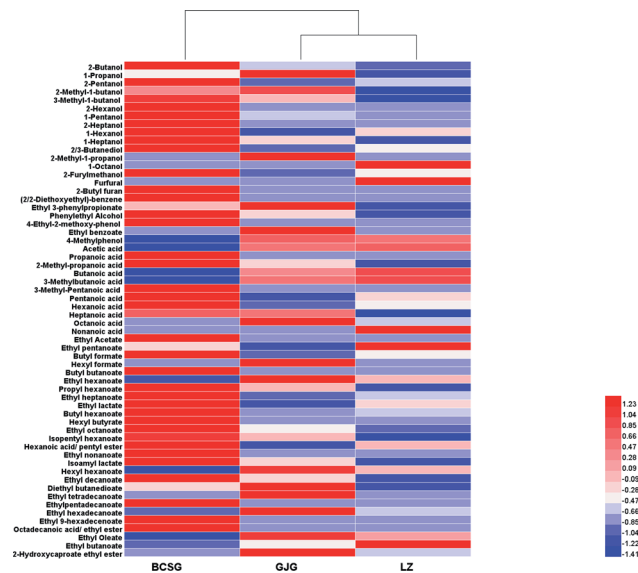


Fig. 4 Heatmap for the concentration of aroma compounds in three representative Nongxiangxing Baijiu samples.

references. As shown in Table 3, a total of 18 aroma compounds were preliminarily confirmed as profile aroma compounds with  $\text{OAVs} \geq 1$  in the three representative Nongxiangxing Baijiu samples. Among them, it was not surprising that the highest OAV was observed from ethyl hexanoate, which exhibited its extremely high OAV above 36 000 in all Nongxiangxing Baijiu samples. These compounds were deemed to be the profile aroma compounds affecting the aroma profile of Nongxiangxing Baijiu attributed to their higher OAVs. However, the OAVs of these 18 aroma compounds in the three Nongxiangxing Baijiu samples were also significantly different. For example, as shown in Fig. 5, 1-propanol, ethyl hexanoate, and ethyl hexadecanoate had higher OAVs in GJG, and these compounds mainly presented the aroma of fermented grain, pineapple and sweet, respectively. Meanwhile, the OAVs of 2-methylpropanoic acid, pentanoic acid, and ethyl acetate were higher in BCSG, with the aroma of acidity, cheese and ripe fruits. This may be one reason for the difference in the aroma profiles of the three representative Nongxiangxing Baijiu samples. Furthermore, the OAVs of some aroma compounds were greater than or equal to 1 in individual Nongxiangxing Baijiu samples. For example, 1-pentanol, 2-butylfuran, and butyl butanoate with the aroma characteristics of fermented grain, fruity and sweet, respectively, only had higher OAVs in BCSG, while the OAVs of 4-methylphenol and 3-methylbutanoic acid were greater than 1 in GJG and LZ. Roughly, in the three representative Nongxiangxing Baijiu samples, the OAVs of esters and alcohols were significantly different. These compounds mainly showed the aroma characteristics of fruit and fermented grain, and made a great contribution to the aroma profile of Nongxiangxing Baijiu. Meanwhile, it can be seen that the OAVs of the same aroma compounds in the three representative Nongxiangxing Baijiu samples were quite different, which may be one of the reasons that cause a slight diversity in the aroma characteristics of the three representative Nongxiangxing Baijiu samples. As shown in



Table 3 OAVs of aroma compounds in three representative Nongxiangxing Baijiu samples

No. <sup>a</sup>	Category	Compounds	CAS	Odor thresholds <sup>b</sup> (mg L <sup>-1</sup> )	OAV <sup>c</sup>			Aroma characteristics <sup>d</sup>
					BCSG	GJG	LZ	
1	Alcohols	2-Butanol	78-92-2	50.00	1	1	0	Fruity
2		1-Propanol	71-23-8	53.95	2	4	1	Fermented grain
38		2-Pentanol	6032-29-7	45.00	1	0	0	Green
39		2-Methyl-1-butanol	137-32-6	50.00	2	3	0	Banana
4		3-Methyl-1-butanol	123-51-3	179.19	2	2	1	Ripe fruit
40		2-Hexanol	626-93-7	1.51	16	0	0	Fruity
5	Aromatic compounds	1-Pentanol	71-41-0	4.00	3	0	0	Fermented grain
41		2-Heptanol	543-49-7	1.43	2	0	0	Fruity
6		1-Hexanol	111-27-3	5.37	11	0	5	Green
3		2-Methyl-1-propanol	78-83-1	40.00	0	1	0	Fermented grain
45		2-Furan methanol	98-00-0	2.00	2	0	1	Roasted sesame
10		Furfural	98-01-1	15.00	0	0	1	Sweet
46		2-Butylfuran	4466-24-4	0.01	1157	0	0	Oranges
7		Ethyl 3-phenylpropionate	2021-28-5	0.13	40	85	0	Honey
48		4-Ethyl-2-methoxy-phenol	2785-89-9	0.12	16	0	0	Wood
49		Ethyl benzoate	93-89-0	1.43	0	1	0	Fruity
8	Acids	4-Methylphenol	106-44-5	0.17	0	8	7	Narcissus
12		Acetic acid	64-19-7	160.00	2	3	3	Acidity
50		2-Methylpropanoic acid	79-31-2	0.13	49	40	35	Cheesy
14		Butanoic acid	107-92-6	0.96	132	194	212	Cheesy
15		3-Methylbutanoic acid	503-74-2	1.05	0	7	9	Dairy
51		3-Methyl pentanoic acid	105-43-1	0.15	38	0	0	Cheesy
16		Pentanoic acid	109-52-4	0.39	61	20	36	Dairy
17		Hexanoic acid	142-62-1	2.52	197	128	141	Fatty
18		Heptanoic acid	111-14-8	13.82	1	1	0	Honey
19		Octanoic acid	124-07-2	2.70	2	6	2	Fatty
52		Nonanoic acid	112-05-0	3.56	0	0	2	Acidity
20		Esters	Ethyl acetate	141-78-6	32.55	71	37	36
22	Ethyl pentanoate		539-82-2	0.03	2674	0	6665	Apple
23	Butyl formate		592-84-7	0.80	89	64	71	Fruity
24	Butyl butanoate		109-21-7	0.11	310	0	0	Fruity
25	Ethyl hexanoate		123-66-0	0.06	37 901	53 306	44 759	Fruity
28	Propyl hexanoate		626-77-7	12.80	3	1	0	Grape
26	Ethyl heptanoate		106-30-9	13.15	29	5	8	Pineapple
27	Ethyl lactate		97-64-3	128.08	7	4	5	Dairy
29	Butyl hexanoate		626-82-4	0.70	113	21	29	Fruity
31	Hexyl butyrate		2639-63-6	0.25	38	0	0	Sweet
30	Ethyl octanoate	106-32-1	0.01	21 313	10 273	5625	Ripe fruit	
36	Isopentyl hexanoate	2198-61-0	1.40	71	36	0	Banana	
54	Ethyl nonanoate	123-29-5	3.15	1	0	0	Grape	
33	Hexyl hexanoate	6378-65-0	1.89	14	27	20	Green	
34	Ethyl decanoate	110-38-3	1.12	13	6	0	Floral	
35	Ethyl hexadecanoate	628-97-7	1.50	10	53	16	Toffee	
21	Ethyl butanoate	105-54-4	0.08	1828	2011	2558	Ripe fruit	

<sup>a</sup> The numbers are the same as the numbers listed in Tables 1 and 2. <sup>b</sup> OAVs were calculated by dividing the concentration by the respective odor threshold. <sup>c</sup> Odor thresholds were taken from ref. 41 and 42. <sup>d</sup> Aroma characteristic, aroma characteristics of aroma compounds smelled by assessors.

Fig. 5, the correlation between GJG and LZ was higher, while BCSG was more different from GJG and LZ due to the variances in the OAVs of esters and alcohols.

### 3.4 The relationship between aroma compounds and aroma characteristic of Nongxiangxing Baijiu was analyzed by molecular matrix and correlation network analysis

In order to establish the correlation between aroma compounds and various aroma characteristics of Nongxiangxing Baijiu, and

to explore the profile aroma compounds which contribute to different sensory attributes (aroma and taste) of Nongxiangxing Baijiu in different regions, the relationship between aroma compounds and flavor characteristic of Nongxiangxing Baijiu was analyzed by molecular matrix and correlation network analysis. In sensory evaluation experiments, the assessors respectively scored 0–5 for 10 attributes of three representative Nongxiangxing Baijiu samples from two aspects of aroma and taste. The 10 sensory characteristics were pit aroma (fatty,





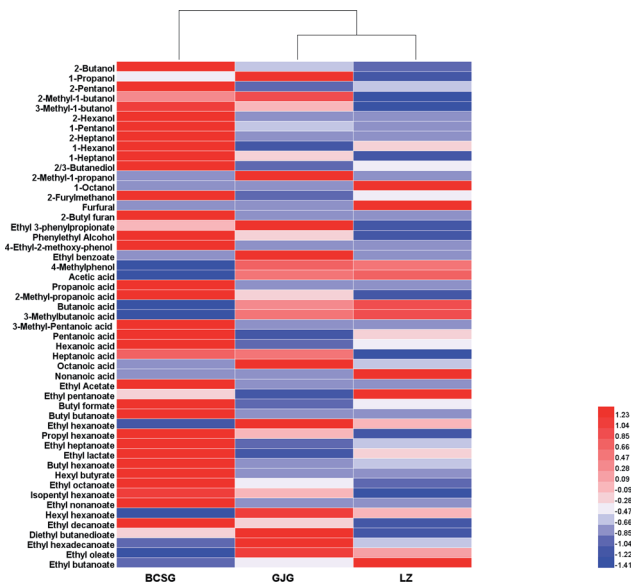


Fig. 5 OAVs of aroma compounds in three representative Nongxiangxing Baijiu samples.

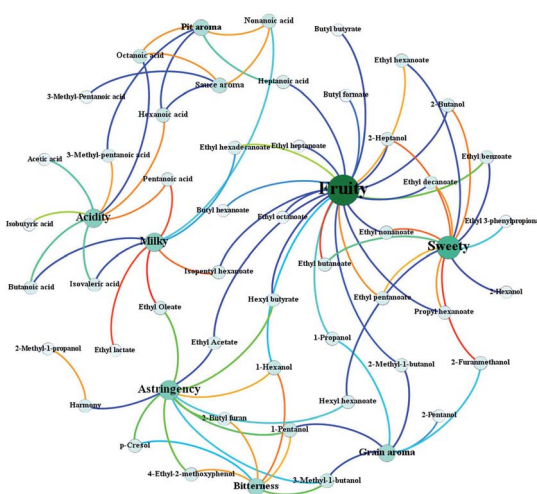


Fig. 6 Contribution of different aroma compounds to distinct aroma characteristics of Nongxiangxing Baijiu samples.

cheesy, dairy), fruity, sweet, milky, grain aroma, sauce aroma, bitterness, astringency, acidity and harmony. Although the FD values from AEDA-GC-O and calculated OAVs could be used to evaluate the odor intensities and contributions of aroma compounds, the contribution of these aroma compounds to the corresponding aroma characteristics of Nongxiangxing Baijiu still needed further study. Hence, the relationship between aroma compounds and aroma characteristics of Nongxiangxing Baijiu which was obtained from previous sensory evaluation was established by molecular matrix and correlation network analysis. The contribution of important aroma compounds to different aroma characteristics of Nongxiangxing Baijiu was preliminarily analyzed, and the colors of the lines in the graph represent the degree of correlation between them. As shown in

Fig. 6, various aroma compounds contributed different flavor characteristics to Nongxiangxing Baijiu. As a result, a total of 22 compounds were associated with a fruity aroma note, followed by a sweet aroma note, associated with 13 compounds, while 10 compounds were associated with an astringent note. Thus, it can be seen that fruit aroma and sweet aroma were typical aroma characteristics of Nongxiangxing Baijiu. In particular, most esters were significantly related to a fruit note, while most alcohols were related to a sweet note and a grain aroma note, and acids were related to acidity and a pit aroma note, which were partly consistent with previous research.<sup>8</sup> For instance, ethyl pentanoate and ethyl hexanoate were correlated with a fruity note. While 2-furan methanol, ethyl decanoate, propyl hexanoate and ethyl pentanoate were initially identified with a correlation with a sweet note in Nongxiangxing Baijiu. Moreover, hexanoic acid and octanoic acid had a notable correlation with acidity and a pit aroma note.

Combined with the above OAV results, some aroma compounds had relatively high OAVs in all three representative Nongxiangxing Baijiu samples. At the same time, they also had a strong correlation with flavor attributes. For example, ethyl hexanoate had a strong correlation with fruity and sweet, hexanoic acid had an impact on acidity, pit aroma and soy sauce aroma, while pentanoic acid had a strong correlation with acidity and milky, *etc.* In addition, some aroma compounds only had high OAVs in an individual sample; they also significantly influenced the aroma characteristics of Nongxiangxing Baijiu and had a strong correlation with corresponding flavor attributes. For instance, the OAVs of ethyl nonanoate and 2-heptanol only in BCSG were greater than or equal to 1, but they also had a strong correlation with fruity and sweet. Isopentyl hexanoate only had higher OAV in BCSG and GJG, but it had a strong correlation with fruity and milky. The OAV of 2-furan methanol in BCSG and LZ were higher, but it was strongly related to sweet. Meanwhile, the OAV of ethyl benzoate in GJG was greater than or equal to 1, and it had a strong correlation with sweet. Based on the above results, 3-methyl-1-butanol, 2-heptanol, 2-furan methanol, butanoic acid, pentanoic acid, hexanoic acid, octanoic acid, ethyl acetate, ethyl hexanoate, ethyl lactate, ethyl octanoate, isopentyl hexanoate, and ethyl butanoate were tentatively defined as crucial profile aroma compounds due to their high aroma expression intensity and remarkable contribution to the flavor characteristics of Nongxiangxing Baijiu in different regions.

## 4. Conclusions

In summary, this study identified a total of 50, 41, and 35 trace components in Banchengshaoguo, Gujinggong, and Luzhou Laojiao samples, respectively, by direct injection combined with GC-O-MS. Among them, 18 aroma compounds were further recognized as the important aroma compounds owing to their relatively high OAVs, which were mainly esters, acids and alcohols. Based on the results of sensory evaluation and aroma compound analysis, the relationship between the aroma compounds and flavor characteristics of Nongxiangxing Baijiu was established. According to analysis of the correlation



network, most esters were strongly correlated with aromas of fruity and sweet, and alcohols mainly had a strong correlation with grain aroma and sweet, while acids contributed to acidity and pit aroma. Based on these results, the crucial profile aroma compounds which significantly affected the flavor characteristics of Nongxiangxing Baijiu in different regions were 3-methyl-1-butanol, 2-heptanol, 2-furan methanol, butanoic acid, pentanoic acid, hexanoic acid, octanoic acid, ethyl acetate, ethyl hexanoate, ethyl lactate, ethyl octanoate, isopentyl hexanoate, and ethyl butanoate. This study provides a theoretical basis for improving the brewing standard of Nongxiangxing Baijiu and realizing the modernization of Baijiu production.

## Author contributions

Jiixin Hong: conceptualization, data curation, investigation, methodology, validation, visualization, writing – original draft, writing – review & editing.

Junshan Wang: conceptualization, data curation, methodology, validation, visualization, writing – original draft, writing – review & editing.

Chunsheng Zhang: investigation, methodology, validation.

Zhigang Zhao: validation, writing – review & editing.

Wenjing Tian: validation, writing – review & editing.

Yashuai Wu: data curation, formal analysis, validation.

Hao chen: data curation, formal analysis, validation.

Dongrui Zhao: conceptualization, methodology, writing – review & editing.

Jinyuan Sun: validation.

## Conflicts of interest

There are no conflicts to declare.

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