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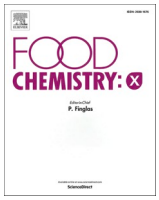

Analysis of volatile compounds in Xiangjiao baijiu from different storage containers and years based on HS-GC-IMS and DI-GC–MS

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ABSTRACT

The volatile compounds in 16 different storage containers and years of Xiangjiao Baijiu (XJBJ) were compared and analyzed via direct injection (DI) combined with gas chromatography–mass spectrometry (GC–MS) and headspace extraction (HS) coupled with gas chromatography-ion mobility spectrometry (HS-GC-IMS) for the first time. Through HS-GC-IMS analysis, it was found that the succession rules of 14 compounds such as furfural during aging process. A total of 60 compounds were identified using DI-GC–MS. Twenty-five of these compounds were further quantified, and 19 compounds had odor activity values (OAVs) > 1, which were important contributor to aroma of XJBJ. Among them, those with OAVs >1000 included ethyl hexanoate, ethyl octanoate, ethyl butanoate, and ethyl pentanoate. Combining the results of quantitative, OAVs and partial least squares-discriminant analysis (PLS-DA) revealed that 10 compounds such as ethyl octanoate were the important compounds that lead to the differences between different storage types of XJBJ.

1. Introduction

Baijiu is a unique distilled liquor in China with a long history, and is one of the six largest distilled liquors in the world, including brandy, whisky, vodka, gin and rum. Distilled liquor is made from grains and other main raw materials through fermentation, distillation, and blending (Zheng et al., 2017). At present, Chinese Baijiu has been mainly divided into 12 flavor types, namely, strong, sauce (Moutai flavor), rice, mild (light), Feng, Te, sesame, Laobaigan, Fuyu, Dong (herbal), Chi, and Jian (mixed) flavor type (Liu and Sun, 2018). Among them, the Jian flavor type Baijiu (JFB) is the combination of strong and sauce flavor type Baijiu. Xiangjiao Baijiu (XJBJ) is a typical JFB and is produced in Hunan Province, China, with five types of grains as raw materials, such as sorghum, corn, glutinous rice, rice, and wheat. After the grains are mixed with Longshan rock spring water and Jiuqu (saccharification fermentation starter), the mixture is fermented in the old cellar of Baoqing Prefecture in the central part of Hunan Province. After fermentation, the fermented grains are distilled to obtain the original Baijiu, which is aged in the jar or other container. Because of its unique "Longshan microclimate" geographical environment, XJBJ has a unique and harmonious aroma and taste.

Aroma is an important factor to evaluate the quality of Baijiu, and the aroma of Baijiu is mainly formed by its volatile compounds. Therefore, many studies in recent years have been conducted to identify and characterize the volatile compounds of baijiu via various methods and techniques (He et al., 2021; Wang et al., 2021; Wang, Ye, et al., 2022; Yin et al., 2023; Zhu et al., 2021). Direct injection (DI) and headspace injection (HS) are two common sample pretreatment methods. DI is easy to operate, fast to analyze, and avoids contamination of organic solvents and loss of certain trace components during sample processing (Yang et al., 2024). HS also prevents contamination of columns due to non-volatile components (Wang, Yi, et al., 2022). In addition, gas chromatography–mass spectrometry (GC–MS) and gas chromatography-ion mobility spectrometry (GC-IMS) are commonly used methods to identified volatile compounds of Baijiu. Among them, GC–MS shows good selectivity, high sensitivity, and a wide range of applications (Wang, Yi, et al., 2022). GC-IMS only needs a small sample size and a simple pre-treatment method (Wang et al., 2020). Moreover, IMS is very sensitive in detecting aroma compounds with functional groups, such as esters, alcohols, ketones, and aldehydes. And the

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detection results can be displayed through two-dimensional spectrum and fingerprints to visualized the changes of aroma compounds, so this method is also usually used to study the changes of volatile components in foods. For example, using DI with gas chromatography-olfaction-mass spectrometry, 55 compounds were identified and combining with odor activity values (OAVs) and aroma intensity values, ethyl acetate, ethyl butanoate, ethyl pentanoate, ethyl hexanoate, ethyl heptanoate, ethyl octanoate, acetic acid, butyric acid, pentanoic acid, hexanoic acid, heptanoic acid and octanoic acid were regarded as the main aroma compounds of JFB (Qiao et al., 2019). The differences of aroma compounds in JFBs with different aging years produced from Hubei Baiyunbian Liquor Industry Co., Ltd. via headspace solid-phase microextraction coupled with GC–MS were studied, which found that the total content of acids, esters, and pyrazine increased with the extension of aging (Zhou et al., 2020). He et al. (2021) studied the changing trend of aroma compounds in different distillation fractions of Baijiu also through HS-GC-IMS and GC–MS. Compared to the middle and tail Baijiu, the aroma compounds in the head Baijiu had higher concentration. Most low molecular weight and alcohol-soluble compounds exhibited a decreasing tendency when the distillation duration was extended, whereas the water-soluble, large molecular weight, and high boiling point compounds exhibited an opposite trend. However, there is no research on the volatile aroma compounds of XJBJ, especially the differences between different storage containers and the changes occurring in these compounds with increasing years of XJBJ storage. In addition, differential substances in XJBJ with different containers and vintages are not yet clear.

Therefore, the purposes of this study were 1) to obtain the difference comparison chart and fingerprint of volatile compounds in 16 XJBJ with different storage containers and years using HS-GC-IMS; 2) to qualitatively analyze the volatile compounds in XJBJ by HS-GC-IMS and DI-GC–MS; 3) to quantitate important volatile compounds in XJBJ via the standard curve method, and further calculate their OAVs to evaluate the aroma contribution of the compounds to XJBJ; 4) to predict the important aroma compounds of different types of XJBJ and the differential substances in different storage type and years of XJBJ by partial least squares-discriminant analysis (PLS-DA).

2. Materials and methods

2.1. Materials and chemicals

The basic information of XJBJ is shown in Table 1. All samples were purchased from Hunan Xiangjiao Liquor Industry Co., Ltd., China.

Table 1
Basic information of Xiangjiao Baijiu samples.

Codes	Storage methods[i]	Storage years	Ethanol contents (*v/v*)
XJDX0Y	Xiangjiao dixia	0	70
XJDX1Y	Xiangjiao dixia	1	72
XJDX2Y	Xiangjiao dixia	2	76
XJDX3Y	Xiangjiao dixia	3	70
XJDX5Y	Xiangjiao dixia	5	70
XJDX10Y	Xiangjiao dixia	10	80
XJMT0Y	Xiangjiao Matan	0	78
XJMT1Y	Xiangjiao Matan	1	76
XJMT2Y	Xiangjiao Matan	2	80
XJMT3Y	Xiangjiao Matan	3	74
XJMT5Y	Xiangjiao Matan	5	72
XJMT10Y	Xiangjiao Matan	10	74
XJZN1Y	Xiangjiao Zunianfen	1	57
XJZN2Y	Xiangjiao Zunianfen	2	64
XJZN3Y	Xiangjiao Zunianfen	3	60
XJZN5Y	Xiangjiao Zunianfen	5	57

i, Xiangjiao dixia means that Xiangjiao Baijiu is stored in a underground cement tank; Xiangjiao Matan means that Xiangjiao Baijiu is stored in a Matan, a type of porcelain jar; Xiangjiao Zunianfen means that Xiangjiao Baijiu is stored in a glass bottle.

Ethyl acetate (99.5 %), ethyl butanoate (95.0 %), ethyl pentanoate (98.0 %), ethyl hexanoate (99 %), ethyl heptanoate (99.0 %), ethyl octanoate (99 %), ethyl hexadecanoate (99 %), ethyl 3-methylbutanoate (99.0 %), ethyl lactate (99.0 %), 1,1-diethoxy ethane (98.0 %), guaiacol (99.0 %), ethyl 2-hydroxy-4-methylpentanoate (98.0 %), 1-propanol (99.0 %), 2-methyl-1-propanol (99.0 %), 3-methyl-1-butanol (99.0 %), 2-methyl-1-butanol (99.0 %), 1-hexanol (99 %), 1-pentanol (99.0 %), acetic acid (99.7 %), pentanoic acid (99.0 %), 2-methylpropionic acid (99 %), furfural (99.0 %), and acetoin (95.0 %) were purchased from J&K (Beijing, China). Octanoic acid (99.0 %) and hexanoic acid (98.0 %) were purchased from ADMAS (Beijing, China). 1-Butanol (99.7 %) was purchased from Aladdin (Shanghai, China). Butanoic acid (99.0 %), heptanoic acid (98.0 %) and 1,1-diethoxy-3-methyl-butane (97.0 %) were purchased from Macklin (Shanghai, China).

The internal standards were 4-octanol (IS1, 97.0 %) and 2-methylhexanoic acid (IS2, 99 %) from J&K (Beijing, China). The n-alkane mixture (C_5-C_{25}) was obtained from Sigma Aldrich (Shanghai, China). Anhydrous sodium sulfate (99.8 %), sodium chloride (99.8 %), and sodium carbonate (99.8 %) were purchased from Beijing Sinopharm Chemical Reagent Co., Ltd., China.

2.2. Preparation of samples

HS-GC-IMS sample pre-treatment: the Baijiu samples were diluted to 10 % ethanol concentration (*v/v*) using ultra-pure water (Thermo Scientific™ Barnstead™ GenPure™ Pro). Then, 1.0 mL of the diluted solutions and 0.36 g of sodium chloride were added into 20 mL headspace bottles. Finally, the bottles were sealed and waited for HS-GC-IMS analysis.

DI-GC–MS sample pre-treatment: 0.40–0.50 g of anhydrous sodium sulfate and 980.0 μL Baijiu were added into 2.0 mL glass bottles, then a mixed standard solution of 20.0 μL was also added. The mixed standard solution contained 4-octanol (85.0 mg/L) and 2-methylhexanoic acid (84.6 mg/L). After being sealed, the samples were placed at −20 °C in a refrigerator for 12 h and passed through a membrane (0.22 μm) before GC–MS analysis.

2.3. HS-GC-IMS analysis

Conditions of HS Autosampler system (He et al., 2021): the furnace temperature (equilibrium temperature) was 60 °C, the tube temperature was 90 °C, and the valve temperature was 85 °C. The pressurization time was 30 s, the sampling time was 20 s, the injection time was 20 s, the back flushing time was 1.0 min, and the analysis cycle was 47 min.

A gas chromatograph (GC, Agilent 7890B, Santa Clara, CA) and an IMS instrument (FlavourSpec® from G.A.S., Dortmund, Germany) were combined for aroma profile analysis of 16 XJBJ. A DB-5 (15 m × 0.25 mm × 0.25 μm; J & W Scientific, Folsom, CA) chromatographic column was used to separate the volatile aroma compounds. The carrier gas was N_2 (purity ≥99.999 %).

GC-IMS analysis conditions (He et al., 2021): the oven temperature was initially maintained at 35 °C for 2 min, then raised to 50 °C at 0.5 °C/min and maintained for 2 min, then raised to 70 °C at 6 °C/min and maintained for 1.0 min, and finally raised to 220 °C at 18 °C/min. β-Ray and ^{3}H were used as the radiation source, the drift gas was N_2 (purity ≥99.999 %) with a flow rate 150 mL/min, the drift tube temperature was 45 °C, and the positive ionization mode was adopted. Each sample was analyzed three times.

2.4. GC–MS analysis

A GC–MS (Thermo Fisher Trace 1310 gas chromatograph and an ISQ mass spectrometer) (Thermo Fisher Science, Waltham, MA) was used for qualitative and quantitative analysis of samples (Wang et al., 2021). The used capillary column was DB-FFAP capillary column (60 m × 0.25 mm × 0.25 μm ; J&W Science , Folsom, CA).

GC–MS analysis conditions: the initial temperature was 40 °C, then increased to 50 °C at 2 °C/min and held for 5.0 min, then increased to 80 °C at 3 °C/min and held for 5.0 min, and finally increased to 240 °C at 5 °C/min and held for 10.0 min. The carrier gas was helium (99.999 %), with a flow rate of 1.0 mL/min. The injection volume was 1.0 μL. The split ratio of injector was 20:1. The GC injector temperature was 250 °C. The temperature of transmission line and MS ion source was 230 °C. The temperature of the quadrupole was 150 °C. MS fragments were collected in electron impact mode (EI, 70 eV), and the collection range was *m/z* 40–450 in full scan mode.

The qualitative analyses were achieved by the NIST17 (National Institute of Standards and Technology) spectral library (match >700) and retention index (RI) (Ye et al., 2022). Under the same chromatographic conditions, the RI of aroma compounds calculated using C7-C27 n-alkanes (Supelco, USA) were compared with those previously reported in literatures, where the absolute values differing by 50 or less were determined to be the same compound (Wang, Ye, et al., 2022).

Fifteen different concentrations of mixed standard solutions were prepared for quantitation using 80 % (*v/v*) ethanol/water solution. Then, they were performed the same analysis with GC–MS as the corresponding samples mentioned above, after being added with mixed internal standards. The analytical conditions were consistent with the qualitative methods used. Each analysis was conducted three times. By plotting the relationship between the response rate of standard compounds and internal standards and their corresponding concentration ratios, the standard curves were obtained. Then, the concentrations of volatile compounds were gotten.

2.5. Calculation of odor activity values

The odor detection threshold refers to previous studies(Du et al., 2021; Fan and Xu, 2011; Liu and Sun, 2018; van Gemert, 2011; Zhang et al., 2019). Calculating the OAVs of volatility compounds based on the ratio of their concentration to their odor threshold.

2.6. Statistical analysis

The standard curves were processed by Microsoft Excel 2016. The PLS-DA was drawn by SIMCA 14 (Umetrics Inc., Sweden). For HS-GC-IMS analysis, the analysis software LAV (Laboratory Analytical Viewer) and the IMS library (IMS database) were used for compound characterization. The HS-GC-IMS spectral contrasts of samples were used as plug-in reporters in LAV and HS-GC-IMS fingerprinting were used as plug-in Gallery Plot.

3. Results and discussion

3.1. Volatile profiles in Xiangjiao baijiu by GC-IMS

HS-GC-IMS was used to analyze the differences in volatile compounds in different types of XJBJ during aging. It can provide a more intuitive indication of the changes in volatile compounds during aging. A difference comparison model is used to compare the change trends of chemical compound (as shown in Fig. 1), where the horizontal and vertical coordinates represent the drift time of the ion mobility spectrometry and retention time (RI) of the gas chromatograph, respectively. XJDX0Y, XJMT0Y, and XJZN1Y are used as reference samples for three types of products. Each point on the reference sample plot represents a compound. The other samples are subtracted from the reference samples. The color indicates the signal intensity (SI) of the concentration. The white color indicates that the concentrations of the volatile compound in other samples are consistent with the reference samples, and the red indicates higher than those of the reference samples, while the blue color indicates lower than those of the reference samples. The redder the color, the higher the concentration. The bluer the color, the lower the concentration.

It is shown in Fig. 1 that, when the RI is between 0 and 1000 s and the drift time is between 1.0 and 2.0 ms, the volatile compounds appeared are most. The change trends of different compounds during this period are different from each other. As the aging time increases, the differences between the samples and the reference samples become greater. When the RI is 1000–1500 s and the drift time is 1.0–2.0 ms, the concentrations of volatile compounds also increase with the increase in aging time. When the RI is 1500–2750 s and the drift time is 1.0–2.0 ms, the content of most volatile compounds in the three XJBJ increased, while the content of a small part of compounds decreased.

In order to further determine the compounds with differences, the fingerprints are constructed for 16 XJBJ of three product types, as shown in Fig. 2. Each line in the figure is a sample's fingerprint. Each sample was analyzed three times, and the sample code is on the right. Each column provides a visual representation of the relative content of the same volatile compound in different varieties, with the names of the compounds below. “M” and “D” represent the monomer and dimer of the compound, respectively. Through the IMS and NIST database, a total of 40 compounds and 8 dimers were identified, included 13 esters, 7 aldehydes, 8 alcohols, 2 acids, 3 ketones, 3 sulfur compounds, 2 nitrogen compounds, and 2 other compounds, including furfural, octanal, 2-methyl-1-butanal, heptanal, nonanal, benzaldehyde, 3-methyl-2-butanal (M/D), ethyl pentanoate (M/D), ethyl acetate, isopentyl acetate (M/D), ethyl butanoate (M/D), propyl propanoate, methyl hexanoate (M/D), ethyl hexanoate (M/D), ethyl heptanoate (M/D), ethyl propanoate, ethyl 4-methylpentanoate, ethyl lactate, ethyl 3-methylbutanoate, ethyl 2-methylbutanoate, 1-propanol, 1-hexanol, 3-octanol, benzyl alcohol, 1-butanol (M/D), 2-methyl-1-propanol, 2-methyl-1-butanol, 3-methyl-1-butanol, hexanoic acid, butyric acid, 2-nonanone, 2-hexanone, 2-heptanone, 2-ethylpyridine, 2-acetylfuran, 1,1-diethoxy-3-methylbutane, 2-thiazoly-1-propanpne, methylpyrazine, dimethyl trisulfide, and methional. According to the fingerprints, the darker the red color, the higher the concentration of the compound. On the contrary, the more the blue color, the lower the concentration. From this, the change trends of the compounds during aging are revealed in Fig. 2, and the fingerprints are divided into four regions labeled with ABCD.

For the samples of XJDX (Fig. 2 (a)), the contents of furfural, 2-methyl-1-butanal, heptanal, isopentyl acetate (M/D), ethyl acetate, and ethyl lactate in area A decrease. The contents of ethyl pentanoate (M/D), and 1-propanol in region B remain basically unchanged during aging. The contents of these 19 compounds including 1-hexanol, ethyl butanoate (M/D), butyric acid, etc. in area C increased. In the D region, there are 12 compounds that their contents reach their peaks during aging and then decrease, such as 2-heptanone, 2-ethylpyridine, etc. In XJMT (Fig. 2 (b)), the contents of 14 compounds, including furfural, methional, ethyl acetate, 2-methyl-1-butanal,etc., in area A decrease. The contents of hexanoic acid and 1-propanol in region B remain essentially constant during aging. The contents of 15 compounds in area C increased, such as 3-octanol, ethyl 4-methylpentanoate, ethyl 3-methylbutanoate, etc. The contents of 9 compounds, 2-heptanone, benzyl alcohol, 2-nonanone, 1-butanol (M/D), 2-hexanone, 2-methyl-1-propanol, dimethyl trisulfide, 2-thiazoly-1-propanpne, and 2-ethylpyridine in region D reach their peak values during aging and then decrease again. In XJZN (Fig. 2 (c)), the contents of 7 compounds, 2-methyl-1-butanal, 2-methyl-1-propanol, furfural, methional, ethyl hexanoate (M/D), ethyl acetate, and ethyl pentanoate (M/D) in area A decrease. The contents of 1-propanol and hexanoic acid in area B remain unchanged during aging. The contents of 13 compounds, including 3-octanol, ethyl 4-methylpentanoate, ethyl 3-methylbutanoate, etc., in area C increased. In the D region, there were 2-heptanone, 2-ethylpyridine, and other 13 compounds, which reached their peaks during aging and then decrease.

In summary, the change rules of furfural, 2-methyl-1-butanal, ethyl acetate, hexanoic acid, 1-propanol, 1-hexanol, 3-octanol, ethyl 4-methylpentanoate, butyric acid, ethyl butanoate, 2-heptanone, 2-

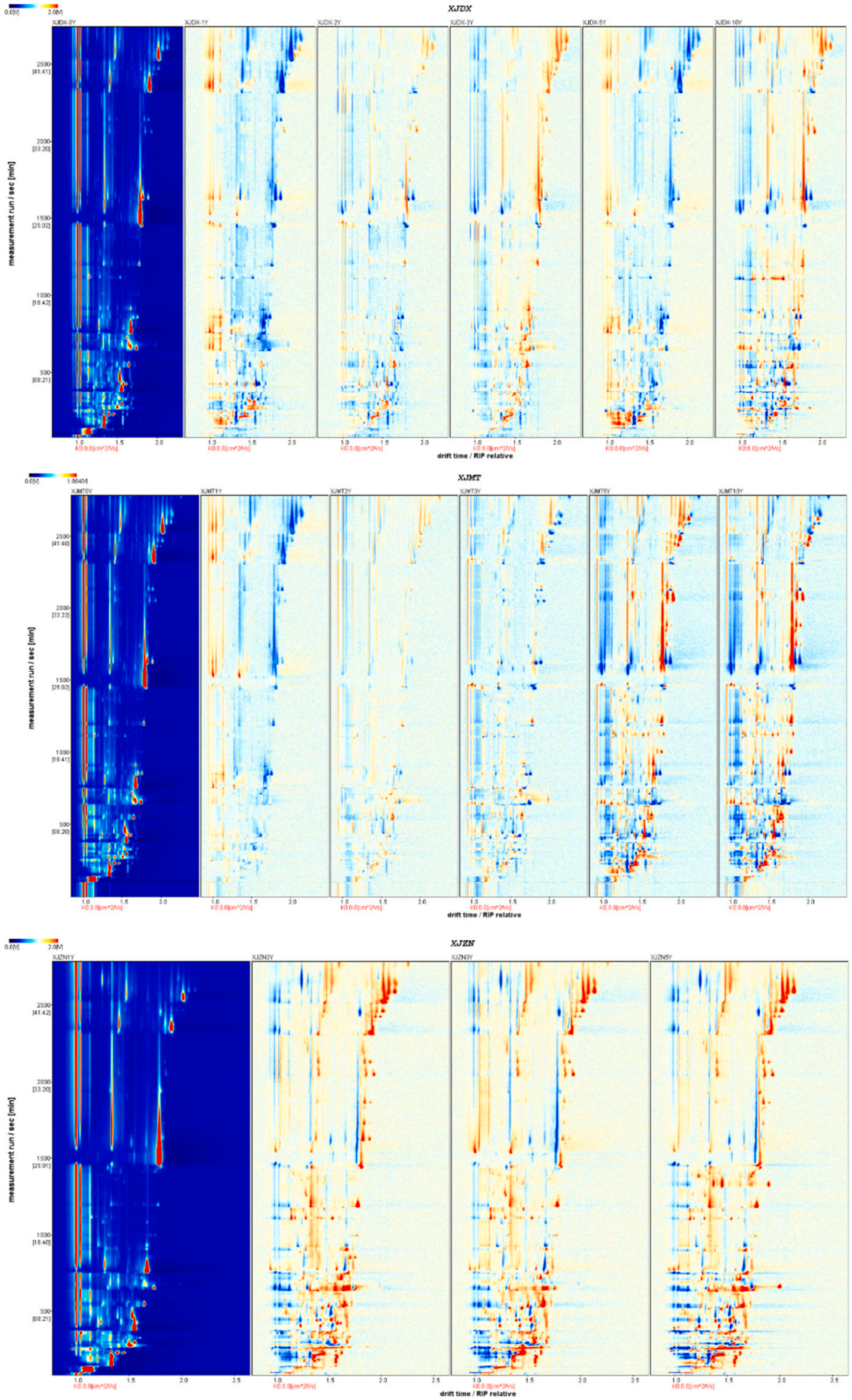

Fig. 1. Comparison models of volatile compounds of 16 Xiangjiao Baijiu in different years and product types. XJDX0Y, XJMT0Y, and XJZN1Y were used as reference samples for different types of products (XJDX, XJMT, and XJZN), respectively. (XJDX, XJMT and XJZN represents the storage methods of Xiaojiao dixia, Xiangjiao matan, and Xiangjiao zunianfen, respectively; 0Y and 1Y represents the storage year of 0 and 1 year.)

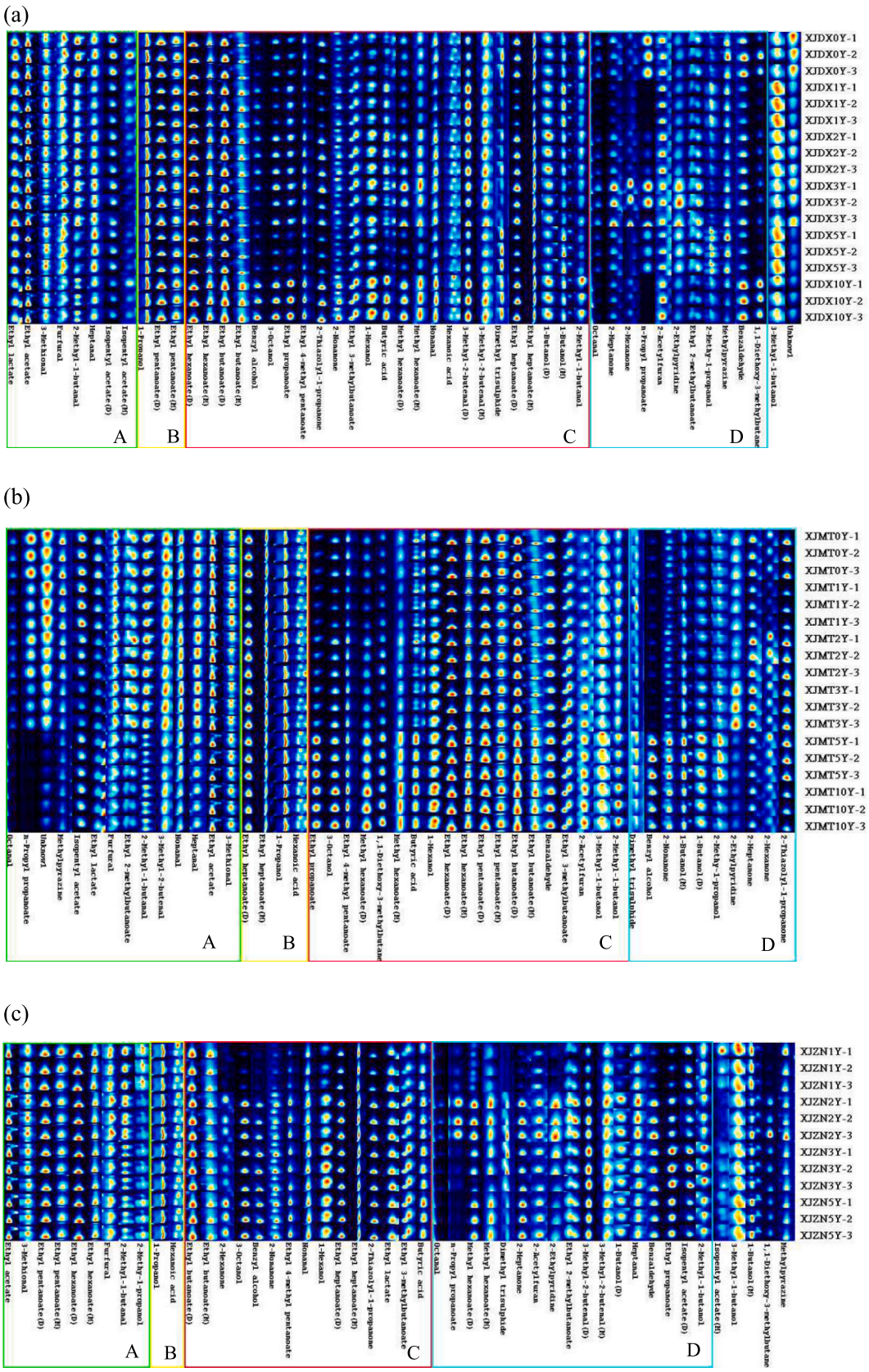

Fig. 2. Gallery plots of the selected signal peak areas form three different storage containers of Xiangjiao Baijiu in different years. (a) XJDX; (b) XJMT; (c) XJZN. (XJDX, XJMT and XJZN represents the storage methods of Xiaojiao dixia, Xiangjiao matan, and Xiangjiao zunianfen, respectively.)

ethylpyridine, methional and ethyl 3-methylbutanoate in the aging process of three different types of XJBJ were the same. The levels of furfural, 2-methyl-1-butanal, methional, and ethyl acetate in the three different storage-type products decreased during the aging process. Due to the hydrolysis and volatility of ethyl acetate, its content showed a decreasing trend with increasing aging (Ren et al., 2015). Furfural decreased with increasing aging, which was consistent with previous studies (Li et al., 2021). Methional was formed by the transamination process of methionine to α-keto-γ-(methylthio) butyric acid, then generated through decarboxylation process (Che et al., 2020; Zhang et al., 2023). The contents of hexanoic acid and 1-propanol remained basically unchanged, which was similar to the change trend of mixed flavor Baijiu (Zhou, 2020). Meanwhile, hexanoic acid was one of the main contributors to the aroma of Baijiu (Qiao et al., 2019). The contents of 1-hexanol, 3-octanol, ethyl 4-methylpentanoate, butyric acid, ethyl butanoate, and ethyl 3-methylbutanoate increased. The change trends of 1-hexanol, 3-octanol, ethyl 4-methylpentanoate and ethyl 3-methylbutyrate were consistent with previous studies (Zhang et al., 2022). Butyric acid was important aroma compounds in Baijiu (Jia and Ren, 2008), and its content played an important role in Baijiu aroma (Qiao et al., 2019). The research of Li et al. (2023) showed that ethyl butanoate was a key marker compound to distinguish the JFB from the strong flavor Baijiu. The compounds including 2-heptanone and 2-ethylpyridine reached their highest contents during the aging process and then decreases. The change rule of 2-heptanone was inconsistent with sauce flavor type Baijiu, which may be related to the different flavor type and storage method (Wang et al., 2024).

3.2. Volatile profiles in Xiangjiao baijiu by GC–MS

Qualitative analysis was conducted on 16 samples of XJBJ using DI combined with GC–MS. A total of 60 compounds were identified, as shown in Supplementary table 1, including 22 alcohols, 11 acids, 22 esters, 1 ketone, 3 aldehydes, and 1 ether. As shown in Fig. 3, In XJZN, there are 2 aldehydes, 1 ketone, 8 acids, 10 esters, and 14 alcohols. There are 12 alcohols, 9 acids, and 16 esters in XJMT, 14 alcohols, 8 acids, 10 esters, 1 ketone, and 2 aldehydes in XJZN. The unique alcohols in XJDX were 2-hexanol and 2-propanoxyethanol. The unique compound in XJMT was 2,5-dimethyl-3-hexanol. The unique compound in XJZN was 1,2-propanediol. 1,3-Propanedioic acid and 3-methylpentanoic acid were unique to XJDX. Other acids can be detected in XJDX, XJMT, and XJZN. Among the esters, the unique compounds in XJDX were ethyl 2-hydroxyhexanoate, hexyl formate, ethyl 3-methyl butanoate, ethyl undecanoate, butyl lactate, and 2-hydroxypropanoate methyl ester. Other esters can be detected in XJDX, XJMT, and XJZN.

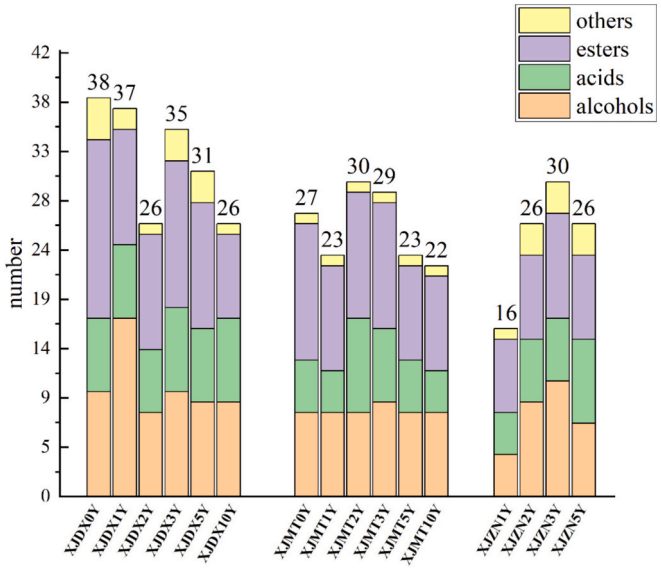

Fig. 3. Content ratio of various volatile compounds in 16 different storage containers and years of Xiangjiao Baijiu identified using DI and GC–MS.

Quantitative analysis was conducted on 25 volatile compounds with larger peak areas based on qualitative results, as shown in Table 2, including 10 esters, 7 alcohols, 5 acids, 1 aldehyde, 1 ether, and 1 ketone. The other quantitation information is shown in Supplementary table 2. The internal standards were 2-methylhexanoic acid and 4-octanol. In XJDX, the compounds with the highest content in XJDX0Y, XJDX1Y, XJDX2Y, XJDX3Y, and XJDX5Y were ethyl lactate, with 1750.16, 1421.46, 1128.17, 1557.84, and 1069.10 mg/L, respectively. The compound with the highest content in XJDX10Y was ethyl hexanoate (2397.74 mg/L). In XJMT, the compound with the highest content in XJMT0Y and XJMT1Y was ethyl acetate with 1480.64 and 1497.59 mg/L, respectively. The compound with the highest content in XJMT2Y, XJMT3Y, XJMT5Y, and XJMT10Y was ethyl hexanoate, which was 1390.40, 1275.92, 3961.18, and 4915.71 mg/L, respectively. Among XJZN, the compound with the highest content in XJZN1Y, XJZN2Y, and XJZN5Y was ethyl hexanoate, with 1241.14, 1071.89, and 1188.31 mg/L, respectively. The compound with the highest content in XJZN3Y was ethyl lactate, which has a content of 903.00 mg/L. The highest average content in XJDX was ethyl lactate (1374.97 mg/L), while the highest average content in XJMT and XJZN was ethyl hexanoate with 2235.91 and 1082.66 mg/L, respectively.Among all quantitative compounds, the ester compounds have the highest content, which was the key factor for the characteristic aroma of Baijiu. The esters in Baijiu were mainly produced by esterification of fatty acids and alcohols (Mo et al., 2009) and the metabolism of ester-producing yeast (Huang et al., 2018). The amounts of esters accounted for 82.96 %–83.56 % of the total aroma compounds in XJBJ. The total content of 10 esters in XJDX and XJMT showed an overall upward trend with aging. This was consistent with previous research results (Zhou et al., 2020; Zhu et al., 2016). The total amount of ester compounds in XJZN showed a decreasing trend with aging, which may be due to the decrease in the content of ethyl lactate with aging. Its accounts for 30.53 % of the total ester in XJZN. Acids generally exhibited fluctuating growth during the aging process, which was consistent with experimental results (Cao et al., 2021; Zhang, 2013). For example, butyric acid, hexanoic acid, and pentanoic acid increased with aging, which may be caused by the oxidation of aldehydes and alcohols (Ma et al., 2014). The total content of alcohols in XJDX, XJMT, and XJZN showed a trend of first increasing and then decreasing. However, a single type of alcohol did not show a significant change trend, which was consistent with previous research (Chen et al., 2023; Zhou et al., 2020).

Based on quantitative results and threshold calculations, there are 17, 16, and 15 compounds with average OAVs >1 in XJDX, XJMT, and XJZN, respectively (as shown in Table 3), included esters, acids, aldehydes, ketones, and alcohols. Among three different Baijiu products, a total of 13 common compounds had average OAVs ≥1, which were ethyl hexanoate (XJDX average OAV = 19,152, XJMT average OAV = 40,653, XJZN average OAV = 19,685, the following statement was the same), ethyl octanoate (2706, 3644, 1948), ethyl butanoate (2367, 3794, 1869), ethyl pentanoate (898, 2229, 274), butyric acid (89, 92, 89), pentanoic acid (85, 262, 31), 1-butanol (57, 93, 21), ethyl acetate (35, 43, 21), hexanoic acid (16, 31, 17), 1-hexanol (14, 19, 8), ethyl lactate (11, 9, 7), 1-propanol (3, 3, 3), ethyl hexadecanoate (2, 2, 1). In XJDX and XJMT, the OAVs of 1-pentanol (2, 3, <1) and ethyl heptanoate (1, 3, <1) were greater than 1, and the OAV of 2-methyl-1-propanol (<1, 1, <1) was only greater than 1 in XJMT. The OAV of furfural (<1, <1, 1) in XJZN was greater than 1. Among compounds with OAVs >1, ethyl hexanoate, ethyl octanoate, and ethyl butanoate have higher OAVs, whose OAVs were all above 1000 in XJDX, XJMT, and XJZN. Ethyl pentanoate only has an OAV > 1000 in XJMT. The highest OAV was ethyl hexanoate, with an OAV > 10,000. Compared to compounds with OAVs >1000 in Baiyunbian Baijiu, they was consistent with each other

Table 2
Concentrations of 25 volatile compounds in 16 different storage containers and years of Xiangjiao Baijiu.

No.	Compounds[i]	Concentrations (mg/L) [ii]																	
		XJDX							XJMT							XJZN				
		0Y	1Y	2Y	3Y	5Y	10Y	average	0Y	1Y	2Y	3Y	5Y	10Y	average	1Y	2Y	3Y	5Y	average
1	Ethyl acetate	1253.42 ± 176.61	886.10 ± 176.14	970.22 ± 185.63	1510.24 ± 84.6	891.45 ± 138.23	1309.34 ± 198.74	1136.80	1480.64 ± 485.10	1497.59 ± 34.12	1265.22 ± 140.77	987.20 ± 189.24	1527.05 ± 218.90	1687.21 ± 251.37	1407.49	732.27 ± 19.42	759.07 ± 67.03	730.10 ± 58	550.38 ± 55.18	692.96
2	Ethyl butanoate	61.26 ± 6.66	77.45 ± 3.11	178.38 ± 23.83	175.06 ± 2.89	176.02 ± 14.25	496.39 ± 75.82	194.09	85.82 ± 16.85	48.49 ± 2.82	120.25 ± 20.48	181.54 ± 27.83	827.55 ± 112.10	603.19 ± 95.26	311.14	121.59 ± 3.23	147.53 ± 14.21	165.77 ± 7.43	178.30 ± 10.99	153.30
3	Ethyl pentanoate	6.46 ± 0.74	6.57 ± 0.93	11.11 ± 1.46	26.91 ± 0.19	41.00 ± 0.29	52.31 ± 6.24	24.06	38.32 ± 4.76	36.07 ± 0.98	31.06 ± 2.09	22.58 ± 4.58	119.21 ± 22.77	110.93 ± 18.86	59.70	8.55 ± 1.34	7.32 ± 0.69	6.95 ± 0.76	6.54 ± 1.03	7.34
4	Ethyl hexanoate	665.64 ± 108.53	794.42 ± 83.11	1049.99 ± 99.95	1011.11 ± 169.62	401.37 ± 53.15	2397.74 ± 281.51	1053.38	1243.66 ± 37.54	628.59 ± 37.79	1390.40 ± 236.19	1275.92 ± 139.38	3961.18 ± 425.57	4915.71 ± 560.61	2235.91	1241.14 ± 19.66	1071.89 ± 50.12	829.31 ± 45.04	1188.31 ± 100.02	1082.66
5	Ethyl lactate	1750.16 ± 243.34	1421.46 ± 86.91	1128.17 ± 63.38	1557.84 ± 22.92	1069.10 ± 101.90	1323.09 ± 39.47	1374.97	1398.99 ± 24.08	1118.76 ± 4.59	861.62 ± 92.57	791.20 ± 44.09	1050.96 ± 86.92	1385.58 ± 112.84	1101.19	1015.03 ± 30.97	801.01 ± 15.26	903.00 ± 16.10	854.66 ± 43.04	893.43
6	Ethyl heptanoate	18.97 ± 2.72	6.39 ± 0.28	19.81 ± 1.29	22.35 ± 4.13	5.68 ± 0.10	36.71 ± 1.64	18.32	37.02 ± 1.59	14.24 ± 0.31	43.26 ± 4.27	42.49 ± 2.41	44.11 ± 2.38	25.75 ± 1.59	34.48	6.31 ± 0.48	14.77 ± 0.23	11.04 ± 0.15	13.91 ± 0.11	11.51
7	Ethyl 3-methylbutanoate	10.53 ± 0.13	16.12 ± 0.03	–	–	–	–	13.33	–	–	–	–	–	–	–	–	–	–	–	–
8	Ethyl 2-hydroxy-4-methylpentanoate	12.05 ± 1.56	15.86 ± 2.24	17.05 ± 1.56	18.21 ± 1.23	7.96 ± 1.55	9.25 ± 0.68	13.40	8.47 ± 0.51	8.09 ± 0.59	55.95 ± 1.18	98.32 ± 13.47	–	–	42.80	–	10.19 ± 1.25	16.96 ± 0.95	12.62 ± 0.37	13.26
9	Ethyl octanoate	7.46 ± 1.52	7.59 ± 0.58	34.35 ± 4.46	37.07 ± 0.13	47.87 ± 1.07	76.71 ± 7.40	120.18	51.19 ± 0.22	13.12 ± 1.99	33.55 ± 3.56	46.35 ± 8.78	85.36 ± 1.03	54.70 ± 4.43	47.38	11.37 ± 0.29	28.37 ± 4.95	28.24 ± 2.80	33.33 ± 1.49	25.33
10	Ethyl hexadecanoate	54.18 ± 2.84	59.69 ± 7.69	51.62 ± 1.83	158.32 ± 24.29	43.84 ± 0.17	40.18 ± 0.48	87.64	158.18 ± 14.48	47.68 ± 0.21	51.22 ± 2.67	56.19 ± 1.99	47.52 ± 0.62	49.77 ± 0.57	68.43	44.46 ± 0.15	48.73 ± 0.52	47.37 ± 0.45	44.36 ± 0.06	46.23
	All esters	**3840.13 ± 544.65**	**3286.06 ± 361.12**	**3460.70 ± 383.39**	**4517.11 ± 310.00**	**2684.29 ± 310.71**	**5859.72 ± 625.98**	**4036.16**	**4502.29 ± 585.13**	**3413.01 ± 83.32**	**3852.53 ± 503.78**	**3501.79 ± 431.77**	**7662.93 ± 870.29**	**8832.83 ± 1045.53**	**5308.50**	**3180.72 ± 75.54**	**2888.88 ± 154.27**	**2738.74 ± 131.68**	**2882.41 ± 212.29**	**2926.00**
11	Butyric acid	83.77 ± 0.75	83.92 ± 0.64	83.63 ± 0.65	88.75 ± 3.13	87.80 ± 3.15	87.04 ± 0.76	85.82	85.44 ± 1.17	88.25 ± 6.24	86.08 ± 1.22	85.50 ± 0.94	86.50 ± 3.88	100.39 ± 2.46	88.69	83.72 ± 0.10	89.86 ± 3.71	84.53 ± 0.15	85.39 ± 0.28	85.88
12	Hexanoic acid	40.64 ± 5.78	34.56 ± 3.39	41.35 ± 7.34	33.19 ± 0.15	34.26 ± 0.37	62.13 ± 0.85	41.02	34.83 ± 1.82	36.22 ± 3.03	52.60 ± 4.49	49.81 ± 5.90	77.43 ± 3.78	218.61 ± 26.72	78.25	34.39 ± 1.59	48.06 ± 4.28	39.16 ± 0.93	50.13 ± 2.54	42.94
13	Acetic acid	67.17 ± 11.28	11.99 ± 1.16	14.88 ± 2.89	85.90 ± 17.56	18.09 ± 3.04	17.79 ± 2.15	35.97	80.92 ± 13.92	37.47 ± 6.93	34.36 ± 5.01	50.46 ± 8.44	33.89 ± 3.46	61.05 ± 8.79	49.69	15.11 ± 2.36	12.14 ± 0.90	18.05 ± 1.90	11.59 ± 1.24	14.22
14	Pentanoic acid	1.96 ± 0.28	7.60 ± 0.39	23.09 ± 3.76	77.33 ± 7.93	42.57 ± 4.40	46.92 ± 6.18	33.25	89.94 ± 11.67	78.86 ± 3.64	54.29 ± 11.06	53.92 ± 4.35	135.53 ± 15.62	199.25 ± 36.25	101.97	6.62 ± 0.90	6.19 ± 0.75	11.30 ± 1.68	24.47 ± 4.09	12.15
15	2-Methylpropionic acid	0.14 ± 0.02	0.06 ± 0.01	–	–	–	–	0.10	–	–	0.42 ± 0.07	–	–	–	0.42	–	–	0.19 ± 0.02	0.14 ± 0.01	0.17
	All acids	**193.68 ± 18.11**	**138.13 ± 5.59**	**162.95 ± 14.64**	**285.17 ± 28.77**	**182.72 ± 10.96**	**213.88 ± 9.94**	**196.16**	**291.13 ± 28.58**	**240.80 ± 19.84**	**227.75 ± 21.85**	**239.69 ± 19.63**	**333.35 ± 26.74**	**579.30 ± 74.22**	**319.02**	**139.84 ± 4.95**	**156.25 ± 9.64**	**153.23 ± 4.68**	**171.72 ± 8.16**	**155.34**
16	1-Propanol	169.50 ± 3.65	155.66 ± 2.85	166.57 ± 4.37	184.38 ± 4.55	156.86 ± 2.42	163.75 ± 3.41	166.12	172.45 ± 1.98	162.93 ± 0.85	187.34 ± 10.13	177.30 ± 4.10	172.61 ± 5.93	228.15 ± 14.31	183.46	139.63 ± 5.83	154.80 ± 5.54	232.34 ± 10.28	151.26 ± 4.10	169.51
17	2-Methyl-1-propanol	13.63 ± 1.49	29.11 ± 2.94	24.71 ± 1.52	12.49 ± 1.24	21.06 ± 4.02	37.32 ± 6.05	23.05	17.33 ± 0.59	19.32 ± 2.39	23.13 ± 3.60	29.32 ± 3.80	46.08 ± 5.01	49.85 ± 8.91	30.84	15.55 ± 1.03	12.19 ± 0.61	24.06 ± 2.00	20.66 ± 0.61	18.12
18	1-Butanol	198.19 ± 35.52	149.10 ± 12.96	150.36 ± 17.94	241.28 ± 40.49	148.67 ± 25.43	47.55 ± 7.60	155.86	281.04 ± 7.17	290.94 ± 39.05	359.34 ± 64.24	257.13 ± 40.80	200.75 ± 23.35	136.38 ± 13.11	254.26	25.91 ± 1.08	140.30 ± 17.67	23.12 ± 4.17	40.37 ± 5.62	57.43
19	2-Methyl-1-butanol	21.61 ± 2.43	51.41 ± 4.51	35.79 ± 2.36	15.87 ± 0.02	19.90 ± 3.05	38.94 ± 1.36	30.59	17.83 ± 2.02	23.25 ± 1.05	25.04 ± 2.97	15.53 ± 0.10	64.06 ± 2.39	81.83 ± 8.49	37.92	–	21.10 ± 0.88	13.75 ± 0.50	–	17.43
20	3-Methyl-1-butanol	26.81 ± 4.45	123.16 ± 15.54	94.34 ± 3.38	41.79 ± 7.21	63.51 ± 7.41	103.83 ± 9.36	75.57	55.06 ± 3.42	72.13 ± 0.52	63.28 ± 6.43	51.48 ± 6.64	143.54 ± 8.93	157.91 ± 16.64	90.57	–	54.80 ± 2.77	–	–	54.80
21	1-Pentanol	11.25 ± 1.96	2.21 ± 0.36	6.68 ± 0.40	13.21 ± 0.40	4.72 ± 0.32	3.91 ± 0.27	7.00	16.30 ± 1.80	16.25 ± 0.19	15.82 ± 1.71	14.20 ± 0.93	5.83 ± 0.78	–	13.68	1.60 ± 0.07	5.85 ± 0.14	3.03 ± 0.34	2.82 ± 0.09	3.32
22	1-Hexanol	84.84 ± 11.87	36.27 ± 2.28	78.09 ± 1.50	135.30 ± 0.44	60.83 ± 3.79	53.20 ± 0.12	74.76	112.42 ± 10.30	82.34 ± 1.91	162.39 ± 23.51	141.94 ± 6.70	57.34 ± 2.50	53.19 ± 3.87	101.60	22.98 ± 0.29	75.23 ± 0.48	31.07 ± 0.60	36.90 ± 1.84	41.55
	All alcohols	**525.83 ± 61.37**	**546.92 ± 41.44**	**556.54 ± 31.47**	**644.32 ± 54.35**	**475.55 ± 46.44**	**448.50 ± 28.17**	**532.94**	**672.43 ± 27.28**	**667.16 ± 45.96**	**836.34 ± 112.59**	**686.90 ± 63.07**	**690.21 ± 48.89**	**707.31 ± 65.33**	**712.34**	**205.67 ± 8.30**	**464.27 ± 28.09**	**327.37 ± 17.89**	**252.01 ± 12.26**	**362.14**

(*continued on next page*)

Table 2 (*continued*)

No.	Compounds[i]	Concentrations (mg/L) [ii]																		
		XJDX							XJMT						XJZN					
		0Y	1Y	2Y	3Y	5Y	10Y	average	0Y	1Y	2Y	3Y	5Y	10Y	average	1Y	2Y	3Y	5Y	average
23	Furfural	42.64 ± 7.38	–	–	35.94 ± 11.86	–	–	39.29	–	–	–	–	–	–	0.00	–	45.39 ± 3.79	85.06 ± 5.72	48.05 ± 1.58	59.50
24	1,1-Diethoxy-3-methylbutane	10.65 ± 1.36	10.80 ± 0.67	11.53 ± 1.65	9.60 ± 0.74	9.95 ± 0.19	14.66 ± 1.94	11.20	9.51 ± 0.61	9.55 ± 0.72	13.37 ± 3.61	16.80 ± 1.63	17.54 ± 3.26	18.78 ± 2.66	14.26	–	6.70 ± 0.57	4.44 ± 0.45	3.65 ± 0.17	4.93
25	Acetoin	14.92 ± 1.53	13.45 ± 0.28	–	–	13.64 ± 0.60	–	14.00	–	–	–	–	–	–	0.00	–	16.42 ± 0.48	23.96 ± 0.30	16.97 ± 0.24	19.12
		68.21 ± 10.27	**24.25 ± 0.95**	**11.53 ± 1.65**	**45.54 ± 12.60**	**23.59 ± 0.79**	**14.66 ± 1.94**	**64.49**	**9.51 ± 0.61**	**9.55 ± 0.72**	**13.37 ± 3.61**	**16.80 ± 1.63**	**17.54 ± 3.26**	**18.78 ± 2.66**	**14.26**	**0.00 ± 0.00**	**68.51 ± 4.84**	**113.46 ± 6.47**	**68.67 ± 1.99**	**83.55**

[i] Important volatile compounds in 16 different storage containers and years of Xiangjiao Baijiu.
[ii] values (means ± SD, $n = 3$); –, concentration below detection limit.

(Zhou et al., 2020).

3.3. Difference of volatile compounds in Xiangjiao baijiu of different containers during aging

Complex physical and chemical changes such as volatilization, hydrolysis, esterification and oxidation occur during the storage of Baijiu, which also affect the trace compounds of Baijiu (Chen et al., 2023; Sun et al., 2024). During the storage of Baijiu, different storage containers also affect the changes of trace compounds. XJMT stores Baijiu in specially made pottery jars and places it in an underground cellar. XJDX uses in an underground cement tank as storage container. XJZN was directly stored in commercial glass bottles. Pottery jars has good air permeability, no liquid leakage, no light transmission, and slow heat conduction, which can accelerate the natural aging of Baijiu and increase the content of trace elements in Baijiu(Yu, 2023). The underground cement cellar has the characteristics of avoiding light, constant temperature and humidity and ventilation characteristics, which is conducive to the aging of Baijiu (Yu, 2023). Glass bottles have the advantages of smoothness, easy cleaning, corrosion resistance, wear resistance etc., but their high light transmittance is not conducive to the aging process of Baijiu (Zuo et al., 2021). These different containers could lead to different change trends in aroma compounds.

From Fig. 2, the trends of octanal, propyl propanoate, ethyl 2-methylbutanoate, 2-acetylfuran, nonanal, ethyl heptanoate, benzyl alcohol, 2-nonanone, 2-thiazoly-1-propanpne, and 3-methyl-1-butanol in XJDX and XJZN were consistent with each other, while the trends of XJMT were different from them. The trends of heptanal, isopentyl acetate, ethyl lactate, ethyl hexanoate, methyl hexanoate, ethyl propanoate, 2-methyl-1-butanol, 2-methyl-1-propanol, and 2-hexanone in XJDX and XJMT were consistent, while the trends of XJZN were different from them. 1-Butanol and dimethyl trisulfide show a trend of first increasing and then decreasing in XJMT and XJZN, while in XJDX, they showed an increased trend. In summary, the trend of volatile compound changes in XJDX was highly similar to that of XJZN and XJMT, while the trend similarity of volatile compounds in XJMT and XJZN was relatively low, which may be due to differences in their storage containers (Li et al., 2008; Wu et al., 2023). The specific aging mechanism requires further comparative research.

3.4. Statistical analysis

In order to study the key differential compounds affecting different types of XJBJ, PLS-DA was used to analyze 25 quantitated compounds in XJBJ. The results of PLS-DA (Fig. 4) indicate significant differences among samples of three product types. The compounds near the sample point have a high correlation with the sample, while the compounds far away from the sample point have a low correlation. As shown in Fig. 4 (a), ethyl 3-methylbutanoate, ethyl octanoate, ethyl lactate, and ethyl hexadecanoate have a great influence on the aroma of XJDX. Acetoin and furfural have a great impact on the aroma of XJZN. Most of the compounds including ethyl pentanoate, 2-methyl-1-propanol, pentanoic acid, etc. have a substantial effect on the aroma of XJMT.

Compounds with variable importance in projection (VIP) > 1.0 are generally regarded as the main cause of differences between samples (Chong and Jun, 2005). As shown in Fig. 4 (b), 10 compounds such as ethyl lactate, ethyl 3-methylbutanoate, 1,1-diethoxy-3-methylbutane, pentanoic acid, ethyl octanoate, ethyl acetate, 1-butanol, ethyl heptanoate, 3-methyl-1-butanol, and furfural were important compounds that lead to differences in different product types of XJBJ. Among them, the OAVs of ethyl octanoate (average OAV = 2706, 3644, 1948), pentanoic acid (85, 262, 31), 1-butanol (57, 93, 21), ethyl acetate (35, 43, 21), and ethyl lactate (11, 9, 7) were above 1, while the OAV of ethyl heptanoate (1, 3, < 1) in XJZN was less than 1, and the OAVs of furfural (<1, <1, 1) in XJDX and XJMT were all less than 1. The OAVs of ethyl 3-methylbutanoate in XJDX0Y and XJDX1Y were respectively 585 and 896, while in

Table 3
Odor thresholds and odor activity values of volatile compounds in 16 different storage containers and years of Xiangjiao Baijiu.

No.	Compounds	Threshold (μg/L)	OAV[i]																	
			XJDX							XJMT							XJZN				
			0Y	1Y	2Y	3Y	5Y	10Y	average	0Y	1Y	2Y	3Y	5Y	10Y	average	1Y	2Y	3Y	5Y	average
4	Ethyl hexanoate	55[a]	12103	14444	19091	18384	7298	43595	19152	22612	11429	25280	23199	72021	89377	40653	22566	19489	15078	21606	19685
9	Ethyl octanoate	13[a]	574	584	2642	2852	3682	5901	2706	3938	1009	2581	3565	6566	4207	3644	875	2182	2172	2564	1948
2	Ethyl butanoate	82[a]	747	945	2175	2135	2147	6054	2367	1047	591	1466	2214	10092	7356	3794	1483	1799	2022	2174	1869
3	Ethyl pentanoate	26.78[b]	241	245	415	1005	1531	1953	898	1431	1347	1160	843	4451	4142	2229	319	273	260	244	274
11	Butyric acid	964[a]	87	87	87	92	91	90	89	89	92	89	89	90	104	92	87	93	88	89	89
14	Pentanoic acid	389[a]	5	20	59	199	109	121	85	231	203	140	139	348	512	262	17	16	29	63	31
18	1-Butanol	2730[a]	73	55	55	88	54	17	57	103	107	132	94	74	50	93	9	51	8	15	21
1	Ethyl acetate	32699[a]	38	27	30	46	27	40	35	45	46	39	30	47	52	43	22	23	22	17	21
12	Hexanoic acid	2520[a]	16	14	16	13	14	25	16	14	14	21	20	31	87	31	14	19	16	20	17
22	1-Hexanol	5370[a]	16	7	15	25	11	10	14	21	15	30	26	11	10	19	4	14	6	7	8
5	Ethyl lactate	128000[a]	14	11	9	12	8	10	11	11	9	7	6	8	11	9	8	6	7	7	7
16	1-Propanol	54000[a]	3	3	3	3	3	3	3	3	3	3	3	3	4	3	3	3	4	3	3
10	Ethyl hexadecanoate	39299.35[c]	1	2	1	4	1	1	2	4	1	1	1	1	1	2	1	1	1	1	1
21	1-Pentanol	4000[a]	3	<1	2	3	1	<1	2	4	4	4	4	1	<1	3	<1	1	<1	<1	<1
6	Ethyl heptanoate	13200[a]	1	<1	2	2	<1	3	1	3	1	3	3	3	2	3	<1	1	<1	1	<1
17	2-Methyl-1-propanol	28300[a]	<1	1	<1	<1	<1	1	<1	<1	<1	<1	1	2	2	1	<1	<1	<1	<1	<1
20	3-Methyl-1-butanol	179000[a]	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
23	Furfural	44029.73[e]	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	1	2	1	1
8	Ethyl 2-hydroxy-4-methylpentanoate	45953.66[d]	<1	<1	<1	<1	<1	<1	<1	<1	<1	1	2	<1	<1	<1	<1	<1	<1	<1	<1
13	Acetic acid	160000[a]	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
19	2-Methyl-1-butanol	179190[a]	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
24	1,1-Diethoxy-3-methylbutane	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
15	2-Methylpropionic acid	1580[a]	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
25	Acetoin	259[a]	58	52	<1	<1	53	<1	27	<1	<1	<1	<1	<1	<1	<1	<1	63	93	66	55
7	Ethyl 3-methylbutanoate	18[a]	585	896	<1	<1	<1	<1	247	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1

[i] The odor activity values corresponding to volatile compounds.
[a] Odor thresholds from reference Liu et al., 2018.
[b] Odor thresholds from reference van Gemert, 2011.
[c] Odor thresholds from reference Zhang et al., 2019.
[d] Odor thresholds from reference Du et al., 2021.
[e] Odor thresholds from reference Fan and Xu, 2011.

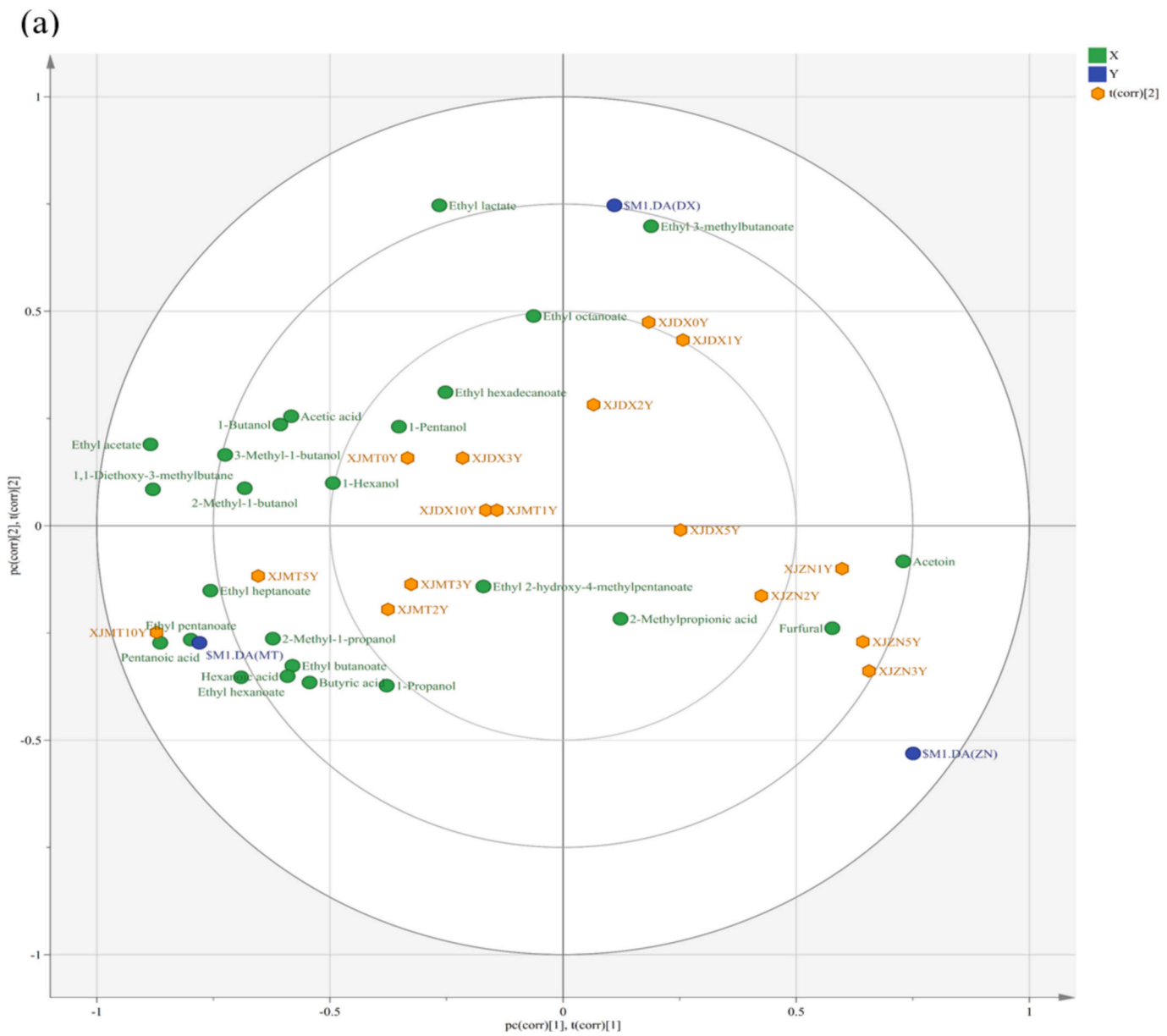

Fig. 4. (a) Biplot showing the correlation between volatile compounds and 16 different storage containers of Xiangjiao Baijiu in different years. (b) Average variable importance for the projection (VIP) values of 8 aroma compounds.

other 14 XJBJ were below 1.

4. Conclusions

The succession rules of XJBJ were first explored during the aging process through HS-GC-IMS and DI-GC–MS, and the differences between different storage methods have also been revealed in this study for the first time. A total of 40 and 60 compounds were identified via HS-GC-IMS and DI-GC–MS, respectively. In the three XJBJ during the aging process, the levels of furfural, 2-methyl-1-butanal, ethyl acetate, and methional showed a downward trend, the contents of hexanoic acid and 1-propanol remained basically unchanged, the concentrations of 1-hexanol, 3-octanol, ethyl 4-methylpentanoate, butyric acid, ethyl butanoate, and ethyl 3-methylbutanoate all showed an upward trend, and the contents of 2-heptanone and 2-ethylpyridine reached highest and then decreases. According to quantitative analysis, ethyl lactate (893.43–1374.97 mg/L), ethyl acetate (692.96–1407.49 mg/L), and ethyl hexanoate (1053.38–2235.91 mg/L) had higher concentrations. A total of 19 compounds had OAVs >1, of which those greater than 1000 included ethyl hexanoate (19,152, 40,653, 19,685), ethyl octanoate (2706, 3644, 1948), ethyl butanoate (2367, 3794, 1869), and ethyl pentanoate (898, 2229, 274). It showed that ester compounds contributed significantly to the aroma of XJBJ. According to PLS-DA analysis, it was found that ethyl octanoate, ethyl lactate, ethyl acetate, pentanoic acid, 3-methyl-1-butanol, 1-butanol, ethyl heptanoate, furfural, 1,1-diethoxy-3-methylbutane and ethyl 3-methylbutanoate were important compounds that lead to difference in XJBJ from different storage containers and years. This study provided a scientific basis the quality control of XJBJ during aging. In addition, more abundant methods should be used to further analyze the trace compounds in XJBJ, so as to provide further reference data for the product quality control and storage process improvement of XJBJ.

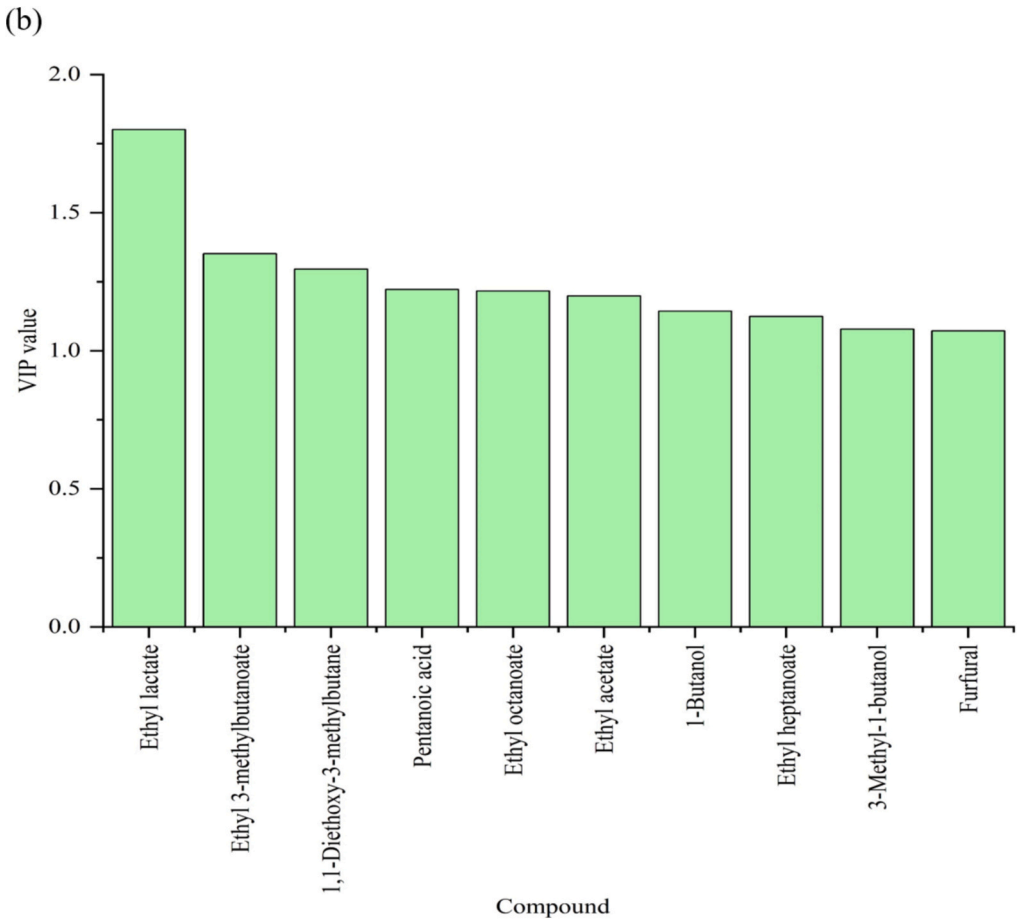

Fig. 4. (*continued*).

CRediT authorship contribution statement

Bing Zhang: Writing – original draft, Visualization, Software, Methodology, Investigation, Data curation, Conceptualization. **Siman Zheng:** Writing – original draft, Visualization, Software, Methodology, Investigation, Data curation, Conceptualization. **Mingquan Huang:** Writing – review & editing, Supervision, Methodology, Investigation, Funding acquisition. **Qiang Wu:** Validation, Supervision, Investigation. **Wei Dong:** Software, Investigation. **Jihong Wu:** Visualization, Software. **Hongqin Liu:** Validation, Supervision, Methodology. **Dongrui Zhao:** Validation, Supervision. **Yougui Yu:** Validation, Supervision. **Jinchen Li:** Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that may affect the work described herein.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fochx.2024.101976.

Data availability

Data will be made available on request.

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