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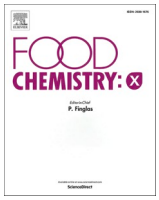

Maillard reaction intermediates in Chinese Baijiu and their effects on Maillard reaction related flavor compounds during aging

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ABSTRACT

This study investigated the Maillard reaction in Baijiu and the effects of extended aging in the presence of Maillard reaction intermediates (MRIs) on aromatic compounds, particularly focusing on heterocyclic changes. MRIs with different aroma types in Baijiu aged 1–18 years and force-aged for 6 weeks were determined. Results revealed that MRIs in soy sauce aroma–type Baijiu were significantly more abundant than those in other types of Baijiu. Changes in MRIs were observed and compared in aging and forced-aging Baijiu. Additionally, the distribution and variation of heterocycles in Baijiu were examined, which revealed an increase in N-heterocycle levels but a decrease in S- and O-heterocycle levels to a certain extent. The results of this study demonstrate that the Maillard reaction during the aging of Baijiu influences heterocycle concentrations, thereby improving flavor of aged Baijiu. Research into heterocycles and the Maillard reaction may help elucidate the aromatic evolution of Baijiu with aging and provide guidance for Baijiu storage.

1. Introduction

The widely recognised Maillard reaction, occurring between a free amino group and the carbonyl group of a reducing carbohydrate, initiates a series of complex chemical reactions within a complex instantaneous cascade reaction network. These reactions significantly affect the sensory properties and value of food (Gupta et al., 2018). The Maillard reaction ubiquitously occurs during food processing and storage, producing numerous reaction products, including Maillard reaction intermediates (MRIs) and volatile flavor compounds (Lan et al., 2010). MRIs are crucial compounds for studying the Maillard reaction owing to their influence on the colour, flavor and quality of food as precursors (Martins, Alcantara, Silva, Melchert, & Rocha, 2022; Shakoor, Zhang, Xie, & Yang, 2022).

MRIs, primarily 5-hydroxymethylfurfural, 5-methylfurfural, furfural, methylglyoxal, glyoxal, 2,3-butanedione, 2,3-pentanedione and 3-deoxyglucosone, can be categorised into α-dicarbonyl and furan compounds. Recently, more insights have been gained regarding the chemical process of the Maillard reaction and the synthesis pathways of over 100 volatile flavor compounds formed by MRIs have been elucidated (Shakoor et al., 2022). Carbon module labelling technology and model response validation experiments have revealed the transformation of MRIs into other Maillard reaction products (MRPs), especially heterocycles (Jiang et al., 2023). In terms of food quality, the presence of α-dicarbonyl compounds is often considered an indicator of optimal maturity or spoilage. These compounds are key precursors of heterocyclic flavor compounds, including pyrazines, oxazoles, furans and thiazoles (Y. Wang & Ho, 2012), and have been identified as key precursors of colour formation during storage in apple juice (Paravisini & Peterson, 2018). Furthermore, α-dicarbonyl compounds influence fermentation and aging processes (Hellwig, Borner, & Henle, 2021), particularly the yellowing degree and flavor of beer (Pieczonka et al., 2021). Similarly, furan MRIs contribute to aroma and taste, serving as potent indicators. Specifically, furfural and 5-methylfurfural are bitter compounds (Li, Wu, Tang, & Yu, 2019), whereas 5-acetoxymethyl-2-furaldehyde, formed from 5-hydroxymethylfurfural and acetic acid, is a novel sweet taste modulator (Hillmann et al., 2012). Additionally, furans influence aroma formation, and 5-hydroxymethylfurfural is often used as a time–temperature indicator for the heat treatment of food (Murkovic & Bornik, 2007), serving as an index compound for beer alongside 5-methylfurfural. Thus, MRIs offer a wide range of information for producers in terms of sensory/taste, flavor, colour and Maillard reaction monitoring.

Baijiu is a typical distilled liquor with low carbohydrate and amino

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acid concentrations. Reportedly, Maillard reactions occur during Baijiu aging and influence its flavor (L. L. Wang, Chen, & Xu, 2023). However, to the best of our knowledge, these reactions have not yet been observed during Baijiu aging. Considering the presence of abundant carbohydrates and amino acids and the use of high temperature during Baijiu fermentation and distillation, Baijiu is expected to be rich in typical MRPs, such as ketones, heterocycles, nitrogenous compounds, aldehydes and sulphur compounds (Hong, Zhao, & Sun, 2021). Thus, it is speculated that Maillard reactions occur during its aging process. Owing to the low temperature and low pH (pH 3–3.5) conditions employed during aging, the Maillard reactions may not progress beyond intermediate stages. In Baijiu, certain MRIs, including furfural and 5-methylfurfural, are abundant (He et al., 2020). However, MRIs such as glyoxal and methylglyoxal have not yet been detected in Baijiu. Thus, one of our objectives was to identify the MRIs and MRPs in Baijiu, aiming to explore the hypothesis regarding the Maillard reaction's contribution to the aroma compounds of Baijiu.

Herein, the volatile compounds and MRIs in Baijiu were quantified via GC × GC–TOF-MS and LC–MS, respectively, to identify any possible associations between aging and MRI and MRP concentrations. Additionally, MRI concentrations in Baijiu with different aroma types were investigated. This study aimed to establish the dynamics of certain MRPs and MRIs during Baijiu aging using real Baijiu as an example and to explore the effects of Maillard reactions and MRIs on the changes in flavor compounds in Baijiu.

2. Material and methods

2.1. Baijiu samples

In this study, 72 Chinese Baijiu samples from different distilleries were included, comprising 8 light aroma–type, 9 strong aroma–type and 15 soy sauce aroma–type samples. All samples were stored for the same duration. The remaining 40 samples were soy sauce aroma–type Baijiu directly stored in pottery jars following fermentation and distillation without blending. Thirty-nine of these samples were from various vintages, ranging from 2022 to 2004, and were stored in pottery jars at room temperature in a Baijiu cellar, whereas the remaining one was soy sauce aroma–type Baijiu with abundant MRPs. All samples were stored at 4 °C before analysis.

2.2. Analytical reagents

Glyoxal (40% solution in water, high-performance LC [HPLC] grade), methylglyoxal (40% solution in water, HPLC grade) and ethanol (99.9%, HPLC grade) were purchased from Sigma-Aldrich (Shanghai, China). Water was purified using a Milli-Q purification system (Millipore, Bedford, MA). Methanol (99.9%, LC grade), acetonitrile (ACN; 99.90%, LC grade), formic acid (99%, LC grade), furfural, 5-hydroxymethylfurfural, 5-methylfurfural, 2,3-butanedione and 2,3-pentanedione were purchased from Macklin Biochemical Co., Ltd. (Shanghai, China). 3-Deoxyglucosone was purchased from Yuanye Bio-Technology Co., Ltd. (Shanghai, China).

2.3. Analysis of MRIs in Baijiu via LC–MS

2.3.1. Sample preparation for analysing MRIs in Baijiu via LC–MS

The presence of 5-hydroxymethylfurfural was directly analysed. Baijiu samples were filtered through a 0.45-μm filter and prepared for analysis. Mingfu Wang's method (D. Liu, He, Xiao, Zhou, & Wang, 2021) was used to analyse dicarbonyls as their corresponding quinoxalines following derivatisation with *o*-phenylenediamine. Subsequently, 1 mL of Baijiu was mixed with 5 μL of 500 mM *o*-phenylenediamine and incubated at 37 °C for 2 h before filtration through a 0.45-μm polytetrafluoroethylene (PTFE) filter membrane. The presence of furfural and 5-methylfurfural was investigated following derivatisation with 2,4-dinitrophenylhydrazine using Naotaka Kuroda's mothed (El-Maghrabey, Suzuki, Kishikawa, & Kuroda, 2021). Then, 500 μL of Baijiu was mixed with 500 μL of 2,4-dinitrophenylhydrazine (2 g/L) and incubated at 50 °C for 2 h before filtration through a 0.45-μm PTFE filter membrane.

2.3.2. UPLC conditions for analysing MRIs in Baijiu via LC–MS

An electrospray ionisation source–equipped triple-quadrupole mass spectrometer (Xevo TQ-S, Waters Corp., USA) was used to determine the MRIs in Baijiu (Yan, Chen, He, Nie, & Xu, 2020). The source was operated under a capillary voltage of 3 kV, spray gas flow of 800 L/h, solvent temperature of 500 °C and conical gas flow of 50 L/h. To optimise the multiple reaction monitoring (MRM) mode associated with acquisition parameters, a direct infusion of the standard solution and derivatised standard solution (20 mg/L) was performed at an infusion flow rate of 5.0 L/min, cone voltage of 5–50 V and collision energy of 5–35 eV. The Sample Tune and Develop Method functions in MassLynx software (Xevo TQ-S, Waters) were employed to optimise the parent ion (*m/z*), product ions (m/z), cone voltage (V) and collision energy (eV) for each MRI detection. The optimised MRM transition for each MRI is listed in Table S1 based on its response and ion fragments.

The chromatographic separation of MRIs was performed using a Waters BEH C18 column (100 × 2.1 mm, 1.7 μm) with the ACQUITY UPLC system (binary solvent manager, Waters Corp., USA). The column temperature was maintained at 30 °C, with an injection volume of 10 μL. The mobile phase comprised 0.1% formic acid in ACN and 0.1% formic acid in water. 5-Hydroxymethylfurfural was detected via a gradient elution from 85% to 78% water in 8 min at a flow rate of 0.3 mL/min. α-Dicarbonyl detection was detected as follows: 0–5 min, 25% B; 5–6 min, 25%–80% B; 6–7.5 min, 80% B; 7.5–10.5 min, 80%–100% B; 10.5–12.5 min, 100% B; and 12.5–16 min, 25% B. Furfural and 5-methylfurfural were detected as follows: 0–5 min, 55% B; 5–6 min, 55%–80% B; 6–7.5 min, 80% B; 7.5–10.5 min, 80%–100% B; 10.5–12.5 min, 100% B; and 12.5–16 min, 25% B.

2.4. Analysis of volatile compounds in Baijiu via headspace-solid phase microextraction–comprehensive two-dimensional gas chromatography-time-of-flight-mass spectrometry

Volatile aroma compounds were quantified via headspace-solid phase microextraction (HS-SPME)–GC × GC − TOF-MS (L. Wang et al., 2020). In a 20-mL screw-capped vial, 5 mL of Baijiu was diluted to a final ethanol concentration of 10% and spiked with 10 μL of a mixed internal standard (n-hexyl-d13-alcohol, 200 mg/L and Is3: 2-phenylethyl acetate-d3, 200 mg/L) saturated with 1.5 g NaCl. Volatile compounds were extracted using an automatic headspace sampling system (MultiPurpose Sample MPS2 with an SPME adaptor, from Gerstel) with a 50/30-μm DVB/CAR/PDMS fibre (2 cm, Supelco, Inc., Bellefonte, PA, USA). The samples were equilibrated at 40 °C for 5 min and extracted under stirring (250 rpm) for 40 min. After extraction, the fibre was placed in a GC injection port at 250 °C for 5 min to allow analyte desorption.

Following extraction, the fibre was inserted into the injection port of a gas chromatograph (250 °C) and desorbed for 5 min. Herein, a LECO Pegasus 4D GC × GC–TOF-MS system (LECO Corporation, St. Joseph, MI, USA) with an Agilent 7890B gas chromatograph (Agilent Technologies, Palo Alto, CA, USA) was employed. GC × GC separation was performed using a polar/moderately polar column arrangement. A DB-FFAP column (60 m × 0.25 mm i.d.; 0.25-μm film thickness, Agilent Technologies Inc.) was used as the first dimension (1D), and an Rxi-17Sil MS Cap. column (1.5 m × 0.25 mm i.d.; 0.25-μm film thickness, Restek Technologies Inc.) was used as the second dimension (2D). The oven temperature of the first column was set at 45 °C for 3 min, increased by 4 °C/min to 150 °C, held for 2 min, increased by 6 °C/min to 200 °C, increased by 10 °C/min to 230 °C and held for 10 min. Throughout the chromatography, the temperature of the second column was maintained

5 °C higher than that of the first column, resulting in a total analysis time of 52.58 min. A quad-jet, dual-stage thermal modulator was installed between the 1D and 2D columns, with a modulation period of 4 s and hot pulse time of 0.8 s. The transfer line and ionisation source temperatures of the TOF-MS system were set at 240 °C and 230 °C, respectively. Electron impact mass spectra were recorded at 70 eV and acquired over a 35,400 amu *m/z* scan range. Standard curves were established as previously described, and all samples were evaluated in triplicate.

2.5. Statistical analysis

Mean comparisons were performed using Tukey's test ($\rho > 0.5$; $P < 0.05$, 0.01, 0.001). Correlation networks were visualised using Gephi (Version 0.9.1) with a classic Fruchterman–Reingold algorithm.

3. Results and discussion

3.1. Detection of MRIs in Baijiu

Only some MRIs, such as 5-methylfurfural, furfural, 2,3-butanedione and 2,3-pentanedione, have been previously detected in Baijiu (H. Liu & Sun, 2018). To gain a better understanding of the occurrence of the Maillard reaction during Baijiu aging, an MRI detection method was used to determine the distribution of MRIs. Variations in the MRIs indicated different degrees of the Maillard reaction during Baijiu aging, resulting in various Maillard reaction–related flavor compounds.

3.1.1. Detection method of MRIs in Baijiu

An MRM method was developed for MRI detection. Calibration curves demonstrate the linearity of all the compounds (Table S1). MRIs exhibited good linearity over a wide concentration range with excellent correlation coefficients ($R^2 > 0.99$). The limits of detection and quantification of the MRIs were estimated at 0.1221–2.3609 and 0.4069–7.8698 μg/L, respectively. Precision measurement was conducted based on a stable instrument status, and the results demonstrating reproducibility were recorded as relative standard deviation values within the triplicates (<20%). Additionally, the recovery rates were between 80% and 120%. These observations validate the LC–MS approach used in this study to quantify the MRIs in Baijiu.

3.1.2. MRI concentrations in different types of Baijiu

Seven box charts were created to compare the average and overall concentrations of 5-hydroxymethylfurfural, 5-methylfurfural, furfural, glyoxal, methylglyoxal, 2,3-butanedione and 2,3-pentanedione in Baijiu with different aroma types (Fig. 1). As expected, certain types of Baijiu exhibited high concentrations of specific MRIs. Furfural demonstrated the highest concentration (3.31–284.21 mg/L), followed by 5-methylfurfural (69.12–127,846.20 μg/L) and 2,3-butanedione (33.48–91,297.47 μg/L). The concentrations of glyoxal and methylglyoxal were 26.34–1582.20 and 51.92–2958.03 μg/L, respectively. The

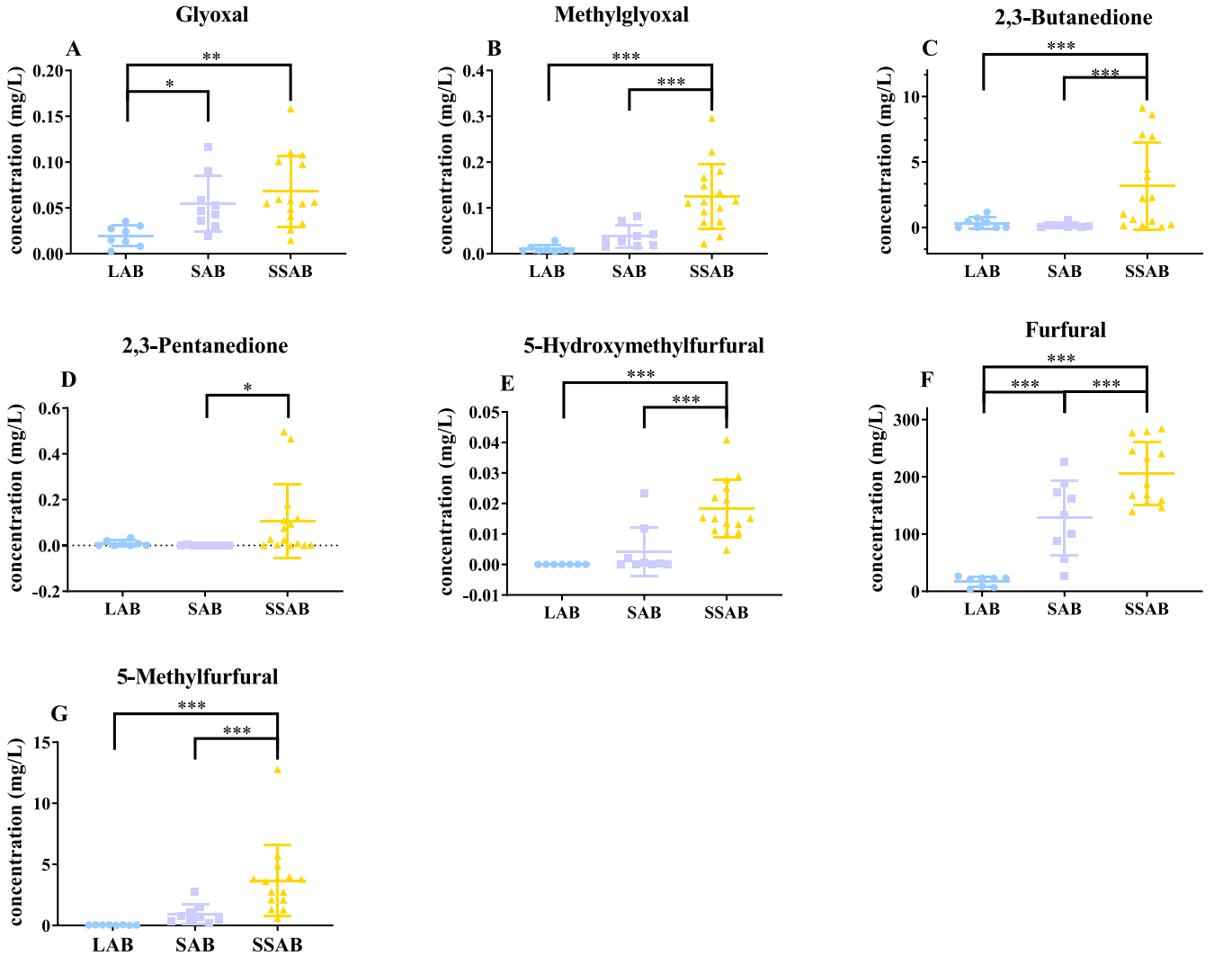

Fig. 1. Simultaneous analysis of different MRIs detected in light aroma–type Baijiu (LAB), strong aroma–type Baijiu (SAB) and soy sauce aroma–type Baijiu (SSAB).

concentrations of 5-hydroxymethylfurfural and 2,3-pentanedione exceeded the detection limit in some Baijiu samples, with their highest values being 289.46 and 1777.44 μg/L, respectively. Moreover, the concentration of 3-deoxyglucosone, an important precursor of aging in beer (Nobis et al., 2021), was below the detection limit in Baijiu with various aroma types; however, it has been detected in red wine and whisky (X. J. Wang et al., 2018). This result can be attributed to the lack of sugars in Baijiu to produce 3-deoxyglucosone. The glucose content was 298.1 ± 135.3 μg/L and 502.8 ± 10.80 μg/L, lower than the values detected in wine or champagne (Jia & Ma, 2023). Moreover, 5-hydroxymethylfurfural, 5-methylfurfural and furfural, which are MRIs derived from furfural, can be detected in various substances, such as coke, milk, coffee, beverages, bread, beer, urine and other solid or liquid substances (da Silva, Gauche, Gonzaga, Costa, & Fett, 2016; Jian-Yuan, Zhi-Guo, & Yu-Qi, 2009). The concentration of 5-hydroxymethylfurfural in light aroma–type Baijiu was below the detection limit, whereas it was the highest in soy sauce aroma–type Baijiu, substantially different from the other two types. Similarly, the highest concentration of 5-methylfurfural was detected in soy sauce aroma–type Baijiu, significantly differing from those in the other two Baijiu types. Among all MRIs in Baijiu, furfural exhibited the highest concentration, with its concentration being the highest in soy sauce aroma–type Baijiu (121.96–284.21 mg/L) (26.20–225.94 mg/L in strong aroma–type Baijiu and 3.31–26.54 mg/L in light aroma–type Baijiu), with the difference being significant. The glyoxal and methylglyoxal concentrations were 14.58–158.23 and 37.23–295.80 μg/L in soy sauce aroma–type Baijiu, 18.84–116.09 and 16.02–81.83 μg/L in strong aroma–type Baijiu and 2.63–35.26 and 5.19–28.29 μg/L in light aroma–type Baijiu, respectively. Glyoxal and methylglyoxal exhibited a low steady-state concentration (Lund & Ray, 2017), explaining their low concentrations in Baijiu. Additionally, the glyoxal concentration significantly differed between light aroma–type Baijiu and the other two types of Baijiu. Methylglyoxal concentrations also significantly differed between soy sauce aroma–type Baijiu and the other two types of Baijiu. In comparison, glyoxal and methylglyoxal concentrations have been estimated at 2.48–4.00 and 0.86–1.07 mg/L (Paravisini & Peterson, 2019) in orange juice and 0.3–1.3 and 0.8–33.0 mg/kg in honey (Marceau & Yaylayan, 2009), respectively. Therefore, glyoxal and methylglyoxal concentrations in Baijiu were considerably lower than those in other foods, indicating suppressed Maillard reactions during Baijiu aging (Wang & Ho, 2012).

Generally, various MRIs are present in Baijiu with different aroma types, owing to its unique traditional brewing and fermentation technology. Interestingly, the soy sauce aroma–type Baijiu exhibited the highest concentrations of MRIs. Its higher fermentation, distillation and accumulation temperatures, along with a longer fermentation time, were conducive to the Maillard reaction and the production of MRIs and other Maillard reaction precursors. These precursors effectively enhanced the quality of Baijiu during the slow aging process, and there is a likelihood that the Maillard reaction occurs during the Baijiu aging process. The elevated concentration of MRIs in the soy sauce aroma–type Baijiu increases the possibility of the occurrence of the Maillard reaction during Baijiu aging, thereby confirming our hypothesis.

3.1.3. MRI concentrations in soy sauce aroma–type Baijiu aged for various time periods

To assess the concentration of various MRIs in aged Baijiu and

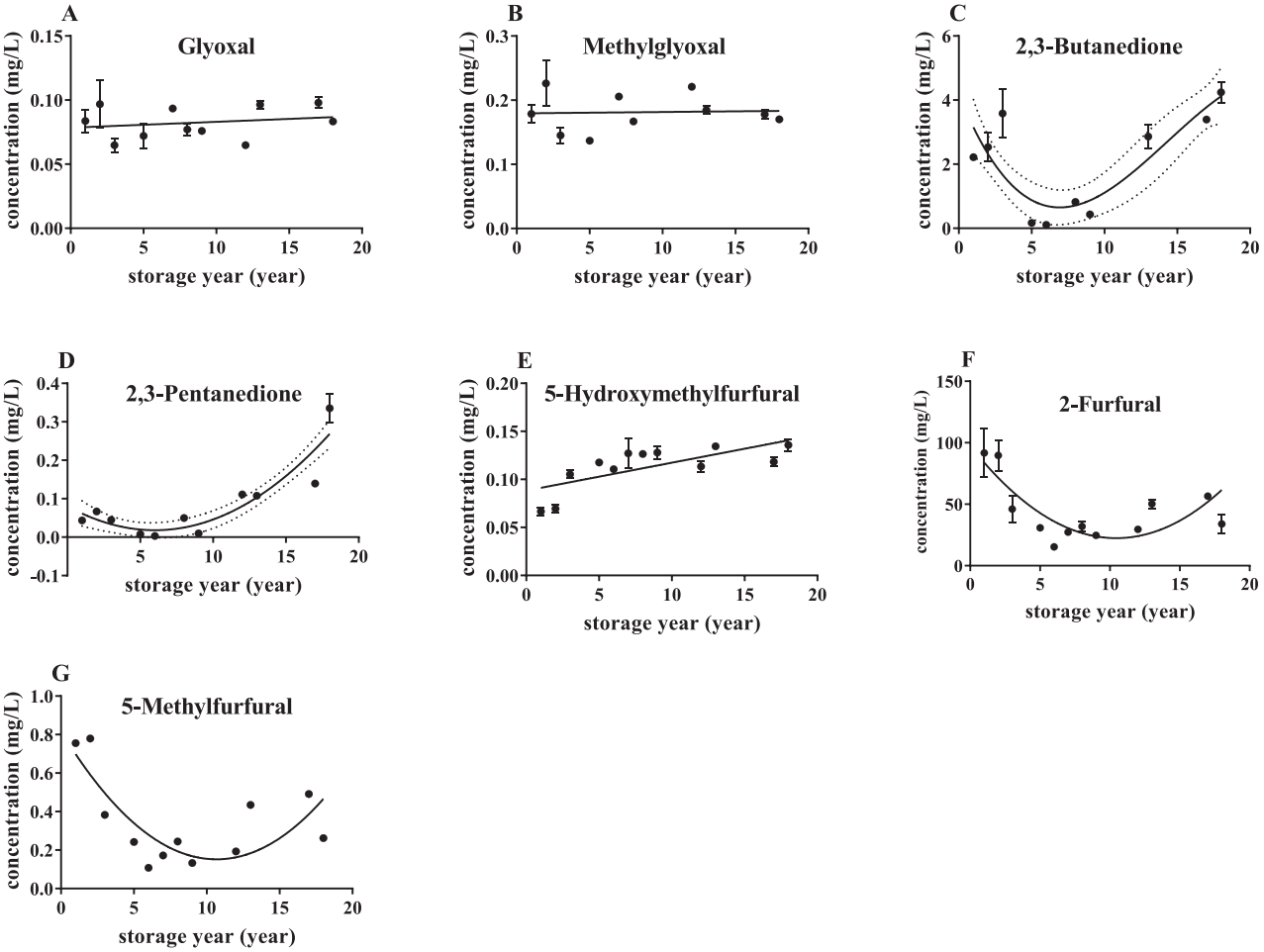

Fig. 2. Analysis of different MRIs detected in Baijiu aged for various time periods.

further confirm the occurrence of the Maillard reaction during Baijiu aging, soy sauce aroma–type Baijiu aged for different years was selected based on the highest MRI concentration in various Baijiu types. The concentration of 5-hydroxymethylfurfural increased gradually from 0.0666 to 0.1358 mg/L (Fig. 2) in the soy sauce aroma–type Baijiu, considered a time–temperature indicator in coffee (Macheiner, Schmidt, Karpf, & Mayer, 2021). In pH lower than 7.0, reducing sugars formed Amadori and Heyns rearrangement products via cyclisation, producing 3-deoxyglucosone, a precursor of 5-hydroxymethylfurfural. The slow accumulation of 5-hydroxymethylfurfural, likely due to a lack of sugar during the aging process, renders it a potential marker of aging time in aged Baijiu. The concentration trend of 5-methylfurfural was similar to that of furfural, decreasing after 9 years of storage and slightly increasing after 12 years of storage. Furfural and 5-methylfurfural are key aroma precursors in the generation of sulphur-containing flavors, with notable examples being 2-furfurylthiol and 2-methyl-3-furanthiol (Yaghmur, Aserin, Abbas, & Garti, 2005). These compounds are considered aroma precursors related to furan flavor compounds in the Baijiu aging process. Glyoxal and methylglyoxal concentrations in aged unblended Baijiu were higher than those in other commercial Baijiu samples. When Baijiu was stored in pottery jars, the Maillard reaction was highly active during the aging process owing to the use of a suitable concentration of oxygen and the catalysis of metal ions. The glyoxal and methylglyoxal concentrations remained stable at 0.08 and 0.2 mg/L, respectively, in aged Baijiu, possibly due to the maintenance of a consistent temperature during the aging process, leading to stable Maillard reaction rates. However, the concentrations of methylglyoxal and glyoxal did not differ, and their dynamic changes could not be confirmed. The concentration of 2,3-butanedione was unstable, decreasing in the first 6 years of storage and increasing with further storage. The 2,3-pentanedione concentration increased and peaked at 18 years of storage at 0.3351 mg/L. Generally, MRIs in aged Baijiu exhibit distinct characteristics, providing evidence of the occurrence of the Maillard reaction during the Baijiu aging process. Furthermore, as precursors of MRPs, changes in MRIs influence the production of aroma compounds during the aging process. Among the MRIs, α-dicarbonyl compounds participate in the formation of heterocyclic compounds such as pyrazines, pyranones, furans, furanones and pyrroles and sulphur-containing compounds such as thiols, thiophenes and thiazoles, which are important for imparting food flavor (Shakoor et al., 2022) and Baijiu quality. Moreover, furfural reacts with organic acids to produce compounds such as furfuryl acetate and furfuryl propanoate. Additionally, furfuryl and 5-methylfurfuryl produce other furan compounds, influencing the flavor of aging Baijiu.

3.2. Effects of the Maillard reaction on volatile compounds in Baijiu

3.2.1. Effects of the Maillard reaction and MRIs on volatile compounds in aged Baijiu

The effects of the Maillard reaction on the flavor of Baijiu and its mechanism of occurrence are unknown. In this study, the GC × GC − TOF-MS data of soy sauce aroma–type Baijiu were evaluated using the following approach. A data table was generated, including sample names, retention times, extracted masses and peak areas. Over 2000 peaks for each sample were observed. The selection method was as follows: LECO ChromaTOFTM Workstation (version 4.44) was used for all acquisition control and data processing. Automated peak detection and spectral deconvolution were employed, setting the minimum signal-to-noise (S/N) ratio necessary to record a chromatographic peak at 30 in GC × GC. A preliminary identification of the compounds was performed by comparing the experimental retention indices of the compounds with the retention index library developed by our lab. A compound was considered preliminarily identified if the mass spectral information for each chromatographic peak was at least 75% similar to the previously established mass spectral library in our lab and if the difference between RI and RIT was no >30 units. Positive identification of compounds was achieved by comparing the retention data and mass spectra of the standard compounds listed in the data table, and 389 volatile compounds were tentatively identified (He et al., 2020). The correlation between these compounds and MRIs and aging time was further analysed via Spearman correlation analysis. Finally, 109 compounds with correlation coefficients higher than 0.6 were selected. Consequently, 109 potential Maillard reaction–related aroma compounds were identified from 13 Baijiu samples aged for different years based on HS-SPME–GC × GC–TOF-MS analysis, including 19 furanoids, 14 aldehydes, 16 sulphur compounds, 14 pyrazines, 11 alcohols, 17 ketones, 7 esters, 4 phenols, 2 oxazoles and 5 terpenes. To visualise the relationship between the MRIs and these 109 aroma compounds, heat map and hierarchical cluster analysis were used (Fig. S1). Furfural, 5-methylfurfural, 2,3-butanedione and methylglyoxal exhibited a highly positive correlation with potential Maillard reaction–related aroma compounds, whereas 5-hydroxymethylfurfural and aging time demonstrated a highly negative correlation with potential Maillard reaction–related aroma compounds. There were 43 aroma compounds with a correlation coefficient of >0.7 with MRIs, and 22 of them were heterocycles. Additionally, 20 aroma compounds exhibited a correlation coefficient of >0.8 with MRIs, and 11 of them were heterocycles. Seven heterocycles were O-heterocycles, and all were furan compounds. Among them, methyl 2-methyl-3-furyl disulphide exhibited flavors of cooked meat and thiamine and a low flavor odour of 0.3 μg/L. There were three pyrazines (2,3-dimethyl-5-ethylpyrazine, 2,3-dimethylpyrazine and 2,3,5,6-tetramethylpyrazine) and one S-heterocycle (2,4,5-trimethyloxazole). Except for the heterocycles, six aroma compounds were ketones, in which 3-hydroxy-2-butanone was a tetramethylpyrazine precursor; two were sulphur compounds, and dimethyl trisulphide was a precursor of S-heterocycles. Furthermore, Maillard reaction–associated products including furans, nitrogen, sulphur and oxygen heterocycles were reported to contribute roasted, bready, nutty and caramel aromas to the overall wine flavor and are believed to be formed through Maillard reaction or Maillard reaction–like activity during wine aging (Charnock, Pickering, & Kemp, 2022). Thus, heterocyclic compounds are highly correlated with MRIs and were selected to examine the effects of MRIs and the Maillard reaction during Baijiu aging.

3.2.2. Effects of the Maillard reaction and MRIs on heterocyclic compounds in aged Baijiu

In total, 53 heterocyclic compounds with a high correlation with the Maillard reaction were selected and considered MRPs. To determine the correlation between MRIs and these 53 MRPs and precursors in Baijiu with different aging years, a Sankey diagram was created (Fig. 3). The low correlation between years of aging and aroma compounds was mainly due to unstable Baijiu quality and flavors owing to different aging years and differences in the brewing craft in some distilleries. Compounds with a correlation coefficient of >0.6 with 5-hydroxymethylfurfural included furfuryl butyrate, furfuryl acetate, 2,4-di-tert-butylphenol, furfuryl hexanoate, furan, 2-methyl furan, 2,2′-methanediyldifuran, 2,2′-bifuran, thiophene, furfuryl alcohol and furfuryl propionate. Nine out of eleven were furan compounds, which also demonstrated a high correlation with 5-methylfurfural and furfural, both having a furan group. 5-Hydroxymethylfurfural and 5-methylfurfural were negatively and positively correlated with furfural, respectively. Thus, 5-hydroxymethylfurfural was considered more stable than furfural and 5-methylfurfural, with its increase, furan compounds such as furfural and 5-methylfurfural may undergo further reactions. Possible mechanisms of furfural and 5-methylfurfural formation from furan, 2-methylfuran, furfuryl alcohol and 2-furoic acid have been reported (Delatour et al., 2020). Thus, furfural and 5-methylfurfural are important precursors of the Maillard reaction and key intermediates in the Baijiu aging process. As shown in Fig. S2, Furfuryl alcohol, formed via furfural reduction, can form furfuryl butyrate, furfuryl acetate, furfuryl hexanoate and furfuryl heptanoate with abundant acids in Baijiu. Furfural can also form 2,2′-difurfuryl ether and 2,2′-methanediyldifuran;

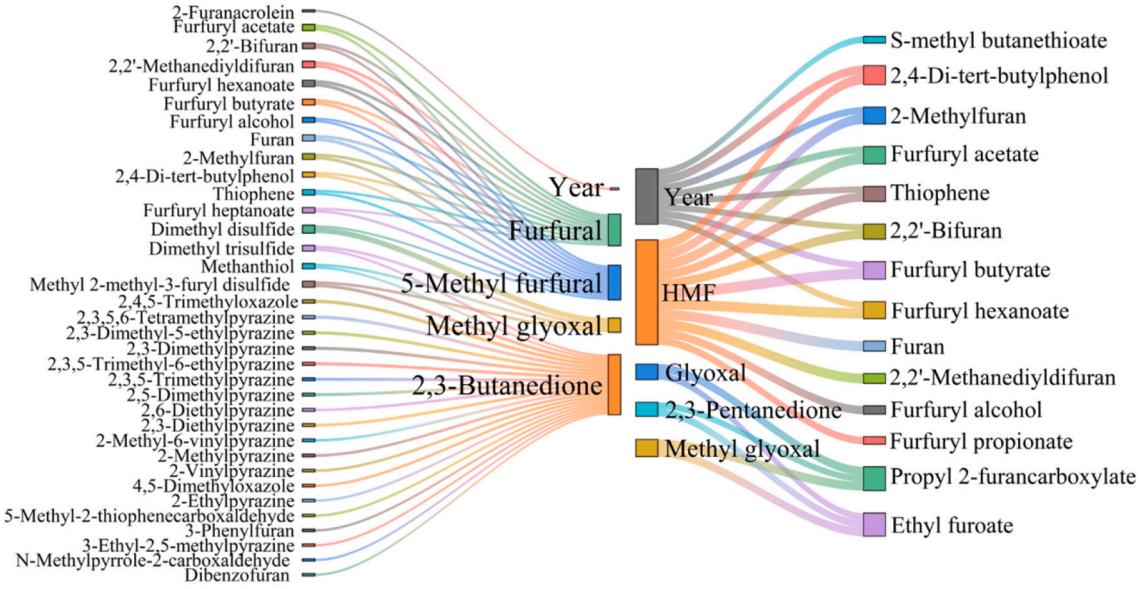

Fig. 3. Sankey diagram of correlation between MRIs and MRPs detected in Baijiu aged for various time periods ($\rho > 0.5$). Left side, positive correlation; right side, negative correlation.

furfuryl and 5-methylfurfural exhibit a high correlation with these compounds. Furans are commonly produced through a nonenzymatic browning Maillard reaction. The dramatic changes in furan concentrations are crucial for the flavor change during Baijiu aging. Furan Maillard reaction compounds commonly exhibit sweet, caramel, nutty and baked aromas, whose intensities reportedly increase during the Baijiu aging process (L. Zhu et al., 2020). Low molecular weight furans decreased in our study; it is considered in the Baijiu aging process that the molecular weight of compounds in Baijiu increased. The correlation of glyoxal and volatile compound concentrations was low; no compounds exhibited a positive coefficient of >0.6, and propyl 2-furancarboxylate and ethyl furoate exhibited a negative coefficient of >0.6. The aroma compounds with a positive correlation coefficient with methylglyoxal of >0.6 included dimethyl trisulphide, dimethyl disulphide, methanethiol, methyl 2-methyl-3-furyl disulphide and dimethyl disulphide. The higher concentrations of methyl 2-methyl-3-furyl disulphide, methanethiol and dimethyl trisulphide were reportedly responsible for the pickle-like off-odour of Moutai aroma–type Baijiu (L. Wang et al., 2020). Therefore, during aging, the Maillard reaction of methylglyoxal with methyl 2-methyl-3-furyl disulphide, methanethiol and dimethyl trisulphide reduces this pickle-like odour. Because of the high positive correlation between methanethiol, dimethyl disulphide, dimethyl trisulphide, dimethyl sulphide and methylglyoxal, these compounds might undergo further reactions in Maillard reactions rather than being volatilised during the aging process. Aroma compounds positively correlated with 2,3-butanedione with a coefficient of >0.8 were 2,4,5-trimethyloxazole, 2,3,5,6-tetramethylpyrazine, methyl 2-methyl-3-furyl disulphide, 2,3-dimethyl-5-ethylpyrazine and 2,3-dimethylpyrazine. Reactive carbonyl species react with amino compounds to form pyrazines. Furthermore, the synthesis pathway of tetramethyl pyrazine from 3-hydroxy-2-butanone has been reported (B. F. Zhu & Xu, 2010); 3-hydroxy-2-butanone and tetramethyl pyrazine constitute important flavor compounds in the soy sauce aroma–type Baijiu and might be related to the soy sauce flavor (Wu & Xu, 2012). Moreover, the high concentrations of methyl 2-methyl-3-furyl disulphide are an important factor in the pickle-like off-odour of the soy sauce aroma–type Baijiu (L. Wang et al., 2020). Through the correlation analysis of the Baijiu with different aging years, it is speculated that MRIs and Maillard reactions play an important role in the aging process of Baijiu, thereby influencing its flavor, the reaction pathways of MRIs to heterocycles were also elucidated.

3.2.3. *Variations in heterocycles concentrations during Baijiu aging*

The principal component analysis model based on the concentrations of heterocycles in relation to Baijiu age is presented in Fig. S3. The first two components explained 69.38% of the total variance. Baijiu age was projected in the second quadrant of the plot. Three clusters of heterocyclic compounds were identified based on their concentration variations in relation to age. Cluster 1 (depicted in green in Fig. S3) comprised furfuryl butyrate, 2,2′-difurfuryl ether, 2-methylfuran, furan, furfuryl hexanoate, thiophene, 2(5H)-furanone and 2-pentylthiophene. These compounds were positioned opposite to the age variable and exhibited a significant negative correlation with Baijiu aging. Heterocycles in Cluster 2 (represented in red in Fig. S3), including 2,3,5,6-tetramethylpyrazine and 2,3,5-trimethylpyrazine, also projected on the opposite side. The principal component analysis plot revealed that nitrogen-containing heterocycles were negatively correlated with Baijiu age; however, oxygen- and sulphur-containing heterocycles were positively correlated with Baijiu age, indicating that oxygen- and sulphur-containing heterocycles can participate in further reactions.

Fig. S4 highlights the heterocycles selected from Baijiu produced from 2001 to 2018. The correlation of the various heterocycle concentrations with Baijiu age mainly revealed a nonlinear regression, reflecting the complexity of the Maillard reaction in the Baijiu aging process. The low correlation between aging years and aroma compounds was chiefly due to the unstable Baijiu quality and flavor owing to different years of aging and changes in the brewing craft of distilleries. The concentration of 2,3-butanedione in a 12-year-old Baijiu was 14.31–14.96 mg/L, which was seven times higher than that in a 13-year-old Baijiu. Similarly, the concentration of pyrazines in a 12-year-old Baijiu was significantly higher than that in other aged Baijiu. Reportedly, 2,3-butanedione is a key precursor of pyrazines (Sun, Ni, Yang, & Qin, 2022). Thus, the 12-year-old Baijiu was considered an abnormal sample and removed from the evaluation of the variations in heterocycle concentrations during Baijiu aging. The results revealed that the concentrations of 2,3,5,6-tetramethylpyrazine and 2,3,5-trimethylpyrazine increased; the former fit a second-degree polynomial while the latter fit a linear polynomial. Furfuryl butyrate, 2,2′-difurfuryl ether and thiophene concentrations decreased and fit a second-degree polynomial, whereas 2-methylfuran, furan and furfuryl hexanoate fit an

exponentiation and decreased and stabilised at 5 years. Other compounds, such as 2(5H)-furanone and 2-pentylthiophene, exhibited a strong Spearman's correlation with aging; however, they did not demonstrate a significant dynamic fit. In brief, pyrazines may accumulate during the aging process in Baijiu, and other furans and sulphur-containing heterocycles may participate in subsequent reactions that have a major influence on colour development. The variations in heterocycles and MRIs concentration indicate the relevance between them, and the given reaction pathway confirms the relationship.

3.3. Verification of the effects of MRIs on volatile compounds in Baijiu

3.3.1. MRI content in forced aging Baijiu

As the sugar and amino acid concentrations in Baijiu were low (highest glucose concentration, 3.3 mg/L (Wang Xiaodan, Li, Fuyan, Chao, & Dongming, 2021); total amino acid concentration, 13.66–34.01 mg/L (Zhang Zhuangying & Yan, 2014)), the concentration of raw materials for the Maillard reaction in Baijiu was limited. Furthermore, because glyoxal and methylglyoxal were stable in differently aged Baijiu with low steady-state concentrations, it was very difficult to determine their concentrations. Thus, forced aging was performed on the original Baijiu at high temperatures to observe the variability of MRIs and eliminate the influence of technology and raw materials. To gain a deeper understanding of variations in glyoxal and methylglyoxal and to investigate their impact on Baijiu during aging, standard glyoxal and methylglyoxal substances were spiked into Baijiu samples. Considering the relatively low levels of glyoxal and methylglyoxal naturally present in Baijiu, 1 mg/L glyoxal and 2 mg/L methylglyoxal (R) were added to the original Baijiu sample at week 0. The samples were then stored for 12 weeks at 75 °C alongside the original unaltered Baijiu (J). The influence of MRIs on Baijiu during aging was also studied. The forced aging Baijiu exhibited high yellow intensity on the surface, thus indicating the contribution of the Maillard reaction to aged Baijiu.

Compared with the aging Baijiu, the glyoxal concentration in forced aging Baijiu drastically decreased during the first week, whereas the methylglyoxal concentration steadily decreased throughout the forced aging process (Fig. 4). Due to the low sugar concentration and Maillard reaction rate in Baijiu, it seems that methylglyoxal and glyoxal underwent dynamic changes in the Baijiu aging process. Conversely, the 2,3-pentanedione concentration increased in the first 6 weeks and decreased in the next 6 weeks in forced aging Baijiu; however, it differed from that in aged Baijiu. This difference might be attributed to the decreased concentration of Maillard reaction raw materials, leading to the decreased generation of MRIs in Baijiu, whose level eventually was lower than that required for further reaction. Moreover, the 2,3-butanedione concentration decreased in the first week, increased in the next 5 weeks, and finally decreased in the last 6 years in forced aging Baijiu. Furfural and 5-methylfurfural concentrations decreased rapidly in week 1 and decreased slowly in the consequent 11 weeks, while the 5-hydroxymethylfurfural concentration increased in 12 weeks. Moreover, the 5-hydroxymethylfurfural concentration showed the same trends in forced aging and aged Baijiu; thus, it demonstrates the potential to be a marker of Baijiu aging time and temperature.

Glyoxal and methylglyoxal in the Maillard reaction could produce alkyl pyrazines, thiophenes and thiazoles. Although they do not produce substances such as methanethiol and phenylacetaldehyde, glyoxal and methylglyoxal participate in some production pathways. In an experiment involving the accelerated heating of regular Baijiu samples over 6 weeks and Baijiu adding glyoxal and methylglyoxal, a semiquantitative analysis of alkyl pyrazines, thiophenes, thiazoles, some aldehydes and

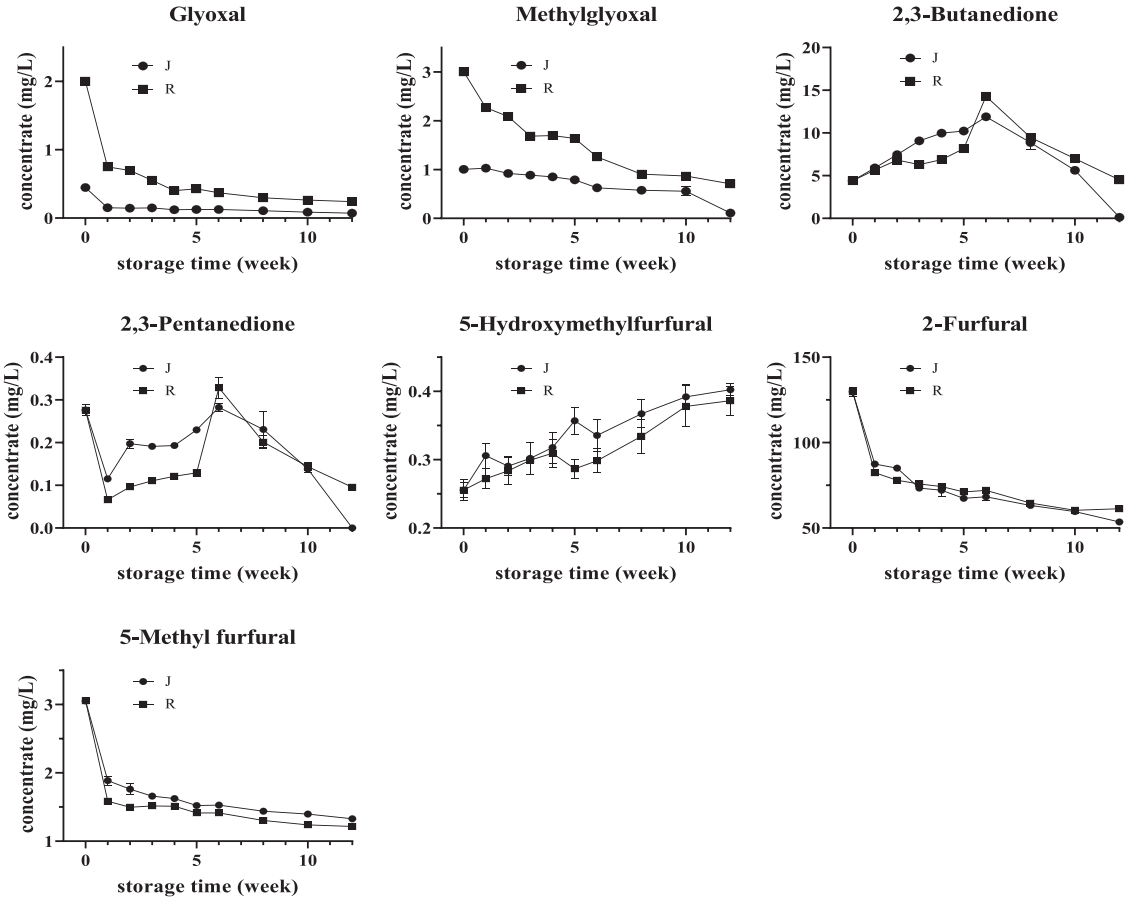

Fig. 4. Simultaneous analysis of different MRIs detected in forced aging Baijiu. R: 1 mg/L glyoxal and 2 mg/L methylglyoxal were added in the original Baijiu sample. J: Baijiu sample.

sulphide compounds was conducted. The results showed that levels of 2,6-dimethylpyrazine, 2,5-dimethylpyrazine, 2-ethylpyrazine and 2-ethyl-6-methylpyrazine increased by 43.78%, 17.98%, 12.47% and 16.35%, respectively. These findings suggest that glyoxal and methylglyoxal act as precursors for alkyl pyrazines, and the Maillard reaction during the aging process may enhance the production of pyrazines, thereby influencing the roast-like flavor. Levels of dimethyl disulphide decreased by 15.72%, 2-n-pentylthiophene increased by 29.14% and thiazole increased by 10.83%, indicating that glyoxal and methylglyoxal may react with dimethyl disulphide and other sulphide compounds, which are prone to volatilisation and contribute to the formation of heterocyclic sulphide compounds. These compounds have low threshold values and make substantial contributions to the desirable and undesirable flavor of Baijiu. Furthermore, the levels of phenylacetaldehyde, propaldehyde and octanal increased by 27.45%, 10.83% and 27.94%, respectively. The increase of carbonyl compound levels, which are reactants of the Maillard reaction, suggests that the addition of glyoxal and methylglyoxal accelerates the rate of the Maillard reaction. Additionally, the initial content of glyoxal and methylglyoxal is crucial for the Baijiu aging process.

3.3.2. Simulated aging of Baijiu to verify the relationship between MRIs and heterocyclic compounds

To verify and reveal the influence of MRIs and the Maillard reaction on changes in the flavor compounds of Baijiu, MRIs and volatile aroma compounds in Baijiu force-aged at 75 °C for 6 weeks were monitored. Network analysis was performed to investigate the potential correlations between the aroma compounds and their precursors. As previously discussed, heterocyclic compounds such as pyrazine, furans and sulphur compounds exhibited higher correlation with MRIs. Thus, GC × GC maximum possibility was used to obtain the maximum possible data on aroma compounds. Then, aldehydes, pyrazine, furans and sulphur compounds were selected and thoroughly assessed for mass spectra and RI similarities (Y. He et al., 2020). Finally, 92 aroma compounds were selected. The Spearman correlation coefficients between the 92 aroma compounds ($P < 0.05$) and 7 MRIs and time were calculated, and a coefficient (ρ) of >0.6 demonstrated the strongly correlated nodes of the network. Network analysis highlighted the important aroma compounds that were predicted as key contributors to aroma changes in MRPs in the soy sauce aroma–type Baijiu (Fig. 5). Through co-occurrence network analysis, 30 nodes and 159 edges were obtained ($|\rho| > 0.6$, $p < 0.05$). Spearman correlation coefficients revealed that 22 aroma compounds were significantly correlated with seven MRPs and time, indicating that these compounds are important contributors to the aroma differences in the Maillard reaction in Baijiu ($p < 0.05$, $\rho > 0.6$). Moreover, 5-hydroxymethylfurfural, 5-methylfurfural, furfural, 2,3-butanedione, 2,3-pentanedione, glyoxal and methylglyoxal were significantly correlated with 18, 22, 27, 23, 17, 7 and 22 types of aroma compounds, respectively, ($p < 0.05$, $\rho > 0.6$). Among the 22 aroma compounds, 12 were highly correlated with the MRPs in differently aged Baijiu: 2,2′-difurfuryl ether, 2,2′-methanediyldifuran, 2,6-dimethylpyrazine, 2-ethyl-6-methylpyrazine, 5-ethyl-2-furaldehyde, dibenzofuran, furfuryl acetate, furfuryl alcohol, furfuryl butyrate, furfuryl methyl sulphide, methyl 2-methyl-3-furyl disulphide, propyl 2-furancarboxylate and thiophene. This indicates that MRIs and the Maillard reaction dominantly contributed to the production of heterocyclic compounds. Two of them were pyrazines, which reportedly exhibited a synergistic effect on the perception of roasted aroma (Y. Yan, Chen, Nie, & Xu, 2021); 2,6-dimethyl pyrazine was positively correlated with time, methylglyoxal, 2,3-butanedione and 2,3-pentanedione; however, it was negatively correlated with furfural, 5-methylfurfural and glyoxal. Three of them were sulphide compounds, which exhibit a roasted aroma and potential application as

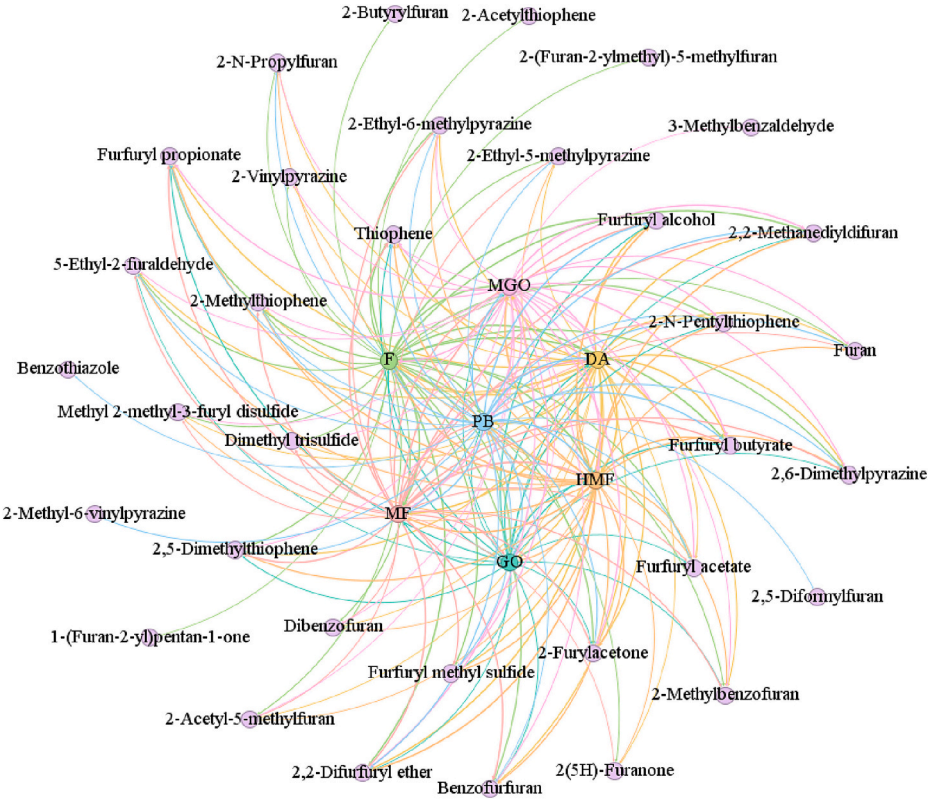

Fig. 5. A: Correlation network between MRIs and MRPs ($p < 0.05$) detected in soy sauce aroma–type Baijiu aged for various time periods. **B:** Correlation network between MRIs and MRPs ($P < 0.05$) detected in soy sauce aroma–type Baijiu aged with accelerated heating over 6 weeks (the thickness of lines is proportional to the value of Spearman's correlation [$\rho > 0.6$, $P < 0.05$]). The size of the circles is linked to the number of MRP edges. The colours of the lines are the same as the MRIs nodes. GO: glyoxal, MGO: methylglyoxal, DA: 2,3-butanedione, PB: 2,3-pentanedione, HMF: 5-hydroxymethylfurfural, F: Furfural, MF: 5-methylfurfural.

odour-active compounds in the soy sauce aroma–type Baijiu (Y. Yan, Chen, Nie, & Xu, 2020). Thiophene and methyl 2-methyl-3-furyl disulphide were positively correlated with furfural and 5-methylfurfural; however, they were negatively correlated with methylglyoxal, 2,3-butanedione, 2,3-pentanedione and time. Heterocycles exhibited an identical trend in aged Baijiu and forced aging Baijiu (Fig. 6). Almost all heterocycles shown in Fig. 6 demonstrated a significant difference in young and aged Baijiu. However, there was no significant difference between middle-aged and very old Baijiu. Additionally, in the manually aged Baijiu, the difference between the first 2 weeks and the last 4 weeks of aging was significant, indicating the change from an unordered to an ordered process of Baijiu aging. The analysis of natural aging indicates

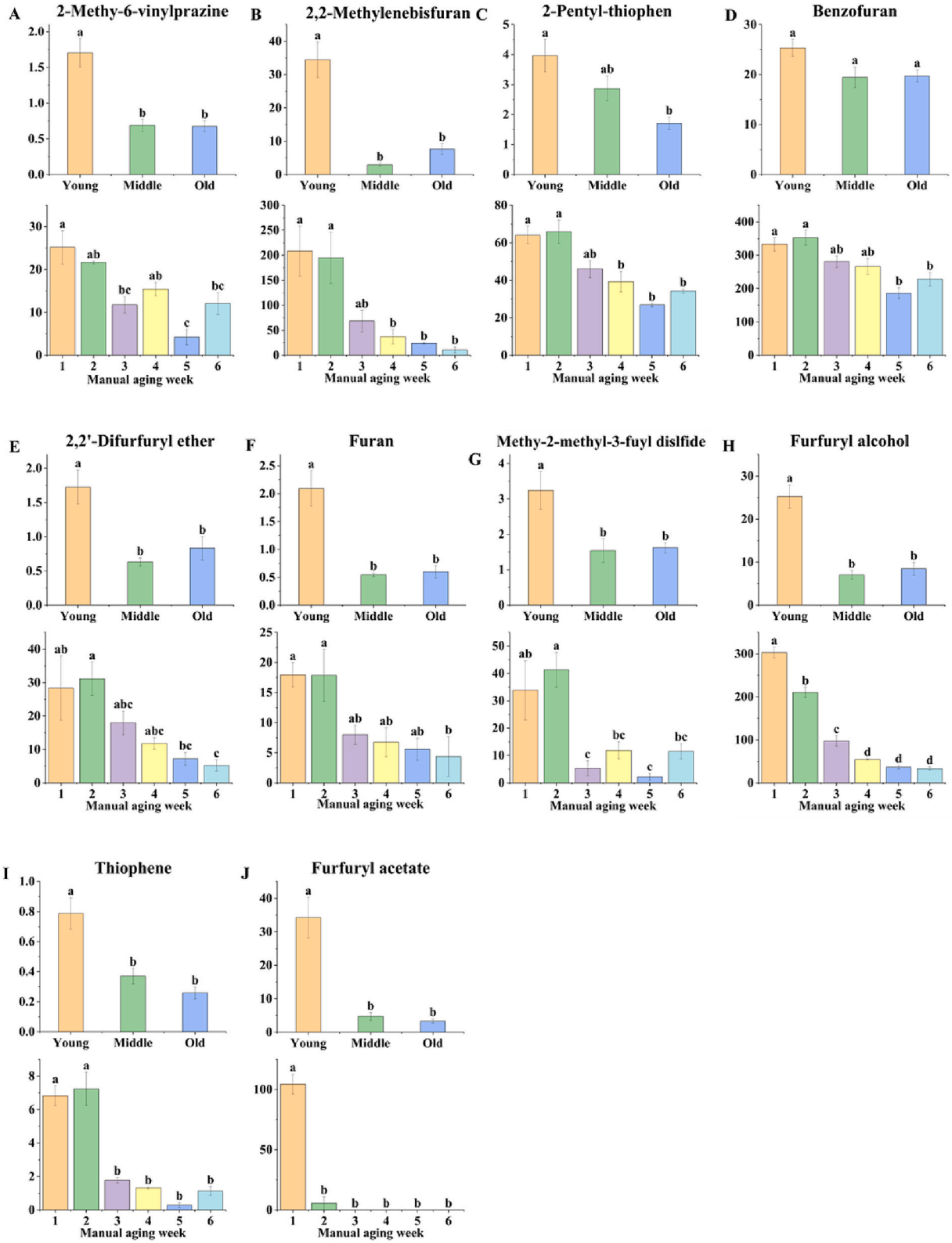

Fig. 6. Content of some heterocycles detected in Baijiu aged for various time periods and in forced aging Baijiu; all values are expressed in mg/L.

that MRIs have an effect on heterocyclic compounds and quality, and the elucidated pathway and variation of heterocycles confirm the finding. Further, forced aging experiments were conducted to exclude additional factors. In brief, the Maillard reaction occurs during Baijiu aging and influences the concentration of heterocycles, thereby leading to flavor changes in Baijiu.

4. Conclusions

In this study, the aging mechanism of soy sauce aroma–type Baijiu was explored by evaluating the potential correlation between the Maillard reaction precursor compounds and MRPs of soy sauce aroma–type Baijiu. This study established a method to systematically detect MRIs in Baijiu for the first time. Overall, the highest MRI content was found in soy sauce aroma–type Baijiu. A total of 53 compounds, mainly heterocycles, were screened that were highly correlated with vintage and Maillard reaction precursors. A high correlation between MRIs and heterocyclic compounds was established, indicating that prolonged aging leads to the generation and further reaction of heterocyclic compounds. The reaction pathway from MRIs to heterocyclic compounds in Baijiu was also elucidated. In the study of MRIs and heterocyclic compounds in accelerated-aged Baijiu, it was found that 22 heterocyclic compounds showed a high correlation between MRIs and reaction time, with 18 of them overlapping with natural aging. This further confirmed the effect of the Maillard reaction on heterocyclic compounds in aged Baijiu. However, the contribution of these compounds to the aroma of aged Baijiu needs further investigation. The description of the aroma of heterocyclic compounds is consistent with that of sensory characteristic changes in stored Baijiu proposed by the study. Additionally, a better understanding of the natural aging process allows for scientifically effective storage while maintaining and improving the quality of the final product.

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CRediT authorship contribution statement

Hao Huang: Writing – original draft, Methodology, Investigation, Data curation. **Yuchen Gao:** Writing – review & editing, Investigation. **Lulu Wang:** Writing – review & editing, Methodology, Investigation. **Xiaowei Yu:** Writing – review & editing. **Shuang Chen:** Writing – review & editing, Project administration, Methodology, Investigation, Funding acquisition. **Yan Xu:** Writing – review & editing, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Appendix A. Supplementary data

UPLC-MS/MS parameters and Method Validity and Reliability for MRI in Baijiu (Table S1); basic information of the aroma compounds in aged Baijiu (Table S2); basic information of the aroma compounds in forced aging Baijiu (Table S3); heat map and HCA clustering results of 109 aroma compounds with a high correlation in different aging years Baijiu ($\rho > 0.5$) (Fig. S1); pathway of MRIs and some typical heterocycles (Fig. S2); PCA correlation circle (total variability = 69.38%) presenting the proximity of heterocycle concentrations to wine age, according to Spearman's procedure (Fig. S3); the concentration and model of some heterocycles in different aging years of Baijiu (Fig. S4). Supplementary data to this article can be found online at [https://doi.org/10.1016/j.fochx.2024.101356].

References

Charnock, H. M., Pickering, G. J., & Kemp, B. S. (2022). The Maillard reaction in traditional method sparkling wine. *Frontiers in Microbiology, 13*, Article 979866. https://doi.org/10.3389/fmicb.2022.979866

Delatour, T., Huertas-Perez, J. F., Dubois, M., Theurillat, X., Desmarchelier, A., Ernest, M., & Stadler, R. H. (2020). Thermal degradation of 2-furoic acid and furfuryl alcohol as pathways in the formation of furan and 2-methylfuran in food. *Food Chemistry, 303*. https://doi.org/10.1016/j.foodchem.2019.125406

El-Maghrabey, M., Suzuki, H., Kishikawa, N., & Kuroda, N. (2021). A sensitive chemiluminescence detection approach for determination of 2,4-dinitrophenylhydrazine derivatized aldehydes using online UV irradiation - luminol CL reaction. Application to the HPLC analysis of aldehydes in oil samples. *Talanta, 233*, 11. https://doi.org/10.1016/j.talanta.2021.122522

Gupta, R. K., Gupta, K., Sharma, A., Das, M., Ansari, I. A., & Dwivedi, P. D. (2018). Maillard reaction in food allergy: Pros and cons. *Critical Reviews in Food Science and Nutrition, 58*(2), 208–226. https://doi.org/10.1080/10408398.2016.1152949

He, Y., Liu, Z., Qian, M., Yu, X., Xu, Y., & Chen, S. (2020). Unraveling the chemosensory characteristics of strong-aroma type baijiu from different regions using comprehensive two-dimensional gas chromatography-time-of-flight mass spectrometry and descriptive sensory analysis. *Food Chemistry, 331*, Article 127335. https://doi.org/10.1016/j.foodchem.2020.127335

Hellwig, M., Borner, M., & Henle, T. (2021). Reduction of 5-Hydroxymethylfurfural and 1,2-Dicarbonyl compounds by Saccharomyces cerevisiae in model systems and beer. *Journal of Agricultural and Food Chemistry, 69*(43), 12807–12817. https://doi.org/10.1021/acs.jafc.1c04760

Hillmann, H., Mattes, J., Brockhoff, A., Dunkel, A., Meyerhof, W., & Hofmann, T. (2012). Sensomics analysis of taste compounds in balsamic vinegar and discovery of 5-acetoxymethyl-2-furaldehyde as a novel sweet taste modulator. *Journal of Agricultural and Food Chemistry, 60*(40), 9974–9990. https://doi.org/10.1021/jf3033705

Hong, J., Zhao, D., & Sun, B. (2021). Research Progress on the profile of trace components in baijiu. *Food Reviews International, 1-27*. https://doi.org/10.1080/87559129.2021.1936001

Jia, W., & Ma, R. (2023). Cross-modal interactions caused by nonvolatile compounds derived from fermentation, distillation and aging to harmonize flavor. *Critical Reviews in Food Science and Nutrition, 1-28*. https://doi.org/10.1080/10408398.2023.2172714

Jiang, W., Wang, X., Ma, Y., Du, M., Wu, C., & Xu, X. (2023). Mechanism of carbon skeleton formation of 2,3,5-Trimethylpyrazine via a conversion reaction between methylglyoxal and Glyoxal. *Journal of Agricultural and Food Chemistry, 71*(13), 5337–5344. https://doi.org/10.1021/acs.jafc.2c08745

Jian-Yuan, W., Zhi-Guo, S., & Yu-Qi, F. (2009). Determination of 5-hydroxymethylfurfural using derivatization combined with polymer monolith microextraction by high-performance liquid chromatography. *Journal of Agricultural and Food Chemistry, 57*(10), 3981–3988. ://FSTA:2009–10-Ha4144.

Lan, X. H., Liu, P., Xia, S. Q., Jia, C. S., Mukunzi, D., Zhang, X. M., … Xiao, Z. B. (2010). Temperature effect on the non-volatile compounds of Maillard reaction products derived from xylose-soybean peptide system: Further insights into thermal degradation and cross-linking. *Food Chemistry, 120*(4), 967–972. https://doi.org/10.1016/j.foodchem.2009.11.033

Li, H., Wu, C. J., Tang, X. Y., & Yu, S. J. (2019). Determination of four bitter compounds in caramel colors and beverages using modified QuEChERS coupled with liquid chromatography-diode Array detector-mass spectrometry. *Food Analytical Methods, 12*(7), 1674–1683. https://doi.org/10.1007/s12161-019-01500-z

Liu, D., He, Y., Xiao, J., Zhou, Q., & Wang, M. (2021). The occurrence and stability of Maillard reaction products in various traditional Chinese sauces. *Food Chemistry, 342*, Article 128319. https://doi.org/10.1016/j.foodchem.2020.128319

Liu, H., & Sun, B. (2018). Effect of fermentation processing on the flavor of baijiu. *Journal of Agricultural and Food Chemistry, 66*(22), 5425–5432. https://doi.org/10.1021/acs.jafc.8b00692

Lund, M. N., & Ray, C. A. (2017). Control of Maillard reactions in foods: Strategies and chemical mechanisms. *Journal of Agricultural and Food Chemistry, 65*(23), 4537–4552. https://doi.org/10.1021/acs.jafc.7b00882

Macheiner, L., Schmidt, A., Karpf, F., & Mayer, H. K. (2021). A novel UHPLC method for determining the degree of coffee roasting by analysis of furans. *Food Chemistry, 341* (Pt 1), Article 128165. https://doi.org/10.1016/j.foodchem.2020.128165

Marceau, E., & Yaylayan, V. A. (2009). Profiling of α-Dicarbonyl content of commercial honeys from different botanical origins: Identification of 3,4-Dideoxyglucoson-3-ene (3,4-DGE) and related compounds. *Journal of Agricultural and Food Chemistry, 57*(22), 10837–10844. https://doi.org/10.1021/jf903341t

Martins, F., Alcantara, G., Silva, A. F. S., Melchert, W. R., & Rocha, F. R. P. (2022). The role of 5-hydroxymethylfurfural in food and recent advances in analytical methods.

Food Chemistry, 395, Article 133539. https://doi.org/10.1016/j.foodchem.2022.133539

Murkovic, M., & Bornik, M. A. (2007). Formation of 5-hydroxymethyl-2-furfural (HMF) and 5-hydroxymethyl-2-furoic acid during roasting of coffee. *Molecular Nutrition & Food Research, 51*(4), 390–394. https://doi.org/10.1002/mnfr.200600251

Nobis, A., Kunz, O. S., Gastl, M., Hellwig, M., Henle, T., & Becker, T. (2021). Influence of 3-DG as a key precursor compound on aging of lager beers. *Journal of Agricultural and Food Chemistry, 69*(12), 3732–3740. https://doi.org/10.1021/acs.jafc.0c08003

Paravisini, L., & Peterson, D. G. (2018). Role of reactive carbonyl species in non-enzymatic browning of apple juice during storage. *Food Chemistry, 245*, 1010–1017. https://doi.org/10.1016/j.foodchem.2017.11.071

Paravisini, L., & Peterson, D. G. (2019). Mechanisms non-enzymatic browning in orange juice during storage. *Food Chemistry, 289*, 320–327. https://doi.org/10.1016/j.foodchem.2019.03.049

Pieczonka, S. A., Hemmler, D., Moritz, F., Lucio, M., Zarnkow, M., Jacob, F., … Schmitt-Kopplin, P. (2021). Hidden in its color: A molecular-level analysis of the beer's Maillard reaction network. *Food Chemistry, 361*, Article 130112. https://doi.org/10.1016/j.foodchem.2021.130112

Shakoor, A., Zhang, C., Xie, J., & Yang, X. (2022). Maillard reaction chemistry in formation of critical intermediates and flavour compounds and their antioxidant properties. *Food Chemistry, 393*, Article 133416. https://doi.org/10.1016/j.foodchem.2022.133416

da Silva, P. M., Gauche, C., Gonzaga, L. V., Costa, A. C. O., & Fett, R. (2016). Honey: Chemical composition, stability and authenticity. *Food Chemistry, 196*, 309–323. https://doi.org/10.1016/j.foodchem.2015.09.051

Sun, H., Ni, B., Yang, J., & Qin, Y. (2022). Nitrogenous compounds and Chinese baijiu: A review. *Journal of the Institute of Brewing, 128*(1), 5–14. https://doi.org/10.1002/jib.686

Wang, L., Fan, S., Yan, Y., Yang, L., Chen, S., & Xu, Y. (2020). Characterization of potent odorants causing a pickle-like off-odor in Moutai-aroma type baijiu by comparative aroma extract dilution analysis, quantitative measurements, aroma addition, and omission studies. *Journal of Agricultural and Food Chemistry, 68*(6), 1666–1677. https://doi.org/10.1021/acs.jafc.9b07238

Wang, L. L., Chen, S., & Xu, Y. (2023). Distilled beverage aging: A review on aroma characteristics, maturation mechanisms, and artificial aging techniques. *Comprehensive Reviews in Food Science and Food Safety, 22*(1), 502–534. https://doi.org/10.1111/1541-4337.13080

Wang, X. J., Gao, F., Li, L. C., Hui, X., Li, H., & Gao, W. Y. (2018). Quantitative analyses of alpha-dicarbonyl compounds in food samples by HPLC using 4-(2,3-dimethy1-6-quinoxalinyl)-1,2-benzenediamine as a derivatizing reagent. *Microchemical Journal, 141*, 64–70. https://doi.org/10.1016/j.microc.2018.05.006

Wang Xiaodan, X. Y., Li, Y., Fuyan, Z. H., Chao, H., Dongming, J., & Yuhang, Z. (2021). Sugars and sugar alcohols of the Laobaigan baijiu. *China Brewing, 40*, 70–74. https://doi.org/10.11882/j.issn.0254-5071.2021.01.014

Wang, Y., & Ho, C. T. (2012). Flavour chemistry of methylglyoxal and glyoxal. *Chemical Society Reviews, 41*(11), 4140–4149. https://doi.org/10.1039/c2cs35025d

Wu, Q., & Xu, Y. (2012). Transcriptome profiling of heat-resistant strain bacillus licheniformis CGMCC3962 producing Maotai flavor. *Journal of Agricultural and Food Chemistry, 60*(8), 2033–2038. https://doi.org/10.1021/jf204270h

Yaghmur, A., Aserin, A., Abbas, A., & Garti, N. (2005). Reactivity of furfural–cysteine model reaction in food-grade five-component nonionic O/W microemulsions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 253*(1–3), 223–234. https://doi.org/10.1016/j.colsurfa.2004.10.114

Yan, Y., Chen, S., He, Y., Nie, Y., & Xu, Y. (2020). Quantitation of pyrazines in baijiu and during production process by a rapid and sensitive direct injection UPLC-MS/MS approach. *Lwt, 128*. https://doi.org/10.1016/j.lwt.2020.109371

Yan, Y., Chen, S., Nie, Y., & Xu, Y. (2020). Characterization of volatile sulfur compounds in soy sauce aroma type baijiu and changes during fermentation by GC x GC-TOFMS, organoleptic impact evaluation, and multivariate data analysis. *Food Research International, 131*. https://doi.org/10.1016/j.foodres.2020.109043

Yan, Y., Chen, S., Nie, Y., & Xu, Y. (2021). Quantitative analysis of pyrazines and their perceptual interactions in soy sauce aroma type baijiu. *Foods, 10*(2). https://doi.org/10.3390/foods10020441

Zhang Zhuangying, F. W., & Yan, X. (2014). Comparative analysis of free amino acid content and composition in different aroma type Chinese liquors. *Science and Technology of Food Industry, 35*(17), 280–284+288.

Zhu, B. F., & Xu, Y. (2010). A feeding strategy for tetramethylpyrazine production by Bacillus subtilis based on the stimulating effect of ammonium phosphate. *Bioprocess and Biosystems Engineering, 33*(8), 953–959. https://doi.org/10.1007/s00449-010-0419-5

Zhu, L., Wang, X. L., Song, X. B., Zheng, F. P., Li, H. H., Chen, F., … Zhang, F. Y. (2020). Evolution of the key odorants and aroma profiles in traditional Laowuzeng baijiu during its one-year ageing. *Food Chemistry, 310*. https://doi.org/10.1016/j.foodchem.2019.125898