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Novel insight into the evolution of volatile compounds during dynamic freeze-drying of *Ziziphus jujuba* cv. Huizao based on GC–MS combined with multivariate data analysis

Min Gou [a,b], Qinqin Chen [a,*], Xinye Wu [a], Gege Liu [a], Marie-Laure Fauconnier [b], Jinfeng Bi [a,*]

[a] *Institute of Food Science and Technology, Chinese Academy of Agricultural Sciences (CAAS)/Key Laboratory of Agro-Products Processing, Ministry of Agriculture and Rural Affairs, 100193 Beijing, China*
[b] *Laboratory of Chemistry of Natural Molecules, Gembloux Agro-Bio Tech, University of Liége, 5030 Gembloux, Belgium*

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ABSTRACT

To understand the evolution of aroma in jujubes during dynamic freeze drying (FD), the relationship between aroma compounds, precursors, and related enzyme activities were analyzed. Fifty-three volatiles were identified during FD processing. After FD, the total aroma contents were increased from 11,004 to 14,603 μg/kg, ketones content was significantly decreased by 54.11 %, resulted in the loss of creamy note in freeze-dried jujube (FDJ). Through the network analysis, serine, glycine, proline, valine, cysteine, arginine, glutamic acid, lysine and leucine had the significant correlation with pyrazines, dominated the roasty note of FDJ. Linoleic acid, α-linolenic acid and oleic acid with lipoxygenase had important effects on the increase of esters (from 412 to 9,486 μg/kg), contributed fruity and sweet notes of FDJ. Besides, through the Mantel test, the influence degree of factors on the formation of FDJ aroma was ranked as temperature > enzyme activity > fatty acids > amino acids.

1. Introduction

Red jujubes (*Zizyphus jujuba* Mill.) are both used as food and medicine in China, their unique flavor is helpful to improve consumers' attraction and enhance market competitiveness (Gou et al., 2022). With the development of freeze drying (FD), freeze-dried red jujube made from *Ziziphus jujuba cv.* Huizao, has become a popular product, with better nutrition, appearance, color and aroma. However, the causes of aroma differences between raw and freeze-dried jujube and the aroma formation pathway during FD are still unclear. The development of aroma in freeze-dried red jujube is a dynamic and complex process that depends on the combined effects of drying condition, aroma precursors and enzyme activities.

Different from lower constant freeze-drying temperature (<30 °C) of experimental FD machine, which usually reported in the published literature, the multi-stage and variable-temperature freeze-dried procedure was used in industry. Fortunately, same procedure could be well achieved by the pilot scale FD. In which, a higher temperature of heating plate (85–65 °C) was used to provide higher latent heat for the sublimation of water, to accelerate the FD rate and shorten the FD time. In this process, the sample temperature will gradually increase from the freezing temperature (−40 °C) to the heating plate temperature (65 °C), chemical and enzymatic reactions will occur and result in the production of different and new aroma.

In addition to higher temperature FD condition, red jujube contains rich aroma precursors, including amino acids, fatty acids and reducing sugars (Song et al., 2019), which could provide a variety of metabolic pathways and chemical reaction, such as Maillard reaction for the aroma formation of freeze-dried red jujube. Fatty acids are the precursors of most aliphatic alcohols, aldehydes, ketones and esters that have a variety of oxidation pathways, among which lipoxygenase (LOX) oxidation pathway is involved in the synthesis of green flavor compounds (C-6 and C-9 aldehydes and alcohols) (Boukobza et al., 2001). Reducing sugar is also a precursor for the metabolic synthesis of alcohols, acids, esters. During anaerobic respiration, monosaccharides are converted to pyruvate, which is catalyzed by dehydrogenases to form acetyl-CoA and further ester compounds (El Hadi et al., 2013; Schwab et al., 2008). In addition, amino acids could also form esters by acetyl-CoA or form pyrazines by Maillard reaction with reducing sugar (Gonda et al., 2010).

Coupled with FD condition and aroma precursors, the aroma production of red jujube by pilot scale FD is more complex, involving lipid oxidation, Maillard reaction and lipid-Maillard interaction. Therefore,

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* Corresponding authors.
E-mail addresses: celerylc@163.com (Q. Chen), bjfcaas@126.com (J. Bi).

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the changes of aroma, reducing sugars, fatty acid and free amino acids, and related enzyme activities in the pilot scale freeze drying process of red jujube will be investigated; and to explore the correlation between aroma and aroma precursors and enzyme activities, main precursors of aroma-active compounds will be identified through the Mantel test and network analysis. It could provide novel insights into the aroma evolution in dynamic FD of red jujube, as well as guidance for future research including optimization of the freeze dried process to improve the aroma profile of red jujube.

2. Materials and methods

2.1. Materials and chemicals

Red jujubes (*Zizyphus jujuba* cv. Huizao) were obtained from local orchard in Akesu, Xinjiang, China, in November 2020. Mature fruits without any physical damage were selected, then collected and transported to Beijing within 2 days. All jujube samples were stored at 4 °C controlled atmosphere storage room until used. The water content of "Huizao" was 25.57 %, the pH was 5.5, and the solid soluble content was 69.0 %.

Oct-1-en-3-ol, 2,3-butanediol, hexanal, (*E*)-2-hexenal, (*E*)-2-heptenal, (*E*)-2-octenal, furfural, benzaldehyde, decanal, butane-2,3-dione, 3-octanone, 3-hydroxybutan-2-one, oct-1-en-3-one, 6-methyl-5-hepten-2-one, 6,10-dimethyl-2-undecanone, acetic acid, butanoic acid 3-methyl-, pentanoic acid, (*E*)-but-2-enoic acid, hexanoic acid, heptanoic acid, (*E*)-2-hexenoic acid, octanoic acid, nonanoic acid, methyl hexanoate, ethyl hexanoate, hexyl acetate, ethyl heptanoate, methyl octanoate, ethy octanoate, methyl decanoate, ethyl decanoate, methyl dodecanoate, ethyl dodecanoate, oxolan-2-one, 5-ethyloxolan-2-one, 6-methyloxan-2-one, 5-propyloxolan-2-one, 5-butyloxolan-2-one, 5-heptyloxolan-2-one, 5-hexyloxolan-2-one, 2,6-dimethylpyrazine, 2,6-diethylpyrazine, 2-ethyl-3,5-dimethylpyrazine, tetramethylpyrazine, limonene, γ-terpinene, naphthalene, 2-cyclohexene-1-one, *n*-alkane (C5-C40), Triton X-100, Dithiothreitol (DTT), crosslinked polyvinylpyrrolidone (PVPP), nicotinamide adenine dinucleotide (NADH), 5,5′-dithiobis-(2-nitrobenzoic acid) (DTNB), acetoacetyl coenzyme A (acetyl CoA), MES-Tris buffer (pH 6.0), Tris-HCl buffer (0.5 mol/L, pH 8.0), acetaldehyde, butanolwere purchased from Yuanye Bio-Technology (Shanghai Yuanye Bio-Technology Co., ltd, Shanghai, China). 3-Oxobutan-2-yl acetate, 2-ethyl-6-methylpyrazine, styrene, α-farnesene, *p*-cymene and $MgCl_2$ were purchased from Macklin (Shanghai Macklin Biochemical Co., ltd, Shanghai, China). All of the chemical standards used above with purity $\geq$ 99 %, and other reagents were analytical grade.

2.2. Freeze drying (FD) treatment

Briefly, the kernel of jujubes was removed and the remaining part was cut into 5 mm slices; then 500 g jujube slices soaked in 80 °C water for 1 min to keep a relatively flat surface before freeze drying. Jujube slices were drained in a colander and put into −40 °C refrigerator for 48 h. A pilot scale freeze dryer (Advantech Co., ltd. China) was used with drying conditions was as follows: The cold trap temperature and vacuum pressure were −30 °C and 60 Pa, respectively; the drying temperature of the heating plate was from room temperature to 85 °C within 45 min and kept for 3 h, then decreased to 70 °C within 30 min and maintained for 5 h, and finally decrease to 65 °C within 30 min and kept for 1 h. The sample tray was in the middle of two heating plates and not directly connected, the diagram was shown in Fig. S1. At the same time, the temperature of jujube slices was monitored online through the temperature probe which equipped in FD machine (Fig. S2). The dynamic FD process included 0–10 stages, with drying time of 0, 105, 165, 225, 285, 345, 405, 465, 525, 585 and 645 min, respectively.

2.3. Volatile compounds analysis

2.3.1. Extraction of volatile compounds by using headspace solid-phase microextraction (HS-SPME)

The extraction method by HS-SPME of red jujube aroma was described by Gou et al. (2022).

2.3.2. Determination of volatile compounds using gas chromatography–mass spectrometry (GC–MS)

The volatile compounds were identified by GC–MS (QP-2010, Shimadzu, Japan) equipped with a DB-Wax column (60 m × 0.25 mm, 0.25 μm). The temperature programs were according to (Gou et al., 2022). The aroma compounds were identified by comparing the NIST17 library of the GC–MS and were confirmed by the retention indices (RI) and authentic aroma standards. The RI was calculated on the basis of the linear retention times of the *n*-alkanes (C5 − C40) in the DB-WAX columns under the same GC–MS conditions. Internal standard method was used for aroma quantitative analysis (2 μL 2-cyclohexene-1-one, 1 mg/L). The content of each volatile compound was calculated based on the GC peak areas related to that of internal standard.

2.3.3. Odor activity value (OAV)

$$OAV = C/OT \tag{1}$$

where C was the concentration of the compound and OT was its orthonasal detection odor threshold. The threshold values referred to the literature in water (Gou et al., 2022).

2.4. Sensory evaluation

The panelist selection and training methods were according to Gou et al. (2022) and Pu et al. (2020). The sensory evaluation was performed by 10 panelists (4 males and 6 females aged 23–28, healthy, without rhinitis, and nonsmokers) who were experienced and engaged in food flavor research for sensory evaluation. Panelists were trained for 4 weeks: Firstly, they were trained to distinguish and describe the aroma standards of red jujube for 4 weeks. Secondly, the panelists proceeded to conduct sensory evaluation of the red jujube sample. The aroma descriptors of red jujube were determined according to the experts' discussion on sensory attributes. In this study, The descriptors of red jujube were creamy (3-hydroxybutan-2-one), floral (5-butyloxolan-2-one), green (hexanal), fruity (methyl dodecanoate), roasty (2,6-dimethylpyrazine), sweet ((*E*)-but-2-enoic acid), sour (acetic acid), rancid (3-methylbutanoic acid) and nut (2-ethyl-6-methyl-pyrazine) (Pu et al., 2022). Finally, the quantitative descriptive analysis (QDA) was conducted in triplicate by panelists, and scores for each sample in 0.5 increments, from 0.0 to 3.0 on the basis of 7-point scales (0, none; 1.5, moderate; and 3, very strong).

2.5. Aroma precursor analysis

2.5.1. Sugar compounds analysis

Sucrose, glucose, and fructose in red jujube were analyzed by high-performance anion-exchange chromatography with pulsed amperometric detection (ICS-3000, DIONEX Co., ltd. China) according to the method of Song et al. (2019).

2.5.2. Free amino acids analysis

Amino acid was analyzed by automatic amino acid analyzer (L-8900, Hitachi, Japan) according to the method of Song et al. (2019).

2.5.3. Fatty acids analysis

The fatty acids of jujube were detected by gas chromatograph (GC) equipped with a flame ionization detector (FID) detector (GC, 2010, Shimadzu, Japan) according to the national standard of China (GB

5009.168-2016).

2.6. Analysis of enzymes activities

2.6.1. Lipoxygenase (LOX) activity

Sodium phosphate buffer (0.50 mol/L, pH 6.5) and 0.5 % Triton X-100 was used for LOX extraction (Lyu et al., 2021). And LOX activity was assayed according to Amanpour et al. (2019).

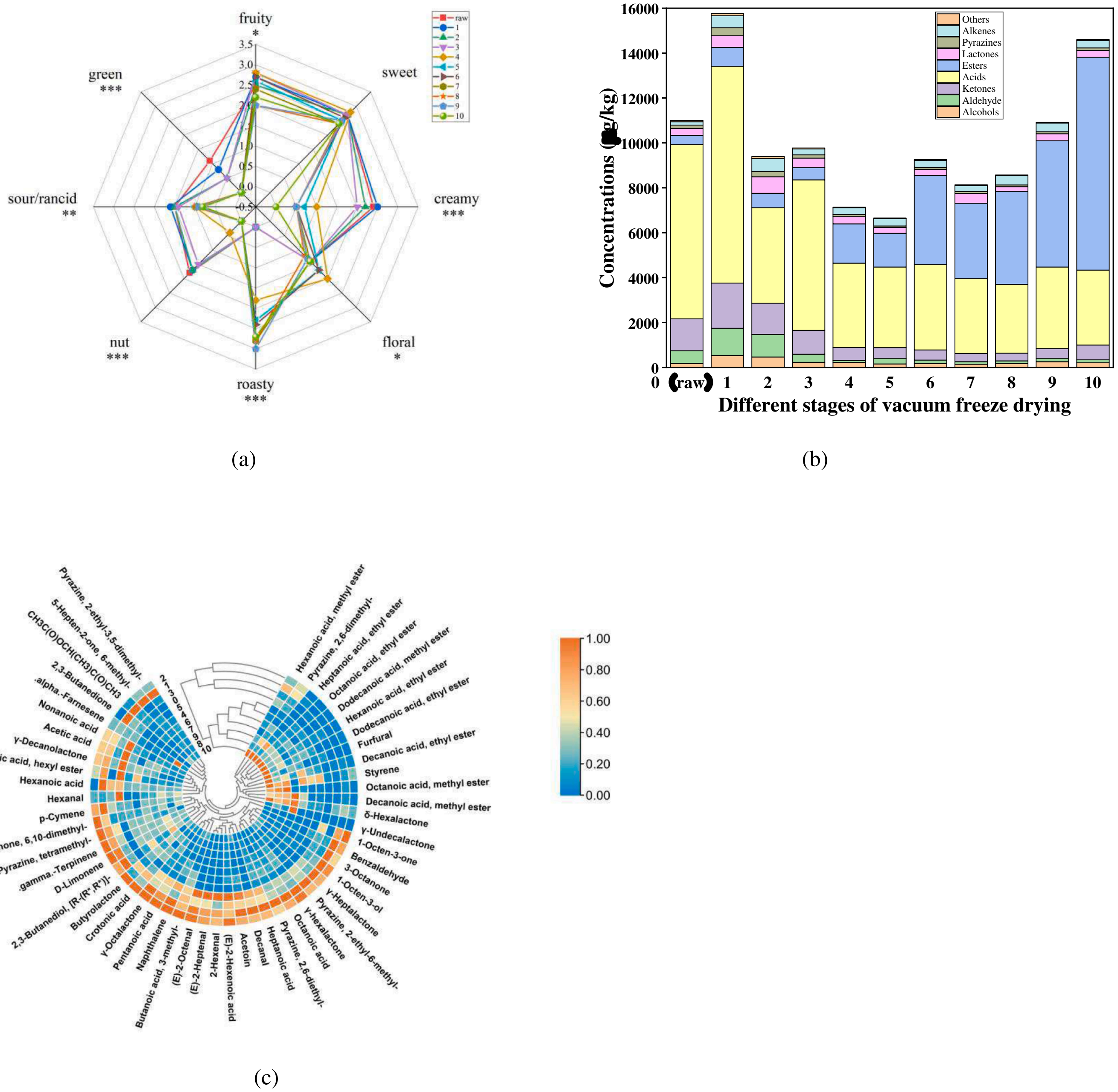
2.6.2. Alcohol dehydrogenase (ADH) activity

The MES-Tris buffer (0.1 mol/L, pH 6.0) with DTT (2 mmol/L) and PVPP (1 %) was used for ADH extraction. ADH activity assayed according to Zhou et al. (2019) and Lara et al. (2003) with slight modifications. The reaction system containing 0.3 mL ADH crude enzyme, 2.4 mL MES-Tris buffer (pH 6.0), 0.15 mL NADH (1.6 mmol/L) and 0.15 mL acetaldehyde (80 mmol/L). The above reaction substrate was mixed and determined at 340 nm for 1 min.

2.6.3. Alcohol acyltransferase (AAT) activity

The Tris-HCl (0.5 mol/L, pH 8.0), containing 0.1 %(V/V)Triton X-100 and 0.3 mg/g PVPP was used for AAT extraction. For AAT activity, the reaction substrate was 2.5 mL Tris-HCl (0.5 mol/L, pH 8.0, containing 0.5 mmol/L $MgCl_2$), 150 μL acetyl CoA (0.5 mol/L, pH 8.0, containing 0.5 mmol/L acetyl CoA), 50 μL butanol (0.5 mol/L, pH 8.0, containing 20 mmol/L acetyl CoA) and 150 μL AAT crude enzyme. The above reaction substrate was incubated at 35 ℃ in water bath for 15 min, then 100 μL 1 mmol/L DTNB was added and allowed to stand at room temperature for 10 min and determined at 412 nm for 1 min (Zhou et al., 2019).

One unit (U) represents the variation of absorbance per minute. The specific activity of all enzymes was defined as U/g.



(a)

(b)

(c)

Fig. 1. The changes in aroma profiles (a), contents of different group of aroma compounds (b) and clustering aroma compounds content heatmap (c) in red jujube during different freeze drying stages. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2.7. Statistical analysis

Software of SPSS version 20.0 (SPSS Inc., Chicago, IL) was applied for statistical treatment. Duncan's multiple test was used to verify significant differences among the samples at $p < 0.05$ level. Contents of different components were presented as the mean ± SD (standard deviation). The clustered heatmap was plotted using TBtools version 1.0686 (Heatmap Illustrator, China). The Mantel test analysis was performed using the OmicStudio tools at https://www.omicstudio.cn/tool. The network correlation analysis was constructed using Cytoscape (v.3.4.0).

3. Results and discussion

3.1. Sensory analysis of red jujube during freeze drying

Aroma profiles of red jujube at different FD stages were evaluated by trained panelists. As shown in Fig. 1(a), the aroma profiles could be divided to two groups, the stages 0 (raw)-3 was one group with sweet (2.7), fruity (2.5), creamy (2.4), nut (1.8), sour/rancid (1.5), floral (1.4) and green (1.1) notes. While the stages 4–10 was the other group with roasty (2.7), sweet (2.4), fruity (2.2), floral (1.4) and sour/rancid (0.8) notes. Among these aroma contributors, the aroma intensity of creamy, sour/rancid, green, and nut decreased significantly with FD time increased, and performed the lowest at the end of FD (stage 10), especially for creamy, green, and nut notes. In addition, the aroma intensity of roasty increased with FD time increased from stage 4. The aroma profile transformed from sweet dominated to roasty dominated during FD processing. To further investigate the aroma differences among samples, GC–MS combined with OAV were applied to analyze the volatile compounds responsible for the aroma differences of samples.

3.2. Dynamic changes in aroma compounds of red jujube during freeze drying

A total of 53 aroma compounds were detected in the red jujube during FD processing for stage 0–10 (0–645 min), including 2 alcohols, 7 aldehydes, 7 ketones, 9 acids, 10 esters, 7 lactones, 5 pyrazines, 4 alkenes and 2 others (Table 1). As shown in Table 1 and Fig. 1(b), the content of total aroma compounds in red jujube was significantly increased from 11,005 μg/kg to 14,605 μg/kg at stage 0–10. As reported, the average loss ratio of volatile compounds of freeze-dried banana slices and carvone in bread crumbs was 37.5 % and 55 %, respectively (Dimelow et al., 2005; Mui et al., 2002). It can be seen, pilot scale freeze drying could enhance the aroma compared with traditional constant FD. However, the concentrations of aroma compounds undergoes complex changes during pilot scale FD processing, where they increased from 11,005 μg/kg to 15,726 μg/kg (stage 0 to 1), then decreased to 6,657 μg/kg (stage 5), and finally increased to 14,605 μg/kg (stage 10). The contents of ketones, aldehydes and acids showed an obviously decreased trend during FD; meanwhile, esters showed an increased trend with FD time increased (Fig. 1(b)). The clustering content heatmap revealed that there were two obvious groups (stage 0–3 and stage 4–10) (Fig. 1(c)), which was in accordance with the sensory evaluation result. These changes of aroma composition could explain the transformation of aroma profile in red jujube after FD.

Furthermore, odor activity value (OAV) was applied to explain the contribution of compounds to the overall aroma profile (Table 2). Thirty aroma-active compounds (OAV > 1) were identified in all freeze-dried samples including 2 alcohols, 4 aldehydes, 5 ketones, 2 acids, 8 esters, 3 lactones, 3 pyrazines, 1 alkenes and 2 others. Stage 0–3 contained 27 important aroma compounds (OAV > 1), in which, ketones, aldehydes, alcohols, esters and pyrazines contributed the higher OAVs, and presented "creamy, fruit, sweet, green, floral and nut" characters. However, in the stage 4–10, there were only 20 aroma-active compounds (OAV > 1) in freeze dried samples, in which, esters and pyrazines dominated the OAVs, they contributed the sweet, fruit and roasty notes, respectively. These results were consisted with above discussed sensory evaluation.

Acids were the most numerous class of volatile compounds detected in the raw red jujube. The most abundant acids were acetic acid and hexanoic acid, with sour note. But they did not contribute a strong sour profile to red jujube due to the higher threshold. Otherwise, hexanoic acid, 3-methyl-butanoic acid and (*E*)-but-2-enoic acid were identified the key aroma-active compounds in "Huizao", they contributed the "sour and sweet" notes to red jujube (Gou et al., 2022). However, the contents of acids decreased significantly during FD processing and no longer provide the sour characteristics of freeze-dried jujube. In Song et al. (2020) study, red jujube had the highest content of total acids after constant lower temperature FD (25 °C). The different result might be due to the totally different drying condition. The multi-stage and higher temperature used in this study could promote the chemical reaction occurred, and leading the acids transformed to esters. In addition, acids might be discharged by vacuum pump, due to they have lower vapor pressure and easily vaporized. Acetic acid also had an obvious loss ratio (45.90 %), which might be due to its polarity and better water solubility and easier evaporation with water, or involved in the chemical reaction.

As the second most abundant class of volatile compound in raw red jujube, ketones also contributed the most OAVs to the overall aroma of raw red jujube. A total of 7 ketones were detected throughout the FD stage, and were mainly existed in the front period of FD (stage 0–3). Among these ketones, butane-2,3-dione, 3-hydroxybutan-2-one and oct-1-en-3-one might contribute the creamy, fruit and green aroma to red jujube because of their relatively low thresholds. Furthermore, butane-2,3-dione, 3-hydroxybutan-2-one, 6-methyl-5-hepten-2-one and 3-oxobutan-2-yl acetate were identified the key aroma-active compounds in "Huizao" (Gou et al., 2022). Similar to acids, most of ketones also decreased obviously with FD time, except for 6,10-dimethyl-2-undecanone, which might be produced by amino acid degradation or unsaturated fatty acid oxidation (Zhang et al., 2019).

Esters provided the fruity, sweet, and floral notes for red jujube. As shown in Table 1, as the FD time increased, the numbers and content of esters increased, especially ethyl esters, which enhance the fruity and sweet note of red jujube. However, in traditional constant FD, esters showed a decreased trendy (Chin et al., 2008). In our previous study, only methyl decanoate, ethyl decanoate and methyl dodecanoate were identified as the key aroma-active compounds, meanwhile, ethyl heptanoate, ethyl dodecanoate and hexyl acetate also been key aroma-active compounds in "Huizao" after FD. Otherwise, esters also contributed the major OAVs during later FD stage (4–10) (Table 2).

Pyrazines are generally results from the Maillard reaction, which are more favorable at high temperature. Though the percentage of pyrazines was decreased from 1.30 % to 0.77 % after FD, the OAVs contribution become higher (from 4.87 % to 19.75 %) (Table 1). They have an important contribution to the nut flavor of raw red jujube and roasty flavor of freeze-dried red jujube due to the low threshold. And the 2-methypyrazine, 2,5-dimethylpyrazine, 2,6-dimethylpyrazine and 2-ethyl-3,5-dimethyl-pyrazine were identified as the key aroma compound in raw red jujube (Gou et al., 2022; Zhu & Xiao, 2018).

A total 7 aldehydes were identified at different stages of FD, some aldehydes were not detected after stage 3, such as (*E*)-2-hexenal, (*E*)-2-heptenal, (*E*)-2-octenal and decanal. Aldehydes have green, fatty, grassy, and fresh characteristics (Gou et al., 2021). Thus, from stage 4, the red jujube samples no longer perceived the green note (Fig. 1). However, the content of furfural increased with FD time, with sweet, caramel, nutty, and baked notes. In general, furfural was commonly produced through non-enzymic browning, which could be promoted by the higher FD temperature. Alcohols were another important class of compounds for red jujube samples. The content of alcohols presented a slightly increase during FD, as was observed with Song et al. (2020). That might be caused by glucose metabolism, amino acid decarboxylation and dehydrogenation with prolonged FD time or oxidation and degradation of polyunsaturated fatty acids (Ye et al., 2022). Among the

Table 1
The contents of aroma compounds in red jujube at different freeze drying stages.

	Compounds (μg/kg)	RI	Freeze drying stage										
			raw	1	2	3	4	5	6	7	8	9	10
A1	Oct-1-en-3-ol	1450	138 ± 21bcd	346 ± 29a	313 ± 7a	153 ± 4b	101 ± 6cde	89.51 ± 12.81de	105 ± 8bcde	79.79 ± 1.24e	82.98 ± 1.66e	117 ± 6bcde	141 ± 10bc
A2	2,3-Butanediol	1556	39.28 ± 9.74e	178 ± 19a	147 ± 4ab	74.59 ± 3.67de	115 ± 7bc	64.11 ± 2.92de	60.26 ± 17.52de	59.22 ± 4.07de	89.00 ± 0.23 cd	136 ± 0b	66.28 ± 5.78de
	Total		177	524	460	228	216	154	165	139	172	253	207
B1	Hexanal	1083	96.46 ± 1.03a	34.12 ± 0.35 cd	37.54 ± 4.70 cd	40.92 ± 1.30 cd	23.56 ± 1.69ef	21.08 ± 3.48f	33.30 ± 0.12de	37.17 ± 0.83 cd	44.15 ± 3.35c	54.98 ± 0.83b	56.51 ± 4.45b
B2	(*E*)-2-Hexenal	1216	35.43 ± 1.81a	28.13 ± 0.37b	24.96 ± 1.12c	11.26 ± 0.16d	nd	nd	nd	nd	nd	nd	nd
B3	(*E*)-2-Heptenal	1323	25.16 ± 0.39a	20.32 ± 0.12b	20.42 ± 0.44b	12.25 ± 1.68c	nd	nd	nd	nd	nd	nd	nd
B4	(*E*)-2-Octenal	1429	81.25 ± 3.37a	76.34 ± 5.45a	77.89 ± 0.95a	41.15 ± 16.28b	nd	nd	nd	nd	nd	nd	nd
B5	Furfural	1460	1.80 ± 0.01d	nd	nd	nd	nd	1.11 ± 0.13e	3.23 ± 0.14c	4.21 ± 0.12b	4.36 ± 0.33b	1.4 ± 0.37de	14.04 ± 0.01a
B6	Benzaldehyde	1480	294 ± 5c	1025 ± 85a	823 ± 43b	233 ± 10 cd	67.42 ± 11.34e	231 ± 0 cd	125 ± 28de	70.75 ± 0.69e	67.84 ± 0.68e	99.67 ± 16.42e	63.41 ± 17.94e
B7	Decanal	1520	29.72 ± 5.20b	39.48 ± 1.45a	27.73 ± 0.62bc	22.33 ± 1.26c	nd	nd	nd	nd	nd	nd	nd
	Total		564	1223	1012	361	90.98	253	162	112	116	156	134
C1	Butane-2,3-dione	979	83.73 ± 1.12b	356 ± 40a	nd	108 ± 2b	nd	nd	nd	nd	nd	nd	nd
*C*2	3-Octanone	1253	18.62 ± 1.25c	67.75 ± 6.20a	41.47 ± 1.77b	13.63 ± 1.47 cd	8.75 ± 0.96d	7.00 ± 0.83d	5.45 ± 0.45d	6.66 ± 0.75d	7.35 ± 0.22d	8.43 ± 0.34d	10.89 ± 0.01 cd
C3	3-Hydroxybutan-2-one	1284	1188 ± 93ab	1258 ± 57a	1019 ± 62bc	844 ± 18c	461 ± 11d	346 ± 35de	305 ± 52de	254 ± 16e	263 ± 20e	267 ± 26e	471 ± 30d
C4	Oct-1-en-3-one	1290	20.84 ± 0.91c	29.89 ± 0.74b	37.96 ± 4.28a	nd	nd	nd	nd	nd	nd	nd	nd
C5	6-Methyl-5-hepten-2-one	1338	28.17 ± 6.20c	105 ± 16a	49.80 ± 1.71b	23.69 ± 0.98c	34.53 ± 0.01bc	35.32 ± 0.02bc	32.08 ± 0.01bc	29.98 ± 0.01bc	29.85 ± 0.01bc	36.43 ± 0.01bc	36.31 ± 0.01bc
C6	3-Oxobutan-2-yl acetate	1378	15.09 ± 1.46c	38.60 ± 1.15a	13.77 ± 0.92c	15.13 ± 0.54c	12.17 ± 0.14c	12.10 ± 0.49c	14.38 ± 2.41c	10.61 ± 0.80c	12.38 ± 0.51c	11.89 ± 1.45c	20.77 ± 2.49b
C7	6,10-Dimethyl-2-undecanone	1450	67.86 ± 19.73cde	152 ± 8b	225 ± 26a	58.37 ± 17.52de	62.87 ± 2.16de	76.87 ± 2.81cde	94.07 ± 1.07 cd	73.71 ± 4.17cde	31.60 ± 5.30e	104 ± 13bcd	114 ± 9bc
	Total		1422	2007	1387	1063	579	477	451	375	344	428	653
D1	Acetic acid	1449	1352 ± 186a	1052 ± 0ab	1041 ± 40ab	687 ± 144bc	535 ± 20c	754 ± 20bc	783 ± 143bc	836 ± 53bc	602 ± 44c	697 ± 87bc	585 ± 86c
D2	3-Methylbutanoic acid	1666	492 ± 5b	565 ± 0b	799 ± 12a	560 ± 10b	284 ± 35 cd	316 ± 46c	90.02 ± 7.96e	50.51 ± 2.70e	74.71 ± 9.00e	50.96 ± 0.01e	213 ± 8d
D3	Pentanoic acid	1733	224 ± 19b	273 ± 0a	303 ± 8a	192 ± 20b	117 ± 1c	112 ± 6c	125 ± 3c	108 ± 21c	105 ± 5c	98.88 ± 14.38c	112 ± 2c
D4	(*E*)-But-2-enoic acid	1745	29.87 ± 0.33bc	34.52 ± 9.08bc	72.34 ± 15.00a	54.1 ± 16.8ab	33.5 ± 13.78bc	16.26 ± 1.20c	31.95 ± 6.52bc	15.21 ± 3.40c	19.55 ± 1.19bc	30.66 ± 4.39bc	22.68 ± 2.31bc
D5	Hexanoic acid	1846	4270 ± 146b	5941 ± 161a	510 ± 75d	4181 ± 676b	2098 ± 50c	1845 ± 147c	2214 ± 90c	1756 ± 7c	1760 ± 119c	2220 ± 420c	1992 ± 466c
D6	Heptanoic acid	1950	502 ± 59b	639 ± 3a	497 ± 1b	410 ± 5c	277 ± 1d	209 ± 17de	245 ± 6d	221 ± 1de	209 ± 7de	217 ± 2de	163 ± 18e
D7	(*E*)-2-Hexenoic acid	1967	156 ± 4a	116 ± 17a	152 ± 13a	115 ± 10a	52.76 ± 27.46b	34.37 ± 5.83b	40.57 ± 6.93b	44.62 ± 1.21b	48.09 ± 0.91b	45.30 ± 13.70b	41.08 ± 5.72b
D8	Octanoic acid	2060	470 ± 23b	894 ± 1a	726 ± 111a	424 ± 14bc	325 ± 15bcd	249 ± 13d	265 ± 16 cd	248 ± 3d	230 ± 75d	238 ± 25d	181 ± 8d
D9	Nonanoic acid	2178	261 ± 57a	143 ± 31b	152 ± 12b	78.1 ± 7.25bc	36.09 ± 1.52c	50.47 ± 7.61c	nd	45.29 ± 0.99c	22.42 ± 0.58c	34.91 ± 0.001c	32.18 ± 0.01c
	Total		7757	9658	4252	6701	3758	3586	3795	3325	3070	3633	3342
E1	Methyl hexanoate	1184	60.73 ± 2.37c	101 ± 0b	53.16 ± 2.58 cd	33.81 ± 2.06cde	22.93 ± 1.25de	15.12 ± 4.08e	30.99 ± 11.81cde	14.06 ± 2.12e	34.00 ± 1.93cde	42.53 ± 16.38cde	142 ± 22a
E2	Ethyl hexanoate	1245	61.59 ± 2.33 cd	19.3 ± 0.76d	27.61 ± 3.91d	60.04 ± 2.32 cd	97.37 ± 3.38bcd	54.14 ± 1.42d	93.03 ± 7.76bcd	26.99 ± 1.26d	142 ± 2bc	176 ± 65b	417 ± 28a
E3	Hexyl acetate	1272	20.88 ± 1.72a	17.90 ± 0.19ab	11.43 ± 0.07c	4.47 ± 0.19e	15.26 ± 1.45b	6.68 ± 0.89de	6.66 ± 0.14de	5.74 ± 0.43de	5.68 ± 0.47de	6.66 ± 0.36de	8.18 ± 0.14d
E4	Ethyl heptanoate	1326											

(*continued on next page*)

Table 1 (*continued*)

	Compounds (μg/kg)	RI	Freeze drying stage										
			raw	1	2	3	4	5	6	7	8	9	10
			6.06 ± 0.96d	35.04 ± 0.24 cd	8.84 ± 0.01d	7.29 ± 0.01d	9.14 ± 0.02d	24.10 ± 0.01 cd	33.75 ± 0.01 cd	41.85 ± 1.41 cd	67.98 ± 9.85c	276 ± 28b	350 ± 32a
E5	Methyl octanoate	1372	15.67 ± 0.70e	43.05 ± 0.79d	24.14 ± 0.51de	15.65 ± 7.54e	18.38 ± 0.03e	23.8 ± 1.66de	42.35 ± 11.12d	19.77 ± 4.10e	265 ± 0b	296 ± 0a	230 ± 10c
E6	Ethyl octanoate	1457	nd	nd	nd	36.84 ± 0.02 h	66.13 ± 0.01 g	85.54 ± 0.01f	117 ± 0d	96.37 ± 0.01e	195 ± 0c	253 ± 0b	672 ± 0a
E7	Methyl decanoate	1593	121 ± 15f	276 ± 7e	164 ± 4f	136 ± 3f	164 ± 4f	212 ± 66ef	979 ± 7d	2155 ± 52a	1494 ± 0b	1566 ± 1b	1292 ± 37c
E8	Ethyl decanoate	1638	35.08 ± 5.80f	220 ± 14ef	147 ± 33ef	39.34 ± 0.43f	576 ± 29 cd	381 ± 115de	1517 ± 30b	413 ± 138de	806 ± 6c	1205 ± 22b	2228 ± 180a
E9	Methyl dodecanoate	1804	90.87 ± 4.64d	127 ± 0d	124 ± 0d	84.09 ± 9.83d	84.09 ± 9.83d	283 ± 65 cd	529 ± 112bc	275 ± 17 cd	541 ± 40bc	682 ± 245b	1644 ± 56a
E10	Ethyl dodecanoate	1841	nd	nd	84.20 ± 10.50def	27.47 ± 1.76ef	698 ± 29bc	418 ± 3cdef	626 ± 6bcd	315 ± 48cdef	593 ± 118bcde	1124 ± 361b	2503 ± 282a
	Total		412	839	644	445	1751	1503	3974	3410	4144	5627	9486
F1	Oxolan-2-one	1632	73.54 ± 4.93de	94.88 ± 14.21cde	318 ± 12a	210 ± 9b	144 ± 0bc	116 ± 16 cd	87.98 ± 38.88cde	151 ± 26bc	40.41 ± 11.50e	131 ± 8 cd	120 ± 12 cd
F2	5-Ethyloxolan-2-one	1694	118 ± 15b	222 ± 10a	215 ± 4a	106 ± 1bc	102 ± 2bcd	69.06 ± 1.96de	102 ± 0bcd	94.74 ± 4.51bcde	61.99 ± 1.84e	76.66 ± 18.18cde	68.96 ± 11.15de
F3	6-Methyloxan-2-one	1773	14.07 ± 2.89f	25.85 ± 0.21d	21.56 ± 0.42de	22.38 ± 0.36de	18.72 ± 1.20ef	18.78 ± 1.15ef	25.31 ± 1.72d	43.86 ± 2.15ab	35.94 ± 2.11c	39.64 ± 0.71bc	45.99 ± 0.98a
F4	5-Propyloxolan-2-one	1787	26.38 ± 0.40c	50.33 ± 1.11a	39.87 ± 1.97b	21.89 ± 1.31 cd	11.39 ± 0.53e	11.25 ± 0.53e	12.80 ± 2.05e	10.73 ± 1.29e	10.99 ± 1.33e	13.59 ± 1.52e	20.16 ± 0.36d
F5	5-Butyloxolan-2-one	1910	58.00 ± 2.38b	83.00 ± 0.49a	83.30 ± 5.90a	51.89 ± 0.71b	35.00 ± 0.34cde	31.19 ± 1.73de	32.87 ± 0.67cde	41.37 ± 1.91c	26.18 ± 2.06e	36.83 ± 2.30 cd	32.68 ± 3.24cde
F6	5-Heptyloxolan-2-one	2024	nd	nd	nd	nd	nd	nd	nd	88.41 ± 0.01a	23.92 ± 0.20b	8.01 ± 0.10c	4.58 ± 1.55d
F7	5-Hexyloxolan-2-one	2152	24.57 ± 0.38a	19.74 ± 2.63ab	17.54 ± 2.75bc	10.57 ± 0.57def	12.44 ± 0.54 cd	10.90 ± 1.00de	10.79 ± 0.59de	9.93 ± 2.37def	4.96 ± 0.28f	5.47 ± 0.28ef	5.73 ± 0.25ef
	Total		315	496	695	423	324	257	272	440	204	311	298
G1	2,6-Dimethylpyrazine	1328	11.87 ± 2.00 g	20.24 ± 0.20c	18.73 ± 0.06d	11.62 ± 1.58 h	6.06 ± 0.12 k	7.75 ± 3.76j	14.36 ± 0.01e	10.85 ± 0.01i	11.87 ± 8.35f	22.62 ± 1.77b	34.49 ± 0.13a
G2	2-Ethyl-6-methylpyrazine	1386	85.52 ± 1.54c	165 ± 6a	123 ± 8b	78.51 ± 2.59c	33.03 ± 0.48def	27.03 ± 2.11ef	31.80 ± 4.59ef	22.94 ± 3.05f	33.00 ± 0.50def	38.07 ± 2.35de	47.06 ± 2.50d
G3	2,6-Diethylpyrazine	1430	22.51 ± 1.28d	69.16 ± 2.39a	40.77 ± 0.81b	27.69 ± 0.92c	18.39 ± 0.01e	8.45 ± 0.36f	11.66 ± 0.43f	9.65 ± 0.36f	nd	nd	nd
G4	2-Ethyl-3,5-dimethylpyrazine	1455	14.96 ± 3.09c	81.7 ± 9.27a	35.55 ± 1.81b	22.96 ± 0.12c	20.33 ± 0.81c	14.96 ± 0.45c	26.25 ± 0.01bc	22.54 ± 0.01c	21.06 ± 0.01c	20.31 ± 0.48c	22.80 ± 0.21c
G5	Tetramethylpyrazine	1470	8.70 ± 0.22j	13.11 ± 0.32b	14.28 ± 1.61a	11.51 ± 0.27c	10.28 ± 0.29f	10.41 ± 0.71e	10.67 ± 1.52d	9.73 ± 0.47 h	10.11 ± 0.84 g	9.28 ± 0.33i	8.56 ± 0.01 k
	Total		144	349	232	152	88	69	95	76	76	90	113
H1	Limonene	1200	90.2 ± 3.18d	449 ± 3a	481 ± 1a	190 ± 20c	216 ± 14bc	229 ± 11bc	201 ± 2c	236 ± 17bc	226 ± 18bc	271 ± 31b	208 ± 0c
H2	*γ*.-Terpinene	1246	nd	18.82 ± 0b	23.71 ± 2.56a	9.51 ± 2.29 cd	8.28 ± 0.26 cd	7.37 ± 0.52 cd	7.09 ± 0.1d	7.68 ± 0.42 cd	6.01 ± 0.09d	11.49 ± 0.56c	7.03 ± 0.06d
H3	Styrene	1261	14.20 ± 1.7gh	18.64 ± 0.99 g	34.28 ± 0.37f	11.86 ± 1.17gh	56.63 ± 3.94e	65.95 ± 0.21d	73.49 ± 1.60bc	8.85 ± 1.53 h	68.17 ± 0.36 cd	78.47 ± 0.70b	91.95 ± 3.23a
H4	*α*-Farnesene	1746	45.33 ± 8.07b	48.70 ± 1.31b	44.18 ± 1.80b	43.81 ± 0.80b	16.38 ± 1.90c	26.11 ± 1.79c	23.90 ± 0.23c	23.31 ± 4.69c	120 ± 0a	21.70 ± 1.23c	26.79 ± 0.55c
	Total		150	535	583	255	297	328	305	276	420	383	334
I1	*p*-Cymene	1270	10.09 ± 1.23b	29.67 ± 4.56a	23.97 ± 0.35a	14.19 ± 1.04b	3.60 ± 0.20c	9.95 ± 0.52b	11.57 ± 0.49b	10.93 ± 1.30b	8.56 ± 1.39bc	12.68 ± 0.05b	12.69 ± 0.22b
I2	Naphthalene	1746	53.54 ± 2.54b	65.75 ± 6.98a	66.11 ± 0.12a	30.60 ± 3.09c	27.67 ± 1.89 cd	19.59 ± 0.55de	27.67 ± 1.89 cd	15.36 ± 1.28e	20.76 ± 1.56cde	19.49 ± 0.24de	24.83 ± 0.01cde
	Total		63.63	95.42	90.08	44.79	31.27	29.54	39.24	26.30	29.32	32.16	37.53

Mean values with different lower-case letters in the same row correspond to significant differences at $p < 0.05$. Data are represented as the mean ± SD; “nd”: Not detected. RI: Retention indices on DB-Wax columns were determined by *n*-alkanes.

Table 2
The odor activity value (OAV) of aroma compounds in red jujube at different freeze drying stages.

	Compounds	Freeze drying stage										
		raw	1	2	3	4	5	6	7	8	9	10
A1	Oct-1-en-3-ol	92	231	209	102	67	60	70	53	55	78	94
A2	2,3-Butanediol	<1	2	2	<1	1	<1	<1	<1	<1	1	<1
B1	Hexanal	19	7	8	8	5	4	7	7	9	11	11
B2	(*E*)-2-Hexenal	<1	<1	<1	<1	nd	nd	nd	nd	nd	nd	nd
B3	(*E*)-2-Heptenal	2	2	2	<1	nd	nd	nd	nd	nd	nd	nd
B4	(*E*)-2-Octenal	27	25	26	14	nd	nd	nd	nd	nd	nd	nd
B5	Furfural	<1	nd	nd	nd	nd	<1	<1	<1	<1	<1	<1
B6	Benzaldehyde	<1	1	1	<1	<1	<1	<1	<1	<1	<1	<1
B7	Decanal	10	13	9	7	nd	nd	nd	nd	nd	nd	nd
C1	Butane-2,3-dione	84	356	nd	108	nd	nd	<1	nd	nd	nd	nd
C2	3-Octanone	<1	3	2	<1	<1	<1	<1	<1	<1	<1	<1
C3	3-Hydroxybutan-2-one	85	90	73	60	33	25	22	18	19	19	34
C4	Oct-1-en-3-one	6946	9962	12,653	nd	nd	nd	nd	nd	nd	nd	nd
C5	6-Methyl-5-hepten-2-one	<1	2	<1	<1	<1	<1	<1	<1	<1	<1	<1
C6	3-Oxobutan-2-yl acetate	/	/	/	/	/	/	/	/	/	/	/
C7	6,10-Dimethyl-2-undecanone	/	/	/	/	/	/	/	/	/	/	/
D1	Acetic acid	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
D2	Butanoic acid, 3-methyl-	<1	1	2	1	<1	<1	<1	<1	<1	<1	<1
D3	Pentanoic acid	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
D4	(*E*)-But-2-enoic acid	/	/	/	/	/	/	/	/	/	/	/
D5	Hexanoic acid	5	7	<1	5	2	2	2	2	2	2	2
D6	Heptanoic acid	1	1	<1	<1	<1	<1	<1	<1	<1	<1	<1
D7	(*E*)-2-Hexenoic acid	/	/	/	/	/	/	/	/	/	/	/
D8	Octanoic acid	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
D9	Nonanoic acid	<1	<1	<1	<1	<1	<1	nd	<1	<1	<1	<1
E1	Methyl hexanoate	<1	1	<1	<1	<1	<1	<1	<1	<1	<1	2
E2	Ethyl hexanoate	12	4	6	12	19	11	19	5	28	35	83
E3	Hexyl acetate	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	0
E4	Ethyl heptanoate	3	18	5	4	5	13	18	22	36	145	184
E5	Methyl octanoate	<1	<1	<1	<1	<1	<1	<1	<1	1	1	1
E6	Ethy octanoate	0	0	0	2	3	4	6	5	10	13	35
E7	Methyl decanoate	28	64	38	32	38	49	228	501	348	364	301
E8	Ethyl decanoate	7	44	29	28	115	76	303	83	161	241	446
E9	Methyl dodecanoate	61	84	83	56	56	189	352	183	361	455	1096
E10	Ethyl dodecanoate	nd	nd	<1	<1	2	1	2	<1	1	3	6
F1	Oxolan-2-one	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
F2	5-Ethyloxolan-2-one	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
F3	6-Methyloxan-2-one	/	/	/	/	/	/	/	/	/	/	/
F4	5-Propyloxolan-2-one	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
F5	5-Butyloxolan-2-one	<1	13	13	8	5	5	5	6	4	6	5
F6	5-Heptyloxolan-2-one	nd	nd	nd	nd	nd	nd	nd	42	11	4	2
F7	5-Hexyloxolan-2-one	22	18	16	10	11	10	10	9	5	5	5
G1	2,6-Dimethylpyrazine	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
G2	2-Ethyl-6-methylpyrazine	2	4	3	2	<1	<1	<1	<1	<1	<1	1
G3	2,6-Diethylpyrazine	4	12	7	5	3	1	2	2	nd	nd	nd
G4	2-Ethyl-3,5-dimethylpyrazine	374	2043	889	574	508	374	656	563	527	508	570
G5	Tetramethylpyrazine	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
H1	Limonene	3	13	14	6	6	7	6	7	7	8	6
H2	γ-Terpinene	nd	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
H3	Styrene	<1	<1	<1	<1	<1	1	1	<1	1	1	1
H4	α-Farnesene	/	/	/	/	/	/	/	/	/	/	/
I1	*p*-Cymene	2	6	5	3	<1	2	2	2	2	3	3
I2	Naphthalene	9	11	11	5	5	3	5	3	3	3	4

detected alcohols, oct-1-en-3-ol was key aroma compound in raw red jujube, and 2,3-butanediol was the key aroma compound in freeze-dried “Huizao” (Zhu & Xiao, 2018). Lactones might be generated from the β-oxidation of fatty acids (Xi et al., 2012). The lactones showed maximum contents at the stage 3, and then decreased, but the contents had no significant changes after FD (Table 1). Among these lactones, 5-propyloxolan-2-one, 5-butyloxolan-2-one and 5-ethyloxolan-2-one with sweet and fruity notes were key aroma compounds in raw “Huizao”, and 5-heptyloxolan-2-one appeared from stage 7, was also identified as the key aroma compound of freeze-dried “Huizao”.

3.3. *Changes in aroma precursors in red jujube during freeze drying*

3.3.1. *Changes in contents of sugars during freeze drying*

Sugars not only enhance the interaction between sweet and aroma compounds but also are the main precursor of aroma (Saint-Eve et al., 2014). Table 3 presents the sugar contents calculated on a dry basis in red jujube samples, revealed that raw samples had the highest content (759 mg/g) of total sugars. Glucose had the highest loss ratio (43.89 %), followed by fructose (28.78 %) and sucrose (26.88 %) after FD. It is illustrated the main components involved in the reaction were reducing sugars, especially glucose. Reducing sugars could form esters under the action of enzymes, and can also undergo Maillard reaction with amino acids at high temperatures to generate pyrazines (Song et al., 2019).

3.3.2. *Changes in contents of fatty acid during freeze drying*

Fatty acids are the most important precursors for the formation of fruit aroma components. The linear aliphatic alcohols, aldehydes, ketones and esters are mainly derived from fatty acid oxidation (Schwab et al., 2008). A total of 9 fatty acids were identified and quantified including lauric acid (C12:0), myristic acid (C14:0), myristoleic acid (C14:1n5), palmitic acid (C16:0), palmitoleic acid (C16:1n7), stearic

Table 3
The contents of reducing sugars, free amino acids and fatty acids (of dry weight basis) in red jujube at different freeze drying stages.

Types	Compositions	Freeze drying stage										
		0	1	2	3	4	5	6	7	8	9	10
Sugars (mg/g)	Glucose	218 ± 13a	169 ± 5abc	207 ± 14ab	168 ± 28abc	91.93 ± 20.89c	155 ± 35abc	116 ± 43bc	177 ± 36abc	129 ± 2abc	124 ± 19abc	123 ± 18abc
	Sucrose	334 ± 5ab	247 ± 57ab	319 ± 22ab	236 ± 43ab	169 ± 36b	265 ± 63ab	210 ± 76ab	311 ± 62ab	272 ± 8ab	255 ± 13ab	245 ± 13ab
	Fructose	207 ± 15a	159 ± 6ab	199 ± 16a	161 ± 29ab	87.48 ± 19.40b	154 ± 37ab	118 ± 46ab	178 ± 38ab	130 ± 2ab	127 ± 18ab	147 ± 14ab
	Total	759	575	725	565	348	574	444	666	531	506	515
Fatty acids (μg/kg)	C12:0	105 ± 3b	132 ± 11ab	143 ± 7a	150 ± 15a	142 ± 7a	142 ± 2ab	140 ± 12ab	140 ± 14ab	135 ± 0ab	139 ± 9ab	136 ± 3ab
	C14:0	144 ± 7b	173 ± 12ab	197 ± 10a	166 ± 13ab	171 ± 5ab	171 ± 1ab	160 ± 1b	173 ± 3ab	174 ± 12ab	173 ± 14ab	157 ± 3b
	C14:1n5	122 ± 6ab	145 ± 14a	134 ± 18ab	103 ± 1b	101 ± 0b	145 ± 1a	105 ± 8b	115 ± 7ab	110 ± 8ab	114 ± 10ab	107 ± 3b
	C16:0	627 ± 3c	77.41 ± 3.31abc	85.09 ± 7.46ab	91.04 ± 5.52a	79.00 ± 3.09abc	74.01 ± 1.15abc	72.08 ± 2.96bc	76.25 ± 4.25abc	76.76 ± 3.11abc	73.51 ± 8.01bc	67.96 ± 1.28bc
	C16:1n7	423 ± 12d	511 ± 16abc	535 ± 20a	504 ± 11abc	436 ± 4d	530 ± 10ab	427 ± 6d	500 ± 14abc	457 ± 12 cd	455 ± 12 cd	475 ± 28bcd
	C18:0	88.01 ± 4.75a	103 ± 7a	91.14 ± 7.37a	107 ± 17a	116 ± 17a	81.87 ± 0.77a	85.33 ± 26.56a	101 ± 2a	95.34 ± 1.52a	96.70 ± 18.89a	nd
	C18:1n9c	184 ± 45b	166 ± 21b	83.33 ± 5.52b	754 ± 112a	118 ± 13b	98.67 ± 19.94b	79.97 ± 28.08b	107 ± 24b	81.42 ± 1.52b	108 ± 26b	53.92 ± 9.81b
	C18:2n6c	337 ± 46b	296 ± 2b	317 ± 23b	609 ± 61a	266 ± 7b	300 ± 8b	233 ± 1b	316 ± 34b	273 ± 37b	248 ± 22b	264 ± 4b
	C18:3n3	67.18 ± 0.01b	80.49 ± 10.35ab	83.33 ± 5.52a	nd	nd	nd	nd	nd	nd	nd	nd
	Total	2097	1684	1669	2484	1429	1543	1302	1528	1403	1407	1261
Free amino acids (μg/kg)	L-Asp	137 ± 5bcd	153 ± 11abc	148 ± 0abc	128 ± 14 cd	172 ± 12ab	179 ± 7a	145 ± 4abc	139 ± 0abcd	128 ± 12 cd	159 ± 4abc	98.52 ± 21.25d
	L-Thr	81.99 ± 5.83bcd	106 ± 6ab	137 ± 0a	80.75 ± 5.39bcd	88.25 ± 1.66bc	102 ± 14b	51.08 ± 14.19d	76.14 ± 3.79bcd	67.44 ± 15.25 cd	80.18 ± 5.22bcd	59.74 ± 3.46 cd
	L-Ser	125 ± 3bc	142 ± 6b	169 ± 0a	114 ± 5c	117 ± 4c	119 ± 8bc	75.18 ± 6.78de	88.30 ± 1.04d	55.9 ± 10.27ef	86.96 ± 6.43d	41.04 ± 3.29f
	L-Glu	390 ± 0d	486 ± 10c	580 ± 0b	265 ± 0e	377 ± 0d	263 ± 12e	43.90 ± 0.01f	68.95 ± 0.02f	374 ± 0.02d	273 ± 0e	648 ± 30a
	L-Gly	25.8 ± 0.39b	29.24 ± 2.04a	26.76 ± 0.01ab	16.40 ± 0.10c	13.04 ± 0.01e	13.51 ± 0.01de	11.12 ± 0.01e	15.86 ±0.010 cd	nd	nd	nd
	L-Ala	50.01 ± 0.01ab	43.54 ± 1.15ab	47.53 ± 0.01ab	37.30 ± 0.61ab	33.49 ± 8.40b	42.60 ± 3.55ab	38.73 ± 3.65ab	54.79 ± 11.96a	33.55 ± 4.39b	34.79 ± 3.70ab	31.37 ± 4.34b
	L-Val	81.89 ± 0.01bc	96.33 ± 3.42b	126 ± 0a	80.63 ± 0.25c	77.83 ± 5.07c	56.97 ± 11.05d	1.13 ± 0.36f	29.88 ± 2.16e	5.43 ± 0.05f	42.18 ± 0.01de	4.17 ± 0.12f
	L-Cys	54.70 ± 0.01a	5.32 ± 0.01e	5.48 ± 0.01e	7.05 ± 0.47e	9.33 ± 3.46e	36.59 ± 1.02 cd	44.28 ± 3.03bc	30.47 ± 4.32d	46.34 ± 1.84ab	33.42 ± 0.52d	50.35 ± 4.34ab
	L-Met	3.21 ± 0.01c	1.64 ± 0.01d	1.83 ± 0.73d	2.09 ± 0.01d	nd	nd	nd	3.84 ± 0.01c	nd	6.54 ± 0.01a	4.78 ± 0.02b
	L-Leu	29.13 ± 0.01b	30.02 ± 3.83ab	34.78 ± 0.81a	19.03 ± 1.24c	14.85 ± 1.5 cd	11.44 ± 0.49de	10.66 ± 0.06de	2.29 ± 0.05f	6.32 ± 0.01ef	17.94 ± 0.03c	1.73 ± 0.07f
	L-Tyr	16.92 ± 0.01c	20.88 ± 0.03b	24.92 ± 1.96a	14.02 ± 0.02d	nd	nd	17.70 ± 0.01c	20.40 ± 0.03b	nd	20.91 ± 0.01b	17.71 ± 0.42c
	L-Phe	25.52 ± 0.01 cd	29.73 ± 4.62bcd	36.66 ± 0.45abc	29.54 ± 4.77bcd	37.73 ± 5.87abc	40.25 ± 1.33ab	28.59 ± 2.83bcd	41.63 ± 5.51ab	30.70 ± 4.88bcd	46.60 ± 0.01a	20.5 ± 2.93d
	L-Lys	19.67 ± 0.45b	20.86 ± 0.15a	17.43 ± 0.43c	16.71 ± 0.21c	13.90 ± 0.01d	13.00 ± 0.01e	9.57 ± 0.03f	1.41 ± 0.01 g	nd	nd	nd
	L-His	14.58 ± 0.01c	24.38 ± 1.52a	25.28 ± 2.06a	18.51 ± 1.34b	18.63 ± 0.96b	2.52 ± 0.24d	nd	nd	nd	nd	nd
	L-Arg	89.97 ± 5.76a	62.76 ± 3.59b	65.54 ± 1.46b	58.32 ± 0.21b	55.77 ± 1.62b	38.85 ± 1.52c	34.95 ± 1.03 cd	39.06 ± 4.20c	29.77 ± 0.92 cd	26.46 ± 0.04d	26.69 ± 2.63d
	L-Pro	4422 ± 112a	4489 ± 236a	4637 ± 692a	2771 ± 136b	4506 ± 156a	5260 ± 284a	4846 ± 104a	4619 ± 71a	4866 ± 60a	5420 ± 13a	4746 ± 421a
	P-Ser	261 ± 88 cd	221 ± 14d	203 ± 0d	285 ± 1bcd	333 ± 0abcd	421 ± 23.56ab	397 ± 32abc	399 ± 55abc	431 ± 9a	451 ± 1a	327 ± 27abcd
	Tau	20.30 ± 3.15d	16.85 ± 2.65d	19.96 ± 0.01d	21.85 ± 2.75 cd	39.73 ± 8.99bc	45.26 ± 0.10ab	54.40 ± 0.01ab	47.71 ± 5.60ab	61.87 ± 9.95a	53.75 ± 0.10ab	62.57 ± 3.26a
	PEA	22.18 ± 0.01d	13.86 ± 0.55d	17.08 ± 0.01d	12.51 ± 2.61d	22.12 ± 2.07d	52.46 ± 0.87bc	65.86 ± 0.01abc	48.03 ± 3.32c	80.32 ± 12.07a	52.3 ± 8.53bc	70.82 ± 3.78ab
	L-Cit	nd	nd	18.36 ± 0.01 h	21.24 ± 0.02 g	26.8 ± 0.02f	57.94 ± 0.02e	65.44 ± 0.01c	61.06 ± 0.01d	91.40 ± 0.01a	nd	75.85 ± 0.01b
	α-AAA	35.73 ± 0.01a	36.50 ± 0.01a	34.1 ± 0.01a	19.59 ± 2.99bc	20.08 ± 0.01bc	30.93 ± 0.03a	nd	35.60 ± 0.01a	17.26 ± 0.01bc	15.07 ± 4.99c	23.92 ± 0.01b
	Cysthi											

(*continued on next page*)

Table 3 (*continued*)

Types	Compositions	Freeze drying stage										
		0	1	2	3	4	5	6	7	8	9	10
		17.02 ± 0.01b	17.2 ± 1.67b	22.86 ± 0.02a	15.98 ± 0.01b	9.41 ± 0.26 cd	11.33 ± 0.01c	8.11 ± 0.01d	5.48 ± 0.01e	1.49 ± 0.25f	0.59 ± 0.01f	0.12 ± 0.01f
	β-AiBA	40.73 ± 0.88b	54.65 ± 4.78a	56.00 ± 0.46a	52.53 ± 1.33a	47.84 ± 1.35ab	38.91 ± 1.42b	23.74 ± 1.17 cd	21.68 ± 4.54 cd	18.95 ± 2.27de	28.54 ± 2.49c	10.63 ± 0.39e
	γ-ABA	227 ± 19a	258 ± 10a	271 ± 5a	241 ± 18a	219 ± 32a	220 ± 15a	120 ± 1bc	153 ± 1b	90.90 ± 0.78 cd	137 ± 0bc	62.77 ± 3.46d
	$EOHNH_2$	15.02 ± 0.64b	17.56 ± 0.03ab	19.36 ± 2.01a	14.67 ± 1.79b	17.09 ± 2.27ab	nd	nd	nd	nd	nd	nd
	Hypro	33.23 ± 6.02ef	29.21 ± 0.02f	24.66 ± 0.31f	40.58 ± 3.5de	44.89 ± 0.07 cd	58.98 ± 1.99a	57.3 ± 0.64ab	47.12 ± 0.62 cd	48.91 ± 1.45bcd	50.50 ± 1.29abc	45.13 ± 0.38 cd
	Total	6240	6406	6771	4383	6315	7115	6150	6050	6485	7037	6430

Mean values with different lower-case letters in the same row correspond to significant differences at $p < 0.05$. Data are represented as the mean ± SD; "nd": Not detected.

C12:0: lauric acid, C14:0: myristic acid, C14:1n5: myristoleic acid, C16:0: palmitic acid, C16:1n7: palmitoleic acid, C18:0: stearic acid, C18:1n9c: oleic acid, C18:2n6c: linoleic acid and C18:3n3: *α*-linolenic acid.

acid (C18:0), oleic acid (C18:1n9c), linoleic acid (C18:2n6c) and *α*-linolenic acid (C18:3n3) (Table 3). These fatty acids were also found in other varieties of jujubes (Song et al., 2019). The fatty acid contents showed a trend of firstly increased from 2,097 μg/kg to 2,484 μg/kg (stage 0–3) and then decreased to 1,261 μg/kg (stage 10), with fluctuations during FD stages. Among these fatty acids, the contents of C12:0, C14:0, C16:0 and C16:1n7 increased slightly at the end of FD. And the others showed a decreased content after FD, especially C18:2n6c and C18:3n3, which were precursors of linear esters compounds through lipoxygenase pathway. This is also consistent with the result that the content of esters increased after FD.

3.3.3. Changes in contents of free amino acids (FAAs) during freeze drying

From Table 3, a total of 26 free amino acids were detected in all red jujube samples. The total free amino acids showed an increasing tendency firstly, and then decreased to 4,383 μg/kg at stage 3, finally

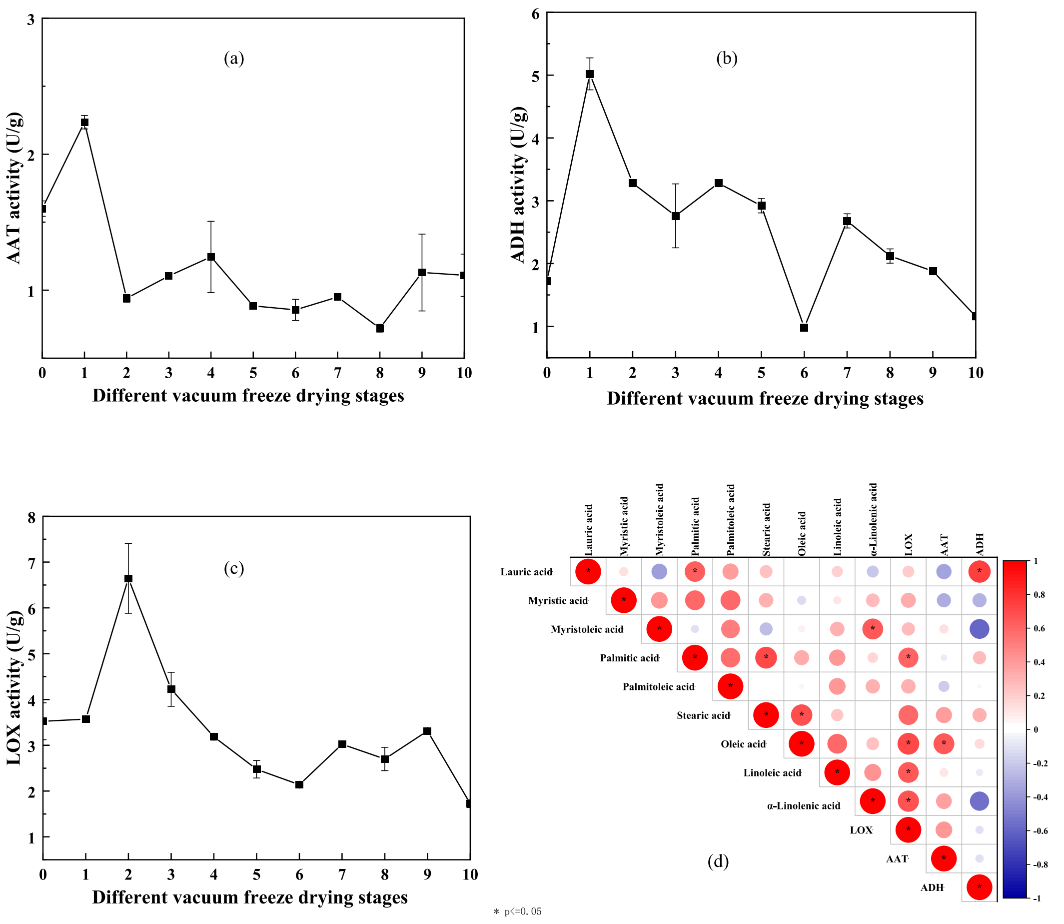


Fig. 2. The enzyme activity changes of lipoxygenase (LOX) (a), alcohol dehydrogenase (ADH) (b) and alcohol acyltransferase (AAT) (c) during the different freeze drying stages, and the correlation between enzyme activities and fatty acids (d).

increased and kept a range from 6,050 μg/kg to 7,115 μg/kg during stage 4–10. FAAs had different changes in red jujube during the whole FD stages. After FD, glycine (Gly), valine (Val), histidine (His), lysine (Lys), Leucine (Leu), cystathionine (Cysthi) and ethanolamine ($EOHNH_2$) were lost more, with a loss ratio of>90 %, followed by serine (Ser), arginine (Arg), β-aminoisobutyric acid (β-AiBA) and γ-aminobutyric acid (γ-ABA), with a loss of 65 %~75 %, aspartic acid (Asp), threonine (Thr), alanine (Ala), phenylalanine (Phe), α-aminoadipic acid

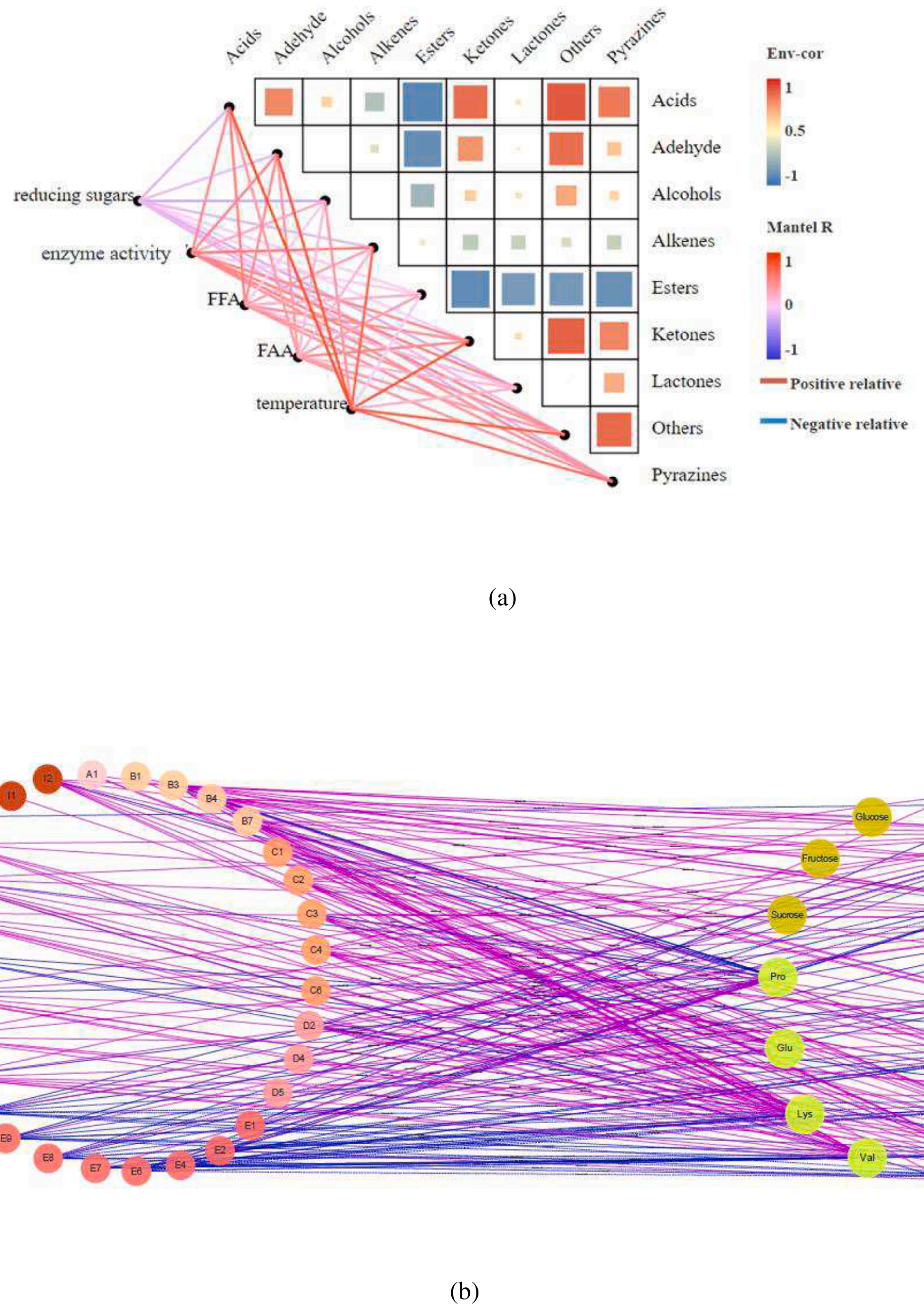


Fig. 3. Correlation analysis between classes of volatile compounds and precursors, enzyme activities and temperature by Mantel test. The upper right diagram showing the Spearman correlation of different classes of aroma compounds. A color gradient denotes the Spearman's correlation coefficients. The bottom left graph shows the Mantel test between effect parameters (reducing sugar, enzyme activies, FFA, FAA, and temperature) and different classes of aroma compounds mentioned above. FFA, free fatty acids; FAA, free amino acids (a) and Spearman correlation networks showing relationships between aroma-active compounds (OAV > 1) and flavor precursors, enzyme activities in red jujube during freeze drying stages. The left-hand circle represents the aroma-active compounds, and the right-hand circle represents the main flavor precursors and enzyme activities in the red jujube during freeze drying. The purple and blue lines respectively represent the positive and negative correlation between the aroma compounds and flavor precursors, enzyme activities. And correlation coefficients between them were calculated using values from all samples. Only significant correlations ($|r|>0.6$, $p < 0.05$) are indicated, and line thickness represents the correlation coefficients of interactions. (For interpretation of the references to color and letter in this figure, the reader is referred to the web version of this article.) (b). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

(α-AAA) and cysteine (Cys) were lost$<$40 %. In addition, proline (Pro), tyrosine (Tyr), serine (Ser) and hydroxyproline (Hypro) increased 4 % ~40 %, while, methionine (Met), glutamic acid (Glu), citrulline (Cit), *o*-phosphoethanolamine (PEA) and taurine (Tau) increased over 50 %. Combined the original content of raw red jujube, data fluctuation and ratio of FAAs, Ser, Gly, Pro, Val, Cys, Arg, Glu, Lys and Leu could be potential precursors for the characteristic aroma of freeze-dried red jujube. These amino acids might involve in Maillard reaction, Strecker degradation, decarboxylation or deamination and other reactions in the thermal reaction process, and form various volatile compounds (El Hadi et al., 2013; Schwab et al., 2008). Pyrazine compounds with roasty and nut notes obtained by Strecker degradation of Cys or thermal reaction of Lys, Gly, Ser, Val, Leu and Arg (Adams & De Kimpe, 2007; Deng et al., 2022; Wang et al., 2021).

3.4. Changes in key enzyme activities in red jujube during freeze drying

Linear-chain aliphatic alcohols, aldehydes, ketones and esters, are commonly derived from the oxidative degradation of fatty acids and are generally formed by LOX pathways in fruits (Wu et al., 2020). LOX, ADH, and AAT are important for the LOX pathway, which results in the synthesis of volatile compounds in red jujube samples. As displayed in Fig. 2(a–c), the activities of ADH and AAT were reached the highest values with 5.02 U/g and 2.24 U/g at the stage 1, and the highest value of LOX was 6.65 U/g at the stage 2. The activity changes of LOX, ADH and AAT showed a consistent trend, increased initially and then declined. Though the enzyme activities had some fluctuation, the activities of ADH, AAT and LOX were lost 76.9 %, 50.3 % and 74.0 % at the stage 10, respectively. In general, the enzyme activity is higher between 30 and 45 °C (Liu et al., 2013), while the temperature was higher than 57 °C after stage 2, which could cause the enzyme activity to decrease or even inactivate (Fig. S1).

From Fig. 2(d), LOX activity showed a significantly positive correlation with palmitic acid, oleic acid, linoleic acid and α-linolenic acid; ADH showed a positive correlation with lauric acid; AAT showed a positive correlation with oleic acid. In general, LOX recognizes the 1,4-pentadiene structure of linoleic acid and linolenic acid in unsaturated fatty acids to make them undergo oxidation and form hydroperoxide fatty acids, and hydroperoxide forms hexanal or hexenal under the action of hydroperoxide lyase (HPL) (Schwab et al., 2008). Under the action of ADH, the corresponding alcohol is formed, such as, (*E*)-2-hexen-1-ol and the alcohol forms the corresponding ester, such as (*E*)-ethyl hex-2-enoate under the action of AAT (Guo et al., 2022).

3.5. Correlation between aroma compounds and precursors and enzyme activities in red jujube during freeze drying

3.5.1. Correlation analysis between classes of aroma compounds and precursors, enzyme activities and temperature

In order to explore the correlation between classes content of aroma compounds, the Spearman correlation analysis was established (Fig. 3 (a) upper right). A correlation was also established between the class content of aroma compounds and precursors and temperature using the Mantel test (Fig. 3(a), bottom left). Spearman correlation showed that esters content was negatively correlated with the content of acids, lactones, pyrazines, aldehydes and ketones. The content of pyrazines, ketones, acids and aldehydes were positively correlated. Butane-2,3-dione and 3-hydroxybutan-2-one with creamy and sweet notes in red jujube as α-dicarbonyl compounds, could participate in the Maillard reaction and form pyrazines with roasty and nut notes (Xiao et al., 2018). This result elucidated the positive correlation between ketones and pyrazines, also explained the aroma profile transformed from creamy and sweet to roasty after FD. With the Maillard reaction occurred, pyrazines as the products of Maillard reaction, ketones and acetic acid as the intermediate products would be produced (Gong et al., 2021). That could be explained the positive correlation between pyrazines, ketones, acids and aldehydes.

Results of the Mantel test indicated that enzyme activity, fatty acids and free amino acids had significant correlations ($p \leq 0.05$) with aldehydes, ketones, acids, lactones, pyrazines, alkenes and others. Amino acids and fatty acids could not only affect the volatile compounds alone, but also their interactions could affect the overall aroma to a great extent, which is mainly played by Maillard reaction. In Maillard reaction, amino compounds could be provided by amino acids, while carbonyl compounds could be converted from reducing sugar or fatty acids (Hou et al., 2017). In addition, some volatile oxidation products of fatty acids, such as acids, ketones, alcohols, would also react with the intermediate products of Maillard reaction to generate flavor compounds and contribute to the overall aroma. They might generate some heterocyclic compounds with long alkyl substituents, such as pyridines, pyrazines and so on (Liu et al., 2020). In addition, temperature had a highly significant correlation ($p \leq 0.01$) with the aldehydes, ketones, acids, lactones, pyrazines, alkenes and others. That illustrated the temperature was also a key influencing factor in the aroma formation during FD which is a complex process involved enzyme reaction and non-enzyme reaction. Li et al. (2022) also found that temperature was an important parameter in aroma formation during drying processing of shiitake mushrooms. And based on PCA analysis, they inferred the aroma formation was dominated by enzymatic reactions in the pre-drying period and by non-enzymatic reactions in the post-drying period, which were all driven by temperature. In our study, combined the correlation value, the influence degree of factors on the aroma formation of freeze-dried jujube was ranked as temperature $>$ enzyme activity $>$ fatty acids $>$ amino acids (Fig. 3(a)).

3.5.2. Correlation analysis between aroma-active compounds and flavor precursors, enzyme activities

Based on the above analysis results, the correlation network among aroma-active compounds (OAV > 1), flavor precursors (including 3 fatty acids, 9 free amino acids and 3 reducing sugars), and enzyme activities was constructed using Cytoscape (v.3.8.2) based on the Spearman correlation analysis. Spearman correlation coefficients and p values were calculated and shown in Fig. 3(b). There were 212 significant ($p < 0.05$) and strong ($|r| > 0.6$) correlations between the aroma-active compounds and flavor precursors and enzyme activities. The letter A ~ I stand for alcohols, aldehydes, ketones, acids, esters, lactones, pyrazines, alkenes, and others, respectively.

From Fig. 3(b), there were 3 fatty acids related to volatile compounds, of which the number of aroma-active compounds related to α-linolenic acid was the most (18), followed by linoleic acid (9) and oleic acid (6). That might be due to these fatty acids have unsaturated double bond, which could more easily form aroma compounds by oxidizing reaction. In addition, there were 9 free amino acids related to volatile compounds. The number of aroma-active compounds related to Lys (23) and Leu (23) was the largest, followed by Arg (21), Ser (20), Val (20) and Gly (19), Pro (15), Glu (8) and Cys (3). This result was consisted with section 3.2.3, these amino acids could be identified as the main FAAs precursors for the aroma-active aroma compounds of freeze-dried red jujube. Glucose had more correlations with aroma-active compounds among the 3 sugars, and LOX had greater correlation with aroma-active compounds than ADH and AAT.

As compounds that contribute greatly to the aroma of freeze-dried jujube, pyrazine compounds were mainly negatively correlated with Pro and Cys, and positively correlated with Gly, Lys, Val, Leu, Arg and Glu. This is consistent with Yu et al., (2021) and Kocadağlı et al., (2021). In addition, there was also a significant positive correlation with α-linolenic acid and LOX, which might be due to the substances produced by fatty acids in the oxidation process involved in the Maillard reaction. Similar to pyrazines, precursors associated with ketones included 8 amino acids, 2 fatty acids and 1 reducing sugar, LOX and AAT also showed correlation with ketones. Among them, Arg, Lys, Leu, Val, Pro, Glu, Ser, Gly and α-linolenic acid were correlated with 3-octanone, 3-hydroxybutan-2-one, and oct-1-en-3-one. Ketone compounds showed a declined trend during the FD process, indicating that ketones were reactant during the FD process, and might be converted to other volatile compounds such as pyrazines or carboxylic acids (Xiao et al., 2018).

There were 9 amino acids, 3 fatty acids and LOX significantly correlated with esters. Among these aroma-active compounds, ethyl decanoate, methyl dodecanoate and methyl decanoate were identified as the aroma-active compounds of “Huizao” and freeze-dried “Huizao”. In addition, ethyl dodecanoate and ethyl heptanoate were identified as aroma-active compounds in freeze-dried “Huizao”, ethy octanoate was also produced after FD. Generally, esters could be divided into two categories, one is acetyl coenzyme A and higher alcohols to produce acetates, the other is fatty acids and ethanol to produce fatty acid ethyl esters. Higher alcohols are mainly derived from amino acid catabolism, while acetyl coenzyme A could be produced through various pathways, including amino acid metabolism and fatty acid oxidation, and LOX is an important pathway for fatty acid oxidation (Schwab et al., 2008). Therefore, it could well explain the strong correlation between the dynamic changes of esters and amino acids, fatty acids and LOX enzyme activity.

Similar to esters, lactones were mainly related to α-linolenic acid, LOX enzyme activity and 8 amino acids. Chemically, they are cyclic esters formed by intramolecular condensation of hydroxy fatty acids (El Hadi et al., 2013). The typical lactones in “Huizao” and freeze-dried “Huizao” were γ-lactones. The 5-propyloxolan-2-one was identified as the key aroma-active compounds in “Huizao” before and after freeze-drying, and the 5-heptyloxolan-2-one was identified as the key aroma-active compounds of freeze-dried “Huizao”. In fact, most of the hypotheses on the biosynthesis of fruit lactones involved two main pathways for fatty acids, β-oxidation and LOX to produce aroma compounds. Although the importance of these compounds in fruit aroma, there is a lack of enzymatic research in fruit (El Hadi et al., 2013).

There were also many precursors related to aldehydes, including 2 fatty acids and 8 amino acids, and 3 sugars. The number of precursors related to (*E*)-2-heptenal and (*E*)-2-octenal were the most (11), followed by decanal (10), and most of the precursors were amino acids. Furthermore, these three aldehydes were not detected after FD stage 4, indicating that aldehydes were intermediate products during the FD process. There were few precursors related to alcohols, including Cys, Leu and α-Linolenic. The content of alcohols increased slightly after FD, oct-1-en-3-ol might be derived from fatty acids under the action of ADH, and 2,3-butanediol might be originated from metabolism of pyruvate (Zhang et al., 2020).

4. Conclusion

A total of 30 aroma-active compounds of 53 aroma compounds were detected in all red jujube samples during FD processing, and the aroma content increased 32.7 % after FD. From stage 3 in FD processing, the aroma profile of freeze-dried red jujube was transformed from sweet dominated to roasty dominated. In addition, there were 9 FAAs (Ser, Gly, Pro, Val, Cys, Arg, Glu, Lys and Leu) and 3 FFAs (oleic acid, linoleic acid and α-linolenic acid) selected as key aroma precursors; and LOX play an important role in aroma formation of freeze-dried red jujube. Through analysis of precursors and enzyme activities combined correlation analysis, glucose and FAAs involved in non-enzymatic reactions, they had the main correlation with the formation of esters, pyrazines and furfural; and the FFAs and LOX involved in lipid oxidation reactions, they had the main correlation with the formation of alcohols, aldehydes and lactones. In addition, the influence degree of factors on the aroma formation of freeze-dried jujube was ranked as temperature > enzyme activity > fatty acids > amino acids. The multi-stage and variable-temperature procedure of FD enhanced lipid pyrolysis reaction and non-enzymatic reaction efficiency, which significantly improved the aroma of red jujube.

Furthermore, this study provides a better understanding of how the aroma of red jujube is modified during the freeze-drying process and the origin of these olfactory changes. And reveals which flavor precursors are most important for the development of the characteristic red jujube flavor sought by consumers, thereby enabling the selection of the most suitable red jujube variety for the targeted technological transformation.

CRediT authorship contribution statement

Min Gou: Data curation, Formal analysis, Methodology, Investigation, Writing – original draft. **Qinqin Chen:** Conceptualization, Writing – review & editing, Methodology, Validation. **Xinye Wu:** Investigation, Methodology. **Gege Liu:** Investigation. **Marie-Laure Fauconnier:** Conceptualization, Supervision. **Jinfeng Bi:** Conceptualization, Resources, Supervision.

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

The data that has been used is confidential.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.foodchem.2022.135368.

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