Comparison of volatile compounds and fatty acids of jujubes (Ziziphus jujuba mill.) before and after blackening process

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ABSTRACT
Blackened jujube, as an emerging fruit processed product, was obtained from red jujube by a blackening processing of Maillard reaction with high humidity and temperature. This study was to compare the volatile compounds (VOCs) and fatty acids (FAs) between red jujubes (RJs) and blackened jujubes (BJs) of six cultivars (UJ, MZ, JSXZ, HZ, YHDZ and TZ) using headspace solid-phase microextraction gas chromatography-mass spectrometry (HS-SPME-GC-MS) and GC-MS respectively. A total of 56 VOCs were detected in these six cultivars (RJs and BJJs), and their types and contents were analyzed. A total of 22 FAs, including 12 saturated fatty acids (SFAs) and 10 unsaturated fatty acids (USFAs), was determined in the RJs and BJJs. The content of essential FAs in BJJs was higher. B-JZ had the greatest increase in linoleic and α-linolenic from 5.3 mg/100 g to 10.0 mg/100 g and from 3.4 mg/100 g to 5.1 mg/100 g, respectively. It indicated that BJZ is better for improving flavor and the composition of FAs by blackening process than other five cultivars. In addition, FAs and VOCs were found to have linear correlation with color. The types of VOCs and FAs between red and blackened jujubes were also discriminated using principal component analysis (PCA).

Introduction

Jujube (Ziziphus jujuba Mill.) originates from China with a history of about 4000 years and belongs to the family of Rhamnaceae. Jujubes are rich in proteins, sugars, organic acids, trace minerals, and polysaccharides which make jujubes possess multiple health benefits, such as anti-cancerous, antioxidant, anti-insomnia, and anti-inflammatory. Recently, jujubes have become popular due to their high nutritional value and medicinal properties and have been used as food additives. Meanwhile, with the attractive color and delicious taste, jujubes can be consumed fresh or in the processed forms, such as jujube drinks, candied jujube, and jujube powder.

Blackened jujube (BJ) that is produced through a blackening process at high temperature and humidity has been considered as an innovative processed product from red jujube (RJ) in recent years after the popularity gained from the development of black garlic. Gao et al. reported the temperature, humidity, time, and moisture required for the processing method to covert RJ to BJ, the results showed that the content of sucrose decreased, while the contents of fructose and reducing...

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FOOTNOTES
1These authors contributed equally to this work.

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sugar increased; the content of functional substances such as polyphenols, flavonoids and 5-hydroxymethylfurfural increased after the blackening process. Hong et al. \[^8\] illustrated physicochemical properties and antioxidant activities of fermented Korean BJ. The transformation of RJ into BJ followed the similar mechanism from white garlic into black garlic. However, the mechanism of the color change in both of jujube and garlic is still not well understood. According to some recent research, the Maillard reaction may be responsible for the transformation of garlic color from white to black.\[^9,10\] Moreover, there has been very few studies on the changes in sensory and nutritional profile during transformation of red to black color of jujube.

Aroma and flavor are very important properties of jujube and influence the preference degree of consumers.\[^5\] The volatile components (VOCs) are generally determinant of aroma and flavor of foods.\[^11\] For the past few years, several researchers investigated the VOCs of fresh jujubes at different maturity stages and under different hydration methods during ripening.\[^5,12–19\]

While the volatiles of black garlic were widely studied,\[^20–23\] the research on the volatiles of BJ was limited in the literature. In 2019, we believe to be the first one who conducted the research in identifying the VOCs in RJ and BJ fruits. However, the effect of different jujube cultivars and color difference on the volatiles have not been studied. Therefore, it is of great interest to study the changes in VOCs of jujubes of different cultivars during transformation from red to black and determine the sources of unique flavor of jujube from this process.

Many lipids not only have unique flavors themselves, but are precursors to many flavor substances.\[^24\] Choi et al. (2008) mentioned that lipids not only provide energy, but are also the source of garlic and black garlic smells.\[^21\] Fat acids (FAs) compositions and contents of red jujubes, including the peel and pulp of organic and conventional fruits, at different ripening stages had been studied.\[^3,25–27\] With regard to blackened jujubes, there are limited studies available on the FAs profile in the literature. Only one study covered the fatty acids profile of Korea BJs without the analysis of correlation between the FAs and VOCs.\[^6\]

Therefore, the objectives of this work were to investigate: (1) the change of VOCs and FAs of six Chinese jujube cultivars while transformation from red to black color, (2) the correlations between the VOCs and jujube color, and (3) the correlations between the VOCs and FAs of jujubes. The information obtained from this study is important to processing and quality control in BJ production.

**Material and methods**

**Chemicals**

The 3-octanol standard was obtained from Shanghai Yuanye Biotechnology Co. (Shanghai, China). The 37 FAMEs standard mixture was obtained from Sigma-Aldrich Inc. (USA), including methyl myristate (C14:0), methyl palmitate (C16:0), methyl linoleate (C18:2n6c), and methyl linolenate (C18:3n3). The n-hexane and methanol were of chromatographic grade purchased from Shandong Yuwang industry Co. Ltd. (Shandong, China), and all other reagents were of analytical grade.

**Materials and sample preparation**

Red jujube fruits of five kilograms for each cultivar ‘Z. jujuba cv. Junzao (JZ),’ ‘Z. jujuba cv. Muzao (MZ),’ ‘Z. jujuba cv. Jinsixiaoza (JSXZ),’ ‘Z. jujuba cv. Huizao (HZ),’ ‘Z. jujuba cv. Yuanhongdazao (YHDZ),’ and ‘Z. jujuba cv. Tanzao (TZ)’ were obtained from their production area in China on December 11, 2019. The physical characteristics of jujube fruits are shown in Table 1. Red jujube samples were sorted to procure fruits of good quality and uniform sizes and then were sun-dried. The processing methods used for producing BJ followed the procedures from Gao et al. (2019) and Sun et al. (2019) with little modification.\[^1,7\] Twenty pieces of jujubes of every kind were selected randomly.
Table 1. The changes in physical characteristics of six jujube cultivars during Blackening processing.

| Category | Name                        | Production place                      | Weight (g) | Length (mm) | Width (mm) | Moisture (%) |
|----------|-----------------------------|---------------------------------------|------------|-------------|------------|--------------|
| ZJ/B-ZJ | Junzao/Blackened Junzao    | Hetian county, Xinjiang Province      | 14.64 ± 2.08<sup>b</sup> | 13.96 ± 1.48<sup>b</sup> | 49.2 ± 3.5<sup>a</sup> | 50.0 ± 3.3<sup>a</sup> | 34.2 ± 1.8<sup>a</sup> | 34.4 ± 1.6<sup>a</sup> | 19.4 ± 1.3<sup>h</sup> | 22.8 ± 0.4<sup>g</sup> |
| MZ/B-MZ | Muzao/Blackened Muzao      | Jia county, Shannxi Province          | 5.51 ± 0.95<sup>d</sup> | 5.73 ± 1.29<sup>d</sup> | 32.3 ± 2.9<sup>d</sup> | 34.2 ± 2.3<sup>cd</sup> | 22.3 ± 2.4<sup>cd</sup> | 23.0 ± 1.8<sup>c</sup> | 22.2 ± 2.5<sup>g</sup> | 27.9 ± 1.5<sup>cd</sup> |
| JSX/ZJ  | Jinsixiaozao/Blackened     | Jinsixiaozao                          | 3.36 ± 0.59<sup>e</sup> | 3.67 ± 0.62<sup>e</sup> | 25.7 ± 2.4<sup>e</sup> | 27.0 ± 1.3<sup>e</sup> | 17.4 ± 1.0<sup>d</sup> | 17.7 ± 1.3<sup>d</sup> | 24.0 ± 2.7<sup>fg</sup> | 29.1 ± 1.4<sup>c</sup> |
| HZ/B-HZ | Huizao/Blackened Huizao    | Akesu county, Xinjiang Province       | 5.18 ± 0.59<sup>d</sup> | 4.87 ± 0.59<sup>d</sup> | 32.4 ± 2.4<sup>d</sup> | 33.5 ± 3.6<sup>cd</sup> | 21.9 ± 1.1<sup>i</sup> | 21.6 ± 4.1<sup>c</sup> | 14.5 ± 2.4<sup>i</sup> | 25.7 ± 0.7<sup>ef</sup> |
| YHDZ/TZ | Yuanhongdazao/Blackened    | Ningyang county, Shandong Province    | 11.88 ± 1.1<sup>c</sup> | 15.68 ± 2.27<sup>a</sup> | 35.6 ± 1.9<sup>cd</sup> | 37.3 ± 4.7<sup>b</sup> | 29.9 ± 1.8<sup>b</sup> | 29.3 ± 2.2<sup>cd</sup> | 31.7 ± 0.5<sup>b</sup> | 34.6 ± 0.8<sup>c</sup> |
| B-YHDZ  | Yuanhongdazao              | Ningyang county, Shandong Province    | 11.88 ± 1.1<sup>c</sup> | 15.68 ± 2.27<sup>a</sup> | 35.6 ± 1.9<sup>cd</sup> | 37.3 ± 4.7<sup>b</sup> | 29.9 ± 1.8<sup>b</sup> | 29.3 ± 2.2<sup>cd</sup> | 31.7 ± 0.5<sup>b</sup> | 34.6 ± 0.8<sup>c</sup> |

Values are expressed as mean ± standard deviation. Means followed by different letters in the same column are significantly different from each other at p< 0.05 level.
and immersed in water with a ratio of 1:5 (weight/volume) for 30 min at 25°C and relative humidity of 60%-80%, and then packaged and sealed in plastic zip-locked bags, and the packaged jujubes were put into the electric heating oven (DHG-9203A, Shanghai Yongguangming medical instrument Co. China) at 70°C for 6 days and turned over once every 12 h to assure that the blackening process was occurring homogenously. Jujubes were pitted and the pulps were stored at a freezer at –18°C until further analysis.

**Measurements of size, weight, and moisture contents of red and blackened jujubes**

The lengths and widths of each jujube sample (RJ and BJ) were measured using a digital caliper (Mitutoyo, Sanfeng Co., Japan) with an accuracy of 0.01 mm. The weights of RJ and BJ samples were measured using an OHAUS electronic balance (Aohaosi Instrument, Jiangsu Changzhou Co., China,) with an accuracy of 0.001 g. The moisture content of RJ and BJ samples was measured by drying those in an oven at 100°C for about 24 h until the samples reached a constant weight by following the methods of Khir *et al.* (2013). Total measurements were conducted with 10 samples in each kind of jujubes and the average values were reported.

**Color measurement**

The surface color of 10 jujubes in each category was measured at two opposite points of the equatorial zone using a spectrophotometer (WSC-2B, Shanghai optical instrument Co. China). Color was assessed according to the Commission Internationale de l’Eclairage (CIELab). The color difference ($\Delta E$) was calculated by Equation 1.

$$\Delta E = \sqrt{(L^* - L_0^*)^2 + (a^* - a_0^*)^2 + (b^* - b_0^*)^2}$$  \hspace{1cm} (1)

Where, $(L^*, a^*, b^*)$ and $(L_0^*, a_0^*, b_0^*)$ are two colors in CIELAB color space.

**Detection of VOCs**

Analyses of the VOCs were performed using headspace solid-phase microextraction gas chromatography and mass spectrometry (HS-SPME-GC/MS) methods. The extraction experiments were performed at the same time and under the same temperature conditions. 20 µL of the internal standard (3-octanol) was added to 10 grams of samples and the samples were placed in a 20 mL vial and then capped with a silicone/PTFE lip. Compounds were extracted at 40°C using the SPME fibers (50/30 µm, DVB/CAR/PDMS, StableFlex™/SS (1 cm), Supelco Bellefonte, USA) and then desorbed for 3 min at 230°C in split mode.

GC-MS analysis was performed by using a Shimazu GCMS-TQ8040 (Shimazu, Kyoto, Japan). The injector temperature was fixed at 230°C, and the injection was performed in the 1/10 split mode. It was then separated in a VF-wax MS column (0.25 mm×60 m, 0.25 µm, Varian). The gas flow was set at 1 mL/min. In the oven temperature was programmed as follows: initial temperature of 40°C (held for 3 min), increased at a rate of 5°C/min to 140°C, and then raised at 8°C/min to 230°C (held for 5 min). The triple quadrupole mass spectrometer was operated in the SIM mode. The interface and source temperatures were set at 250°C and 230°C, respectively. The electron energy was set at 70 eV, and the range of acquisition was 30–450 m/z with a solvent delay of 3 min. VOCs were identified by comparing the mass spectra of the samples with the data system (NIST 11 & NIST 11s). The relative contents (%) of the volatile components were calculated by counting the ratio of peak area of the various volatile components to the sum of the components’ peak areas. The measurements were triplicated.
Measurement of FAs

FAs were extracted and methylated using the method reported by Reche et al.\cite{27} with slight modification. They were analyzed by applying Gas Chromatography-Mass Spectrometry (GC-MS, TQ8040 Shimazu, Kyoto, Japan) with the selected ion monitoring (SIM) mode technique immediately. The injector temperature was fixed at 230°C and the injection was performed in the spitless mode. It was then separated in an HP-5 MS column (0.25 mm×30 m, 0.25 μm, Varian). The gas flow was set at 1 ml/min. The oven temperature was programmed as follows: initial temperature of 50°C and held for 1 min, and then increased at a rate of 6°C/min to 290°C and held for 5 min. The triple quadrupole mass spectrometer was operated in the SIM mode. The interface and source temperatures were set at 200°C and 220°C, respectively, with a solvent delay of 3 min. The calculation of the content (mg/100 g) of fatty acids was referred to the method of Zhang et al.\cite{29} The GC-MS/MS parameters for the 22 fatty acid methyl esters are listed in Table S1.

Statistical analysis

Statistical analyses were performed using SPSS version 22.0 software (SPSS Inc., Chicago, IL, USA). The results of different components were presented as the mean ± SD (standard deviation). Duncan’s Multiple Range Test was performed to verify significant differences between the physical and chemical characteristics of RJ and BJ at a level of α = 0.05. All figures were generated in Origin 9.0. The content of VOCs was shown with total peak area and relative content of percentage.

Results and discussion

Physical characteristics of red and blackened jujubes

RJ samples of the six cultivars were prepared for blackening in the same processing conditions and their physical parameters are shown in Table 1. JZ was the heaviest and JSXZ was the lightest among all of the cultivars. The weight of red YHDZ increased by 32% after transformation to black color

Table 2. Linear regression correlation established between volatile compounds and color difference.

| Volatile compounds          | Equation                     | R²  | F      | Sig. | Method |
|-----------------------------|------------------------------|-----|--------|------|--------|
| dl-Alanyl-l-alanine         | y = 1.525 + 0.016 L -0.081a-0.009b | 0.949| 200.078| 0.000| Enter  |
| Ethyl Acetate               | y = -1.474 + 0.050 L + 0.041a+0.144b | 0.735| 29.553 | 0.000| Enter  |
| Ethyl Butyrate              | y = -0.053 + 0.001 L + 0.007a+0.007b | 0.621| 17.474 | 0.000| Enter  |
| Ethyl Hexanoate             | y = 0.460-0.033 L + 0.005a+0.073b | 0.645| 19.360 | 0.000| Enter  |
| 3-Furaldehyde               | y = 17.231 + 0.211 L-0.720a-0.428b | 0.885| 82.482 | 0.000| Enter  |
| 2-Furyl Methyl Ketone       | y = 0.519 + 0.006 L-0.013a-0.024b | 0.704| 25.344 | 0.000| Enter  |
| Isobutyric acid             | y = 0.913-0.044 L + 0.032a+0.032b | 0.637| 18.724 | 0.000| Enter  |
| 5-Methyl furfural           | y = 1.075 + 0.030 L-0.035a-0.075b | 0.724| 28.041 | 0.000| Enter  |
| Butanoic acid               | y = -1.015 + 0.071 L + 0.108a-0.092b | 0.718| 27.169 | 0.000| Enter  |
| Isovaleric acid             | y = 1.503-0.072 L + 0.073a+0.041b | 0.691| 23.884 | 0.000| Enter  |
| Hexanoic acid               | y = 0.925-0.074 L + 0.237a+0.119b | 0.862| 66.849 | 0.000| Enter  |
| Heptanoic acid              | y = -0.941 + 0.049 L + 0.061a-0.057b | 0.668| 21.422 | 0.000| Enter  |
| Octanoic acid               | y = -0.304 + 0.018 L + 0.045a-0.052b | 0.731| 29.007 | 0.000| Enter  |
| Ketones                     | y = 9.145-0.464 L + 0.221a+0.045b | 0.673| 21.964 | 0.000| Enter  |
| Alkanes                     | y = 6.330-0.283 L + 0.105a+0.041b | 0.248| 3.520  | 0.026| Enter  |
| Aldehydes                   | y = 12.554 + 0.478 L-1.776a-1.659b | 0.579| 14.682 | 0.000| Enter  |
| Acids                       | y = 59.522 + 0.575 L + 1.487a-1.989b | 0.514| 11.298 | 0.000| Enter  |
| Esters                      | y = 8.463-0.284 L + 0.056a+0.292b | 0.212| 2.866  | 0.052| Enter  |
| Furans                      | y = 1.785-0.059 L + 0.034a-0.049b | 0.511| 11.156 | 0.000| Enter  |
| Alkenes                     | y = 0.280-0.004 L-0.008a+0.000b | 0.313| 4.849  | 0.007| Enter  |
| Others                      | y = 0.822 + 0.046 L-0.114a+0.060b | 0.582| 14.842 | 0.000| Enter  |
(B-YHDZ). This may be because the moisture immersion changed differently to different cultivars during blackening process. The moisture of the RJs is an important factor that can influence the Maillard reaction and the lipid’s autoxidation. Table 1 shows the moisture contents of all of the RJs increased by various degrees after transforming into BJs with HZ having the highest increase (77%) after turning into B-HZ.

**Color change of jujubes**

At high temperature and humidity, the color of jujubes changed from original red or peony into brownish or dark red and finally into blackened, which was similar to that reported by Sun et al. The jujube colors of RJs and BJs are shown in Table 3 and Figure 1A. It can be noticed from Table 3 that red JZ and JSXZ jujube cultivars had higher brightness (L) than the other cultivars. However, after their transformation, most of the BJs had no significant (p > 0.05) difference in terms of brightness (Table 3). The color difference (ΔE) of JSXZ was the highest among all of the six jujube cultivars after transformation (Figure 1B). The color difference in RJs may be due to the different cultivars and their different drying degrees.

**VOCs of red and blackened jujubes**

**Changes in VOCs in jujubes:** A total of 66 VOCs were detected and quantified in the RJ and BJ samples and not all VOCs existed in every type of jujubes (Table S2-S3). The types of VOCs in RJs and BJs were 17–27 and 13–25, respectively. In general, there were fewer types of VOCs in the BJ than in the RJ. However, the number of VOCs before and after blackening was the same for YHDZ, both were 25 kinds. After transformation from RJ to BJ, B-JZ occupied one more VOCs than JZ, B-HZ occupied two more VOCs than HZ. The factors affecting the change in VOCs could be mainly due to the varying characteristics of different cultivars, Maillard reactions, and autoxidation and degradation of FAs.

Overall, the number of VOCs found in jujube samples in this study was more than that found in literature. Wang et al. (2016) reported 46 kinds of volatiles in jujubes during their dehydration process through four different methods. 38 kinds of volatiles were determined during infrared processing of jujube. During the thermal process, the Maillard reaction is responsible for the formation of many volatile components, and the degradation of amino acids and lipids in a complex reaction system promotes the formation of ketones, furfural and furan substances. Paravisini & Peterson reported that the Maillard reaction increases dicarbonyl species. Isobutyaldehyde, Butyaldehyde, 3-methylbutyaldehyde, 1,3-Octadiene, D-Limonene, 3-Furaldehyde, 5-Methyl furfural, 2-Acetyl-1 H-pyrrole et al. these new formed

| Cultivar | Color parameters |
|----------|------------------|
|          | L   | a  | b   | L   | a  | b   |
| JZ       | 29.7 ± 3.0abc | 21.5 ± 3.0abc | 3.8 ± 1.7abc | 14.7 ± 4.0abc | 3.1 ± 0.4abc |
| MZ       | 22.1 ± 1.0bc | 21.0 ± 0.9bc | 3.8 ± 1.5bc | 11.8 ± 1.4bc | 2.7 ± 0.3bc |
| JSXZ     | 28.8 ± 1.4abc | 22.8 ± 1.3abc | 1.2 ± 0.3abc | 17.7 ± 1.4abc | 2.6 ± 0.1abc |
| HZ       | 28.0 ± 1.5ab | 23.6 ± 2.3ab | 4.7 ± 1.1ab | 16.2 ± 2.7ab | 2.8 ± 0.2ab |
| YHDZ     | 25.7 ± 2.7ab | 22.4 ± 1.9ab | 0.7 ± 0.3ab | 13.7 ± 2.2ab | 2.7 ± 0.1ab |
| TZ       | 25.2 ± 3.3ab | 20.7 ± 2.1ab | 1.8 ± 1.1ab | 13.3 ± 2.1abc | 2.3 ± 0.3abc |

Note: Values are expressed as mean ± standard deviation. Means followed by different letters in the same column are significantly different from each other at p < 0.05 level. RJ, Red jujube; BJ, Blackened jujube.
VOCs in the Maillard process was detected in the BJs, indicated that the blackening process could have played a major role in adding more new VOCs in jujube and thus enhancing aroma or flavor.

The compositions of volatiles of RJs and BJs covered one alkanes, thirteen aldehydes, one alcohols, ten acids, nineteen esters, five ketones, three furans, two alkenes, one pyrrole, and two others (Table S3). The results showed that the acids were the primary components of VOCs in both RJs and BJs and contributed sour tastes in jujubes. JZ had the highest acid content (89.1%), followed by HZ (88.7%). The acid content in jujube after transformation from red to blackened decreased, except JSXZ in which the acid content increased from 64.3% to 70.2% after transformation to B-JSXZ (Table S3). The results were similar to the findings of Wong et al. (1996) who reported a total acid content of 62.97% in jujubes.[19] The highest relative concentration of acetic acid was found to be 69.6% (JZ) which was higher than the value (26.63%) reported by Wang et al. (2016).[5] The acids, such as acetic acid (Figure 2), propanoic acid, butanoic acid, and isovaleric acid, decreased after the blackening process of jujubes.
Aldehydes are the important VOCs found in jujubes and their concentration changed significantly during the blackening process of jujubes. Thirteen types of aldehydes were detected in the jujube samples and most of the RJs contained a low concentration of aldehydes, except JSXZ (25.6%) and YHDZ (11.9%) (Table S3, Figure 2). The concentration of aldehydes in B-JZ, B-MZ, B-HZ, and B-TZ increased by 23.3%, 20.7%, 18.7%, and 19.7%, respectively. The changes in aldehydes might be due to different cultivars and drying conditions of red jujubes. 3-Furaldehyde and 5-Methyl furfural were the dominant aldehydes which increased during the blackening process (Table S3, Figure 2). The 3-furaldehyde was not detected in JZ, JSXZ, and HZ, however, its concentration significantly increased after blackening process of jujubes for B-JZ (24.4%), B-JSXZ (13.9%), and B-HZ (16.3%). The 5-methyl furfural was detected only in the BJs. The increase of the aldehydes contributed new caramel flavor and other aroma. The changes in hexanal in JZ, JSXZ, and TZ were not detected after the blackening process. The transformation of aldehydes could be the results of Maillard reaction. At high temperature and humidity, the carbonyl group and the amino group were subject to Amadori or Heyns rearrangement, degradation and enolization, dehydration, and deamination process, and finally the furfural and 5-methylfurfural were formed from pentose and hextose, respectively.\[11\]

Nineteen types of esters were detected in the studied jujube samples, including two kinds of lactones. For the RJs, the esters were the second dominant VOCs and their relative contents ranged from 4.7% to 8.5% (Table S3). These values were higher than those of Song et al. (2019) who reported the highest ester content of 4% in jujube at half-red maturity.\[14\] After the blackening process, the ester contents in HZ (4.7%) increased to 6.9% (B-HZ), respectively. The ester in the other four jujube cultivars reduced after blackening, especially a reduction from TZ (7.3%) to B-TZ (0.5%). The ethyl butyrate, ethyl hexanoate, and gamma-hexalactone were detected in all of the RJs, but they were not found in all of the BJs. Meanwhile, the Benzaldehyde of BJs decreased significantly, which could reduce the bitter flavor in BJs and it’s reduction could be mainly due to the gradual hydrolyzation of esters into carboxylic acid and alcohols in high humidity.

Figure 2. Relative contents of some volatiles of RJ and BJ.
### Table 4. Correlations of color value and part of volatile compounds relative concentration of jujubes.

| Color difference value | V1   | V4   | V8   | V10  | V12  | V13  | V15  | V17  | V19  | V20  | V22  | V23  |
|------------------------|------|------|------|------|------|------|------|------|------|------|------|------|
| L                      | -0.762** | -0.367* | 0.743** | -0.636** | 0.590** | 0.284 | -0.418* | 0.655** | 0.467** | 0.517** | 0.020 | 0.283 |
| a                      | -0.973** | -0.344* | 0.839** | -0.587** | 0.419*  | 0.586** | -0.371* | 0.783** | 0.400*  | 0.485** | 0.507** | 0.412* |
| b                      | -0.936** | -0.395* | 0.850** | -0.579** | 0.393*  | 0.612** | -0.411* | 0.777** | 0.561** | 0.478** | 0.411*  | 0.489** |
| L                      | -0.401*  | 0.401*  | 0.543** | 0.388*  | -0.736** | -0.659** | 0.441** | 0.549** | 0.497** | -0.642** | 0.751** | -0.513** |
| a                      | -0.432** | 0.300  | 0.753** | 0.294  | -0.937** | -0.829** | 0.201  | 0.513** | 0.762** | -0.836** | 0.820** | -0.730** |
| b                      | -0.438** | 0.475** | 0.785** | 0.464** | -0.917** | -0.829** | 0.178  | 0.655** | 0.750** | -0.839** | 0.754** | -0.694** |
| L                      | 0.542**  | 0.348*  | 0.579** | 0.722** | 0.737**  | 0.696** | 0.178  | 0.722** | 0.773**  | 0.737**  | 0.696** |
| a                      | 0.806**  | 0.636** | 0.711** | 0.925** | 0.780**  | 0.790** | 0.178  | 0.722** | 0.773**  | 0.737**  | 0.696** |
| b                      | 0.782**  | 0.648** | 0.698** | 0.903** | 0.715**  | 0.679** | 0.178  | 0.722** | 0.773**  | 0.737**  | 0.696** |

Note: ** Correlation was significant at the 0.01 level \((p < 0.01)\) (2-tailed); * Correlation was significant at the 0.05 level \((p < 0.05)\) (2-tailed); V was the code of volatile compounds in Table S3.
Three types of furans were detected in most of the jujube samples. The contents of furans in the BJs ranged from 0.3% to 0.9% (Table S3). Among the RJs, only MZ and TZ had been detected with the presence of 0.7% and 0.9% furans, respectively, which eventually decreased after the blackening process. In addition, two alkenes were also detected in some of the BJs, including B-MZ, B-YHDZ, and B-TZ. Moreover, B-JZ was detected with 0.5% content of a pyrrole. The increase of furans, alkenes, and pyrrole after transformation of jujube samples could be caused by the Maillard reaction and the USFAs oxidation.\cite{11}

Alcohols were detected only in some of the BJs, including B-MZ, B-JSXZ, and B-YHDZ. The content of 1,1,3,3,5,5,7,7-Octamethyl-7-(2-methylpropoxy) tetrasiloxan-1-ol was found to be 4.0% in B-MZ (Table S3). The presence of this alcohol compound in jujube was not noticed prior to this study. The presence of alcohols in BJs might be due to the dehydration and deoxidation of aldehydes and then their transformation into corresponding alcohols.\cite{14}

Correlations between VOCs and color changing: The correlation between VOCs and color of the BJs were examined using the Pearson Correlation test and the results are shown in Table 4. The results indicated that VOCs had a significant correlation with color ($L$, $a$, $b$) at $\alpha = 0.01$ and 0.05. 3-Furaldehyde, a representative product of Maillard reaction, had a significant negative correlation ($p < 0.01$) with color and the correlation coefficients of $L$, $a$, and $b$ were $-0.736^{**}$, $-0.937^{**}$, and $-0.917^{**}$, respectively. A darker blackened jujube possessed a higher content of 3-Furaldehyde. Similarly, ethyl acetate (V8) had a positive significant correlation ($p < 0.01$) with color with correlation coefficients of $0.743^{**}$, $0.839^{**}$, and $0.850^{**}$ for $L$, $a$, and $b$, respectively. A darker blackened jujube resulted in a lower content of ethyl acetate. Overall, the correlation results illustrated that the color changing could be a great indicator to understand the difference in VOCs in jujubes during the blackening processing.

The linear regression correlation results are shown in Table 2 and Figure 3. The VOCs and color exhibited good linear regression significance. For example, the equations representing the correlation of 3-Furaldehyde is $y = 17.231 + 0.211 \times L-0.720a-0.428b$ ($R^2 = 0.885$). These prediction models can be useful tools to understand the change in VOCs and thus flavor based on the color changing during blackening process.

Cluster analysis and principal component analysis of VOCs: Cluster analysis (CA) and principal component analysis (PCA) are helpful tools to understand the relation between VOCs and color of jujube fruits. The results of CA are shown in Figure 4. The distance of different clusters in Figure 4 represented the correlation among different jujube cultivars in terms of volatile components. The results indicated that the BJs and RJs were classified distinctly and the VOCs changed noticeably during the blackening process of jujubes.
The null hypothesis was tested using Bartlett’s test and the results revealed a significant difference ($p<.001$) between the independent factors. Eleven components were confirmed as the principal factors accounting for 93.2% of the total variation in the results obtained for the jujube cultivars (Table 5). The component PC1 and PC2 represented 26.9% and 12.5% of the total variation, respectively. The results of PC1 and PC2 through the factor score 1 and factor score 2 are shown in Figure 5 which indicated that the VOCs of RJs and BJs, especially MZ and BTZ, could be distinguished.

**Fatty acid profile of jujubes**

FAs composition and content of red and blackened jujubes: Twenty-two types of FAs were detected in all of the RJ and BJ samples, meanwhile not all samples contained all FAs (Table S4). The results indicated that the six jujube cultivars (red and blackened) contained USFAs and saturated SFAs. Ten USFAs, including the $\alpha$-linolenic acid (C18:3n3) ($\omega-3$ FA) and linoleic acid (C18:2n6) ($\omega-6$ FA), were found in the RJs and Bjs. The $\omega-3$ and $\omega-6$ FAs are the essential FAs...
Table 5. Eigenvectors, proportion of variation and eigenvectors associated with five principal components for the jujube.

| Principal components | 1      | 2      | 3      | 4      | 5      | 6      | 7      | 8      | 9      | 10     |
|----------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Jujube fruits        | 17.758 | 8.225  | 6.544  | 6.160  | 5.727  | 4.513  | 3.852  | 3.156  | 2.764  | 1.470  |
| Cumulation proportion | 26.9   | 39.4   | 49.3   | 58.6   | 67.3   | 74.1   | 80.0   | 84.8   | 89.0   | 91.2   |

| Characters           | Eigenvectors |
|----------------------|--------------|
| Alanyl-l-alanine     | -0.912       |
| Acetaldehyde        | 0.213        |
| Methyl formate      | -0.364       |
| Isobutyraldehyde    | -0.419       |
| Acetone             | 0.435        |
| Methyl acetate      | -0.241       |
| Butyraldehyde       | 0.349        |
| Ethyl Acetate       | 0.845        |
| Methyl propionate   | -0.19        |
| 3-methylbutyraldehyde| -0.541   |
| 1,3-Octadiene       | -0.266       |
| Ethyl Propionate    | 0.204        |
| 2,3-Butanediene     | 0.658        |
| Pentanal            | 0.299        |
| Methyl Butyrate     | -0.365       |
| Methyl Isovalerate  | 0.215        |
| Ethyl Butyrate      | 0.825        |
| 2-Butenal           | 0.21         |
| Ethyl Isovalerate   | 0.438        |
| Hexanal             | 0.577        |
| Methyl Valerate     | -0.342       |
| 3-Penten-2-one      | 0.644        |
| Ethyl Valerate      | 0.545        |
| 2-Butylfuran        | 0.435        |
| Trimethylpropionate | 0.436        |
| Methyl Hexoate      | 0.462        |
| Heptanal            | -0.249       |
| Limonene            | -0.478       |
| Trans-2-Hexenal     | 0.371        |
| Ethyl Hexanoate     | 0.883        |
| 2-pentylfuran       | 0.555        |
| 3-Octanone          | 0.585        |
| Ethyl Heptanoate    | 0.375        |
| 3-Methyl-2-butyl-1-ol| -0.267      |
| 2-Nonanone          | 0.572        |
| Nonanal             | 0.131        |
| Acetic acid         | -0.224       |
| 3-Furaldehyde       | -0.863       |
| 2-Furyl Methyl Ketone| -0.751     |
| Propanoic acid      | -0.071       |
| Benzyaldehyde       | 0.549        |
| Isobutyric acid     | 0.772        |
| 5-Methyl furfural   | -0.814       |
| Methyl Caprate      | -0.301       |
| Butanoic acid       | 0.701        |
| Methyl Benzoate     | -0.738       |
| 4-hydroxy Butanoic acid| 0.055    |
| Isovaleric acid     | 0.783        |
| Gamma-Hexalactone   | 0.645        |
| Pentanoic acid      | 0.779        |
| Hexanoic acid       | 0.373        |
| 2-Acetyl-1-pyrrolic acid| -0.342   |
| Octanoic acid       | 0.702        |
which must be ingested through food because they cannot be produced in the human body by themselves.\textsuperscript{27} Twelve SFAs, including the palmitic acid (C16:0) and stearate acid (C18:0), were found in all of the jujubes. The composition of jujubes demonstrated that the BJs were richer in the FAs and can provide more health benefits than the RJs.

Blackening process of jujube with high temperature and humidity affected the composition and the contents of FAs (Table S4). The contents of total FAs significantly increased after transformation from the RJs to the BJs (except B-HZ). For instance, the total FAs in JZ increased from 126.4 mg/100 g to 151.8 mg/100 g. The total FAs in TZ almost remained unchanged; however, JSXZ and YHDZ noticed a 5-8-fold increase in the total FAs after transformation into B-JSXZ (1260.5 mg/100 g) and B-YHDZ (1370.6 mg/100 g). The percentage of total FAs in jujubes in this study was about 5-times higher than the FA values (0.24\%) reported by Hong \textit{et al.}\textsuperscript{6} however, it was lower than that in the oils (8.31\%–12.35\% of dry weights) obtained from RJs.\textsuperscript{26} The increase in the total FAs in the BJs with different degree was similar to that the garlic processing where the lipid contents increased from 1.8 g/kg to 5.8 g/kg after transformation of fresh garlic to blackened garlic.\textsuperscript{21} The increase of FAs in jujube after blackening can be a result of hydrolysis of triglyceride, which leads to accumulation of saturated short-chain fatty acids, promising higher health benefits.\textsuperscript{33}

The palmitic acid was found to be the most prominent acid in all of the jujube samples, except B-JSXZ and B-YHDZ and its content increased in most of the jujube cultivars after blackening, except the YHDZ which noticed a reduction from 63.8 mg/100 g to 56.4 mg/100 g in B-YHDZ. In addition, the content of tridecanoic acid increased from 0.7 mg/100 g to 1067.0 mg/100 g and 1.7 mg/100 g to 1181.0 mg/100 g after transformation of JSXZ and YHDZ to B-JSXZ and B-YHDZ, respectively. While the content of lauric acid decreased in half of the jujube cultivars, including B-JZ, B-HZ, and B-YHDZ, it increased in the remaining three jujube cultivars after the transformation of RJs to BJs. The stearate acid was found in all of the jujube samples and increased in four jujube cultivars after transformation from the RJs to the BJs,

Figure 5. Principal component analysis of six jujube cultivars (BJs and RJs).
except YHDZ and TZ which noticed slight decrease. SFAs were subject to oxidation and degradation to form the VOCs, such as aldehydes, methyl ketones, acids, hydrocarbons, lactones, and alcohols.¹¹

USFAs, particularly polyunsaturated FAs (PUFA), including the ω-3 and ω-6 FAs, have many functional activities contributing health benefits.²⁷ The important acids, linoleic and α-linolenic acids, were also found in all of the jujube samples. The content of linoleic acid increased in four jujube cultivars, including JZ, MZ, JSXZ, and TZ. As an example, the content in JZ changed from 5.3 mg/100 g to 10.0 mg/100 g after blackening. Meanwhile, the content of α-linolenic acid also increased in four jujube samples after their transformation from red to blackened, for example, from 3.4 mg/100 g in JZ to 5.1 mg/100 g in B-JZ. Figure 6 shows that the ω-3 and ω-6 FAs increased significantly (p<.05) in JZ, MZ, JSXZ, YHDZ and TZ after transformation to B-JZ, B-MZ, B-JSXZ, B-YHDZ, and B-TZ, respectively. Therefore, these trends indicated that jujubes could gain more health benefits after the blackening process. The augmentation of linoleic acid could be due to the formation of melanoidin which inhibited the peroxidation of linoleic acid.³⁴ However, oxidation of the unsaturated acyl chains of lipids could be a major reason of the formation of VOCs, including the oleic, linoleic, linolenic, and arachidonic acids during heat treatment.¹¹

Correlation analysis of FAs and VOCs: FAs usually are the precursors of VOCs and generate new flavor through thermal oxidation.¹¹ The results of Pearson Correlation of FAs and VOCs are shown in Table 6. The results displayed that many VOCs were correlated with FAs at a significance level, α = 0.01 or 0.05. For example, 3-Furaldehyde (V38) and 2-Furyl Methyl Ketone (V39) were negatively correlated with hexanoic acid (C6:0) (V38: −0.666**; V39: −0.681**) (p<.01) and arachidonic acid (C20:4) (V38: −0.519**; V39: −0.495**) (p<.01). For a better understanding of the relation between FAs and VOCs, the results of linear regression correlation are shown in Table 7. The relation of 2-furyl methyl ketone with hexanoic acid is

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**Figure 6.** Omega-6 and omega-3 of six jujube cultivars during blackening processing.
**Table 6. Correlation coefficient between the parts of fatty acids and volatile compounds of jujubes.**

| Volatile compounds | C6:0 | C10:0 | C12:0 | C13:0 | C14:1n5 | C14:0 | C15:0 | C16:1 | C16:0 | C17:1 | C17:0 | C18:3n6 | C18:2 | C18:1n9 | C18:0 | C20:4 | C20:2 | C20:1 | C21:0 | C22:0 | C23:0 |
|--------------------|------|------|------|------|--------|------|------|------|------|------|------|--------|------|--------|------|------|------|------|------|------|------|
| V2                 | 0.530** | 0.713** | 0.585** | 0.128 | 0.714** | 0.475** | 0.437** | 0.513** | 0.464** | 0.244 | 0.011 | 0.098 | 0.092 | −0.53 | 0.328 | 0.214 | −0.131 | −0.130 | −0.131 | 0.240 | −0.021 | 0.287 |
| V1                 | −0.307 | 0.407* | 0.504** | 0.711** | 0.218 | 0.533** | −0.577** | 0.509 | 0.302 | −0.248 | −0.046 | 0.966** | −0.142 | −0.37 | 0.342** | −0.360** | −0.133 | −0.132 | 0.115 | 0.260 | −0.187 | 0.256 |
| V3                 | 0.641** | 0.454** | 0.502** | −0.020 | 0.556** | 0.425** | −0.015 | 0.234 | 0.586 | −0.420** | −0.206 | 0.118 | −0.080 | −0.194 | 0.076 | 0.183 | 0.000 | −0.014 | −0.238 | 0.055 | −0.102 | 0.035 |
| V6                 | 0.544** | 0.732** | 0.600** | −0.310 | 0.731** | 0.489** | 0.403** | 0.524** | 0.478** | −0.248 | −0.005 | −0.089 | 0.099 | −0.153 | 0.341** | 0.215 | 0.000 | 0.252 | −0.015 | 0.302 | 0.007 | −0.011 |
| V11                | 0.655** | 0.374** | 0.609** | −0.028 | 0.722** | 0.491** | 0.407** | 0.533** | 0.478** | −0.244 | 0.003 | −0.088 | 0.103 | −0.148 | 0.345** | 0.238 | 0.213 | −0.130 | −0.016 | 0.264 | 0.004 | 0.336* |
| V27                | 0.190 | 0.397* | 0.481** | 0.690** | 0.206 | 0.530** | −0.531** | 0.095 | 0.313 | −0.228 | −0.008 | 0.875** | −0.135 | −0.304 | 0.367** | −0.339** | −0.122 | −0.121 | 0.144 | 0.294 | −0.131 | 0.300 |
| V13                | −0.666** | −0.188 | 0.111 | 0.229 | 0.244 | −0.081 | −0.027 | 0.537 | 0.203 | 0.369 | 0.206 | 0.179 | 0.310 | 0.244 | 0.287 | −0.319** | 0.051 | 0.086 | 0.218 | 0.198 | 0.245 | 0.201 |
| V9                 | −0.681** | −0.233 | −0.013 | 0.100 | −0.311 | −0.192 | 0.003 | −0.082 | 0.192 | 0.263 | 0.285 | 0.126 | 0.352** | 0.290 | 0.318 | −0.495** | −0.074 | −0.045 | 0.363* | 0.214 | 0.263 | 0.240 |
| V14                | −0.164 | 0.488** | 0.714** | 0.870** | 0.484** | 0.359** | 0.042* | 0.174 | 0.527** | −0.370 | −0.070 | 0.902** | −0.098 | −0.373** | 0.487** | −0.149 | −0.198 | −0.197 | 0.112 | 0.345* | −0.114 | 0.444** |
| V2                 | −0.209 | 0.425** | 0.525** | 0.710** | 0.223 | 0.506** | −0.593** | 0.068 | 0.328 | −0.250 | −0.010 | 0.988** | −0.147 | −0.331** | 0.367** | −0.372** | −0.134 | −0.133 | 0.140 | 0.286 | −0.172 | 0.286 |
| Furan             | −0.491** | −0.493** | −0.533** | −0.048 | −0.407** | −0.415** | −0.118 | −0.118 | 0.070 | 0.314 | 0.383** | 0.018 | 0.471** | 0.594** | 0.346 | −0.509** | 0.249 | 0.237 | 0.173 | 0.264 | 0.509** | 0.195 |

Note: ** Correlation was significant at the 0.01 level (p < 0.01) (2-tailed); * Correlation was significant at the 0.05 level (p < 0.05) (2-tailed); V was the code of volatile compounds in Table S3.
represented by the equation, \( y = 0.438 - 0.768 \text{FA6} \) \( (R^2 = 0.464) \). The equation indicated that the relative content of 2-furyl methyl ketone would decrease with the increase in the content of hexanoic acid.

**Principal component analysis of FAs in jujubes:** Principal component analysis (PCA) results that were used to illustrate the correlation and differences in 22 FAs among the RJs and BJs are shown in Table 8 and Figure 7. The null hypothesis was tested using Bartlett’s test and the results revealed a significant difference \( (p<.01) \) between the independent fatty acids factors. Five components were confirmed as the principal factors, accounting for 89.5% of the total variation in the results obtained for the jujube cultivars (Table 8). The components PC1 and PC2 represented 39% and 21.7% of the total variation, respectively (Table 8 and Figure 7A).

The groupings of RJs and BJs based on their features were performed using PCA by extracting the PC1 and PC2 of their FAs (Figure 7B). For the RJs, the six jujube cultivars could be distinguished and separated with no overlaps using FAMEs content method. Similarly, the BJs could also be distinctly discriminated. The results also indicated that the changes in FAs of different jujube cultivars during the blackening process may produce different compositions in them.
Conclusion

A total of 56 VOCs were detected in the samples of six jujube cultivars (RJs and BJs), including one alkane, thirteen aldehydes, one alcohol, ten acids, nineteen esters, five ketones, three furans, two alkenes, one pyrrole, and one other. The 3-furfural (24.4%) and 5-methylfurfural (2.1%) produced in the blackened JZ contributed to the caramel flavor. The content of some of the VOCs had the preferable linear regression correlation with color, which can be valuable to control the flavor quality of blackened jujubes based on their colors. A total of 22 FAs, including 12 SFAs and 10 USFAs, were

Figure 7. A) Principal component analysis (PC1 and PC2) of FAs of jujubes; B). PCA results of fatty acids during blackening processing
The composition and content of FAs, including linoleic acid (ω-6) and linolenic acid (ω-3), changed after the blackening process of jujubes. Especially B-JZ showed the largest increase in the content of VOCs and essential FAs like linoleic and ω-linolenic, which is better for improving flavor and the composition of FAs by blackening process than the other five cultivars. The blackening process of jujube produced a special attractive aroma and made the VOCs and FAs more abundant and beneficial for people’s health. The present work provides a theoretical basis for the control of the blackening process. In addition, the change mechanism of bioactive substances during the blackening process and the bioactive function of BJ need to be further studied.

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**References**

[1] Sun, X.; Gu, D.; Fu, Q.; Gao, L.; Shi, C.; Zhang, R., et al. Content Variations in Compositions and Volatile Component in Jujube Fruits during the Blacking Process. *Food Sci. Nutr.* 2019, 7(4), 1387–1395.

[2] Reche, J.; Hernandez, F.; Almansa, M. S.; Carbonell-Barrachina, A. A.; Legua, P.; Amoros, A. Effects of Organic and Conventional Farming on the Physicochemical and Functional Properties of Jujube Fruit. *Vol. 99. Lwt-Science and Technology.* 2019, 438–444. doi:10.1016/j.lwt.2018.10.012

[3] Gao, Q. H.; Wu, C. S.; Wang, M. The Jujube (Ziziphus Jujuba Mill.) Fruit: A Review of Current Knowledge of Fruit Composition and Health Benefits. *J. Agric. Food Chem.* 2013, 61(14), 3351–3363. DOI: 10.1021/jf4007032.

[4] Reche, J.; Hernandez, F.; Almansa, M. S.; Carbonell-Barrachina, A. A.; Legua, P.; Amoros, A. Physicochemical and Nutritional Composition, Volatile Profile and Antioxidant Activity Differences in Spanish Jujube Fruits. *Vol. 98. Lwt-Science and Technology.* 2018, 1–8. doi:10.1016/j.lwt.2018.08.023

[5] Wang, R. R.; Ding, S. H.; Zhao, D. D.; Wang, Z. F.; Wu, J. H.; Hu, X. S. Effect of Dehydration Methods on Antioxidant Activities, Phenolic Contents, Cyclic Nucleotides, and Volatiles of Jujube Fruits. *Food Sci. Biotechnol.* 2016, 25(1), 137–143. DOI: 10.1007/s10068-016-0021-y.

[6] Hong, J.-Y.; Nam, H.-S.; Yoon, K.-Y.; Shin, S.-R. Physicochemical Properties and Nutritional Components of Fermented Black Jujube. *Korean J. Food Preserv.* 2012, 19(2), 243–248. DOI: 10.11002/kjfp.2012.19.2.243.

[7] Gao, L.; Gu, D.; Sun, X.; Zhang, R. Investigation of Processing Technology for Aged Black Jujube. *Food Science and Nutrition Studies.* 2019, 3, 107. DOI: 10.22158/fsns.v3n4p107.

[8] Hong, J.-Y.; Nam, H.-S.; Yoon, K.; Shin, S.-R. Antioxidant Activities of Extracts from Fermented Black Jujube. *Korean J. Food Preserv.* 2012, 19. DOI: 10.11002/kjfp.2012.19.6.901.
[9] Rios-Rios, K. L.; Montilla, A.; Olano, A.; Villamiel, M. Physicochemical Changes and Sensorial Properties during Black Garlic Elaboration: A Review. Vol. 88. Trends in Food Science & Technology. 2019, 459–467. doi:10.1016/j.tifs.2019.04.016

[10] Qu, Z.; Zheng, Z.; Zhang, B.; Sun-Waterhouse, D.; Qiao, X. Formation, Nutritional Value, and Enhancement of Characteristic Components in Black Garlic: A Review for Maximizing the Goodness to Humans. Compr. Rev. Food Sci. Food Saf. 2020, 19(2), 801–834. DOI: 10.1111/1541-4337.12529.

[11] Whitfield, F. B. 1992. Volatiles from Interactions of Maillard Reactions and Lipids. Crit. Rev. Food Sci. Nutr. 31 (1–2), 1–58. DOI: 10.1080/1040899209527560.

[12] Wang, L.; Wang, Y.; Wang, W.; Zheng, F.; Chen, F. Comparison of Volatile Compositions of 15 Different Varieties of Chinese Jujube (Ziziphus jujuba Mill.). J. Food Sci. Technol. Mysore. 2019, 56(3), 1631–1640. DOI: 10.1007/s13197-019-03689-7.

[13] Hernandez, F.; Noguera-Artiaga, L.; Burlo, F.; Wojdylo, A.; Carbonell-Barrachina, A. A.; Legua, P. Physicochemical, Nutritional, and Volatile Composition and Sensory Profile of Spanish Jujube (Ziziphus jujuba Mill.) Fruits. J. Sci. Food Agric. 2016, 96(8), 2682–2691. DOI: 10.1002/jsfa.7386.

[14] Song, J.; Bi, J.; Chen, Q.; Wu, X.; Lyu, Y.; Meng, X. Assessment of Sugar Content, Fatty Acids, Free Amino Acids, and Volatile Profiles in Jujube Fruits at Different Ripening Stages. Food Chem. 2019, 270, 344–352. DOI: 10.1016/j.foodchem.2018.07.102.

[15] Chen, Q.; Song, J.; Bi, J.; Meng, X.; Wu, X. Characterization of Volatile Profile from ten Different Varieties of Chinese Jujubes by HS-SPME/GC-MS Coupled with E-nose. Food Res. Int. 2018, 105, 605–615. DOI: 10.1016/j.foodres.2017.11.054.

[16] Galindo, A.; Noguera-Artiaga, L.; Cruz, Z. N.; Burlo, F.; Hernandez, F.; Torrecillas, A., et al. Sensory and Physico-chemical Quality Attributes of Jujube Fruits as Affected by Crop Load. LWT Food Sci. Technol. 2015, 63(2), 899–905. DOI: 10.1016/j.lwt.2015.04.055.

[17] Bi, J.; Chen, Q.; Zhou, Y.; Liu, X.; Wu, X.; Chen, R. Optimization of Short- and Medium-Wave Infrared Drying and Quality Evaluation of Jujube Powder. Food Bioprocess. Technol. 2014, 7(8), 2375–2387. DOI: 10.1007/s11947-013-1245-y.

[18] Yang, L.; Liu, J.; Wang, X.; Wang, R.; Ren, F.; Zhang, Q., et al. Characterization of Volatile Component Changes in Jujube Fruits during Cold Storage by Using Headspace-Gas Chromatography-Ion Mobility Spectrometry. Molecules. 2019, 24(21). DOI: 10.3390/molecules24213904.

[19] Wong, K. C.; Chee, S. G.; Tan, C. H. Volatile Constituents of the Fruit of Zizyphus jujuba Mill. Var. Inermis (Bge.) Rehd. J. Essent. Oil Res. 1996, 8(3), 323–326. DOI: 10.1080/10412905.1996.9700625.

[20] Abe, K.; Hori, Y.; Myoda, T. Characterization of Key Aroma Compounds in Aged Garlic Extract; Food chemistry: 126081. 2020; Vol. 312.

[21] Choi, D.; Lee, S.; Kang, M.-J.; Cho, H.-S.; Sung, N.-J.; Shin, J.-H. Physicochemical Characteristics of Black Garlic (Allium Sativum L.). J. Korean Soc. Food Sci. Nutr. 2008, 37(4), 465–471. DOI: 10.3746/jkfn.2008.37.4.465.

[22] Martinez-Casas, L.; Lage-Yustys, M.; Lopez-Hernandez, J. Changes in the Aromatic Profile, Sugars, and Bioactive Compounds When Purple Garlic Is transformed into Black Garlic. J. Agric. Food Chem. 2017, 65(49), 10804–10811. DOI: 10.1021/acs.jfc.7b04423.

[23] Molina-Calle, M.; Priego-Capote, F.; Luque De Castro, M. D. Headspace-GC-MS Volatile Profile of Black Garlic Vs Fresh Garlic; Evolution along Fermentation and Behavior under Heating. Vol. 80. Lwt-Food Science and Technology. 2017, 98–105. doi:10.1016/j.lwt.2017.02.010.

[24] Forss, D. A. 1972. Odor and Flavor Compounds from Lipids. Progress in the Chemistry of Fats and Other Lipids. 13(4), 177–238. DOI: 10.1007/978-6832(73)90007-4.

[25] Aloui, M. E.; Mguis, K.; Laamouri, A.; Albouchi, A.; Cerniy, M.; Mathieu, C., et al. Fatty Acid and Sterol Oil Composition of Four Tunisian Ecotypes of Ziziphus zizyphus (L.) H.Karst. Acta Botanica Gallicana. 2012, 159(1), 25–31. DOI: 10.1080/12538078.2012.671633.

[26] Elaloui, M.; Laamouri, A.; Albouchi, A.; Cerniy, M.; Mathieu, C.; Vilarem, G., et al. Chemical Compositions of the Tunisian Ziziphus Jujuba Oil. Emir. J. Food Agric. 2014, 26(7), 602–608. DOI: 10.9755/efja.v26i7.17513.

[27] Reche, J.; Soledad Almansa, M.; Hernandez, F.; Carbonell-Barrachina, A. A.; Legua, P.; Amoros, A. Fatty Acid Profile of Peel and Pulp of Spanish Jujube (Ziziphus jujuba Mill.) Fruit. Vol. 295. Food Chemistry. 2019, 247–253. doi:10.1016/j.foodchem.2019.05.147.

[28] Khir, R.; Pan, Z.; Atungulu, G. G.; Thompson, J. F.; Shao, D. Size and Moisture Distribution Characteristics of Walnuts and Their Components. Food Bioprocess. Technol. 2013, 6(3), 771–782. DOI: 10.1007/s11947-011-0717-1.

[29] Zhang, R. T.; Sun, X.; Zhang, K. Q.; Zhang, Y. L.; Song, Y. R.; Wang, F. Z. Fatty Acid Composition of 21 Cultivars of Chinese Jujube Fruits (Ziziphus jujuba Mill.). J. Food Meas. Charact. 2021, 15(2), 1225–1240. DOI: 10.1007/s11694-020-00718-4.

[30] Cui, H. P.; Yu, J. H.; Zhai, Y.; Feng, L. H.; Chen, P. S.; Hayat, K., et al. Formation and Fate of Amadori Rearrangement Products in Maillard Reaction. Trends in Food Science & Technology. 2021; Vol. 115, 391–408. 10.1016/j.tifs.2021.06.055.
[31] Aktag, I. G.; Gokmen, V. *Investigations on the Formation of Alpha-dicarbonyl Compounds and 5-hydroxymethylfurfural in Fruit Products during Storage: New Insights into the Role of Maillard Reaction*. Food Chemistry, 2021; pp 363. doi: 10.1016/j.foodchem.2021.130280.

[32] Paravisini, L.; Peterson, D. G. *Mechanisms Non-enzymatic Browning in Orange Juice during Storage*. Vol. 289. Food Chemistry. 2019, 320–327. doi:10.1016/j.foodchem.2019.03.049

[33] Yoshida, H.; Tatsumi, M.; Kajimoto, G. *Influence of Fatty Acids on the Tocopherol Stability in Vegetable Oils during Microwave Heating*. J. Am. Oil Chem. Soc. 1992, 69(2), 119–125. DOI: 10.1007/BF02540560.

[34] Win, M. M.; Abdul-Hamid, A.; Baharin, B. S.; Anwar, F.; Saari, N. *Effects of Roasting on Phenolics Composition and Antioxidant Activity of Peanut (Arachis Hypogaea L.) Kernel Flour*. Eur. Food Res. Technol. 2011, 233(4), 599–608. DOI: 10.1007/s00217-011-1544-3.