Research Article

Volatile Profile Characterization of Winter Jujube from Different Regions via HS-SPME-GC/MS and GC-IMS

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A combined untargeted and targeted approach was established for fingerprinting volatile organic compounds in winter jujubes from eight regions of China. Volatiles, including alcohols, aldehydes, acids, esters, and alkenes, were identified by gas chromatography-ion mobility spectrometry (GC-IMS). Benzyl alcohol, octanoic acid, 2-hexenal, linalool, 2-nonenal, and ethyl decanoate were the most common compounds present in all jujubes. Principal component analysis (PCA) from GC-IMS and untargeted E-nose showed that the main volatile organic compounds (VOCs) of most jujubes were similar. The volatile organic compounds of winter jujubes from Yuncheng city, Shanxi province, and Aksu region, Xinjiang province, were significantly different from those from other regions. 1-Penten-3-ol, ethylhexanoate, methyllaurate, and 2-formyltoluene were the markers of XJAKS with green and fruity aroma, and SXYC could be labeled by acetone and 2-methoxyphenol with woody and pungent aroma. GC-IMS was an effective method for volatile fingerprinting of jujubes with high sensitivity and accuracy.

1. Introduction

Winter jujube (Ziziphus jujuba Mill. cv. Dongzao) is a unique late-ripening jujube cultivar which originated in China [1]. It is widely distributed in China, including Hebei, Shandong, Shaanxi, Shanxi, and Xinjiang provinces after years of domestication and cultivation [2]. As a representative variety of fresh jujube, it is recognized by its delicious taste and pleasant aroma [1, 3]. As a vital factor considered by consumers, sensory quality can be affected by aroma characteristics, which was correlated with VOCs. The VOCs of fresh winter jujube were composed by alkanes, alcohols, esters, and amines [4]. Geographic region and variety will cause the change of VOCs as reported for different varieties of red jujube [5, 6]. There were significant differences in contents of alcohols, acids, and aromatic compounds among different red jujube varieties [6]. However, there is no systematic study on the geographical differentiation of winter jujube, especially on the VOCs.

At present, headspace solid phase microextraction gas chromatography-mass spectrometry (HS-SPME-GC/MS) and electronic nose (E-nose) are widely applied for the analysis of VOCs in jujube [4, 6]. HS-SPME-GC/MS combines the high separation ability of SPME and the superior identification ability of MS for VOCs [7]. E-nose distinguishes samples via the values of VOCs on different metal-oxide sensors. It defects in the identification of differential components [8]. In contrast to these analytical methods, IMS is a complementary way to detect compounds with low concentration (ppbv levels) with an advantage of fast response [9]. In IMS, vapors from the sample are firstly transferred into the ionization region by carrier gas. Secondly, the product ions formed from the interaction between neutral sample molecules and buffer gas, or bath gas...
molecules in the drift tube will be transported by the electric field into the separation region. Thirdly, the product ions with different drift velocities will reach the detector with different times. At last, the drift time will be used for the qualitative analysis [9]. GC-IMS combines the separation characteristics of GC and the fast response of IMS [10]. GC-IMS has been proved successful in regional identification and varieties classification based on differentiation of VOCs [11–13]. GC-IMS was also used to monitor the changes of VOCs in winter jujube during cold storage [14]. Besides, the combined analysis of GC-IMS and GC-MS has been successfully applied in the differentiation of VOCs from food matrices [15–17]. However, few investigations on the fingerprinting of volatile profiles in winter jujubes from different regions have been done by GC-IMS.

Principal component analysis (PCA) is an effective way to classify samples using unsupervised statics and has been widely employed in chemometrics and bioinformatics today [18]. Variable influence on projection (VIP) is a powerful tool to identify primary and specialized metabolites that are responsible for the discrimination of fruit and vegetables [19]. PCA and VIP scores would be effective for differentiation and selection of potential aroma maker of winter jujubes.

In this study, the geographic differentiation of winter jujubes was investigated by GC-IMS and E-nose based on VOCs. Furthermore, the potential markers of winter jujube from each specific region were identified and quantified by GC-IMS and GC-MS.

2. Material and Methods

2.1. Winter Jujube Preparation and Chemicals. Winter jujubes from eight different regions were purchased from China’s famous jujube trading market (Beiyuanchun Jujube Market in Xinjiang, Xinzheng Jujube Market in Henan, and Cuierzhuang Jujube Market in Hebei). The information of jujube samples is shown in Table 1. 50 kg of winter jujube samples was collected from each region. Fresh fruits free from pests and diseases were washed, and pits were removed, sliced, and frozen by liquid nitrogen and then stored at −40°C for testing as soon as possible.

The reagent of C4–C20 alkanes was purchased from O2si Smart Solution (Charleston, West Virginia, USA), cyclohexane was purchased from Genenode Trading Co., Ltd. (Beijing, China), and n-hexane was purchased from Hushi Co., Ltd. (Shanghai, China). Standards used in this project were as follows: benzyl alcohol, octanoic acid, 2-hexenal, 2-heptenal, linalool, methyl myristolate, 2-nonenal, styrene, hexanoic acid, hexanal, ethyl decanoate, pentanoic acid, 1-penten-3-ol, 1-octen-3-ol, E-2-hexen-1-ol, butanoic acid, heptanoic acid, (E)-3-hexanoic acid, nonanoic acid, acetone, 3-pentanone, 2-hexanone, acetoin, 6-methyl-5-hepten-2-one, (E)-4-undecenal, butanal, E-2-heptanal, heptanal, 2,4-heptadienal, 2-decenal, 3-buten-2-one, ethyl hexanoate, methyl decanoate, methyl laurate, limonene, 2-formyltoluene, 2-formylphenol, 2-nitrophenol, 2-nitrophenol, 2-methoxyphenol, and 2-pentylfuran were all purchased from MilliporeSigma (St. Louis, MO, USA).

2.2. Sample Preparation. About 100 g of frozen winter jujube slices was ground for 60 s with Joyounger juicer (JYL-CO20, Joyounger Co., Ltd., Shandong, China). Accurate 2.0 g of winter jujube pulp was put into a 20 mL vial sealed with a magnetic screw cap and septum before testing.

2.3. GC-IMS Analysis. A FlavourSpec instrument (G.A.S. Gesellschaft für analytische SensorSysyteme mbH Dortmund, Germany) was used for GC-IMS analysis. Procedures were referred to previous studies with small modifications [20]. The sample vial was incubated at 50°C for 20 min, and then 500 μL of headspace was injected at 85°C in splitless mode. Tritium (6.5 keV) was used as the ionization source in this project. A FS-SE-54-CB-1 (15 m × 0.53 mm ID) column was used for separation at 60°C. Linear pressure program of the column was as follows: 2 mL/min for 2 min, ramped up to 10 mL/min over 8 min, then reached to 100 mL/min over 10 min, and at last got to 150 mL/min over 5 min. Nitrogen of 99.99% purity was the drift gas at a flow rate of 150 mL/min and the drift tube was operated at 45°C. All standards were run under the same test procedure to supplement GC×IMS Library Search for qualitative analysis.

The spectrum was analyzed by Laboratory Analytical Viewer (LAV), where retention time and drift time were analyzed for the differentiation of VOCs. Reporter plug-in was used to compare spectrogram differences among samples from the two-dimensional and three-dimensional view. Gallery Plot plug-in was used to compare the differences of volatile fingerprints visually. PCA plug-in was used for classification analysis.

2.4. E-Nose Analysis. A commercial PEN 3.5 E-Nose (Airsense Analytics, GmBH, Schwerin, Germany) containing ten metal-oxide semiconductors was used to distinguish the overall flavor perception of winter jujubes from eight regions. The detailed procedure of sample preparation was referred to Chen et al. [6]. Sample preparation was the same as that in GC-IMS analysis.

2.5. HS-SPME-GC/MS Analysis. HS-SPME conditions and GC-MS analysis were referred to Chen et al. with small modifications [6]. The vials (the same as those in GC-IMS analysis) were equilibrated at 50°C for 40 min. Polydimethylsiloxane/divinylbenzene (PDMS/DVB) fiber was used for extraction and desorbed at 250°C for 3 min in splitless mode. DB-WAX capillary column (30 m × 0.25 mm × 0.25 μm) was used for separation. The oven temperature program was as follows: 40°C for 3 min, heating to 120°C (5°C/min), then rising to 200°C (10°C/min), and holding at 200°C for 5 min. Helium was the carrier gas at a flow rate of 1.0 mL/min. Electron Impact mode with the ion source temperature set at 200°C and the ionization energy of 70 eV was performed in the MS detector. The acquisition was full-scan mode and mass acquisition range was 35–550 m/z.

The standards were qualitatively analyzed under HS-SPME-GC/MS analysis. Retention index (RI) of the
compounds was calculated based on the retention time of C4–C20 alkanes mixture and used as additional support for the identification of compounds. A 2 mg/L solution of cyclohexanone as the optimized internal standard was used for the relative quantitative analysis of VOCs. NIST 17 database was used for identification of the compounds.

Table 1: Geographical distribution information of winter jujubes from eight regions.

| Abbreviation | Geographical origin                                      | Longitude and latitude |
|--------------|----------------------------------------------------------|------------------------|
| HBHH         | Hebei province, Huanghua city                           | E 117.30, N 41.03      |
| SDZH         | Shandong province, Zhanhua city                          | E 118.14, N 37.7       |
| SDYT         | Shandong province, Yantai city                           | E 121.17, N 36.76      |
| SXYC         | Shanxi province, Yuncheng city                           | E 110.15, N 34.35      |
| SXLY         | Shanxi province, Linyi city                              | E 110.77, N 35.15      |
| SNXDL        | Shaanxi province, Dali city                              | E 109.93, N 34.80      |
| XJKEL        | Xinjiang Uygur Autonomous Region, Kuerle city            | E 86.06, N 41.68       |
| XJAKS        | Xinjiang Uygur Autonomous Region, Aksu                   | E 80.29, N 41.15       |

![Figure 1](image-url)  

Figure 1: (a) 2D topographic plots of VOCs from eight regions of winter jujube. (b) VOCs qualitative comparisons of eight regions of winter jujube by GC-IMS.
| No. | Compound                     | Cas       | Formula      | Molecular weight | RI [sec] | Rt [RIrel] | Identification approach |
|-----|-----------------------------|-----------|--------------|------------------|----------|------------|------------------------|
| 1   | Benzyl alcohol (monomer)    | 100-51-6 | C₇H₈O        | 108              | 1090     | 758.55     | RI, DT, Std            |
| 2   | Unknown (monomer)           |           |              |                  |          |            |                        |
| 3   | Hexanoic acid (monomer)     | 142-62-1 | C₆H₁₂O₂      | 116              | 989      | 573.49     | RI, DT, Std            |
| 4   | Cyclohexane (monomer)       | 108-94-1 | C₆H₁₀O       | 98               | 904      | 410.86     | RI, DT, Std            |
|     | Cyclohexane (dimer)         | 108-94-1 | C₆H₁₂O       | 98               | 904      | 402.28     | RI, DT, Std            |
| 5   | Hexanal (monomer)           | 66-25-1  | C₆H₁₂O       | 100              | 796      | 269.29     | RI, DT, Std            |
| 6   | Unknown (monomer)           |           |              |                  |          |            |                        |
| 7   | 2,4-Heptadienal (monomer)  | 5910-85-0 | C₇H₁₀O       | 110              | 1427     | 242.38     | RI, DT, Std            |
| 8   | 2-Nonenal (monomer)         | 2463-53-8 | C₈H₁₆O       | 140              | 687      | 181.34     | RI, DT, Std            |
| 9   | 3-Buten-2-one (monomer)     | 79-77-6  | C₅H₁₀O       | 192              | 1914     | 179.98     | RI, DT, Std            |
| 10  | Acetone (monomer)           | 67-64-1  | C₆H₁₂O       | 58               | 814      | 110.75     | RI, DT, Std            |
| 11  | Styrene (monomer)           | 100-42-5 | C₈H₁₀        | 104              | 602      | 140.40     | RI, DT, Std            |
| 12  | Unknown (monomer)           |           |              |                  |          |            |                        |
|     | E-2-heptenal (monomer)      | 18829-55-5 | C₇H₁₂O       | 112              | 570      | 127.33     | RI, DT, Std            |
| 13  | Unknown (monomer)           |           |              |                  |          |            |                        |
| 14  | 1-Octen-3-ol (monomer)      | 3391-86-4 | C₅H₁₀O       | 128              | 1349     | 226.98     | RI, DT, Std            |
| 15  | Limonene (monomer)          | 138-86-3 | C₈H₁₆O       | 136              | 1032     | 647.98     | RI, DT, Std            |
| 16  | Limonene (dimer)            | 138-86-3 | C₈H₁₇        | 136              | 1032     | 647.00     | RI, DT, Std            |
| 17  | Ethyl hexanoate (monomer)   | 123-66-0 | C₈H₁₆O₂      | 144              | 1405     | 600.99     | RI, DT, Std            |
| 18  | Unknown (monomer)           |           |              |                  |          |            |                        |
|     | Nonanoic acid (monomer)     | 112-05-0 | C₉H₁₈O₂      | 158              | 2083     | 256.62     | RI, DT, Std            |
| 19  | Butanoic acid (monomer)     | 107-92-6 | C₄H₈O₂       | 88               | 1538     | 218.01     | RI, DT, Std            |
| 20  | Unknown (monomer)           |           |              |                  |          |            |                        |
| 21  | Unknown (dimer)             |           |              |                  |          |            |                        |
| 22  | Unknown (monomer)           |           |              |                  |          |            |                        |
| 23  | Limonene (monomer)          | 3777-69-3 | C₉H₁₄O       | 138              | 1134     | 122.26     | RI, DT, Std            |
| 24  | Butanoic acid (dimer)       | 110-93-0 | C₈H₁₄O       | 126              | 1542     | 116.99     | RI, DT, Std            |
| 25  | Unknown (monomer)           |           |              |                  |          |            |                        |
| 26  | Unknown (monomer)           |           |              |                  |          |            |                        |
|     | Methyl decanoate (monomer)  | 68820-35-9 | C₁₁H₂₂O      | 168              | 2719     | 203.77     | RI, DT, Std            |
| 27  | 2-Heptenal (monomer)        | 2463-63-0 | C₇H₁₂O       | 112              | 663      | 169.06     | RI, DT, Std            |
| 28  | 2-Formyltoluene (monomer)   | 529-20-4 | C₈H₈O        | 120              | 1555     | 121.67     | RI, DT, Std            |
| 29  | 1-Penten-3-ol (monomer)     | 616-25-1 | C₅H₁₀O       | 86               | 1134     | 122.26     | RI, DT, Std            |
| 30  | 2-Formylphenol (monomer)    | 90-02-8  | C₈H₁₂O       | 122              | 1542     | 116.99     | RI, DT, Std            |
| 31  | Unknown (monomer)           |           |              |                  |          |            |                        |
| 32  | Unknown (monomer)           |           |              |                  |          |            |                        |
| 33  | Unknown (monomer)           |           |              |                  |          |            |                        |
| 34  | (E)-4-Undecenal (monomer)   |           |              |                  |          |            |                        |
| 35  | 3-Hexenoic acid, (E)-(monomer) | 1577-18-0 | C₆H₁₂O₂      | 114              | 1876     | 730.66     | RI, DT, Std            |
| 36  | Methyl laurate (monomer)    | 111-82-0 | C₆H₁₂O₂      | 214              | 1765     | 709.01     | RI, DT, Std            |
| 37  | 2-Pentylfuran (monomer)     | 3777-69-3 | C₅H₁₀O       | 138              | 1218     | 317.26     | RI, DT, Std            |
| 38  | Unknown (monomer)           |           |              |                  |          |            |                        |
| 39  | 6-Methyl-5-hepten-2-one     | 110-93-0 | C₆H₁₂O       | 126              | 1335     | 652.47     | RI, DT, Std            |
| 40  | Unknown (monomer)           |           |              |                  |          |            |                        |
| 41  | Unknown (monomer)           |           |              |                  |          |            |                        |
| 42  | Unknown (dimer)             |           |              |                  |          |            |                        |
| 43  | Methyl decanoate (dimer)    | 110-42-9 | C₁₁H₂₂O      | 186              | 1613     | 185.05     | RI, DT, Std            |
| 44  | 2-Hexanone (monomer)        | 591-78-6 | C₆H₁₂O       | 100              | 1087     | 260.91     | RI, DT, Std            |
| 45  | Unknown (monomer)           |           |              |                  |          |            |                        |
| 46  | Heptanal (monomer)          | 111-71-7 | C₇H₁₂O       | 114              | 1280     | 373.42     | RI, DT, Std            |
| 47  | Methyl myristoleate (monomer) | 56219-06-8 | C₁₃H₂₆O      | 240              | 670      | 172.37     | RI, DT, Std            |
| 48  | 2-Decenal (monomer)         | 3913-71-1 | C₁₀H₁₈O      | 154              | 1638     | 171.40     | RI, DT, Std            |
| 49  | Unknown (monomer)           |           |              |                  |          |            |                        |
| 50  | Unknown (monomer)           |           |              |                  |          |            |                        |
| 51  | Linalool (monomer)          | 78-70-6  | C₅H₁₀O       | 154              | 981      | 556.52     | RI, DT, Std            |
| 52  | Phenol, 2-nitro-(monomer)   | 88-75-5  | C₆H₅NO₃      | 139              | 1810     | 359.18     | RI, DT, Std            |
2.6. Statistical Procedures. Data standardization was performed using SPSS 13.0 software (SPSS Inc, Chicago, IL). MetaboAnalyst was used for biplot and calculation of LDA analysis and VIP scores (https://www.metaboanalyst.ca/MetaboAnalyst/home.xhtml). Morpheus was applied for the correlation analysis by heatmap (https://software.broadinstitute.org/morpheus/). Each sample was repeated in triplicate.

3. Results and Discussion

3.1. Determination of VOCs from Eight Regions of Winter Jujube by GC-IMS. VOCs of winter jujube samples from eight regions of China were analyzed by GC-IMS, and the result is shown in Figure 1(a). The red baseline on the left is the reaction ion peak (RIP). RIP represents the total number of ions in the ionization chamber, described as H^+(H_2O)^n (n represents the number of water molecules) [17]. The points on the right of RIP represent the signal (monomer, dimer, and even trimer) of volatiles extracted from the samples. Most of the signals appeared in the retention time of 100–600 s and the drift time of 6.0–14.0 ms. The red color represents the higher signal intensity (higher concentration) of the substance, while the white color indicated weaker intensity (lower concentration) [21]. In IMS, the formation of product ions mainly depends on the affinity of analytes to

| No. | Compound                        | Cas          | Formula       | Molecular weight | RI  | Rt [sec] | Dt [RIPrel] | Identification approach |
|-----|---------------------------------|--------------|---------------|-----------------|-----|----------|-------------|------------------------|
| 53  | E-2-Hexen-1-ol (monomer)        | 928-95-0     | C_6H_{12}O    | 100             | 1361| 346.71   | 1.18         | RI, DT, Std             |
| 53' | E-2-Hexen-1-ol (dimer)          | 928-95-0     | C_6H_{12}O    | 100             | 1361| 344.37   | 1.51         | RI, DT, Std             |
| 54  | 2-Methoxyphenol (monomer)       | 90-05-1      | C_6H_{12}O    | 124             | 1831| 309.46   | 1.25         | RI, DT, Std             |
| 55  | Octanoic acid (monomer)         | 124-07-2     | C_8H_{16}O_2  | 144             | 756 | 232.43   | 1.10         | RI, DT, Std             |
| 56  | Pentanoic acid (monomer)        | 109-52-4     | C_8H_{16}O_2  | 102             | 754 | 231.26   | 1.35         | RI, DT, Std             |
| 57  | 3-Pentanone (monomer)           | 96-22-0      | C_6H_{10}O    | 86              | 898 | 188.76   | 1.35         | RI, DT, Std             |
| 58  | 2-Nitrophenetole (monomer)      | 610-67-3     | C_6H_{14}NO_3 | 167             | 1651| 162.82   | 1.19         | RI, DT, Std             |
| 59  | Unknown (monomer)               | —            | —             | —               | 164 | 652      | 1.31         | RI, DT                 |
| 60  | Acetoin (monomer)               | 513-86-0     | C_2H_{4}O     | 88              | 1120| 204.55   | 1.05         | RI, DT, Std             |
| 61  | Ethyl decanoate (monomer)       | 110-38-3     | C_{12}H_{26}O | 200             | 682 | 179.01   | 0.94         | RI, DT, Std             |
| 62  | 2-Hexenal (monomer)             | 505-57-7     | C_6H_{10}O    | 98              | 633 | 154.04   | 1.02         | RI, DT, Std             |
| 63  | Unknown (monomer)               | —            | —             | —               | 525 | 111.14   | 1.17         | RI, DT                 |
| 64  | Butanal (monomer)               | 123-72-8     | C_4H_{8}O     | 72              | 568 | 126.55   | 1.10         | RI, DT, Std             |
| 64' | Butanal (dimer)                 | 123-72-9     | C_4H_{8}O     | 72              | 864 | 124.99   | 1.28         | RI, DT, Std             |
| 65  | Unknown (monomer)               | —            | —             | —               | 537 | 115.24   | 1.15         | RI, DT                 |

Figure 2: PCA plot of eight regions of winter jujube.
Figure 3: Continued.
protons. Product ions could also be affected by the concentration of the analyte, the chemical properties, and the temperature of the drift tube [20].

Varieties of fruits have distinct aroma depending on the composition, concentration, aroma description, and odor threshold of VOCs [22]. The composition of VOCs varied in winter jujubes from different regions. In order to identify the specific differences and make a quantitative comparison, all peaks were identified and numbered for fingerprint comparison. The direct comparison of the components in each sample was shown in Figure 1(b). VOCs in the black frame were the common components among eight regions of winter jujubes. VOCs in the yellow and red frame were the ones present only in SXYC and XJAKS. VOCs in the green frame were the differential ones in eight regions of winter jujube. The corresponding data of retention time (RT) and drift time (DT) are presented in Table 2.

The X-axis represented the code of the compound, corresponding to the information in Table 2.

Common compounds included alcohols, aldehydes, acids, esters, and alkenes (Figure 1(b)). In particular, benzyl alcohol, octanoic acid, 2-hexenal, 2-heptenal, linalool, methyl myristoleate, 2-nonenal, styrene, hexanoic acid, hexanal, ethyl decanoate, and pentanoic acid presented small concentration difference (Figure 1(b)). These identified volatiles, as well as their aroma characteristics, would be important for the whole aroma of winter jujube.

Alcohols were formed by sugar catabolism and/or acid degradation in the food matrix [23]. Benzyl alcohol contributes to a slightly fruity aroma, while linalool, a
monoterpenoid, contributes to floral, lavender, lemon, and rose flavor [23, 24]. Aldehydes were thought to be mainly produced via lipid oxidation and decomposition, contributing most to the overall aroma among all categories because of relatively low odor thresholds. Hexanal derived from linoleic acid contributes to flavor of fruity, grass, and green, with a low odor threshold of 1.1 ng/L [25]. 2-Nonenal is a plant metabolite and derives from linoleate decomposition, with flavor of paper [25]. 2-Heptenal is a plant metabolite with soapy and fatty aroma and existed in white pomelo peel [26]. Acids like octanoic acid, hexanoic acid, and pentanoic acid might be related to cheese aroma [27]. Ethyl decanoate is present in fruits like cherry and pineapple with fruity aroma [26]. Styrene was reported to have sweet, balsamic, and almost floral odor that was extremely penetrating [28]. Esters endow fruity aroma for fruits and methyl myristoleate

![Figure 4: PCA results of eight regions of winter jujubes differentiated by E-nose.](image)

Table 3: Sensors and response characteristics of E-nose.

| Number | Sensors | Response characteristics |
|---|---|---|
| 1 | W1C | Aromatic compounds |
| 2 | W5S | Nitroide |
| 3 | W3C | Ammonia and aromatic components |
| 4 | W6S | Hydrogen selective |
| 5 | W5C | Alkanes and aromatic components |
| 6 | W1S | Methane |
| 7 | W1W | Sulfides |
| 8 | W2S | Ethyl alcohol |
| 9 | W2W | Aromatic components and organic sulfide |
| 10 | W3S | Alkanes |
| Compound                        | CAS     | RI lit | SNXDL | SDZH | XIAKS | HRHH | SDYT | SXYC | SXLY | Aroma description                  |
|--------------------------------|---------|--------|-------|------|-------|------|------|------|------|------------------------------------|
| **Alcohols (3)**               |         |        |       |      |       |      |      |      |      |                                    |
| 1-Penten-3-ol (*)              | 616-25- | 1162   | 6.11  | 0.39 | 2.28  | 0.23 | 52.08| 5.74 | 3.45 | 0.45 | 1.75 ± 0.20 | 2.03 ± 0.30 | 30.7 ± 3.12 | 5.21 ± 0.14 | Grassy, green |
| 1-Octen-3-ol                   | 3391-86-| 1455   | 8.06  | 0.15 | 10.85 | 1.13 | 0.12 | 0.02 | 4.34 | 0.14 | 0.44 ± 0.01 | 18.63 ± 2.01 | —             | —             |                        |
| E-2-hexen-1-ol                | 928-95-0| 1420   | 8.98  | 0.45 | 7.46  | 0.45 | 5.64 | 0.22 | 8.76 | 3.26 | 8.70 ± 1.34 | —             | —             | —             |                        |
| **Acids (3)**                  |         |        |       |      |       |      |      |      |      |      |                                    |
| Butanoic acid                 | 107-92- | 1634   | 3.98  | 0.22 | 16.56 | 2.23 | 5.65 | 1.21 | 1.03 | 0.02 | 0.45 ± 0.02 | —             | —             | —             | —               |
| 3-Hexenoic acid, (E)-nonanoic acid | 1577-18-| 1929   | 0.70  | 0.11 | 0.78  | 0.11 | 5.19 | 0.11 | —   | 3.00 | 0.23 | 36.11 ± 7.89 | 8.28 ± 2.33 | —             | —             | Fruit            |
| **Ketones (6)**                |         |        |       |      |       |      |      |      |      |      |                                    |
| Acetone(*)                    | 67-64-1 | 825    | 1.39  | 0.32 | 38.80 | 3.15 | 0.34 | 0.02 | —   | 4.45 | 0.21 | 19.16 ± 3.02 | —             | —             | —             | —               |
| 3-Pentanone (*)                | 96-22-0 | 975    | 25.43 | 2.45 | 38.80 | 3.15 | 0.34 | 0.02 | —   | 13.95 | 3.1 | 10.84 ± 1.23 | —             | —             | —             | —               |
| 2-Hexanone                    | 59-71-6 | 1124   | 4.56  | 0.82 | 4.34  | 0.82 | —   | —   | —   | 4.45 | 0.21 | 19.16 ± 3.02 | —             | —             | —             | —               |
| Acetoin                        | 513-86-0| 1272   | 5.45  | 0.90 | 9.43  | 0.20 | 9.99 | 0.43 | —   | 4.88 | 0.32 | —             | —             | —             | —             | —               |
| 6-Methyl-5-hepten-2-one        | 110-93-0| 1548   | 9.88  | 0.32 | 38.22 | 4.61 | 9.77 | 0.22 | 10.9 | 0.24 | 25.06 | 2.03 | 17.99 ± 3.59 | 50.79 ± 6.53 | 19.16 ± 3.02 | —               |
| **Aldehydes (5)**              |         |        |       |      |       |      |      |      |      |      |                                    |
| Butanal                        | 123-72- | 898    | 1.39  | 0.22 | 1.11  | 0.22 | 1.37 | 0.22 | 8.99 | 1.52 | 2.02 ± 0.52 | 0.88 ± 0.09 | —             | —             | —               |
| Heptanal                       | 111-71-7| 1194   | 0.97  | 0.11 | 3.43  | 0.21 | —   | —   | 9.43 | 0.21 | 16.43 | 2.11 | —             | —             | —             | —               |
| 2,4-Heptadienial              | 5910-85-| 1490   | 2.45  | 0.04 | 2.17  | 0.04 | 9.36 | 2.04 | 9.87 | 1.23 | 7.70 ± 1.23 | 11.39 ± 1.12 | —             | —             | —               |
| 2-Decenal                     | 3913-71-| 1645   | 0.23  | 0.01 | 4.34  | 0.11 | 6.70 | 0.31 | 0.54 | 0.11 | —   | 4.45 ± 0.32 | 19.16 ± 1.52 | —             | —             | Fat, fish, orange |
| (E)-4-undecenal               | 68820-35-| 2992  | 0.87  | 0.02 | 1.70  | 0.02 | 4.34 | 0.02 | —   | 5.65 | 0.34 | 1.03 ± 0.31 | 0.45 ± 0.02 | —             | —             | —               |
| **Esters (3)**                 |         |        |       |      |       |      |      |      |      |      |                                    |
| Ethyl hexanoate                | 123-66- | 1435   | 7.03  | 1.01 | 1.84  | 0.41 | 33.22| 0.41 | 4.56 | 0.52 | 3.58 ± 0.37 | 8.67 ± 0.69 | 4.49 ± 0.21 | —             | —               |
| Methyl decanoate               | 110-42- | 1640   | 16.34 | 1.23 | 0.11  | 0.01 | 7.98 | 2.01 | 30.47 | 3.23 | 23.52 | 2.89 | 5.51 ± 2.11 | 0.34 ± 0.04 | —             | —               |
| Methyl laurate (*)             | 111-82-0| 1805   | 1.03  | 0.01 | 0.45  | 0.01 | 34.43| 3.01 | 9.43 | 3.22 | 0.43 ± 0.01 | 7.70 ± 0.21 | 9.34 ± 2.33 | —             | —               |
| **Total**                      |         |        |       |      |       |      |      |      |      |      | 24.4 ± 2.4 | 2.4 ± 0.43 | 67.74 ± 3.43 | 21.97 ± 4.85 | 30.9 ± 3.24 | 27.1 ± 3.26 | 21.88 ± 3.01 | 14.17 ± 2.58 |
| Compound          | CAS     | RI cal | RI lit | SNXDL | SDZH | XJAKS | HBHH | SDYT | XJKE | SXYD | SXLY | Aroma description               |
|-------------------|---------|--------|--------|--------|------|-------|------|------|------|------|------|----------------------------------|
| **Alkenes (1), benzenes (5)** |         |        |        |        |      |       |      |      |      |      |      |                                 |
| Limonene          | 138-86-3| 1192   | 1189   | 0.98 ± 0.05cd | 18.80 ± 2.05a | 0.34 ± 0.05d | 4.34 ± 0.35c | 1.60 ± 0.32cd | 13.95 ± 4.33d | 10.84 ± 1.87b | 1.45 ± 0.05d | Lemon-like aroma                |
| 2-Formyltoluene*  | 529-20-4| 1646   | 1621   | nd.    | nd.  | 19.02 ± 2.02a | 0.12 ± 0.02c | nd.  | 0.44 ± 0.09c | 8.63 ± 1.98b | nd.  | Chaes and bitter almond          |
| Alkenes (1), benzenes (5) |        |        |        |        |      |       |      |      |      |      |      |                                 |
| 2-Formylphenol    | 90-02-8 | 1679   | 1636   | 0.44 ± 0.02d | 7.70 ± 1.01b | 2.17 ± 0.03c | 9.36 ± 1.23a | nd.  | 2.43 ± 0.10f | nd.  | Almond, pungent, spice           |
| 2-Nitrophenetole  | 610-67-3| 1816   | —      | 4.56 ± 0.21b | 4.34 ± 0.21b | nd.    | nd.  | nd.  | 17.70 ± 0.23a | nd.  | —                                |
| 2-Nitro-phenol    | 88-75-5 | 1819   | 1812   | 0.34 ± 0.01a | nd.    | nd.    | 7.98 ± 0.10c | 10.47 ± 0.02a | 3.52 ± 0.04d | 8.67 ± 0.21b | nd.  | Peculiar sweet smell              |
| 2-Methoxyphenol*  | 90-05-1 | 1866   | 1862   | 5.45 ± 0.32c | 2.22 ± 0.30ad | 1.43 ± 0.21d | nd.  | 4.88 ± 1.31b | nd.  | 28.63 ± 1.31a | 2.89 ± 0.14g | Burnt, phenol, wood              |
| **Furans (1)**    |         |        |        |        |      |       |      |      |      |      |      |                                 |
| 2-Pentylfuran     | 3777-69-3| 1229  | 1249   | nd.    | nd.  | 1.75 ± 0.11b | nd.  | 0.54 ± 0.08c | nd.  | 4.45 ± 1.29b | 25.63 ± 2.89a | Butter, floral, fruit, green bean |

*RI cal" means RI calculated by the retention time of alkanes. "RI lit" means RI listed in the literature. Compounds with "*" mean variables with VIP score >1. "nd." means not detected.
was found to be with aroma of honey and iris [29]. Mutual comprehensive effect of VOCs is the basis of the formation of the overall aroma of winter jujubes. Most of these common volatiles were found to be aroma attributes of fruity, grass, or green, which was in agreement with Pu et al. [4].

As is shown in Figure 2, PCA of GC-IMS data showed that SXYC and XJAKS were individually apart from the other winter jujubes. All the jujubes studied in this study were distributed in the middle latitude of the northern hemisphere, among which SXYC had the smallest latitude and XJAKS has the smallest longitude (Table 1). The special geographical location and associated climatic factors of SXYC and XJAKS might be the reason why the jujube aroma of these two regions was different from others. SXYC and XJAKS had their own specific VOCs that are framed with yellow and red color separately in Figure 1(b). The substances identified in the yellow frame, including acetone, 6-methyl-5-hepten-2-one, 2-nitrophenol, 2-methoxyphenol, and 2-nitrophenetole, were the specific chemicals in SXYC. XJAKS was characterized by compounds in the red frame, including (E)-3-hexenoic acid, 1-penten-3-ol, ethyl hexanoate, 2-methyl-benzaldehyde, 2-hydroxy-benzaldehyde, trans-4-undecenal, methyl laurate, 2-pentylfuran, and heptanal. The volatile markers of SXYC and XJAKS would be confirmed by the correlation analysis between E-nose and the relative quantitative results of GC-MS for the discriminating components in the following parts.

3.2. E-Nose Analysis. Aromacharacteristics and PCA results based on E-nose of winter jujubes are shown in Figures 3 and 4. Sensors and response characteristics of E-nose are shown in Table 3. E-nose results were not specific information on sample composition but rather a simple fingerprint through pattern recognition.

Figures 3(b), 3(g), and 3(i) show that VOCs of SNXDL, SDZH, HBHH, SDYT, XJKEL, and SXLY responded almost the same tendency on sensors W5S, W1W, and W2W. Aroma of SXYC had the highest response value on sensors W1C, W3C, and W5C (Figures 3(a), 3(c), and 3(e)). XJAKS had the highest response value on sensors W5S, W1S, and W2S inferred from Figures 3(b), 3(f), and 3(h). PCA results (Figure 4) based on Figure 3 showed that SNXDL, SDZH, HBHH, SDYT, XJKEL, and SXLY relatively clustered. SXYC and XJAKS were far away from others. The classification results of aroma characteristics obtained by E-nose (Figure 4) showed the same trend as those obtained by GC-IMS (Figure 2). The classification results of the two technologies strongly indicated that GC-IMS and E-nose had advantages in rapid classification and accuracy. Although targeted and qualitative analysis of winter jujubes was performed well by GC-IMS, the identification and quantitation of potential contributed markers in different winter jujubes were further combined with GC-MS analysis.

3.3. Potential Markers Analysis. HS-SPME-GC/MS was performed targeting the different VOCs (volatiles in the
green, yellow, and red frame in Figure 1(b) of winter jujubes). The results are shown in Table 4. Partial least squares discriminant analysis (PLS-DA) assesses the relationship between a descriptor matrix $X$ and a response matrix $Y$ in a supervised way [19]. The differential variations were amplified to illustrate the relationships between the groups in biplot. Identification of the most important variables for the prediction ability of the PLS-DA model is generally performed by analyzing the regression coefficients. VIP scores provide information about the importance of each
variable used in the grouping model of PLS-DA [30]. VIP scores greater than 1.0 are always treated as the discriminating factor. PLS-DA has been applied to identify primary and specialized metabolites that are responsible for the discrimination of fruits and vegetables [31].

PLS-DA and biplot (Figures 5(a) and 5(b)) got from Table 4 showed the same tendency as the PCA results got from GC-IMS and E-nose (Figures 2 and 4). SNXDL, SDZH, HBHH, SDYT, XJKEL, SXLY, SXYC, and XJAKS were apart from others. As shown in Figure 6, 1-penten-3-ol, acetone, 2-methoxyphenol, methyl laurate, 3-pentanone, 2-formyltoluene, and ethyl hexanoate were the components with VIP scores >1, indicating that they were crucial components for the discrimination of...
winter jujubes from eight regions. The relationship between the differential VOCs (Table 4) and sensors (Figure 3) was analyzed by heatmap (Figure 7). The potential markers for SXYC and XJAKS were analyzed according to the VIP scores and heatmap.

For SXYC, the sensors with higher response values (W1S, W3S, and W5S) were in close relationship with heptanal, acetone, 6-methyl-5-hepten-2-one, 2-methoxyphenol, and 2-nitrophenetole (Figure 7). However, only acetone and 2-methoxyphenol had VIP scores over 1. Research showed that 2-methoxyphenol was a product of pyrolysis of lignin with woody odor. Acetone existed naturally in plants with pungent odor [32]. The quantitative results in GC-MS showed that 2-methoxyphenol and acetone accounted for 31.67% of the differential VOCs in SXYC (Table 4). Their concentration in SXYC was several times higher than that in other jujubes (Table 4). Hence, 2-methoxyphenol and acetone might be the potential markers of SXYC with woody and pungent aroma.

For XJAKS, the sensors with higher response values (W5S, W1S, and W2S) were in close relationship with acetoin, (E)-4-undecenal, 2-formylphenol, butanoic acid, 1-penten-3-ol, 2-formyltoluene, ethyl hexanoate, and methyl laurate (Figure 7). However, 1-penten-3-ol, ethyl hexanoate, methyl laurate, and 2-formyltoluene were the ones with VIP scores >1, and their amount comprised 74.65% of the different VOCs in XJAKS. 1-Penten-3-ol was one of the secondary lipid oxidation products. It was once found in oolong tea infusions and was responsible for butter and pungent odor [33]. Ethyl compounds like ethyl hexanoate exist in kinds of fruits [34]. Methyl laurate could effectively inhibit enzyme activities and thus could help to prevent the green color of fruits from fading away [35]. Methyl-benzaldehydes were present in tomato, cider, elderberry juice, tea, and so forth [36]. 2-Formyltoluene was found in winter jujube for the first time. Thus 1-penten-3-ol, ethyl hexanoate, methyl laurate, and 2-formyltoluene might be the potential markers for XJAKS with green and fruity-like aroma (Figure 8).

4. Conclusion

In conclusion, the difference and similarity in VOCs of winter jujube from eight regions of China were well analyzed by GC-IMS, E-nose, and GC-MS. All results showed that SNXDL, SDZH, HBHH, SDYT, XJKEI, and SXLY clustered together with the differentiation of SXYC and XJAKS. As is shown in Figure 9, benzyl alcohol, octanoic acid, 2-hexenal, linalool, 2-nonenal, and ethyl decanoate were the common volatiles of winter jujubes from eight regions of China. The combined analysis of VIP scores, heatmap, and aroma description indicated that 1-penten-3-ol, ethyl hexanoate, methyl laurate, and 2-formyltoluene were the potential markers for green and fruity aroma profile of SXYC, and XJAKS could be labeled by acetone and 2-methoxyphenol with wood-like and pungent aroma.

Data Availability

Data are contained within this article.

Conflicts of 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.

Authors’ Contributions

The authors’ contributions are as follows: conceptualization, methodology, and formal analysis: Jinfeng Bi, Qin Qin Chen, Giorgia Purcaro, Yening Qiao, and Xinye Wu; investigation, Yening Qiao; writing-original draft preparation: Yening Qiao; writing-review and editing: Jinfeng Bi, Qin Qin Chen, and Giorgia Purcaro; supervision: Giorgia Purcaro, Min Gou, Haonan Hou, and Xinwen Jin. All authors have read and agreed to the published version of the manuscript.

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