Comparison of sugars, organic acids and aroma components of five table grapes in Xinjiang

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Abstract. The sugar, organic acid and aroma Components are very important quality characteristics of fruits. In this study, sugars, organic acids and volatile substances in five varieties of Xinjiang table grape pulp were determined by high-performance liquid chromatography and gas chromatography-mass spectrometry. The results showed that among the five varieties of table grapes in Xinjiang, fructose and glucose were the main sugars, accounting for 46.53-48.82% and 49.35-51.49% of the total sugar content, respectively. Tartaric acid and malic acid were the main organic acids, accounting for 55.72-60.07% and 28.54-39.52% of the total organic acids, respectively. The composition of sugars and organic acids ratio plays a significant role in the taste of table grapes. The sweetness of Red Globe was the highest while the acidity of Centennial Seedless was the highest. In addition, 87 varieties of volatile compounds were identified in table grape pulp with aldehydes as the major compounds (30.93-71.83%). In particular, trans-2-hexenal accounted for 19.33-44.56% of the total volatiles. Analysis of active odorants showed that nerol, geraniol, (Z)-3-hexenal, trans-2-hexenal, phenylacetdehyde, citral and β-myrcene had great contributions to the flavors of Centennial Seedless and Muscat Hamburg, providing flowery, fruity, green and grassy flavors. Hexanol, trans-2-hexen-1-ol, damascone and ethyl butyrate had great contributions to the flavors of Rizamat, providing flowery, green and fruity flavors. Nonanal and 1-octen-3-one had great contributions to the flavors of Manaizi, providing mushroom and fruity flavors. The results provided the complete chemical characteristics of sugar, organic acids and volatile compounds of five varieties of table grapes in Xinjiang, China.

1. Introduction

As a kind of fruit with a high edible value, grapes can not only be eaten directly (table grapes) but also be used to produce wine. The yield of table grapes in China accounts for 80% of the total yield of grapes [1]. As the largest grape-producing area in China, Xinjiang has abundant grape resources.

Appearance, nutritional content and volatile flavor are three important qualities of fresh fruits. The appearance of table grapes depends on the shape, size and weight, which are the first impressions of the grape quality. In addition, organic acids are the major metabolites existing in grapes whose compositions and concentrations are the essential parameters related to grape processing and quality evaluation [2]. The content can affect the taste balance, chemical stability, and pH value directly. Another main
metabolite related to quality existing in grapes is sugar \cite{3}. The content and composition of sugar have great influences on the flavor, color and other nutritional components of grapes. As an important nutrient in grapes, sugar is also one of the important signs showing the ripeness of grapes \cite{4, 5}. The aroma of grapes is one of the important sensory factors measuring the quality. Different varieties of grapes have different aromas, resulting in significant differences in flavors and typical characteristics of grapes \cite{6}.

At present, the study on the quality of table grapes is significantly less than that of wine grapes. There are few complete analyses on the taste and aroma of table grapes in Xinjiang. In this study, the high-performance liquid chromatography (HPLC) and the headspace solid-phase microextraction with the combination of gas chromatography-mass spectrometry (HS-SPME-GC-MS) were used to detect the organic acid, sugar and aroma substances of five varieties of table grapes in Xinjiang, including Red Globe, Rizamat, Manaizi, Muscat Hamburg and Centennial Seedless. Furthermore, influences of chemical components and aroma substance on the quality of different varieties of table grapes were elaborated. The results will provide an important theoretical basis for the quality research on high-quality table grapes in local areas.

2. Materials and Methods

2.1. Raw materials of grapes

Five varieties of table grapes were taken from CITIC Guoan Wine’s grape planting base in Manas County, Xinjiang, China, including Red Globe, Rizamat, Manaizi, Muscat Hamburg and Centennial Seedless. Grapes were picked at the commercial stage of ripeness based on their exterior color and size uniformity.

2.2. Analysis of morphological characteristics and basic physical-chemical indicators

The morphological characteristics of grapes are expressed by the average weight (Wm), density (ρ) and morphological coefficient (Cs) of the grapes. Cs = average height of grapes (mm) / average diameter of grapes (mm). The varieties can be divided into three categories according to Cs: Cs <0.8, short; 0.8 <Cs <1: round; Cs> 1: long. The soluble solids content (SSC) and the titratable acidity (TA) were mainly conducted based on the method of Lichter et al. \cite{7}.

2.3. Measurement of sugars and organic acids

After washing and drying, 15-20 grapes of the same color and uniform size are crushed and mixed with a juicer. 1.00 g of homogenates were obtained and reached 25 mL with ultrapure water in a volumetric flask to weigh. After extracting in the ultrasound for 30 minutes at room temperature, the samples were taken out and added with pure water to equal weight. The extracted samples were centrifuged at 10,000 r/min for 15 minutes at normal temperature to obtain the supernatant liquid, which was filtered with a 0.22 μm filter membrane for tests.

Some modifications were made in this study based on the research conducted by Lima et al. \cite{8}. High-performance liquid chromatography (HPLC) was used to conduct quantitative analyses of tartaric acid, malic acid, citric acid, succinic acid and ascorbic acid. A diode array (DAD) detector was equipped with high-performance liquid chromatography and used the Spursil C18 (250 mm × 4.6 mm, 5 μm) chromatographic column. The mobile phase was 0.025 mol/L KH2PO4-methanol, the H2PO4 was acidified to a pH value of 2.6. The operation time was 15 minutes and the flow rate is 0.6 mL/min at 26 °C, the injection volume was 10 μL. The diode array (DAD) detection wavelength was 250 nm and 210 nm (ascorbic acid corresponded to a wavelength of 250 nm, tartaric acid, malic acid, citric acid and succinic acid corresponded to a wavelength of 210 nm).

Some modifications were made in this study based on the research conducted by Gancedo and Luh et al \cite{9}. High-performance liquid chromatography (HPLC) was used to conduct quantitative analyses of glucose, fructose and sucrose. A differential refractive index detector (RID) was equipped with high-performance liquid chromatography and used the CAPCELL PAK NH2 (250 mm×4.6 mm, 5 μm) chromatographic column. The mobile phase was acetonitrile-water (78; 22 by volume). The operation
time was 20 min, the flow rate was 1 mL/min at 30 °C, the injection volume was 10 μL, and the detection wavelength of differential refractive index (RID) was 210 nm.

2.4. Measurement of volatile compounds [10]
Volatile compounds extraction: The volatile compounds in grape pulp were extracted by HS-SPME and analyzed by gas chromatography/mass spectrometry (GC-MS). 5 mL of peeled pulp juice, 1 g of NaCl and 2.5 μL of 0.98% 2-octanol were added to a 15 mL sample bottle. A magnetic stirring rotor was placed in the bottle after the mixture. The bottle was then sealed with a diaphragm cap made of Teflon. The sample was then placed on a magnetic stirrer at 300 rpm and equilibrated at 40 °C for 10 min. The extraction head of the 50/30μm (DVB/CAR/PDMS) solid-phase microextraction (SPME) was used to continuously heat and stir the sample at 40 °C for 60 minutes to extract and enrich the volatile compounds in the fermentation broth.

Chromatographic conditions: The desorption and analysis of volatile compounds previously extracted with HS-SPME were carried out using a gas chromatograph equipped with an HP-InnOAVx capillary column (60 m × 0.25 mm, 0.25 μm) and mass spectrometer equipped with a selective detector (MSD). Specifically, the SPME extraction head was inserted into the gas chromatograph syringe for thermal desorption at 250 °C, and then separated on an HP-INNOWAX capillary column. The temperature program was: 50 °C for 5 minutes, up to 86 °C at 3 °C/min, up to 90 °C at 1 °C/min, up to 180 °C at 3 °C/min for 3 minutes, up to 230 °C at 15 °C/min, then returned to the initial value after 5 minutes. The flow rate of the carrier gas (He) was 1 mL/min. The ionization energy was 70 eV. The m/z acquisition range was 35-450.

Qualitative and quantitative analysis: The extracted volatile components were identified by comparing spectra and data analysis obtained by mass spectral library search (NIST). Quantification was performed using the internal standard 2-octanol.

3. Results and discussion
3.1. Morphological characteristics and physical-chemical indicators
This study analyzed the morphological characteristics and Physical-Chemical indicators of five varieties of table grapes (Table 1). The average weights (Wm) were sorted as follows: Red Globe > Rizamat > Muscat Hamburg > Manaizi > Centennial Seedless. There’s no obvious difference in density, but the pH values ranged from 3.31 to 4.07. Muscat Hamburg and Red Globe had smaller morphological coefficients (Cs) and were close to round shapes. The other three were long shapes. The soluble solids (SSC) of these five varieties of grapes ranged from 13.55 °Bx to 23.20 °Bx. Except for Rizamat, the SSC of other grapes was greater than 14 °Bx. Studies have shown those table grapes have good sensory qualities when they are harvested at a Brix level above 14 °Bx [11]. In addition, their total acid (TA) was low, ranging from 2.69 g/L to 4.03 g/L. The sugar-acid ratio has a great effect on the taste of fresh fruits, there was a good positive correlation with consumer preferences [12]. Muscat Hamburg and Red Globe had high SSC/TA allowing them to have excellent tastes. In a word, the five varieties of table grapes had wonderful tastes, of which Muscat Hamburg and Red Globe had the highest sugar-acid ratio and the best taste.
### Table 1  Morphological analysis and physical-chemical indicators.

| Grape Varieties         | Appearance | Wm (g)   | ρ (g/ml) | Cs    | pH    | SSC (°Bx) | TA (g/L) | SSC/TA |
|-------------------------|------------|----------|----------|-------|-------|-----------|----------|--------|
| Manaizi                 |            | 7.24±0.05b | 1.01±0.03a | 1.62±0.01d | 4.04±0.06d | 18.45±0.18c | 3.39±0.12b | 5.44±0.16c |
| Centennial Seedless     |            | 4.50±0.04a | 1.09±0.03b | 1.41±0.01c | 3.66±0.04b | 17.35±0.29b | 4.03±0.06c | 4.31±0.01a |
| Muscat Hamburg          |            | 7.80±0.04c | 1.05±0.02ab | 1.11±0.01a | 4.07±0.03d | 22.20±0.31d | 3.42±0.07b | 6.49±0.04c |
| Red Globe               |            | 10.54±0.05c | 1.02±0.02a | 1.09±0.01a | 3.31±0.02a | 23.20±0.24c | 3.85±0.06c | 6.03±0.05d |
| Rizamat                 |            | 8.25±0.03d | 1.01±0.03a | 1.29±0.02b | 3.78±0.03c | 13.55±0.33a | 2.69±0.12a | 5.04±0.22b |

Notes:  
1. Data are expressed as means ± standard deviation of triplicate samples.  
2. Different lowercase letters between columns represent significant differences between cultivars (p < 0.05).

### 3.2. Composition and content of sugar

The composition and content of sugar also affect the taste of table grapes greatly. Three sugars were identified in grape pulp, including glucose, fructose and sucrose (Figure 1). The total sugar was sorted from high to low: Red Globe > Muscat Hamburg > Manaizi > Centennial Seedless > Rizamat. Among these five varieties of grape pulp, glucose and fructose accounted for 46.53-48.82% and 49.35-51.49%.
of the total sugar, respectively. Their contents were 69.25-92.35 mg/g FW and 73.13-102.21 mg/g FW, respectively, constituting the main sugar in the grape pulp. Sucrose accounted for a low proportion of the total sugar content, which was only 1.82-1.98%. The total sugar content ranged from 145.02 to 198.49 mg/g FW.

The composition and content of sugar are important factors determining the quality of fruits [13-15]. Sugar in grapes is mainly accumulated in the form of glucose and fructose [6], during harvest, fructose is slightly higher than glucose [16], which is consistent with the results obtained in this study. At the same time, the content of sucrose in grape pulp was relatively low in this study because most of the sucrose was hydrolyzed during the transportation from grape leaves to fruits, which was converted into the reducing sugar, resulting in the low content of sucrose in grape berries [17] less than 4% of the total sugar and mainly concentrated in the vascular bundle tissue area [18], which was also consistent with the results obtained by Tissues et al [16].

The sweetness of grapes has much to do with the type and composition ratio of sugar components. Different sugar components have different contributions to sweetness. The sweetness of fructose, sucrose and glucose were 1.75, 1.00, and 0.75 [19], respectively. Therefore, grape varieties with a higher content of fructose had a higher sweetness. Meanwhile, the ratio of glucose to fructose + sucrose once was defined as the α ratio, which was used as an indicator to evaluate the sugar composition of grapes [20]; table grapes whose α < 1 were sweeter. To sum up, among the five varieties of grapes in this study, the main factors affecting the sweetness were fructose and glucose whose α was less than 1. They were sweeter grape varieties. Red Globe had the highest absolute content of fructose and the highest sweetness, that is why it is favored by consumers who like sweet fruits.

3.3. Composition and content of organic acid

The organic acid is also an important factor determining the taste of table grapes. The total content of organic acids was sorted from high to low: Centennial Seedless > Red Globe > Muscat Hamburg > Manaizi > Rizamat (Figure 2). The content of tartaric acid was the highest, accounting for 55.72-60.07% of the total organic acid content. The content of Malic acid was the second highest, accounting for 28.54-39.52% of the total organic acid. Tartaric acid and malic acid held a dominant position in organic acids in grape pulp, which is also consistent with previous research [21]. In addition, In this study, the contents
of ascorbic acid, citric acid and succinic acid were all relatively low, accounting for less than 6% of the total organic acid content. No succinic acid was detected in Manaizi, but ascorbic acid and citric acid were both detected. The content of ascorbic acid in Centennial Seedless was significantly higher than that of other grape varieties. Ascorbic acid has a strong antioxidant capacity and citric acid has a great protective effect on the myocardium \[22\].

Similar to the effect of sugar on the sweetness of fruits, the absolute content and proportion of each organic acid component also result in differences in acidity \[23\]. Different organic acids have various acidity intensities. Studies have shown that the comparison of acidity was: tartaric acid > malic acid > citric acid \[24\]. In this study, the ratio of tartaric acid, malic acid, citric acid and succinic acid of the five grapes was about 4: 2: 1: 1, which may determine the acidity characteristics of grapes. The total contents of organic acid, malic acid and tartaric acid of Centennial Seedless were the highest among these five varieties of grapes, namely, the highest acidity.

### 3.4. Composition and content of volatile compounds

A total of 87 kinds of volatile compounds were identified in these 5 varieties of table grapes (Table 2). The Muscat Hamburg Grapes had the most varieties and the highest contents.

| NO. | Volatiles | Content (μg/kg FW) | Red Globe | Rizamat | Manaizi | Muscat Hamburg | Centennial Seedless | RI |
|-----|-----------|--------------------|-----------|---------|---------|----------------|---------------------|----|
| 1   | Ethanol   | 179.82±2.07 c      | 670.70±3.52 c | 57.33±0.98 b | 191.91±0.93 d | 62.29±0.52 b | 932                |
| 2   | 2-Hexyn-1-ol | 5.34±0.10 a          | -         | 13.74±0.41 b | 25.28±0.32 d | 19.30±0.16 c | 1207               |
| 3   | 3-Methyl-1-butanol | 19.95±0.38 c         | 11.00±0.13 b | 5.61±0.12 a | 44.36±0.34 d | -          | 1209               |
| 4   | Pentanol  | 28.34±0.17 a        | 117.73±0.99 b | 139.47±0.97 c | -         | -          | 1242               |
| 5   | 1-Bromo-2-propanol | -                 | -         | 10.35±0.27 a | -         | -          | 1159               |
| 6   | 2-Nonyl-1-ol | 5.57±0.21 a          | -         | -         | -         | -          | 1306               |
| 7   | Hexanol   | 305.01±2.28 c       | 688.60±0.91 c | 157.21±0.97 b | 355.89±0.73 d | 185.66±0.59 b | 1355               |
| 8   | trans-3-Hexen-1-ol | 11.12±0.33 a          | 39.71±0.66 c | 18.19±0.40 b | 73.10±0.52 d | -          | 1382               |
| 9   | trans-2-Hexen-1-ol | 438.93±1.56 a         | 378.25±3.02 d | 39.03±1.00 e | 146.56±1.10 b | 166.00±1.47 c | 1405               |
| 10  | 2,2,6-Trimethyl-6-vinyltetrahydro-2h-pyran-3-ol | - | - | - | 121.26±0.86 b | 36.84±0.77 b | 1444               |
| 11  | Sulcatol  | -                  | 90.71±0.18 a | 106.18±0.89 b | 1159               |
| 12  | trans-2-Octenol | 9.64±0.23 a          | 38.41±1.01 d | 52.21±0.65 c | 28.39±0.28 b | 15.79±0.19 b | 1614               |
| 13  | 2-Ethylhexanol | 39.11±0.46 a          | 23.85±0.30 c | 29.93±0.44 b | 18.12±0.28 b | 5.99±0.16 a | 1491               |
| 14  | (R)-3-Ethyl-4-methylpentan-1-ol | - | 35.75±0.49 b | - | 167.37±0.38 c | 16.10±0.55 a | 1509               |
| 15  | (2Z)-2-Hepten-1-ol | - | 50.03±0.66 a | - | - | 1521               |
| 16  | Octan-1-ol | 37.10±0.50 c        | 51.65±0.84 d | 52.50±1.20 d | 24.44±0.37 b | 11.62±0.22 b | 1557               |
| 17  | 1-Octadecanol | 3.00±0.10 a         | 11.48±0.30 c | 9.40±0.27 b | -         | 11.87±0.13 c | 1596               |
| 18  | 2,6-Dimethylcyclo-3,7-diene-2,6-diol | - | - | - | 23.33±0.28 b | 223.26±2.18 b | 1612               |
|   | Chemical Name                      | Value   |   | Value   |   | Value   |   | Value   |   | Value   |   | Value   |   |
|---|----------------------------------|---------|---|---------|---|---------|---|---------|---|---------|---|---------|---|
| 19| trans-2-Octenol                  | 10.80±0.24<sup>b</sup> | 31.85±0.45<sup>c</sup> | 35.99±0.35<sup>c</sup> | 10.58±0.28<sup>b</sup> | - | 1806    |
| 20| 2,4-Decadien-1-ol                | 16.97±0.29<sup>b</sup> | 13.55±0.15<sup>a</sup> | - | - | - | 1642    |
| 21| 1-Nonanol                        | 29.15±0.39<sup>d</sup> | 32.06±0.52<sup>c</sup> | 12.56±0.35<sup>c</sup> | 11.17±0.18<sup>b</sup> | 6.45±0.29<sup>a</sup> | 1660 |
| 22| 2,2,6-Trimethyl-6-vinyltetrahydro-2H-pyran-3-ol | - | - | - | 14.81±0.12<sup>a</sup> | 249.03±2.65<sup>b</sup> | 1760 |
| 23| Benzyl alcohol                   | - | 15.34±0.35<sup>b</sup> | - | 19.96±0.19<sup>c</sup> | 11.34±0.30<sup>b</sup> | 1870 |
| 24| Phenylethyl alcohol              | - | 35.88±0.53<sup>c</sup> | 20.88±0.35<sup>d</sup> | 68.39±0.22<sup>d</sup> | 15.65±0.35<sup>b</sup> | 1907 |
|   | **Aldehydes**                    |         |   |         |   |         |   |         |   |         |   |         |   |
| 25| Acetaldehyde                     | 136.53±0.64<sup>e</sup> | 104.61±0.99<sup>c</sup> | 59.85±1.36<sup>b</sup> | 124.58±0.90<sup>d</sup> | 6.73±0.16<sup>a</sup> | 702  |
| 26| Hexanal                          | 449.78±0.90<sup>c</sup> | 122.06±0.92<sup>d</sup> | 699.78±7.38<sup>e</sup> | 1430.99±1.89<sup>c</sup> | 311.26±3.14<sup>b</sup> | 1083 |
| 27| 3-Hexenal                        | 23.88±0.36<sup>b</sup> | - | - | 34.37±0.64<sup>a</sup> | 19.05±0.39<sup>a</sup> | 1146 |
| 28| trans-2-Hexenal                  | 1138.08±0.83<sup>a</sup> | 1265.33±1.11<sup>a</sup> | 2527.37±10.6<sup>d</sup> | 3724.72±8.35<sup>e</sup> | 2388.02±2.56<sup>c</sup> | 1216 |
| 29| trans,trans-2,4-Nonadienal       | 12.01±0.27<sup>b</sup> | - | - | - | - | 1255 |
| 30| Octanal                          | 85.63±0.98<sup>c</sup> | 43.85±0.78<sup>b</sup> | 59.46±0.99<sup>d</sup> | 56.08±0.84<sup>e</sup> | 30.63±0.30<sup>c</sup> | 1289 |
| 31| trans-2-Heptenal                 | 91.85±0.73<sup>b</sup> | 157.42±1.41<sup>d</sup> | 286.18±2.22<sup>e</sup> | 111.68±2.14<sup>b</sup> | 84.32±0.61<sup>c</sup> | 1322 |
| 32| Nonanal                          | 187.71±2.20<sup>d</sup> | 142.63±0.61<sup>b</sup> | 199.48±2.14<sup>c</sup> | 146.97±0.99<sup>c</sup> | 70.95±0.62<sup>a</sup> | 1391 |
| 33| trans,trans-2,4-Heptadienal      | 7.43±0.13<sup>a</sup> | 15.49±0.47<sup>d</sup> | 18.14±0.32<sup>c</sup> | 12.29±0.31<sup>b</sup> | - | 1495 |
| 34| Decanal                          | 112.73±0.88<sup>d</sup> | 83.05±1.25<sup>a</sup> | 47.16±0.40<sup>b</sup> | 155.90±1.63<sup>d</sup> | 32.15±0.86<sup>c</sup> | 1498 |
| 35| Benzaldehyde                     | 5.97±0.15<sup>b</sup> | - | 16.57±0.36<sup>b</sup> | - | - | 1507 |
| 36| Non-2-enal                       | 32.99±0.38<sup>d</sup> | 19.55±0.46<sup>b</sup> | 23.96±0.30<sup>d</sup> | 17.20±0.29<sup>c</sup> | 23.08±0.33<sup>d</sup> | 1534 |
| 37| Octodecanal                      | 4.27±0.15<sup>c</sup> | - | - | - | - | 1555 |
| 38| 2-trans,6-trans-Nonadienal       | 21.82±0.23<sup>a</sup> | 11.67±0.31<sup>b</sup> | 21.16±0.35<sup>d</sup> | 8.73±0.18<sup>a</sup> | 19.40±0.19<sup>c</sup> | 1584 |
| 39| Undecanal                        | 2.90±0.08<sup>b</sup> | - | - | - | - | 1602 |
| 40| Phenylacetaldehyde               | 6.33±0.12<sup>c</sup> | 10.08±0.27<sup>b</sup> | 5.72±0.19<sup>a</sup> | 146.43±1.67<sup>d</sup> | 16.46±0.23<sup>c</sup> | 1640 |
| 41| 2-Undecenal                      | 19.02±0.22<sup>b</sup> | 48.45±1.11<sup>c</sup> | 109.71±0.98<sup>d</sup> | 9.37±0.19<sup>c</sup> | - | 1758 |
|   | **ketones**                      |         |   |         |   |         |   |         |   |         |   |         |   |
| 42| 1-Octen-3-one                    | 30.40±0.41<sup>b</sup> | 46.20±0.73<sup>d</sup> | 66.88±0.87<sup>e</sup> | 23.39±0.41<sup>a</sup> | 39.40±0.70<sup>b</sup> | 1300 |
| 43| 2,3-Octandione                   | 17.98±0.26<sup>b</sup> | 13.12±0.15<sup>d</sup> | - | - | - | 1317 |
| 44| 6-Methylhept-5-en-2-one          | 71.51±0.59<sup>b</sup> | 96.28±0.75<sup>a</sup> | 95.89±1.52<sup>a</sup> | 153.60±2.38<sup>b</sup> | 153.04±1.14<sup>b</sup> | 1338 |
| 45| Damascone                        | 15.62±0.18<sup>a</sup> | 86.44±0.75<sup>b</sup> | 7.45±0.12<sup>a</sup> | - | - | 1801 |
| 46| Geranylacetone                   | 32.44±0.59<sup>a</sup> | - | - | - | - | 1836 |
|   | **acids**                        |         |   |         |   |         |   |         |   |         |   |         |   |
| 47| Acetic acid                      | 119.27±1.10<sup>d</sup> | 183.72±1.47<sup>d</sup> | 212.62±3.35<sup>c</sup> | 107.59±0.91<sup>b</sup> | 57.97±1.17<sup>c</sup> | 1450 |
| 48| 1-Hexanoic acid                  | 17.28±0.27<sup>b</sup> | - | 27.78±0.40<sup>b</sup> | - | - | 1516 |
| 49| trans-2-Hexenoic acid            | 5.36±0.17<sup>b</sup> | - | - | 13.37±0.37<sup>e</sup> | 10.79±0.11<sup>b</sup> | 1980 |
|   | Component                  | Amount                  | Amount                  | Amount                  | Amount                  | Amount                  |
|---|----------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| 50| Linoleic acid              | 5.70±0.16<sup>a</sup>  | 5.50±0.16<sup>a</sup>  | -                       | 254.99±5.95<sup>c</sup> | 64.65±1.32<sup>b</sup> |
| 51| Undecanoic acid            | 9.92±0.25<sup>a</sup>  | -                       | 25.45±1.27<sup>b</sup> | -                       | 29.31<sup>b</sup>      |
|   | **Esters**                 |                         |                         |                         |                         |                         |
| 52| Ethyl acetate              | 68.70±0.99<sup>a</sup> | 1550.91±13.0<sup>b</sup> | -                       | 63.60±1.27<sup>a</sup>  | 888                     |
| 53| Ethyl butyrate             | 22.69±0.38<sup>b</sup> | 98.28±1.09<sup>c</sup>  | 22.20±0.46<sup>b</sup> | 10.41±0.15<sup>a</sup>  | 1042                    |
| 54| Geranyl propionate         | -                       | -                       | 9.76±0.16<sup>a</sup>  | -                       | 1152                    |
| 55| Ethyl hexanoate            | -                       | 29.06±0.35<sup>a</sup>  | -                       | -                       | 1212                    |
| 56| Ethynyl hexanoate          | -                       | 43.81±1.17<sup>c</sup>  | 22.32±0.50<sup>b</sup> | 11.42±0.14<sup>a</sup>  | 1335                    |
| 57| Ethyl benzoate             | -                       | 18.21±0.16<sup>a</sup>  | -                       | -                       | 1675                    |
| 58| Linalyl Propionate         | -                       | -                       | 55.71±1.44<sup>a</sup> | 65.86±0.68<sup>b</sup>  | 1697                    |
| 59| Methyl salicylate          | -                       | 34.45±0.10<sup>b</sup>  | -                       | -                       | 1762                    |
| 60| Citronellol acetate        | 4.82±0.15<sup>a</sup>  | -                       | 7.03±0.12<sup>c</sup>  | 180.92±3.43<sup>a</sup> | 39.33±0.70<sup>b</sup> |
|   | **Terpenes**               |                         |                         |                         |                         |                         |
| 61| β-Myrcene                  | -                       | -                       | -                       | 104.18±1.97<sup>b</sup> | 1161                    |
| 62| Limonene                   | -                       | -                       | -                       | 10.29±0.22<sup>a</sup>  | 1622                    |
| 63| trans-β-Ocimene            | -                       | -                       | 29.65±0.53<sup>b</sup> | 49.99±0.87<sup>a</sup>  | 1250                    |
| 64| α-Ocimene                  | -                       | -                       | 112.72±1.55<sup>b</sup> | 85.12±1.90<sup>a</sup>  | 1235                    |
| 65| α-Copaene                  | -                       | 26.85±0.23<sup>a</sup>  | 168.59±1.47<sup>b</sup> | -                       | 1483                    |
| 66| γ-Terpinene                | -                       | 23.73±0.43<sup>a</sup>  | -                       | -                       | 1691                    |
| 67| α-Phellandrene             | -                       | 48.49±0.45<sup>b</sup>  | 50.01±0.48<sup>b</sup> | -                       | 1706                    |
| 68| α-Muurolone                | -                       | 6.61±0.18<sup>a</sup>   | -                       | -                       | 1721                    |
| 69| cis-Calamene               | -                       | 12.93±0.37<sup>b</sup>  | -                       | -                       | 1826                    |
| 70| Citronellol                | 9.82±0.29<sup>a</sup>  | 19.51±0.20<sup>b</sup>  | 24.62±0.42<sup>b</sup> | 26.77±0.23<sup>d</sup> | 31.41±0.28<sup>c</sup> |
| 71| Phytol                     | 9.26±0.28<sup>a</sup>  | -                       | 102.50±1.69<sup>b</sup> | -                       | 1502                    |
| 72| Linalool                   | -                       | -                       | 3367.94±3.23<sup>a</sup> | -                       | 1547                    |
| 73| (-)-Terpinen-4-ol          | -                       | 20.83±0.41<sup>b</sup>  | -                       | 18.73±0.12<sup>a</sup>  | 1581                    |
| 74| α-Terpineol                | 8.35±0.13<sup>b</sup>  | -                       | 7.05±0.23<sup>a</sup>   | -                       | 1712                    |
| 75| Nerol                      | -                       | -                       | 528.14±2.30<sup>a</sup> | 601.44±7.53<sup>b</sup> | 1797                    |
| 76| Geraniol                   | -                       | -                       | 1407.86±4.13<sup>a</sup> | 2554.20±23.1<sup>b</sup> | 1847                    |
| 77| Perilla alcohol            | -                       | -                       | -                       | 12.75±0.25<sup>a</sup>  | 2016                    |
| 78| Citral                     | -                       | -                       | -                       | 99.68±1.76<sup>a</sup>  | 130.51±1.17<sup>b</sup> |
|   | **Other**                  |                         |                         |                         |                         |                         |
| 79| (3R,6S)-2,2,6-Trimethyl-6-vinyl-tetrahydro-pyran-3-ol | - | - | 29.53±0.76<sup>a</sup> | - | 1739 |
| 80| 1,2,3-Trimethylbenzene      | 4.91±0.10<sup>a</sup>  | -                       | -                       | -                       | 1665                    |
| 81| Olivetol                   | -                       | 8.31±0.16<sup>a</sup>   | -                       | -                       | 2216                    |
82 2,4-Di-t-butylphenol 2.56±0.07a 9.36±0.21c 3.23±0.05b - 3.36±0.07b 2318
83 4-Nitrophthalamide 5.47±0.16a - 10.65±0.11c 8.47±0.22b - 1528
84 (-)-Rose oxide - - - - - - 85 8-Hexyl-8-pentyldodecane - - 13.93±0.51a - - 1065
86 trans-3,4-Dimethyl-2-pentene - - 25.31±0.25a - - 1092
87 3-Chloro-1-methylcyclohex-1-ene - - - - 9.69±0.24a 1661
Total 3940.82 6544.72 5672.24 14105.64 8244.16

Notes: 1 “-“ represents not detectable;
2 Data are expressed as means ± standard deviation of triplicate samples;
3 Different lowercase letters between rows represent significant differences between cultivars (p < 0.05).

Aldehydes (30.93–71.83%) were the main volatile component in all grape pulp. In addition, the Alcohols (28.92% and 34.32%) of Red Globe and Rizamat were significantly higher than that of other varieties, the esters (26.45%) of Rizamat were significantly higher than that of other varieties, and the terpenes (40.25% and 44.19%) of Muscat Hamburg and Centennial Seedless were significantly higher than that of other varieties. Among aldehydes, trans-2-hexenal was the main volatile compound in five varieties of grape pulp, accounting for 19.33-44.56% of the total volatile components. Many existing studies on table grapes have shown that C6 compounds have higher concentrations in the grape pulp while trans-2-hexenal is the main C6 compound [25]. In addition, acetaldehyde, hexanal, octanal, trans-2-heptenal, nonanal, decanal, non-2-enal, 2-trans, 6-trans-nonadien and phenylacetalddehyde were detected in each group. trans, trans-2,4-nonadien, octadecanal and undecanal were detected only in Red Globe. Alcohols are the most abundant types with ethanol, hexanol and trans-2-hexen-1-ol as the main alcohols. Similar findings have been shown in previous studies [26]. (2Z)-2-hepten-1-ol was detected only in Rizamat, and 1-bromo-2-propanol was detected only in Muscat Hamburg. Many existing studies have shown that esters are the main component of grape pulp [1], of which Ethyl acetate is the main ester. In this study, only Rizamat had similar results. Ethyl acetate was detected only in Red Globe, Rizamat and Muscat Hamburg, while ethyl hexanoate, ethyl benzoate, and methyl salicylate were only detected only in Rizamat. Among the acids, Acetic acid was the main type, which was detected in each group. Linoelaidic acid was detected in other grapes excluding Manaizi. 1-Hexanoic acid only existed in Red Globe and Manaizi, while trans-2-hexenoic acid only existed in Red Globe, Muscat Hamburg and Centennial Seedless. The content of ketones was relatively low with 6-methylhept-5-en-2-one as the main type. 1-octen-3-one and 6-methylhept-5-en-2-one were detected in each group, and 2,3-octandione was detected in both Red Globe and Rizamat. Damacone was detected in Red Globe, Rizamat, and Manaizi, while geranylacetone was detected only in Red Globe. Among these five varieties of grape pulp, the types and contents of terpenes had great differences. Muscat Hamburg had the highest content of terpenes with Linalool as the main type. Linalool only existed in Muscat Hamburg. β-Myrcene, trans-β-ocimene, α-ocimene, nerol, geraniol and citral were detected only in Muscat Hamburg and Centennial Seedless. α-Copaene and α-phellandrene were detected only in Rizamat and Manaizi. γ-Terpinene, α-muurolene and cis-calamene were detected only in Manaizi. Limonene and perilla alcohol were detected only in Centennial Seedless. Phytol and α-terpineol were detected only in Red Globe and Manaizi. Only citronellol was detected in all grapes. Terpene alcohols were vital volatile compounds in grapes. Barbera et al [27] believed that the main aroma compound of Muscat Hamburg were linalool and geraniol with nerol and citronellol as the supporting compounds.

3.5. Analysis of active odorants
Compounds with OAVs> 1 can be considered as active odorantsl [28]. To further analyze the different contributions made by volatile compounds to samples, volatile compounds (OAVs > 1) in each sample...
were selected for the principal component analysis of their OAVs and five varieties of grapes (Table 3 and Figure 3).

Table 3 Odour descriptors, odour thresholds (ppb in water) of the studied compounds

| NO. | Volatiles       | OAVs                      | OT (μg/L) [1, 29-32] | OD [1,30, 33, 34] |
|-----|----------------|---------------------------|----------------------|------------------|
| 1   | Hexanol         | Red Globe: 0.61           | 1.38                 | 500              | flowery         |
|     |                 | Rizomat: 0.31             | 0.71                 |                  |
|     |                 | Manaizi: 0.31             | 0.71                 |                  |
|     |                 | Muscat Hamburg: 0.37      | 0.37                 |                  |
| 2   | trans-2-Hexen-1-ol | 4.39               | 3.78                 | 100              | green           |
|     |                 | Centennial Seedless: 1.47 | 1.66                 |                  |
| 3   | Linalool        | 0.00                      | 0.00                 | 6                | fruity          |
| 4   | Nerol           | 0.00                      | 0.00                 |                  |
| 5   | Geraniol        | 0.00                      | 0.00                 | 300              | flowery         |
| 6   | (Z)-3-Hexenal   | 95.50                     | 0.00                 | 76.18            | 0.25            |
| 7   | trans-2-Hexenal | 66.95                     | 74.43                | 140.47           | 17              |
| 8   | Nonanal         | 187.71                    | 142.63               | 70.95            | 1               |
| 9   | Phenylacetaldehyde | 1.58                   | 2.52                 | 4.11             | 1               |
| 10  | Citral          | 0.00                      | 0.00                 | 3.12             | 4               |
| 11  | 1-Octen-3-one   | 1899.94                   | 2887.50              | 1462.00          | 0.016           |
| 12  | Damascone       | 312.48                    | 1728.74              | 2462.19          | mushroom        |
| 13  | Ethyl butyrate  | 22.69                     | 98.28                | 10.41            | 1               |
| 14  | Ethyl hexanoate | 0.00                      | 29.06                | 0.00             | 1               |
| 15  | β-Myrcene       | 0.00                      | 0.00                 | 2.89             | 36              |
| 16  | Limonene        | 0.00                      | 0.00                 | 1.03             | 10              |

Notes: OT: Odour threshold; OD: Odour descriptor.

Figure 3 PCA of aroma compounds with OAVs greater than 1 to the first two principal components (HT: Red Globe; LZ: Rizamat; MN: Manaizi; MG: Muscat Hamburg; WH: Centennial Seedless).

The interpretation rates of PC1 and PC2 were 56.7% and 20.2%, respectively. These five varieties of grapes can be clearly divided into three groups. Nerol (flowery), geraniol (flowery), (Z)-3-hexenal (grassy), trans-2-hexenal (grassy), phenylacetaldehyde (flowery), citral (fruity) and β-myrcene (green) had great contributions to the flavors of Centennial Seedless and Muscat Hamburg, hexanol (flowery), trans-2-hexen-1-ol (green), damascone (fruity) and ethyl butyrate (fruity) had great contributions to the flavors of Rizamat, nonanal (fruity) and 1-octen-3-one (mushroom) have great contributions to the
flavors of Manaizi. However, Red Globe has no substances making significant contributions to its flavor, which is jointly affected by multiple volatile compounds.

4. Conclusion
Sugars, organic acids and aroma substances in five varieties of Xinjiang table grape pulp were analyzed in detail in this study. This study provides an essential theoretical basis for the quality evaluation of table grapes.

Acknowledgments
We are grateful for the financial support from the Science and Technology Research Project of the Eighth Division (No. 2020GY07), the Science and Technology Research Project of the Fifth Division (No. 20GY01) and Science and the Technology Research Project of the Xinjiang Production and Construction Corps (No. 2020AB014).

References
[1] Wu Y, Duan S, Zhao L, et al. (2016) Aroma characterization based on aromatic series analysis in table grapes. Scientific reports, 6: 1-16.
[2] Jediyi H, Naamani K, Elkoch A A, et al. (2019) First study on technological maturity and phenols composition during the ripeness of five Vitis vinifera L grape varieties in Morocco. Scientia horticulturae, 246: 390-397.
[3] Eyduran S P, Akin M, Ercisli S, et al. (2015) Sugars, organic acids, and phenolic compounds of ancient grape cultivars (Vitis vinifera L.) from Igdir province of Eastern Turkey. Biological research, 48: 1-2.
[4] Liu H, Wu B, Fan P, et al. (2006) Sugar and acid concentrations in 98 grape cultivars analyzed by principal component analysis. Journal of the Science of Food Agriculture, 86(10): 1526-1536.
[5] Piazzolla F, Pati S, Amodio M, et al. (2016) Effect of harvest time on table grape quality during on-vine storage. Journal of the Science of Food Agriculture, 96(1): 131-139.
[6] Meng J, Xu T, Song C, et al. (2015) Melatonin treatment of pre-veraison grape berries to increase size and synchronicity of berries and modify wine aroma components. Food chemistry, 185: 127-134.
[7] Lichter A, Zutkhyy Y, Sonego L, et al. (2002) Ethanol controls postharvest decay of table grapes. Postharvest Biology, 24: 301-308.
[8] Lima M D S, Da Concei??O Prudêncio Dutra M, Toaldo I M, et al. (2015) Phenolic compounds, organic acids and antioxidant activity of grape juices produced in industrial scale by different processes of maceration. Food Chemistry, 188: 384-392.
[9] Gancedo M C, Luh B. (1986) HPLC analysis of organic acids and sugars in tomato juice. Journal of Food Science, 51: 571-573.
[10] Antalick G, Perello M-C, De Revel G. (2010) Development, validation and application of a specific method for the quantitative determination of wine esters by headspace-solid-phase microextraction-gas chromatography–mass spectrometry. Food Chemistry, 121: 1236-1245.
[11] Bondada B, Harbertson E, Shrestha P, et al. (2017) Temporal extension of ripening beyond its physiological limits imposes physical and osmotic challenges perturbing metabolism in grape (Vitis vinifera L.) berries. Scientia Horticulturae, 219: 135-143.
[12] Xu C, Yagiz Y, Zhao Lu, et al. (2017) Fruit quality, nutraceutical and antimicrobial properties of 58 muscadine grape varieties (Vitis rotundifolia Michx.) grown in United States. Food chemistry, 215: 149-156.
[13] M Massot C, Génard M, Stevens R, et al. (2010) Fluctuations in sugar content are not determinant in explaining variations in vitamin C in tomato fruit. Plant Physiology, 48: 751-757.
[14] Silva G M C, Silva W B, Medeiros D B, et al. (2017) The chitosan affects severely the carbon metabolism in mango (Mangifera indica L. cv. Palmer) fruit during storage. Food chemistry,
237: 372-378.

[15] Nicoletto C, Tosini F, Sambo P. (2013) Effect of grafting and ripening conditions on some qualitative traits of ‘Cuore di bue’tomato fruits. Journal of the Science of Food Agriculture, 93: 1397-1403.

[16] Davies C. (1996) Sugar accumulation in grape berries. Cloning of two putative vacuolar invertase cDNAs and their expression in grapevine tissues. Plant Physiology, 111(1): 275-283.

[17] Xie Z, Li B, Forney C F, et al. (2009) Changes in sugar content and relative enzyme activity in grape berry in response to root restriction. Scientia horticulturae, 123: 39-45.

[18] ZHANG Xiaoyan, WANG Xiuling, WANG Xiaofang, et al. A shift of phloem unloading from symplasmic to apoplasmic pathway is involved in developmental onset of ripening in grape berry[J]. Plant physiology, 2006, 142(1): 220-232.

[19] Zheng L, Nie J, Yan Z. (2015) Advances in research on sugars, organic acids and their effects on taste of fruits. Journal of Fruit Science. 32(02): 304-312.

[20] Coelho E, Da S, Miskinis G, et al. (2018) Simultaneous analysis of sugars and organic acids in wine and grape juices by HPLC: Method validation and characterization of products from northeast Brazil[J]. Journal of Food Composition Analysis, 66: 160-167.

[21] Soyer Y, Koca N, Karadeniz F. (2003) Organic acid profile of Turkish white grapes and grape juices. Journal of food composition analysis, 16: 629-636.

[22] Tang X, Liu J, Dong W, et al. (2013) The cardioprotective effects of citric acid and L-malic acid on myocardial ischemia/reperfusion injury. Evidence-Based Complementary Alternative Medicine, 2013.

[23] Zheng H, Zhang Q, Quan J, et al. (2016) Determination of sugars, organic acids, aroma components, and carotenoids in grapefruit pulps. Food chemistry, 205: 112-121.

[24] Xia Y. (2004) Food chemistry. China Agriculture Press, Beijing.

[25] WU Yusen, ZHANG Wenwen, DUAN Shuyan, et al. In-depth aroma and sensory profiling of unfamiliar table-grape cultivars[J]. 2018, 23(7): 1703.

[26] Wu Y, Zhang W, Duan S, et al. (2018) In-depth aroma and sensory profiling of unfamiliar table-grape cultivars. Molecules, 23: 1703.

[27] Barbera D, Avellone G, Filizzola F, et al. (2013) Determination of terpene alcohols in Sicilian Muscat wines by HS-SPME-GC-MS. Natural product research, 27: 541-547.

[28] Fenoll J, Manso A, Hellin P, et al. (2009) Changes in the aromatic composition of the Vitis vinifera grape Muscat Hamburg during ripening. Food Chemistry, 114: 420-428.

[29] Buttery R G, Teranishi R, Ling L C, et al. (1990) Quantitative and sensory studies on tomato paste volatiles. Journal of Agricultural Food Chemistry, 38: 336-340.

[30] Czerny M, Christlbauer M, Christlbauer M, et al. (2008) Re-investigation on odour thresholds of key food aroma compounds and development of an aroma language based on odour qualities of defined aqueous odorant solutions. European Food Research Technology, 228: 265-273.

[31] Ferreira V, Lopez R, Cacho J F. (2000) Quantitative determination of the odors of young red wines from different grape varieties. Journal of the Science of Food Agriculture, 80: 1659-1667.

[32] Yuan F, Qian M C. (2016) Aroma potential in early-and late-maturity Pinot noir grapes evaluated by aroma extract dilution analysis. Journal of agricultural food chemistry, 64: 443-450.

[33] García-Carpintero E G, Sánchez-Palomo E, Gómez Gallego M A, et al. (2011) Effect of cofermentation of grape varieties on aroma profiles of La Mancha red wines. Journal of food science, 76: 1169-1180.

[34] Genovese A, Lamorte S A, Gambuti A, et al. (2013) Aroma of Aglianico and Uva di Troia grapes by aromatic series. Food research international, 53: 15-23.