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Changes in the Volatile Compounds and Chemical and Physical Properties of Kuerle Fragrant Pear (*Pyrus serotina* Reld) during Storage

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Volatiles from stored Kuerle fragrant pears (*Pyrus serotina* Reld) were studied using high-resolution gas chromatography and the solid-phase microextraction (SPME) method of gas chromatography/ mass spectrometry (GC/MS). The dominant components were hexanal, ethyl hexanoate, ethyl butanoate, ethyl acetate, hexyl acetate, ethanol, α -farnesene, butyl acetate, and ethyl (*E*,*Z*)-2,4-decadienoate. By using GC–olfactometry, it demonstrated that the volatile compounds from SPME were responsible for the aroma of the Kuerle fragrant pear. The levels of sugars, organic acids, and phenolic acids in Kuerle fragrant pears were investigated using high-performance liquid chromatography (HPLC). Fructose was the dominant sugar, followed by glucose and sucrose. With increasing storage time, sucrose levels decreased; however, changes in fructose and glucose levels were not remarkable. There was a slight decrease in flesh firmness during storage. The general soluble solids concentration (SSC) declined slightly after 5 months storage. Some aroma-related volatile components increased during storage, while others decreased, especially the esters. The organic acids and phenolic acids also changed. The flavor of the Kuerle fragrant pears was affected by the change of volatile compounds and changes in chemical and physical properties.

KEYWORDS: *Pyrus serotina* Reld; Kuerle fragrant pear; volatile compounds; GC-olfactometry; chemical and physical properties; solid-phase microextraction (SPME)

INTRODUCTION

Xinjiang Kuerle city, in northwest China, is an important fragrant pear producing area. Xinjiang Kuerle fragrant pears belong to super white pears, and have been planted for more than 1300 years. They have long been valued by consumers for their special fragrance, sweetness, juiciness, unique shape, jade green color, and scent. They are exported to many countries, such as Canada, Indonesia, Malaysia, Singapore, Thailand, and Cambodia. The annual output is about 100 000 tons. The exported fragrant pears are normally harvested at minimum soluble solids levels of 12 ° Brix, and the fruits can be stored for nearly 1 year.

Sugar and organic acid contents have a marked influence on the sensory quality of fruit. Phenolic acids and their derivatives are widely distributed in plants and perform a range of essential metabolic functions. The levels of phenolic acids in plants can be affected by the processes of germination, drying, ripening, storage, processing (1), fruit development (2), and maturation (3). They may contribute to the dark color, bitter taste, and

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objectionable flavor of some fruits, leaves, and seeds (1, 4, 5). There is currently little information available on changes in the levels of sugars, acids, and phenolic acids of Kuerle fragrant pear fruit during storage.

Aroma is one of the most important sensory attributes of fruit. Fruit flavor is particularly sensitive to compositional alterations. The volatile compounds that contribute to fruit flavor are produced through metabolic pathways during ripening, harvest, postharvest, and storage, and are influenced by many factors related to species, variety, and technological treatments (6). There is a considerable amount of literature that examines the volatile components of fruits such as apples, oranges, mangos, and berries. There have been many studies on pears. However, most of these are limited to the examination of physiology and nonvolatile chemical constituents. There also have been 20 papers on pear aroma since 1997, for example, changes in the composition of the France pear during maturation (7) and the volatile constituents of the Asian pear (Pyrus serotina Reld) (8). However, there have been few studies on the volatile compounds and the chemical and physical properties of the Kuerle fragrant pear during storage. The objective of this research was to study the changes of sugars, organic acids, phenolic acids, volatile compounds, and other physical and

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chemical properties of Kuerle fragrant pear (*Pyrus serotina* Reld) and to provide basic information on and evaluate the quality of this pear variety during the entire period of storage.

MATERIALS AND METHODS

Chemicals. All chemicals used in the experiment were of analytical or HPLC grade, purchased from Sigma. They were fructose, sucrose, glucose, gallic acid, chlorogenic acid, caffeic acid, epicatechin, *p*-coumaric acid, quercetin, quercitrin, morin, phloretin xyloglucoside, quinic acid, malic acid, shikimic acid, lactic acid, acetic acid, citric acid, fumaric acid, and succinic acid. The authentic standards of volatiles (ethyl acetate, ethyl propionate, ethyl butanoate, butyl acetate, ethyl 2-methylbutanoate, 1-hexanol, ethyl hexanoate, (*Z*)-ethyl 3-hexenoate, (*E*)-ethyl 3-hexenoate, nonanal, ethyl octanoate, octyl acetate, butyl butanoate, ethyl decanoate, and ethyl (*E*,*Z*)-2,4-decadienoate) used as gas chromatography (GC)–olfactometry reference compounds were supplied by T. Hasegawa Co. Ltd., Japan.

Plant Materials. Xinjiang fragrant pears (*Pyrus serotina* Reld) were harvested in the Shayidong horticultural field in Kuerle city, Xinjiang, China, in mid-September 2003. The soluble solids concentration was 12 ° Brix. Fragrant pear fruits were loosely packed inside a conventional modular bulk container with a polyliner and stored at 0 °C and 88–90% relative humidity. The humidity inside the polyliner was approximately 95%. The air was exchanged with fans four times daily to remove ethylene.

Design of Experiments. The volatile compounds of fragrant pear fruits after storage of 1, 2, 3, 4, and 5 months were analyzed. Firmness, soluble solids, sugar content, organic acid content, and phenolic acid content, and volatile compound content were determined during storage.

Measurement of Flesh Firmness. Flesh firmness was measured using a handheld electrometer (Model GY-1, Mudan River, China); 10 fruits were randomly selected from 30 to 40 stored fruits at each storage period of 1, 2, 3, 4, and 5 months. The flesh firmness of each fruit was measured twice, on opposing sides of the fruit equator. The skin was removed using a slicer to a 1 mm cutting depth, prior to the fruit being placed on a hard surface and held firmly during testing (9).

Measurement of Soluble Solids Concentration (SSC). Soluble solids concentration was measured using a manual refractometer (Model ATC-1 E, Brix 0-32%, ATAGO, Japan). Ten fruits were randomly selected from 30 to 40 stored fruits at each storage period of 1, 2, 3, 4, and 5 months. The fruit flesh, excluding core and seeds, was milled into slurry with a juice extractor and centrifuged to remove coarse particles; the resultant pear juice was used for SSC measurement. Each sample was measured in triplicate.

Standard Materials. Standards of sugars, organic acids, and phenolic acids were used to obtain the linear curve. The linearity of the response to an RI and UV detector was tested for each compound with five different concentrations prepared in distilled water, K₂HPO₄ solution, and methanol solution. All correlation coefficients were in the required range. Qualitative and quantitative analyses of the sugars, the organic acids, and the phenolic acids were according to their respective standard material and the linear curve method.

Composition of Sugars. The composition of sugars was determined using the method of Dolenc and Stampar (10) with modifications. Samples were prepared from seven to ten fresh Kuerle fragrant pears after each storage period of 1, 2, 3, 4, and 5 months. Fruit flesh excluding cores and seeds was squeezed into juice using a commercial turmix blender. The juice was pooled and then filtered through filter paper. The fruit juice (5 g) was diluted to 100 mL with bidistilled water and then centrifuged in a refrigerated centrifuge at 3000g for 10 min. The extract was filtered through 0.45 μ m Millipore filters, and a 20 μ L sample was used for current high-performance liquid chromatographic (HPLC) analysis of sugars. The analysis was in triplicate. The HPLC conditions were as follows: column, PRONTOSIL, 120-10-Amino 10.0 μ m, 250 \times 4.6 mm i.d. (KNAUER, Germany); solvent $CH_3CN/H_2O = 85:15$ as mobile phase, at a flow rate of 1.5 mL/min, at 30 °C, equipped with an RI detector (Model K-2301, KNAUER, Germany).

Composition of Organic Acids. Fruits were treated for organic acids determination. Fruit juice (2 g) was diluted to 50 mL with K₂HPO₄•

3H₂O (0.01 M, pH 2.6) and centrifuged in a refrigerated centrifuge at 3000g for 10 min. The extract was filtered through 0.45 μ m Millipore Organic filters, and a 20 μ L sample was used for current HPLC analysis of organic acids. Each sample was measured in triplicate. The HPLC conditions were as follows: column, PRONTOSIL, 120-10-C18 H 10.0 μ m, 250 × 4.6 mm i.d. (KNAUER, Germany); solvent 0.01 M K₂-HPO₄·3H₂O, pH 2.6 as mobile phase, at a flow rate of 0.5 mL/min, at 30 °C, equipped with a UV detector with wavelength set to 210 nm (Model K-2301, KNAUER, Germany).

Composition of Phenolic Acids. Seven to ten Kuerle fragrant pears were selected after 1, 2, 3, 4, and 5 months of storage, and the fruit flesh excluding cores and seeds was pressed into juice. Three times 10 g of pear juice was extracted with ethyl acetate (10 mL the first time, then 5 mL the remaining times). The combined extracts were dried with pure nitrogen each time, and the extracts were removed. The residue was dissolved in methanol (1 mL) and then filtered through a 0.45 μ m organic membrane prior to HPLC analysis. The separation of phenolic compounds was performed on a KNAUER chromatograph equipped with BF-2000 chemstation software, a K-001 pump, and a PRONTOSIL 120-10-C18 (150 \times 4.6 mm i.d.) column, and was operated at the temperature of 30 °C. The mobile phase consisted of 100% (v/v) acetonitrile (eluent A) and 0.1% (v/v) formic acid in water (eluent B). The gradient program was as follows: 2% A + 98% B (0-5 min), 12% A + 88% B (5-25 min), 45% A + 55% B (25-50 min), performed at 280 nm with a flow rate of 1.0 mL/min. The injection volume for all samples was 20 µL. Each sample was measured in triplicate.

Isolation of Volatile Compounds Using Solid-Phase Microextraction (SPME). Seven to ten fruits were washed, and excluding the fruit flesh cores and seeds were pressed into pulp. A 8 g sample was quickly transferred into a 15 mL headspace flask containing 2.2 g of NaCl, in order to minimize the loss of volatile components and avoid browning. The volatiles were sampled by manual headspace solid-phase microextraction at 40 °C while stirring. The fiber (100 μ m PDMS, Supelco) was inserted into the injection port of the GC/MS after 30 min of sampling and then desorbed at 250 °C for 10 min. Each analytical sample was measured in triplicate.

Gas Chromatography/Mass Spectrometry (GC/MS) Condition. A Hewlett-Packard 6890 GC/MS with a flame ionization detector and GC-olfactometric port (J&W Scientific Inc., Germany) was used, with the injector and detector maintained at 250 and 270 °C, respectively. The column dimensions were 0.32 mm i.d. \times 30 m, with 0.5 μ m film thickness (Hewlett-Packard). The carrier gas (He) had a flow rate of 1.0 mL/min. The temperature program was isothermal at 35 °C for 2 min, increase to 250 °C at 4 °C/min, and then hold for 15 min. The analysis was in triplicate.

The identification of compounds was based on comparison of their spectra and relative abundances with the NIST/Wiley Registry of Mass Spectral Data (Hewlett-Packard Co., USA). The identity of a component was confirmed by comparison of the Kováts retention index and mass spectrum with a standard of the corresponding compound (if available). In the absence of a matched index and matched reference spectrum, Kováts retention indices were used for tentative compound identifications and confirmed by fragmentation patterns of tested mass spectra. Calculation of Kováts retention indices (K index) for individual peaks was done by using retention time data from a series C₆-C₁₅ alkane standards. For identification of the dominant esters, such as ethyl acetate, ethyl propionate, ethyl butanoate, butyl acetate, ethyl 2-methylbutanoate, 1-hexanol, ethyl hexanoate, (Z)-ethyl 3-hexenoate, (E)-ethyl 3-hexenoate, nonanal, ethyl octanoate, octyl acetate, butyl butanoate, ethyl decanoate, and ethyl (E,Z)-2,4-decadienoate, the GC/MS data were directly compared with those of authentic compounds.

GC Chromatography–Olfactometry (GC–O). Five olfactometry panelists, trained in GC sniffing and odor recognition, sniffed the humidified effluent of the GC four times each. The intensity of each compound with aroma activity was recorded on a sliding scale from 0 to 15, and the aroma quality was noted. The output of the variable potentiometer was connected to a separate channel in the ChromPerfect software used to gather GC-FID data, and time intensity data were continuously recorded. The method, equipment, and software used are detailed in ref 11. A compound was deemed aroma active if it was

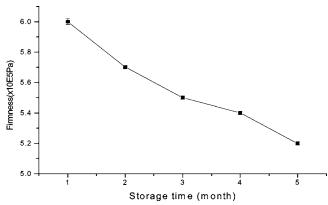


Figure 1. Changes of Kuerle fragrant pear firmness during storage.

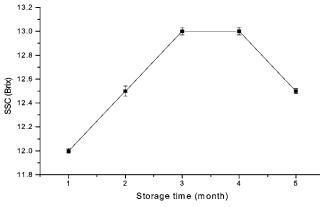


Figure 2. Changes of Kuerle fragrant pear SSC during storage.

detected in at least half of all sniffs (8-16 runs). The intensity of each run was normalized, so the highest intensity had a score of 100. The normalized intensities of all the runs where the compound was detected were then averaged. If the compound was not detected in a run, its value was treated as missing, not zero.

Statistical Analysis. The results were statistically evaluated by oneway analysis of variance (AVOVA). Statistical differences with *P*-values under 0.05 were considered significant. All experiments were replicated three times.

RESULTS AND DISCUSSION

Flesh firmness is a very important physical property of fruit tissue, as it directly affects eating quality and texture. A change in flesh firmness may be due to modification of the chemical structure of the cell wall, for example in ref *12* ascribed the massive breakdown of avocado cell wall to hydrolysis of polysaccharides by hydrolytic enzymes. In contrast, Kuerle fragrant pear firmness decreased very slowly during storage (**Figure 1**). The response of flesh firmness to storage conditions and harvest date was dependent on the growing location.

As shown in **Figure 1**, during Kuerle fragrant pear storage, the firmness can keep to a certain degree, which is not common in other fruits. For example, during kiwi fruit development, the flesh became remarkably soft, so the fruit was soft enough to be damaged during handling and transportation from the field to the market. However, during storage, Kuerle fragrant pear flesh remained hard enough for the fruit to be transported to the market. A few researchers described a similar pattern of Chinese pear (including Kuerle fragrant pear and Yali pear) firmness change; for example, Zhang (13) described a similar pattern of Kuerle fragrant pear firmness change and Ning (14) also described a similar pattern of Yali pear firmness change.

As shown in **Figure 2**, Kuerle fragrant pear SSC developed with fruit ripening, increasing slowly from 1 month after storage

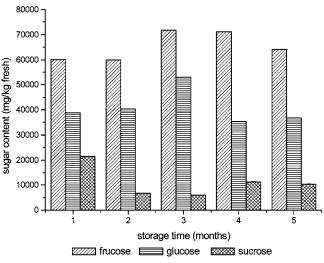


Figure 3. Changes of Kuerle fragrant pear sugars content during storage.

(12 ° Brix) (stage 1) to 3 months after storage (13 ° Brix) (stage 3), stabilizing from stage 3 to stage 4, and then decreasing only slightly. The SSC total change was not remarkable. This suggested that even if Kuerle fragrant pear fruit were stored for half a year, SSC would change only slightly, and the flesh quality could be maintained during the storage period. This was similar to the results of Zhang (13).

The most important sugars were fructose, glucose, and sucrose (**Figure 3**). Fructose and glucose content increased from stage 1 to stage 3, while there was a general decline in sucrose content. This may be ascribed to the hydrolysis of sucrose by sucrase to yield glucose and fructose from stage 1 to stage 3. Sucrose content increased slightly after stage 3, perhaps due to fruit respiration and loss of water during Kuerle fragrant pear storage and decrease in the hydrolysis of starch, as indicated by a concurrent decrease in fructose and glucose content.

There have been numerous studies attributed to increasing levels of fructose, glucose, and sucrose at advanced stages of fruit maturity, such as in an apple variety (var. Glockenapfel) (15). Gao (16) indicated that during a Kuerle fragrant pear storage period there was a close relationship between the sugar change and respiration change. In first storage period, the pear respiration was rising, and the sugar was consumed. However, with the hydrolysis of starch, the individual sugar content of pear dropped slightly. In the middle of the storage period, Kuerle fragrant pear respiration intensity decreased, and consumed little individual sugar. Thus the sugar content can keep to a certain degree. With a long storage time, the pear respiration intensity increased and the total sugar content was reduced. Our results were similar to this.

Quinic acid, malic acid, shikimic acid, lactic acid, acetic acid, citric acid, fumaric acid, and succinic acid were detected in the Kuerle fragrant pear fruit (**Figure 4**). Ackerman and others (15) reported citric acid as the most abundant acid and malic acid as the second most abundant acid determined in an apple variety throughout ripening and storage in a decreasing trend. However, in Kuerle fragrant pear the most important acid was malic acid, followed by citric acid. Malic and citric acid contents increased from stage 1 to stage 3, and then decreased. The reason for this may be attributed to a dilution effect caused by mass increase during the cell growth phase. After storage, increased respiration is also responsible for the decline since malic acid is the principle metabolic substrate together with the sugar. Acetic acid content decreased during storage, possibly due to its function as respiration precursor, or its role in the synthesis of

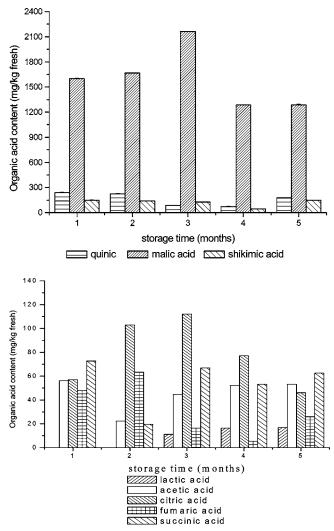


Figure 4. Changes of Kuerle fragrant pear organic acids content during storage.

esters. Lactic acid was not detected in stages 1 and 2, but was detected after stage 2. Our result was similar to that of Zhang (13).

Forty-three compounds were obtained from SPME (**Table 1**). The most important volatile compounds were ethyl hexanoate (12.96%), ethyl butanoate (11.29%), α -farnesene (2.31%), hexanal (17.80%), ethyl acetate (9.69%), and hexyl acetate (2.94%). Isopropyl palmitate was found in Kuerle fragrant pear; it probably originated from Kuerle fragrant pear waxiness in the pear skin or from the SPME extraction course.

Takeoka et al. (8) reported that the following compounds are important contributors to pear aroma: ethyl 2-methylbutanoate, ethyl hexanoate, ethyl butanoate, ethyl 2-methylpropanoate, hexyl acetate, ethyl heptanoate, hexanal, ethyl pentanoate, and ethyl propanoate. Shiota and others (7) reported that the principal volatile components in the La France Pear were ethyl, propyl, butyl, and hexyl acetates. In our research, gas chromatography olfactometry (sniffing) was used to determine whether the compounds from the SPME method have significant contributions to the aroma of Kuerle fragrant pear. From the odor description (**Table 1**), we can conclude that compounds from SPME could be present in the aroma of Kuerle fragrant pear, such as ethyl acetate, ethyl propionate, ethyl butanoate, ethyl-2-methylbutanoate, ethyl hexanoate, hexyl acetate, ethyl octanoate, octyl acetate, and ethyl (*E*,*Z*)-2,4-decadienoate; this is

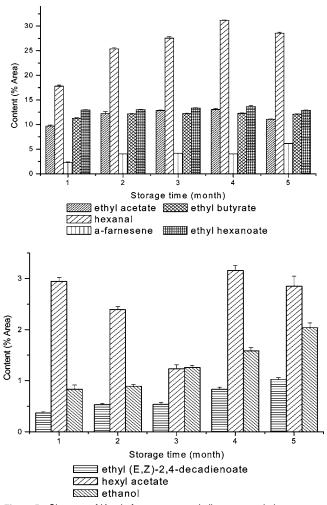


Figure 5. Changes of Kuerle fragrant pear volatiles content during storage.

similar to the previous work on the aroma components of Asian pear and European pears (8).

As shown in **Figure 5**, ethyl acetate, ethyl butyrate, ethyl hexanoate, hexyl acetate, and ethanol contents increased from stage 1 to stage 4, and then decreased. Hexanal and α -farnesene contents decreased, while ethyl (E,Z)-2,4-decadienoate changed slightly during this period. Zhang (13) found that the volatiles of climacteric fruit accumulated after the respiratory climacteric, but decreased during storage. Kuerle fragrant pear fruit follows this pattern. Hexanal content concentrated in skin of the immature Kuerle fragrant pear fruit after harvest, but decreased during storage as fruit matured. Hexyl acetate and ethyl (E,Z)-2,4-decadienoate are important contributors to the flavor composition of Bartlett pear (17), and these compounds were detected in Kuerle fragrant pear fruit; however, further research is required to determine whether ethyl (E,Z)-2,4-decadienoate is also the special flavor compound of Kuerle fragrant pear. α-Farnesene was a major compound in Kuerle fragrant pear. Shiota and others (18) suggested that α -farnesene could be responsible for the "fresh green" odor of the La France pear fruit, since it was the main volatile compound of Japanese pear peel. The role of α -farnesene in Kuerle fragrant pear fruit requires further study.

In general, European pears are ripened by storage after picking. During storage, the fruit develops a soft flesh and a strong pleasant aroma and becomes suitable for eating. The changes in the composition of volatile components during maturation were also investigated by Shiota and others (18). The results from this showed that the concentration of the esters,

Table 1. Principal Volatile Compounds of Kuerle Fragrant Pear Identified from SPME/GC/MS

| compound | content (% area) | retention index ^a | identification ^b | odor quality (ref) | odor threshold ^c (ref) | |
|------------------------------------|------------------|------------------------------|-----------------------------|---|-----------------------------------|--|
| ethanol | 1.83 | 396 | A, C | alcohol (24) | | |
| ethyl acetate | 9.69 | 600 | В | fruity (22) | | |
| acetic acid | 0.20 | 610 | A | sour (<i>23</i>) | 32 300 (25) | |
| ethyl propionate | 0.17 | 681 | В | banana, apple (24) | 10 (<i>8</i>) | |
| ethyl 2-methylpropionate | 0.07 | 738 | A, C | sweet, fruity, apple, banana (7) | 0.1 (26) | |
| hexanal | 17.80 | 776 | В | green, fruity (17) | 5 (26) | |
| ethyl butanoate | 11.29 | 789 | В | strawberry, apple, banana (24) | 1 (27) | |
| butyl acetate | 1.68 | 796 | В | fruity, pear (24) | 66 (27) | |
| ethyl 2-methylbutanoate | 0.60 | 842 | В | green, apple, floral (24) | | |
| 1-hexanol | 0.80 | 851 | В | grass, fruity (24) | 2500 (<i>28</i>) | |
| propyl butyrate | 0.01 | 879 | A, C | pineapple (24) | | |
| ethyl pentanoate | 0.22 | 881 | A, C | apple (24) | 5 (28) | |
| ethyl tiglate | 0.11 | 923 | A, C | fruity (24) | 65 (<i>8</i>) | |
| butyl butanoate | 0.02 | 947 | С | pear, pineapple (7, 24) | | |
| ethyl hexanoate | 12.96 | 975 | В | fruity, green, apple, brandy, winelike (20) | 1 (<i>8</i>) | |
| (Z)-ethyl 3-hexenoate | 0.21 | 981 | A, B | fatty, citruslike (24) | | |
| (E)-ethyl 3-hexenoate | 0.27 | 982 | A, B | | | |
| hexyl acetate | 2.94 | 984 | B | apple, pear, floral (24) | 2 (26) | |
| ethyl 2-hexenoate | 0.40 | 1020 | В | green (24) | | |
| 1-octanol | 0.08 | 1053 | A, C | 5 () | | |
| ethyl heptanoate | 0.11 | 1082 | A, C | fruity (24) | 2.2 (28) | |
| ethyl 3-(methylthio)propionate | 0.24 | 1084 | A, C | | () | |
| nonanal | 0.15 | 1085 | B | fatty (24) | | |
| ethyl benzoate | 0.10 | 1143 | A, C | fruity (24) | | |
| ethyl 4-octenoate | 0.03 | 1169 | A, C | | | |
| ethyl octanoate | 0.39 | 1180 | B | floral (24) | 92 (<i>8</i>) | |
| decanal | 0.03 | 1192 | A, C | | | |
| octyl acetate | 0.07 | 1194 | В | pear, fruity (24) | 12 (<i>8</i>) | |
| ethyl 2-phenylacetate | 0.01 | 1221 | A, C | floral (24) | | |
| (E,E)-2,4-decadienal | 0.03 | 1286 | A, C | green (24) | | |
| ethyl decanoate | 0.02 | 1376 | В | 5 | 122 (<i>8</i>) | |
| tetradecane | 0.03 | 1381 | A, C | | () | |
| 6,10-dimethyl-5,9-undecadien-2-one | 0.02 | 1419 | C | | | |
| ethyl (E,Z)-2,4-decadienoate | 0.37 | 1444 | В | pear (17, 24) | 100 (<i>8</i>) | |
| α -farnesene | 12.31 | 1495 | A, C | | | |
| pentadecane | 0.03 | 1500 | C | | | |
| butylated hydrotoluene | 0.30 | 1510 | С | | | |
| diethyl phthalate | 0.02 | 1629 | C | | | |
| hexadecane | 0.10 | 1635 | C C C | | | |
| eicosane | 0.01 | 1904 | C | | | |
| 1-octadecene | 0.05 | 1910 | C C | | | |
| dibutyl phthalate | 0.03 | 1923 | Č | | | |
| isopropyl palmitate | 0.12 | 1979 | Ă, C | | | |

^a Retention index, using paraffins (C₆-C₁₅) as references. ^b A, identification by retention index; B, identification by external standard; C, identification by GC/MS. ^c Threshold in nanograms per milliliter of water (ng/mL).

| Table 2. | Changes | of Phenolic | Acid Corr | pounds | during | Storage | Time | (ma/ka | Fresh) |
|----------|---------|-------------|-----------|--------|--------|---------|------|--------|--------|
| | | | | | | | | | |

| compound | stage 1 (month) | stage 2 (month) | stage 3 (month) | stage 4 (month) | stage 5 (month) |
|-------------------------|------------------|------------------|------------------|------------------|------------------|
| chlorogenic acid | 46.5 ± 0.3 | 48.0 ± 0.3 | 49.1 ± 0.03 | 44.91 ± 0.03 | 38.58 ± 0.02 |
| quercitrin | 4.251 ± 0.02 | 3.396 ± 0.02 | 4.1 ± 0.02 | 4.24 ± 0.02 | 4.352 ± 0.02 |
| phloretin xyloglucoside | 1.271 ± 0.03 | 1.302 ± 0.02 | 1.495 ± 0.02 | 1.62 ± 0.01 | 1.672 ± 0.01 |
| morin | 4.468 ± 0.04 | 4.043 ± 0.03 | 4.509 ± 0.03 | 4.479 ± 0.02 | 4.078 ± 0.02 |
| quercetin | 2.310 ± 0.03 | 2.254 ± 0.03 | 2.251 ± 0.03 | 2.248 ± 0.02 | 2.22 ± 0.02 |

especially ethyl, propyl, butyl, and hexyl acetates, increased markedly with increasing maturity of the fruit. During our research, Kuerle fragrant pears have not developed a soft flesh like European pears, although the firmness deceased. Perhaps there are different changes of volatile compounds between European pears and Kuerle fragrant pears.

Chlorogenic acid was the dominant phenolic acid, followed by morin, quercetin, phloretin xyloglucoside, and quercitrin (**Table 2**). Zhang (13) determined that the phenolic acid content of apple was relatively stable during maturation and storage. Wu and others (19) reported that chlorogenic acid was the main contributor to core browning of Yali pear fruit, but there is little literature about the functions of individual phenolic acids in Kuerle fragrant pear. The composition of phenolic acids in the Kuerle fragrant pear fruit changed during storage, especially the content of chlorogenic acid. From stage 1 (46.5 mg/kg) to stage 5 (35.58 mg/kg), total phenolic acid content decreased. Ju (20) reported that with the ripening of Yali pear the phenolic acid content dropped. Harel and others (21) described a similar pattern of apple phenolic acid change. This can be explained by the concurrent decrease in polyphenoloxidase (PPO) activity. Change in the composition of phenolic acids has little effect on the flavor of Kuerle fragrant pear fruit; however, further research is required to determine the effects on processing for juice and other products.

In conclusion, the physical and chemical properties of Kuerle fragrant pear fruit were investigated after 1, 2, 3, 4, and 5 months

of storage. Flesh firmness and SSC changed slightly. The composition of sugars, organic acids, and phenolic acids was determined by HPLC. Fructose was the dominant sugar in Kuerle fragrant pear fruit, malic acid was the principal organic acid, and chlorogenic acid was the most important phenolic acid. The volatiles of Kuerle fragrant pear (*Pyrus serotina* Reld) during storage were first studied by high-resolution gas chromatography and GC/MS using SPME, and by using the GC– olfactometry port. The results demonstrated that the volatile flavor compounds from SPME were responsible for the aroma of Kuerle fragrant pear fruit. The volatiles and physical and chemical properties of Kuerle fragrant pear fruit change during storage; however, the cultivar retains good quality during storage.

LITERATURE CITED

- Maga, J. Simple phenol and phenolic compounds in food flavor. Crit. Rev. Food Sci. Nutr. 1978, 10, 323–372.
- (2) Ayaz, F. A.; Kadioglu, A.; Reunanen, M. Changes in phenolic acid contents of Diospyros lotus L. during fruit development. J. Agric. Food Chem. 1997, 45, 2539–2541.
- (3) Peleg, H.; Naim, M.; Rousel, R. L.; Zehavi, U. Distribution of bound and free phenolic acids in oranges (Citrus sinensis) and grapefruits (Citrus paradisi). J. Sci. Food Agric. 1991, 57, 417– 426.
- (4) Lee, H. S.; Nagy, S. Formation of 4-vinyl guaiacol in adversely stored orange juice as measured by an improved HPLC method. *J. Food Sci.* **1990**, *55*, 162–163, 166.
- (5) Makkar, H. P. S.; Dawra, R. K.; Singh, B. Tannin levels in leaves of some oak species at different stages of maturity. *J. Sci. Food Agric.* **1991**, *54*, 513–519.
- (6) Rizzolo, A.; Lombardi, P.; Vanoli, M.; Polezello, S. Use of Capillary Gas Chromatography/Sensory Analysis as an additional tool for sampling technique comparison in peach aroma analysis. *J. High Resolut. Chromatogr.* **1995**, *18*, 309–314.
- (7) Shiota, H. Changes in the volatile composition of La France pear during maturation. J. Sci. Food Agric. 1990, 52 (3), 421–429.
- (8) Takeoka, G. R.; Buttery, R. G.; Flath, R. A. Volatile constituents of Asian pear (Pyrus serotin). J. Agric. Food Chem. 1992, 40, 1925–1929.
- (9) Watkins, C.; Harman, J. Use of penetrometer to measure firmness of fruit. Orchardist N. Z. 1981, 54, 14–16.
- (10) Dolenc, K.; Stampar, F. An investigation of the application and conditions of analyses of HPLC methods for determining sugars and organic acids in fruits. *Res. Rep. Biotech. Fac. Univ. Ljubljana* **1997**, *69*, 99–106.
- (11) Bazemore, R.; Goodner, K. L.; Rouseff, R. L. Volatiles from unpasteurized and excessively heated orange juice analyzed with solid phase microextraction and GC-olfactometry. *J. Food Sci.* **1999**, *64*, 800–803.
- (12) Sakurai, N.; Nevins, D. J. Relationship between Fruit Softening and Wall Polysaccharides in Avocado (Persea Americana Mill) Mesocarp Tissues. *Plant Cell Physiol.* **1997**, *38*, 603–610.

- (13) Zhang, W. Y. *The Biology and Physiology of Fruit*; Agricultural Publishing Company: Beijing, China, 1990.
- (14) Ning, B. The relationship between the storage and the temperature in China Yali pear. *Hortic. Rec.* **1981**, 645.
- (15) Ackerman, J.; Fischer, M.; Amado, R. Changes in sugars, acids, and amino acids during ripening and storage of apples (cv. Glockenapfel). J. Agric. Food Chem. 1992, 40, 1131–1134.
- (16) Gao, H. F.; Wang, Y. Z. Respiration and sugar-catabolism of Kuerle fragrant pear during storage. *Acta Hortic. Sin.* **1983**, *10* (2), 141–142.
- (17) Heinz, D. E.; Jennings, W. G. Volatile components of Bartlett pear V. J. Food Sci. 1966, 31, 69–80.
- (18) Shiota, H.; Minami, T.; Sawa, T. Aroma constituents of Japanese pear fruit. *Kajuu Kyokai Ho* **1981**, *279*, 36–40.
- (19) Wu, G. X.; Zhou, H. W.; Wang, J. M. Biochemical mechanism and substances determination of enzymic browning of yali pear (Pyrus Bretschneideri Rehd). *Acta Hortic. Sin.* **1992**, *19* (3), 198–202.
- (20) Ju, Z. G. Effect on the Laiyang pear pheonolic acid mechanism and texture browning in harvest time. *Chin. Agric. Sci.* 1991, 24 (2), 63–68.
- (21) Harel, E.; Mayer, A. M.; Shain, Y. Catechol oxidase, endogenous substrates and browning in developing apples. *J. Sci. Food Agric.* **1966**, *17*, 389–392.
- (22) Muench, P.; Hofmann, T.; Schieberle, P. Comparison of Key Odorants Generated by Thermal Treatments of Commercial and Self-Prepared Yeast Extracts: Influence of Amino Acid Composition on Odorant Formation. J. Agric. Food Chem. 1997, 45, 1338–1344.
- (23) Buettner, A.; Schieberle, P. Characterization of the Most-Odor-Active Volatiles in Fresh Hand-Squeezed juice of Grapefruit (Citrus paradisi Macfayden). J. Agric. Food Chem. 1999, 47, 5189–5193.
- (24) Lin, J. N. Production and Application of Natural and Edible Essence and Flavor; Beijing Light Industry Press: Beijing, 1991.
- (25) Guth, H.; Grosch, W. Identification of the Character Impact Odorants of Stewed Beef Juice by Instrumental Analysis and Sensory Studies. J. Agric. Food Chem. 1994, 42, 2862–2866.
- (26) Buttery, R. G.; Seifert, R. M.; Ling, L. C.; Soderstrom, E. L.; Ogawa, J. M.; Turnbaugh, J. G. Additional Aroma Components of Honeydew melon. J. Agric. Food Chem. **1982**, 30, 1208– 1211.
- (27) Flath, R. A.; Black, D. R.; Guadagni, D.; McFadden, W.; Schultz, T. Identification and Organoleptic Evaluation of Compounds in Delicious Apple Essence. J. Agric. Food Chem. **1967**, 15, 29– 35.
- (28) Takeoka, G. R.; Flath, R. A.; Mon, T. R.; Teranishi, R.; Guentert, M. Volatile Constituents of Apricot (Prunus armeniace). J. Agric. Food Chem. 1990, 38, 471–477.

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