



Article

Comprehensive Evaluation of the ‘Shixia’ Longan Quality under Postharvest Ambient Storage: The Volatile Compounds Played a Critical Part

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Abstract: Longan fruit generally undergoes rapid quality deterioration during the postharvest stage, with the manifestation of flavor loss as well as pronounced off-odor production. Nevertheless, the unapparent aroma makes people ignore the odor change in postharvest longan. Sensory analysis serves as an indispensable method combining instrumental detection and the perceptibility of human sensation in a comprehensive evaluation of quality during production and consumption. In this study, we established the evaluating data of the appearance, flavor, taste substances, volatile profiles, and deterioration of ‘Shixia’ longan throughout room-temperature storage using instrument assessment and descriptive measurements. Our results indicated that both the appearance state and the taste condition notably engendered confusion or trouble for consumers to judge under the quality transition period. Conversely, the development of odor was highly consistent with that of quality deterioration. Some unpleasant volatile substances including alcohol (ethanol), acid (acetic acid), and esters (acetic acid methyl ester and ethyl acetate) were probably the cause of off-odor during the storage. The result of the sensory evaluation also presents a more significant relevance between the overall quality and the odor. Generally, the work paved the way to reveal the importance of odor profiles for assessing the comprehensive quality condition of postharvest room-temperature stored longan.

Keywords: longan fruit; postharvest storage; sensory evaluation; electronic tongue; electronic nose; volatile profile



Citation: Li, J.; Luo, T.; Xu, J.; Zhu, D.; Han, D.; Wu, Z. Comprehensive Evaluation of the ‘Shixia’ Longan Quality under Postharvest Ambient Storage: The Volatile Compounds Played a Critical Part. *Horticulturae* **2024**, *10*, 585. <https://doi.org/10.3390/horticulturae10060585>

Academic Editor: Elazar Fallik

Received: 18 April 2024

Revised: 22 May 2024

Accepted: 30 May 2024

Published: 3 June 2024



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1. Introduction

Longan (*Dimocarpus longan* Lour.), one of the renowned evergreen tropical or subtropical fruit trees of high economic value in Sapindaceae family, originated from South China or South Asia and has been commercially cultivated in China for over 2000 years [1,2]. At present, it has been extensively grown in many countries such as China, Thailand, Vietnam, India, and so on. Among these regions, China has the largest planting area (over 300,000 hectares) and the highest total production (more than 1.5 million tons) [2,3]. Longan fruit is commonly called dragon eye. Its edible aril accumulates high-leveled nutritive phytochemicals such as polysaccharides, vitamin C (about 0.8 mg g^{−1} fresh weight), polyphenols (about 0.75 mg g^{−1} fresh weight), and carbohydrates (about 150 mg g^{−1} fresh weight), which confers it not only the unique and appealing flavor but also the bioactive effects including antitumor, immunomodulatory and antioxidant capacity [4,5]. Thus, it is widely consumed and gains popularity with the global people [6].

Longan fruit ripens and is harvested in hot summer with high prevailing temperatures (25–33 °C) and humidity (>75%), which results in the extreme irreversibility to postharvest long-term storage and long-distance transportation [6–9]. In general, longan fruit can be stored for about 30 days at 4–5 °C, but its shelf life is shorter (6–7 days) under ambient conditions (about 25–33 °C, >75% relative humidity) without any postharvest handlings due to its rapid peel browning, highly perishable nature, and susceptibility to postharvest pathogens such as *Phomopsis longanae* Chi [10] and *Lasiodiplodia theobromae* (Pat.) Griff. & Maubl. [11]. In China, ‘Shixia’ is the main cultivar with the largest cultivated area and yield, followed by ‘Chuliang’. Up to now, in China, longan is still a fruit present on the local market for the purpose of fresh sales and consumption, although it can be processed into products such as juices, wines, and vinegars [12]. Accordingly, postharvest quality control and maintenance are crucial for fresh longan fruit, and meanwhile, a correct estimate for the fruit quality condition seems indispensable for consumers when purchasing.

Fruit quality can be defined as the degree of excellence in a given product, which includes the formation and postharvest maintenance of both the external appearance and the internal quality such as flavor and nutrition substances of the fruit [13]. As one of the major quality aspects, flavor consists of taste and odor that have a direct impact on the individual purchase preferences of consumers [13]. However, the flavor quality of fruits may generally decline rapidly and undergo the processes of flavor loss as well as the production of off-flavor during the postharvest period [14]. Longan fruit, one of the typical non-climacteric fruits, is prone to rot and deteriorate in the postharvest stage manifested by pericarp browning and aril breakdown, along with the production of an unpleasant and strong off-odor, especially during storage under an ambient environment [7]. Although a series of strategies comprising physical, chemical, and biological treatments have been applied to reduce postharvest loss and extend the storage life of longan fruit over the past several decades, it cannot reverse the ultimate declining trend of quality [7,8,15–17]. Most previous studies focused on the mechanisms of the pericarp browning and aril breakdown, which are the common appearance indexes that affect the color of the longan pericarp and indicate of interior quality deterioration, respectively [9]. In fact, it seems difficult for consumers to distinguish the actual quality condition of longan fruit from the apparent color or the internal pulp conditions, because studies have found that the mesocarp of longan was the first to turn brown, followed by the endocarp, and then the exocarp during postharvest storage [18]. Moreover, even if the aril of longan has already broken down or become bland after harvest and storage, the pericarp appears sound [18]. In this instance, seeking other aspects to help consumers correctly appraise the quality status of postharvest longan becomes extremely urgent.

Odorants, a mixture bestowed by diverse volatile compounds, constitute an intuitive sensory characteristic of fruit [19]. It is easily perceived by humans, which makes it an important indicator for consumers to evaluate the quality and freshness of fruit [13,20]. Those volatiles emitted by fruits may undergo transformation during postharvest storage by reflecting in the degradation of the original characteristic aroma of the fruit or leading to an increase in the content of off-odor substances [14]. Longan fruit, usually eaten fresh, bears a succulent, sweet, and aromatic flavor but without apparent aroma, which makes people pay far too little attention to the volatile compounds to ignore the severe off-odor produced by the fruit during postharvest storage. Whilst a published study has been carried out on the volatile substances of different longan landraces [21], there appear to be no empirical investigations aiming at understanding the changes in volatile profiles that occur under ambient storage and the relevance with the quality of postharvest longan.

Given that longan fruits are temporarily stored under normal temperatures in general for quick sales and consumption during the fresh period, an ambient storage experiment was carried out by using the longan fruits harvested from a main cultivar named ‘Shixia’. For comprehensively estimating the storability and quality status, a systematic detection with regard to the changes in some parameters including appearance, color, taste, volatile profiles, cell state, and deterioration condition after a period of normal temperature storage

was conducted using techniques including electronic tongue, electronic nose, and gas chromatography. Moreover, sensory evaluation was conducted to analyze the relationship between the longan fruit quality indexes and the quality attribute under storage. This study attempts to provide a new perspective to learn about the quality deterioration process of longan during the postharvest ambient storage and promote the marketing and purchasing of this fruit.

2. Materials and Methods

2.1. Longan Fruit Materials, Treatments, Storage, and Sampling

The commercial mature fruits of longan (cv. ‘Shixia’, SX) were harvested from the orchard of Fruit Research Institute, Guangdong Academy of Agricultural Sciences in July 2022, put into a plastic basket, packed with PE plastic wrap to prevent water loss, placed in a truck with refrigeration air conditioning (about 18–20 °C), and immediately delivered to the laboratory. The individuals with uniform color, maturity, shape (longitudinal diameter/transverse diameter, about 0.90–0.94), and size (single fruit weight, about 8.0–9.0 g), and free of disease or blemishes were selected for the subsequent experiments.

A total of 600 longan fruits were selected and dipped into 500 mg/L prochloraz solution for 2 min, and subjected to a natural air-dry at room temperature for 30 min. Then, a precise weight (200 ± 1 g) of the longan fruits was packed into a rectangle perforated polyethylene wrap box (650 mL), which was sealed with a 0.025 mm thick polyethylene (PE) bag and then stored at room temperature (25 ± 1 °C) and 85% relative humidity (RH). Three boxes of the longan samples were randomly taken at three days interval to determine the following quality indexes.

2.2. Determination of Chromatic Value

Three wrap boxes of the fruits (about 60 fruits in total) were randomly selected at 0, 3, 6, 9, and 12 days after storage to determine the chromatic value of each fruit according to the method reported in our previous work [22]. The L^* (lightness, 0 to 100: black-white), a^* (negative to positive: green to red), b^* (negative to positive: blue to yellow), and C^* (represents the color saturation) values on the equatorial plane of each fruit were measured using a color analyzer (NH310, 3nh Technology Co., Ltd., Shenzhen, China). The measurement at each time point was subjected to three repetitions.

2.3. Sampling and Determination of Total Soluble Solid (TSS) and Vitamin C (VC) Content

Three wrap boxes of the longan fruits were randomly selected at 0, 3, 6, 9, and 12 DAS for sampling. Ten fruits from each wrap box were separated into pericarp and aril. The collected aril was immediately used for juicing to determine the TSS content (%) by a digital refractometer (PAL-BX/ACID F5, ATAGO Co., Ltd., Tokyo, Japan). The VC content of longan pulp was determined by an ultraviolet-visible spectrophotometer method according to a previously reported method [7]. A total of 10 µL longan juice was diluted with 9900 µL oxalic acid solution (2%, *w/v*, pH6.0 adjusted with NaOH) and then the absorbance was measured at 267 nm. The VC content was calculated by a standard curve. Three biological replicates of the sampling and measurement of the TSS and VC content were performed.

2.4. Determination of Relative Electrolytic Conductivity, Decay Rate, Pericarp Browning Index, and Aril Breakdown Index

Relative electrical conductivity, an indicator of membrane permeability, was measured according to [17] with minor modifications. Thirty pericarp discs were derived from ten longan fruits using a puncher (5 mm in diameter) and washed three times with deionized water. Then, twenty discs were transferred into 25 mL deionized water. After incubation at 25 °C for 30 min, the electrolyte value (D1) of the bathing solution was determined using a conductivity meter (STARTER3100C, Ohaus International Trading (Shanghai) Co., Ltd., Shanghai, China). Afterwards, the solution with discs was boiled for 15 min and quickly cooled to room temperature for detecting the total electrolyte value (D2) again. The

electrolyte value of deionized water (D0) was used as a blank control. Relative conductivity rate was calculated according to Equation (1):

$$\text{Relative electrical conductivity (\%)} = (D1 - D0)/(D2 - D0) \times 100\%, \quad (1)$$

If a fruit showed an occurrence of white mycelium, became soft, and the color of its exocarp darkened, it was considered as rotted. According to the method mentioned in [7], three boxes of longan fruits were randomly selected for examining the decay rate at 0, 3, 6, 9, and 12 DAS.

The browning index of the inner pericarp was calculated according to the reported method [8]. The browned area (BNA) of each fruit was estimated using the following scales: score = 0, no browning; score = 1, BNA was 0.1% to 25%; score = 2, BNA was 25.1% to 50%; score = 3, BNA was 50.1% to 75%; score = 4, BNA was 75.1% to 99.9%; score = 5, BNA was 100%. The pericarp browning index was calculated according to Equation (2):

$$\text{Pericarp browning index} = \sum (\text{BNA score of each fruit})/30, \quad (2)$$

The aril breakdown index was calculated according to a reported method [8]. The breakdown area (BDA) of each longan aril was evaluated using the following scales: score = 0, no breakdown; score = 1, BDA was 0.1% to 25%; score = 2, BDA was 25.1 to 50%; score = 3, BDA was 50.1% to 75%; score = 4, BDA was 75.1% to 99.9%; score = 5, BDA was 100%. The aril breakdown index was calculated using Equation (3):

$$\text{Aril breakdown index} = \sum (\text{BDA score of each fruit})/30, \quad (3)$$

2.5. E-Tongue Analysis

E-tongue (ISENSO SuperTongue, New York, NY, USA) measurements were performed on the juice of long fruit to evaluate the taste sense properties according to the method described by [23] with minor modifications. A total of 10 g frozen powder of longan pulp was dissolved into 30 mL ultrapure water. After ultrasonic extraction for 10 min, the sample was centrifuged at $10,000 \times g$ and 35 mL supernatant was transferred to the electronic tongue special beaker. Another 30 mL distilled water was prepared as lotion. In order to avoid the fluctuation of the sensor detection value, the data were collected for three biological replicates and three technical repetitions.

2.6. E-Nose Analysis

The PEN3 portable electronic nose (AIRSENSE, Mecklenburg, Germany) was used to detect the volatile of longan in the package during storage, according to the method described by [24] with minor modifications. The detector is equipped with 10 metal oxide sensor arrays to evaluate aromatic benzenes (W1C), nitrogen oxides (W5S), ammonia (W3C), hydrogens (W6S), alkanes (W5C), methane (W1S), terpenes, hydrogen sulfides (W1W), alcohols (W2S), aromatic components & organic sulfides (W2W), and aromatic alkanes (W3S). In loading analysis, the larger the value of the sensor gets on PC1, the more effectively the samples separate from each other. Additionally, the closer the sensor distribution is to the origin, the less it distinguishes the sample. Three biological replicate measurements of the volatile in the package were performed.

2.7. GC-MS Analysis of Volatile Compounds

The identification and quantification of volatiles were performed with headspace gas chromatography as in reference [25] using an Agilent 1890B gas chromatograph and a 5977A mass spectrometer (Agilent, Santa Clara, CA, USA) with a DB-5MS column (20 m $\times$ 0.18 mm $\times$ 0.18 μ m film thickness). A solid-phase microextraction device consisting of divinylbenzene/carboxylic acid/polydimethylsiloxane (DVB/CAR/PDMS) fibers (50/30 μ m inner diameter, 2 cm length; Supelco, Darmstadt, Germany) was inserted into

headspace vials and the compounds were extracted at 40 °C thermostatic water bath for 30 min. After extraction, the SPME fibers were inserted into the GC-MS at 250 °C for 1 h.

The carrier gas was high-purity helium (purity $\geq 99.99\%$) at a flow rate of 1.0 mL/min. The temperature program started at 35 °C for 5 min and was ramped up to 150 °C at a rate of 3 °C/min, then continued to heat up to 240 °C at a rate of 10 °C/min and was then held at 240 °C for 2 min, and the electron impact (EI) ionization source operated at 70 eV. The mass spectrometer scanned the range of 35–500 amu.

The quantification of the volatile compounds within the package was based on area normalization. Compound identification was achieved through the National Institute of Standards and Technology (NIST) MS database (<https://webbook.nist.gov/>; accessed on 6 January 2023). The compounds with $p < 0.05$ and variable importance in projection (VIP) > 1 were thought to have a statistically significant contribution.

2.8. Odor Evaluation

The odor emitted by the SX longan samples was tested according to the method mentioned in the reference [26] with minor modifications. The grade of off-odor concentration was evaluated by a continuous scale ranging from 0 (odorless) to 5 (strong and unbearable odor).

2.9. Sensory Analysis

The longan samples were evaluated and scored by a group of sensory panels that were uniformly trained on the sensory indexes and scoring methods before the evaluation. Since SX longan was inedible after storage longer than 6 days, the samples from 0, 3, and 6 DAS were used to perform an organoleptic flavor evaluation. Nine people made up the sensory panel, and they were trained by the standard mentioned in [27] with slight changes. Each longan was randomly numbered, and then placed on a plate and distributed to the evaluators. Each sample was tasted and scored, and then the next sample was evaluated at 2 min intervals after gargling with water. The evaluators rated the appearance, sweetness, flavor, texture, and overall taste preference of longan in 3 rounds. The evaluation guidelines considered a continuous scale ranging from 1 (the lowest score) to 9 (the highest score) [27]. The overall acceptability was presented in weighted average calculated as follows.

$$\text{Score} = \sum (\text{score} \times \text{total number of raters}) / \text{total number of raters} \times 100\%, \quad (4)$$

2.10. Statistical Analysis

The original data from three replicates were processed using Microsoft Excel 2021. A one-way analysis of variance (ANOVA) with Tukey's post hoc test was conducted using the SPSS 26 software package (SPSS Inc., Chicago, IL, USA) to analyze significant differences. Softwares including the Origin 2022 statistical software (OriginLab Corporation, Northampton, MA, USA) and Adobe Illustrator 2021 were used to edit the graphs. The WinMuster software (version 1.6.2.14), a software coming with e-nose, was used to process e-nose data for LDA (linear discriminant analysis) and loading analysis. The analyses of the electronic tongue data were performed by the ISENSO Tongue software (version 2.1.0.7). Orthogonal partial least-squares discriminant analysis (OPLS-DA) and VIP were performed using the SIMCA (Version 14.1, Umetrics, Umea, Sweden) software. TBtools (Version 1.115, Guangzhou, China) was used to plot the heatmaps.

3. Results

3.1. Changes in Appearance of Longan during Storage

Appearance state is the primary attribute affecting the quality of fruits [28]. In contrast to the desire of most consumers to give high importance to good taste, the fruits with poor appearance will not be welcomed and chosen even if the taste is guaranteed. In this study, we conducted a room temperature storage experiment by mimicking the ambient storage environment in production with the use of a 0.025 mm polyethylene bag, and the outward status of the longan fruits was assessed in several visual parameters. On the whole, the

overall appearance of the SX longan pericarp showed no significant change during the early stages of storage (0 DAS to 6 DAS) (Figure 1a). In detail, the skin colors of most of the longan samples from 0 DAS, 3DAS, and 6 DAS were yellow-brown and showed no distinction. Furthermore, the pulp samples of the longan from 0 DAS and 3 DAS were grape-like in texture, translucency, and crystal white of good quality. Nevertheless, the pericarp gradually turned brown after being stored for 6 days, and finally to obvious dark and lusterless at 9 DAS and 12 DAS. Meanwhile, disease infection was commonly found in the longan fruit during the later storage stages (6 DAS, 9 DAS, and 12 DAS), which was characterized by white pathogenic fungi around the surface. In particular, the phenomenon of aril breakdown, characterized by juice extravasation and decay in the longan pulp, appeared severe in the later storage period (Figure 1a).

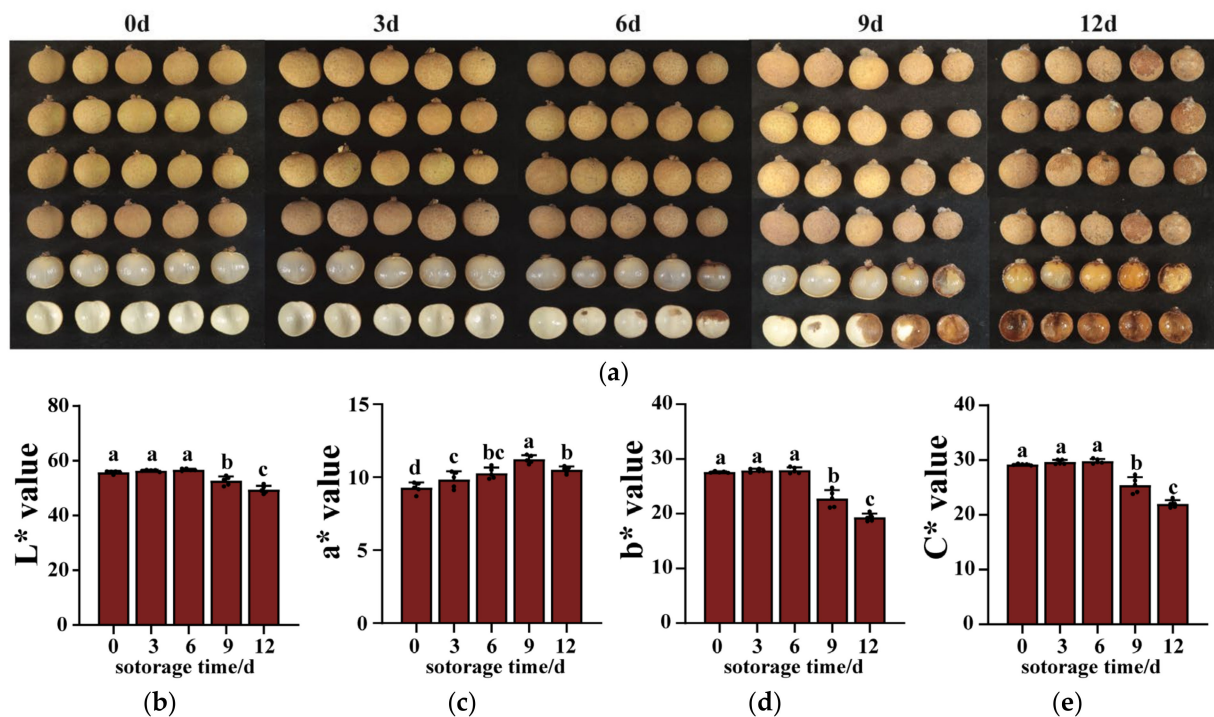


Figure 1. The appearance status of the SX longan during room-temperature storage. (a) The appearance of SX; (b–e) the chromatic analysis of the pericarp. Different letters indicate statistically significant differences according to one-way ANOVA with Tukey’s post hoc test, $p < 0.05$.

For appropriately reflecting the discrepancy and change in the pericarp color during storage, chromatic L^* , a^* , b^* , and C^* values were accurately detected (Figure 1b). The L^* value (brightness) ranged from 47.9 to 57.0 in the SX longan samples, which maintained a stable and high level from 0 DAS to 6 DAS, but significantly decreased at 9 DAS and 12 DAS (Figure 1b). Similarly, b^* value and C^* values showed no significant changes from 0 DAS to 6 DAS, but gradually decreased from 9 DAS to 12 DAS. In total, the b^* value of the pericarp ranged from 18.8 to 28.3, while C^* ranged from 21.4 to 30.1 (Figure 1d,e). However, the a^* value (more red) dramatically increased from 9.1 to 11.3 during the first 9 days of storage but then decreased (Figure 1c). Altogether, the changes in the above chromatic parameters clearly indicated that the pericarp color of the longan became darker, less green, and less shiny along with the storage.

3.2. Detection of Cell State and the Quality Deterioration of Longan during Storage

As clearly shown in Figure 1, quality spoilage definitely emerged in the longan, indicated by its changes in appearance during storage. Pericarp browning is one of the severe postharvest problems that gives rise to the unappealing color of longan fruit. The browning degree is generally evaluated by the longan inner pericarp due to the unobvious

change in the exocarp's superficial color during storage. In this study, obvious pericarp browning in the SX longan appeared at 3 DAS and then rapidly raised from 0.93 to 4.53 during 6 DAS to 12 DAS (Figure 2a). Aril breakdown, also called pulp autolysis or pulp breakdown, is a key factor that leads to the decreases in nutritional and market values of postharvest longans [29]. As shown in Figure 2b, aril breakdown showed a similar tendency as the pericarp browning index, which began rising after three days' storage, and subsequently went up sharply after 6 DAS.

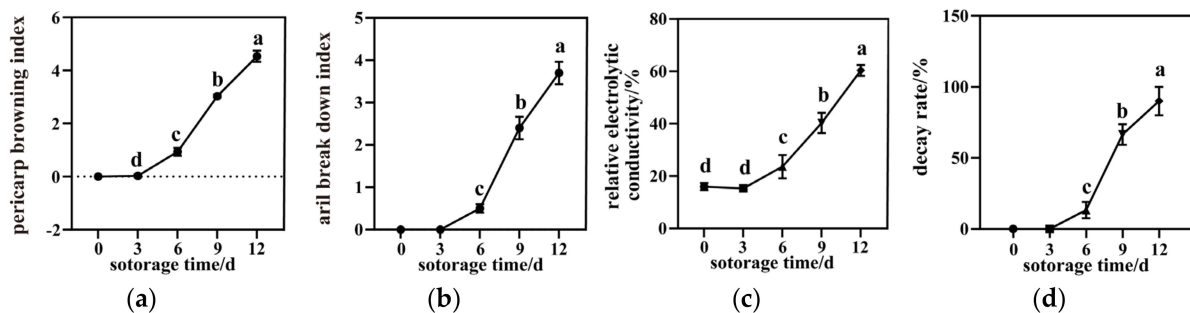


Figure 2. Measurement of the pericarp browning index (a), aril breakdown index (b), cell relative electrolytic conductivity (c), and decay rate (d) of the SX longan during the ambient storage. Different letters indicate statistically significant differences according to one-way ANOVA with Tukey's post hoc test, $p < 0.05$.

The stability of the cell membrane is of vital significance to maintaining the physiological activities of organisms. To assess the structure integrity of the membrane and the extent of membrane damage in the SX longan pericarp during storage, relative electrolytic conductivity was tested as a crucial parameter (Figure 2c). As illustrated in Figure 2c, the cell membrane relative conductivity remained at a low level within the initial 3 days' storage and started to ascend gently (at a rate of 2.77% per day) during 3 DAS to 6 DAS, and then more quick increases were observed from 6 DAS to 9 DAS (5.57%/d) and 9 DAS to 12 DAS (6.70%/d).

Decay is a severe appearance symptom of postharvest problems for longans, which directly affects the consumer's acceptance and purchasing possibilities [30]. Prior reports found that the pulp breakdown of longan fruit was largely caused by decay induced by pathogen infection. Figure 2d exhibited that the rot of the SX longan was not observable within the initial 3 days' storage, whereas it displayed an uptrend throughout the later storage period especially 6 DAS to 12 DAS.

The above findings indicated that the disease and quality deterioration of the longan in the first 3 days of room temperature storage were in a slow and latent development state, whereas in the later period of storage, especially after 6 days of storage, the disease develops rapidly, which may be the cause of the rapid quality deterioration.

3.3. Measurements of Taste Profiles of Longan Fruit during Storage

Taste sensations are the aggregate of the sensations created by food when it is inserted into the mouth [28]. The occurrence of fruit flavor deterioration during storage may generally cause a decline in the unique taste. Taste assessment is one important quality-control parameter for monitoring the quality changes in fruits after harvesting and during storage [28]. An electronic tongue is a taste-sensing analytical device that can be trained to accurately screen the taste attributes of fruit internal complicated compositions within a rapid time frame [31].

For detecting the detailed changes in taste profiles of longan pulp samples during the whole storage, the present work carried out a taste-sensing analysis by means of an electronic tongue with six sensors to provide eighteen characteristic values. Principal component analysis (PCA) was firstly used for analysis, but it could not distinguish the SX longan samples of different storage periods from each other (Figure S1). Subsequently,

another algorithm named the linear discriminant analysis (LDA) model, which was proved to be a useful tool for discrimination in prior studies, was adopted and successfully achieved a rough separation (Figure 3a). As demonstrated in Figure 3a, the first principal component (PC1) of LDA accounted for 60.79% of the total variance while PC2 explained 27.91%. The samples at 0 DAS, 3 DAS, 6 DAS, and 12 DAS showed significant separation from each other; nevertheless, the LDA model was not able to well separate the samples at 6 DAS from that at 9 DAS, because these two samples had a little physical overlap (Figure 3a). It might be concluded that there was no significant difference in the taste compounds between these two groups of samples.

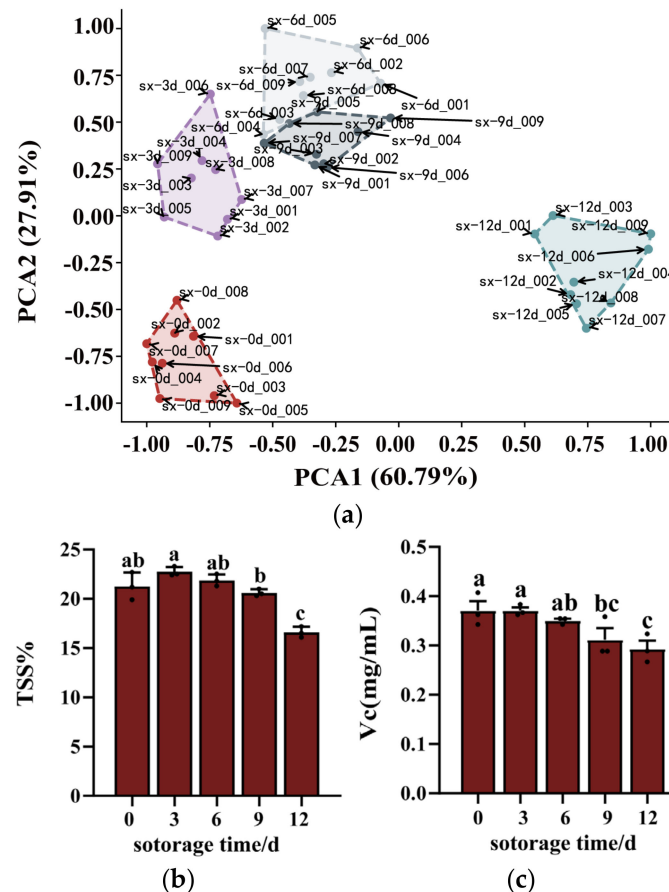


Figure 3. Measurements of taste condition of the SX longan in storage period. (a) The detection of longan flavor change by electronic tongue. (b) The TSS content. (c) The Vc content. Different letters indicate statistically significant differences according to one-way ANOVA with Tukey's post hoc test, $p < 0.05$.

TSS, VC, and titratable acidity (TA) are primary components affecting longan taste and nutritional value; however, TA accounts for an extremely low content in longan fruit [32]. TSS includes sugars, acids, vitamins, minerals, etc., which is normally utilized as an indicator for measuring fruit flavor and quality [33]. To gain a specific understanding of taste profiles, the changes in TSS and VC content in the SX longan during storage were further tested (Figure 3b,c). The TSS content of the SX longan increased from 0 DAS to 3 DAS, but then slowly decreased from 3 DAS to 9 DAS. Interestingly, the fluctuation was not significant within 0 DAS to 9 DAS, yet TSS significantly declined from 9 DAS to 12 DAS (Figure 3b). Similar to the trend of TSS, the VC content in the SX longan pulp dropped slowly within 0 DAS to 6 DAS, indicating insignificant difference among these stages, hereafter declining slightly till the end of the storage (Figure 3c). The above findings corroborated the idea that these two classes of compounds that determined the taste characteristics were insignificantly different between the samples of 6 DAS and 9 DAS,

which was consistent with the indistinct discrimination of these two samples concluded by the electronic tongue.

3.4. Identification of Odor Volatile Compounds from Ambient Stored Longan

The odor fraction of fruit plays one of the determining parts of acceptability [28]. Changes in the proportion of the composition and categories of volatiles during postharvest handlings will profoundly alter the fruit odor. The onset of pronounced off-flavor generally indicated a significant deterioration of fruit flavor [14]. For a better understanding of the volatile profile in longan during storage, an e-nose equipped with several electronic gas sensors was applied to test the complex chemical constituents, and the results were presented with an LDA (Figure 4a). As demonstrated in Figure 4a, the accuracy of this analysis was 90.07%, with the first principal component (PC1) contributing to 79.07% of the total variance while PC2 explaining 11.23%, respectively. Nevertheless, LDA was not able to identify all of the sample differentiation well, because great overlaps were found among the samples at 0 DAS, 3 DAS, and 6 DAS (Figure 4a). Furthermore, to confirm the contribution rate of each sensor to the sample differentiation, loading analysis was carried out to investigate which major category of volatiles played the decisive effect (Figure 4b). According to Figure 4b, sensors including W2S (alcohols), W2W (aromatic components and organic sulfides), W5S (nitrogen oxides), W1S (methane), and W1W (terpenes, hydrogen sulfide) had the highest responses, which indicated that they gave an excellent contribution to distinguish the samples.

SPME-GC-MS was utilized to quantify the change in specific volatile components in the SX samples during storage. As illustrated in Figure 4c, 35 volatile compounds classified into 17 terpenes, 2 alcohols, 7 aromatic hydrocarbons, 4 esters, 2 alkanes, and 1 acid, and 2 'other' compounds were identified (Figure 4c; Table S1). On the one hand, the terpenes ranked the first portion in the SX longan samples at 0 DAS (76%), then their portion experienced a precipitous decline to 21% at 12 DAS. A similar descendent trend was observed in aromatic hydrocarbons (7% to 5%), although the reduction was not obvious. On the other hand, the proportion of the rest volatiles shared a rising tendency across the storage. In detail, the alcohols (3% to 25%) and the esters (7% to 27%) increased the highest ratios, followed by the alkanes (1% to 4%), acids (3% to 12%) and 'other' compounds (3% to 6%) (Figure 4c).

Moreover, we used the multivariate statistical analysis to assess the 35 volatile components. The PCA model displayed a favorable separation of the two principal components that accounted for 90.76% of the total variance, and exhibited a noticeable difference between the 0 DAS and 12 DAS SX longan samples (Figure 4d). To identify characteristic volatiles for different storage stages, an OPLS-DA model was constructed to determine the VIP values, confirming its reliability with 200 permutation tests ($R^2 = 0.683$ and $Q^2 = -0.706$; Figure 4e). From the data, the OPLS-DA results highlighted five discriminative volatile compounds ($p < 0.05$, $VIP > 1$; Figure 4f; Table S1), including ethanol (Voc_2), acetic acid methyl ester (Voc_3), ethyl acetate (Voc_4), acetic acid (Voc_5), and β -ocimene (Voc_13). In detail, β -ocimene (Voc_13) was the only terpene that accounted for the highest proportion (61.82%) at 0 DAS and showed the biggest drop at the end of storage (Figure 4g) among the five identified compounds. The rest of the marked volatiles comprising one alcohol (ethanol), one acid (acetic acid), and two esters (acetic acid methyl ester and ethyl acetate) augmented significantly in relative content during the storage progress (Figure 4g).

Although some of the differences between the volatile compound profiles of the SX longan samples at different storage stages were able to be detected instrumentally, these differences were probably imperceptible to human olfactory sensation. Thus, an odor evaluation of the SX samples was performed in this study as a complementary experiment (Table S2). Table S2 detailedly showed that fresh SX longan at 0 DAS possesses a smell of Chinese herbal medicine as well as a smell of spice, which could be kept, and the concentration and intensity of odorants were enhanced within the initial 3 days of storage. A kind of wood and dirt odor came over at 6 DAS, indicating the transformation of

compositions of the odorants. After storage for 9 days, the odor changed over to a kind of acid, mildew, and rot smell with a palpable sense of off-odor; afterwards, its concentration rapidly went up till the end of the storage (Table S2).

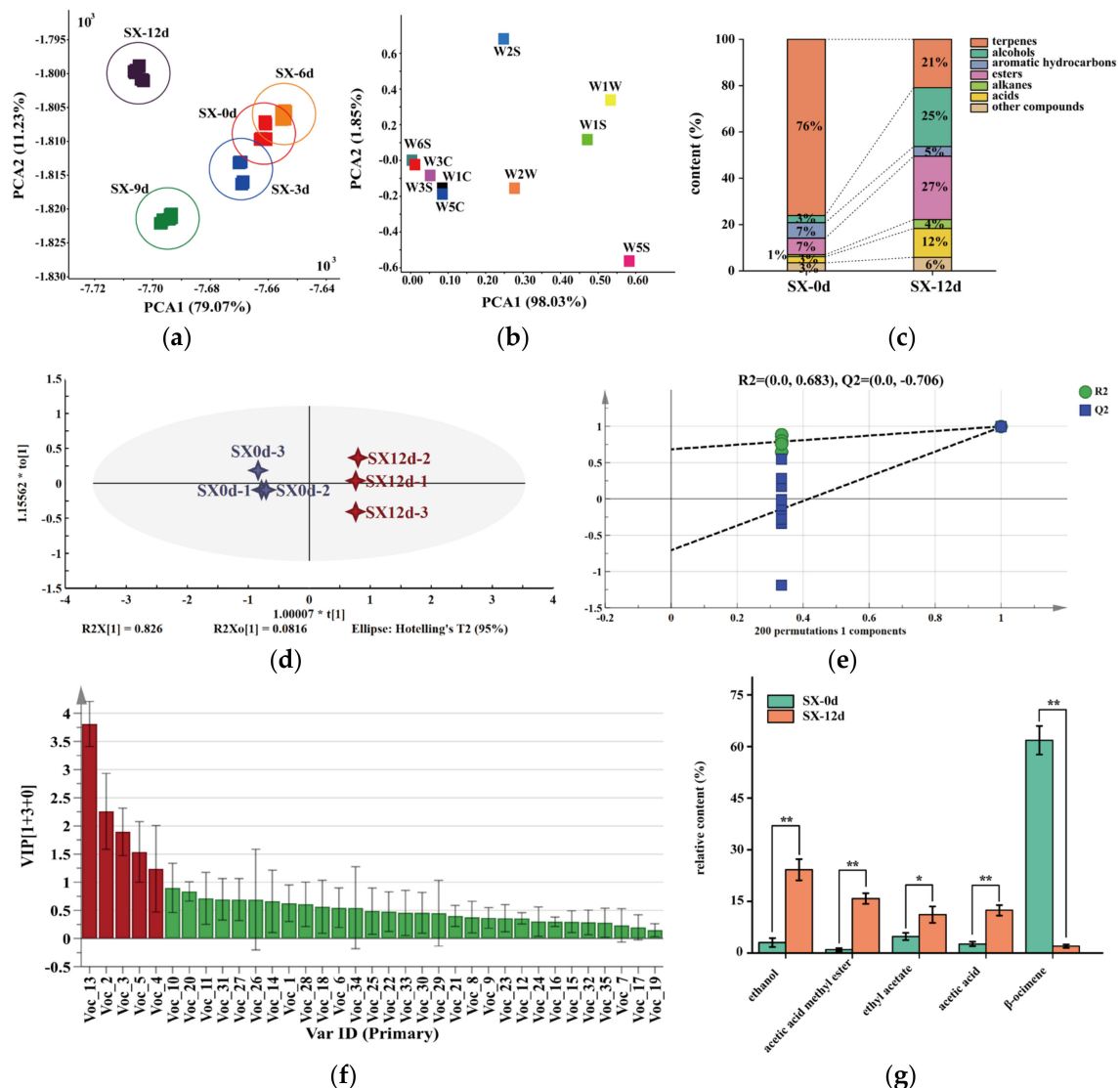


Figure 4. Quantification and multiple analysis of volatile components during storage. (a) The LDA results of electronic nose data. (b) The loading analysis of electronic nose data. (c) The dynamic changes in content and categories of the volatile substances from 0 DAS and 12 DAS. Multivariate statistical analysis: (d) PCA score plot; (e) cross-validation results. The intercept of the Q2 regression line of the cross-validation model with 200 tests of alignment was less than 0, indicating that the OPLS-DA discriminant model was not over-fitted and the model was relatively reliable; (f) VIP score plot: red bars represented volatile compounds with VIP > 1 and green bars represented VIP < 1. (g) The relative content analysis of the identified marked volatile components. Asterisks indicate significant difference between the two samples at the same time point: *, $p < 0.05$; **, $p < 0.01$.

3.5. Sensory Evaluation Analysis of the Fruit Quality

Sensory evaluation is an available way to help realize the analysis and comparison of sensory properties, as well as the quality control for different fruits [34]. Consumer sensory perception is ultimately the most important assessment of changes in fruit flavor. Therefore, we submitted the longan fruit samples which had finished the instrument-based analyses to a panel of trained judges for overall sensory quality evaluation to clarify which quality attribute had an effective impact on the comprehensive quality (Figure 5).

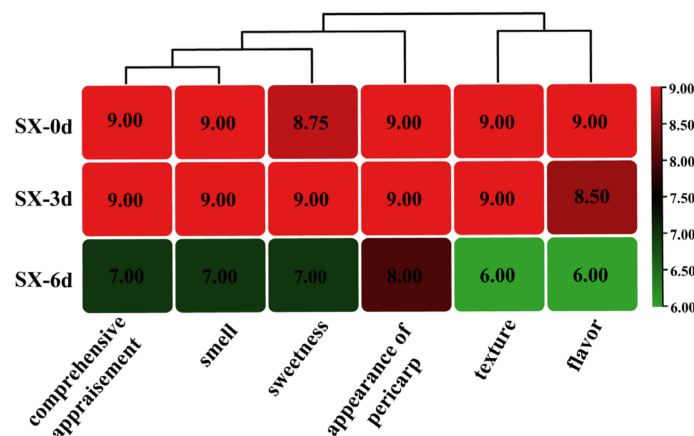


Figure 5. The heatmap of the scores of the comprehensive sensory qualities of SX during storage.

Figure 5 detailedly exhibited that a similar score pattern can be seen between the comprehensive appraisal and the smell of different samples, both of which were clustered together much closer than that of the other quality attributes. Notably, compared to the comprehensive appraisal, the appearance of the pericarp of the SX longan samples presented a higher scoring trend, particularly with the increase in the storage time, which suggested that changes in fruit appearance lag behind the changes in other quality attributes. Furthermore, the score modes of the sample texture and flavor appeared a lower tendency than the others along with the storage, indicating a faster transformation in the texture and flavor of the SX longan samples (Figure 5).

4. Discussion

Fruit is a kind of popular food product appreciated for its appealing color, fragrance, and taste, as well as its unique nutritional properties and high flavor quality [14]. Recently, due to the augmentation of consumer awareness in all aspects associated with fruit quality, quality control of preharvest or postharvest fruit has become an issue of major importance. Monitoring the fruit quality and freshness has attracted a great deal of interest from both the consumer and the fruit industry [6]. Longan, praised as the king of fruits for its high nutritional values and valuable pharmacological effects, is widely cultivated and well-liked all over the world [1,2]. Nevertheless, its bad resistance to postharvest rot and deterioration, which was primarily induced by the fragility of the fruit pericarp structure, the continuously relatively strong metabolism, and the vulnerability to pathogen infection, not only damages the overall sensory flavor quality but also sets a pronounced limit for long-term storage or distant transportation [18,35]. Thus, available means to monitor and ensure the after-harvested quality becomes essential.

Fruit quality, consisting of sensory or organoleptic quality, nutritional quality, microbiological quality, and so on, is of great importance in affecting fruit acceptance and consumer satisfaction [28]. Among them, sensory experiences evoked by the sensory quality of various fruit products are the key to prompt a feeling of pleasure and commercial success [28]. Sensory or organoleptic properties comprising appearance, color, flavor, taste, odor, texture, and overall acceptability are the significant determinants to assess the fruit's sensory quality [13]. To judge and measure these quality characteristics, sensory analysis that is conventionally realized by two common techniques, namely subjective or qualitative and objective or quantitative methods serves as an essential tool [28]. The subjective measurement of fruit sensory properties is managed through organoleptic responses that are normally measured by a rating test with a group of trained panelists, whereas objective or discriminative measurement demands the application of instrument or equipment to accurately check the routine quality [28,34]. In this study, we established a set of data from instrument assessment and descriptive measurements of 'Shixia' longan for evaluating the quality condition during postharvest storage.

The appearance of fruit, generally designated by the surface properties such as color, shape, and texture, can reflect some information about the preference of human sight sensation. In general, desirable surface characteristics like glossy or shiny superficial color can be determined as the superior manifestation of fruits with high quality [28]. Interestingly, however, consumers may face confusion or trouble when judging the quality condition of longan fruit simply by the apparent state presented in the external pericarp with naked human eyes. Longan fruit is such a particular fruit that the change in its superficial yellow-brown color in the exocarp lags behind the endocarp during the early storage [17]. Only when the quality deterioration is too severe in the late storage period does the outer peel color of the longan fruit show a significant darkening color (Figure 1). Alternatively, it is worth noting that the longan fruit has been undergoing a quality transformation since storage day 3 from indexes reflecting the fruit's external or internal condition that have clearly exhibited an accordant decline in quality within the storage day 3 to day 6 (Figure 1c; Figure 2). However, a similar good apparent state during the storage days 0, 3, and day 6 has no difference in these three sampling days, which can be verified by the detection of L^* , b^* , and C^* values (Figure 1).

As one of the major aspects among the fruit quality attributes, the flavor of the fruit is the combination and interaction in taste and odor, and has a direct impact on the individual purchase preference of consumers [20]. Taste is an important organoleptic property that governs the human acceptance and appreciation of fruits through the mouth. Some taste-related metabolites such as sugars, acids, and phenolics jointly contribute to the unique perception in the mouth (sweetness, acidity, or bitterness) [13]. Remarkably, the present work has identified that the taste substance of the SX longan starting to rot (at 6 DAS) can not significantly be told apart from that of the clearly deteriorated SX longan (at 9 DAS) by instrument detection (Figure 2A). Similarly, the main taste compounds TSS and VC are insignificant between these two storage periods (Figure 2B).

In parallel to taste, odor is another kind of key factor that is made up of a wide range of volatile compounds to jointly convey the flavor of fruits [13,20]. Generally, these odor-developing components are firstly perceived by the human olfactory system and then transmitted the odor signals to the brain, which has a decisive influence on consumption [28]. Fresh longan is a kind of distinctive fruit with a special flavor but without an obvious aroma, resulting in little attention to the volatile compounds emitted by the fruit. Different from the previous results that esters (68.4%) and terpenoids (27.1%) were quantitatively the most significant among longan volatiles, among which ethyl acetate (66.2%) and (E)-Pocimene (26.7%) were clearly dominant in fresh longan [21], our findings pointed out that the terpene compounds are obviously dominant in quantity with the content of β -ocimene far ahead of other volatile substances (Table S1). Moreover, β -ocimene has a sweet herbaceous scent according to the Flavornet and Human Odor Space database (<https://www.flavornet.org/flavornet.html>, accessed on 8 January 2023), which is consistent with the odor evaluation result in fresh longan (storage day 0). Thus, some discrepancy probably could be observed between different *D. longan* varieties, and meanwhile, the accumulated β -ocimene may be the characteristic aroma volatile in fresh SX longan.

Based on the consideration of the distinct production of strong and unpleasant odor in longan fruit in the postharvest stage, we firstly emphasize on confirming the change in volatiles during postharvest storage in this work. Contrary to the insignificant difference shown in the result of taste, the odor under the transition period (storage day 6) significantly separates from the obvious deterioration stage (after storing 9 days) (Figure 4A), and is further demonstrated by drastic increasing off-odor concentration grade in odor evaluation (Table S2). Furthermore, some unpleasant volatile substances including alcohol (ethanol), acid (acetic acid), and esters (acetic acid methyl ester and ethyl acetate) of longan fruits were increased gradually with the extension of storage, which is possibly the explanation for the cause of off-odor from postharvest physiological processes (Figure 4; Table S1). Backed by numerous studies, ethanol is the most common odor alcohol found in fruits and the alcohols may emit odors such as 'musty, mushroom, fatty, oily, bitter, burnt' that are not part

of the fruits flavor [36,37]. Moreover, it has been found that the increase in esters may lead to 'overripe' odor, among which ethyl acetate has been studied as an off-flavor indicator of fruit anaerobic metabolism [38]. Alternatively, acids can emit a powerful sour-rancid odor that has a negative impact on the quality of fruit flavor, especially acetic acid that has the characteristics of 'sharp, pungent, sour' odor [14]. Hence, the significant change in odor profile during longan fruit spoilage suggests a joint influence by the decrease in aromatic substance (β -ocimene) and the increase in specific off-odor components (alcohol, acid, and esters). The result of the sensory evaluation in accordance with the perceptibility of human sensation also presents a more important relevance between the comprehensive appraisal and the odor, rather than the other sensory parameters (Figure 5). It should be noted that the results and conclusion of this experiment were obtained in the longan fruit stored at room temperature conditions (25–33 °C, humidity >75%). These results may not provide an accurate reference for the sensory and quality evaluation of longan fruit under other storage and logistics conditions such as low-temperature storage and controlled atmosphere storage.

5. Conclusions

In this study, a complete set of data that evaluated the appearance, flavor, taste substances, volatile compounds, and deterioration condition of 'Shixia' longan during postharvest storage were established by the combination of instrument assessment and descriptive measurements. Nevertheless, the index of appearance state of the fruit displayed no significant differences between the fresh period (0–3 DAS) and the quality transition stage (6 DAS), while the taste condition could not tell the difference from the quality transition stage (6–9 DAS) and the late storage period (9–12 DAS), which seems unsuitable for judgement for generating confusion or trouble for consumers. In contrast, the significant change in odor profiles shows obvious statistical differences at each sampling time point and is consistent with the quality deterioration process. Remarkably, some unpleasant volatile substances including alcohol (ethanol), acid (acetic acid), and esters (acetic acid methyl ester and ethyl acetate) of longan fruit were increased along with storage, which is possibly the cause of off-odor. The result of the sensory evaluation also presents a more important relevance between the comprehensive appraisal of sensory quality and the odor rather than sensory parameters. This study provided a new perspective to learn about the quality deterioration process of longan during room-temperature storage with an emphasis on the importance of odor change.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/horticulturae10060585/s1>, Figure S1: The PCA analysis of longan taste profile; Table S1: The content of volatile compounds in the SX longan under the ambient storage; Table S2: Odor evaluation of the smell in the SX longan during storage.

Author Contributions: Conceptualization, J.L. and T.L.; methodology, J.L., J.X. and T.L.; software, J.L.; validation, J.L. and T.L.; formal analysis, J.L.; investigation, J.L., D.Z. and J.X.; resources, J.X. and D.H.; data curation, J.L. and J.X.; writing—original draft preparation, J.L. and T.L.; writing—review and editing, J.L. and T.L.; visualization, J.L.; supervision, T.L., D.H. and Z.W.; project administration, D.H. and Z.W.; funding acquisition, T.L. and Z.W. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Key Research and Development Program of China (2022YFD2100103), the Earmarked Fund for China Agricultural Research System-Litchi and Longan (CARS-32), the Science and Technology Plan Projects of Guangzhou City (2023B01J2001) and Guangdong Basic and Applied Basic Research Foundation (2022A1515012049).

Data Availability Statement: The original contributions presented in the study are included in the article; further inquiries can be directed to the corresponding authors.

Conflicts of Interest: The authors declare no conflicts of interest.

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