Analysis of volatile compounds in *Annona squamosa* L. fruit under cold storage based on HS-GC-IMS

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**Abstract:** *Annona squamosa* L., also known as sugar apple, sweetsop, is listed as one of the world’s five largest tropical fruits and is commercially cultivated in tropical and subtropical regions of China. To analyze the effect of different preservatives on the volatile aroma components of sugar beets during cold storage, the samples were stored at 4 °C and sampled every two days. The change in volatile aroma components was studied by changing the composition of the preservative. The volatile aroma components in the storage of sweetsop were analyzed by GC-IMS. The results indicated that the preservation of the sweetsop by 1-MCP made the volatile aroma as much as possible with the fresh components under the condition of cold storage. The findings of this study are of great significance for the research and development of the future preservation method of *Annona squamosa* L. fruit and will provide theoretical support for the preservation technology of tropical fruits.

1. Introduction

*Annona squamosa* L. also called sugar apple, sweetsop or sugar pineapple, is one of the world’s five largest tropical fruits, and is cultivated in Zhejiang, Taiwan, Fujian, Guangdong, Guangxi, Hainan and Yunnan provinces in China $^{[1]}$. It is called "Aquila" for its lychee shape, and has a high nutritional value containing about 2.34% protein, 0.30% fat and 20.42% sugar $^{[2, 3]}$, and rich bioactive components, such as vitamins, crude fiber, Fe, Ca, P and other mineral elements. It could lower blood sugar level, promote metabolism, facilitate bowel movements and anti-oxidation $^{[4]}$. *Annona squamosa* L. is heart-shaped and is about 150 g per fruit, it has a very bumpy skin $^{[5]}$. The pulp is slightly, creamy yellow or white, sweet with a good flavor and low acidity $^{[6]}$, and is considered as a delicious and nutritionally valuable fruit meant for table purpose.

The formation of flavor is important for fruit ripeness, and is regarded as an important indicator for the evaluation of fruit quality. The unique aroma in *Annona squamosa* L. fruit is very attractive to consumers $^{[7]}$. However, custard apple is climacteric fruits, generally characterized by high respiration...
and ethylene production, and are chilling sensitive, so it is highly susceptible to spoilage, soften very rapidly during ripening, and become squashy and not easy to consume. Being highly perishable, the fruits could not be sent to distant markets. Therefore, there is an urgent need to develop a suitable method to minimize postharvest losses\cite{9,10}. In this work, the postharvest fruit was treated with exogenous NO (SNP) and 1-methylcyclopropene (1-MCP), respectively, and then stored at 4 °C. The effect of different preservation agents on flavor of *Annona squamosa* L. fruit was analyzed using Gas Chromatograph-Ion Mobility Spectrometer (GC-IMS). The appropriate preservative agent was expected to selected and for extending its shelf life.

### 2. Materials and methods

#### 2.1. Materials

The fruit of *Annona squamosa* L. at eight maturity stage was harvested from the South Asian Tropical Crops Research Institute of the Chinese Academy of Tropical Agricultural Sciences (Zhanjiang, China). Fruits were collected for uniformity of size, maturity and absence of physical injuries or infection. Then, the fruits were randomly divided into three groups and stored at 4°C for 7 days\cite{11}.

#### 2.2. Methods

**Headspace injection conditions.** Headspace incubation temperature: 40 °C; incubation time: 20 min; incubation speed: 500 rpm; syringe temperature: 60 °C; injection volume: 500 μL; Carrier gas: high purity N₂ (99.999%) with splitless mode.

**GC-IMS conditions.** Column temperature: 40°C; running time: 25 min; flow rate: initial 2.0 ml/min, and then linearly increased to 150 ml/min after 2 min; drift tube length: 5 cm; tube linear voltage: 400 V/cm; drift tube temperature: 40°C; drift gas: high purity N₂ (99.999%); flow rate: 150 ml/min; detection temperature of IMS: 45°C.

#### 2.3. Designing experiments

Sample processing and analysis: 5 g flesh of the *Annona Squamosa* L. was weighted, and place into a 20 mL headspace sample bottle, incubate at 40 °C for 20 min, and tested on a FlavourSpec® flavor analyzer. Each sample is volatilized by GC-IMS Library Search Software for qualitative analysis of volatile compounds. The analytical spectra were normalized using Laboratory Analytical Viewer (LAV), and Principal Component Analysis (PCA) was performed. Three samples were randomly selected from the control and treated groups, and each measurement was repeated twice. The results were expressed as mean ± standard deviation (SD).
Fig. 1 Volatile fingerprints of Annona squamosa L. treated with different preservation agents

Fig. 1 shows that the changes of volatile compounds of *Annona squamosa* L. treated with different preservation agents (100 mmol/L of exogenous NO and 70 mmol/L of 1-MCP) for 1.5 h at 4 °C. The fresh fruit and samples on the 7th day storage was selected, and their volatile compounds were analyzed using GC-IMS method. The *Annona squamosa* L. fruit with no treatment was considered as control. The fingerprints of these samples were divided into eight regions including A, B, C, D, E, F, G, and H areas, and the highest content of volatile compounds was found in the *Annona squamosa* L. fruit treated with NO group under 4 °C storage. As shown in the regions of G, F and E, the characteristic volatile compounds were observed. The volatile compounds identified in sample treated with 1-MCP are shown in region A.

Compounds such as hexane-2-one, and limonene were only present in the *Annona squamosa* L. fruit treated with 1-MCP at 4 °C. These substances may be characteristic volatility for the preservation treatment during the whole storage period. The volatile compounds detected in the area B, such as 2,6-dimethylpyrazine and other unknown compounds, were found in both groups treated with exogenous NO and 1-MCP, respectively, while it was not found in the fresh and control groups. The compounds, such as 2,3-pentanedione marked in the region D, have the highest content in the fresh *Annona squamosa* L. After 7 days storage, the content of the compounds in the fresh sample declined obviously, indicating that the cold storage could keep the content of this compound. In the area H, volatile compounds such as butyraldehyde, 1-butanol, 1-propanol, and ethanol are the same as those shown in the D area, and after cold storage, the content of these compounds increased. The content of volatile compounds such as ketone, 2-pentanone, and pentanol had hardly changed under the cold storage with no treatment. In area C, such as 2,3-butanedione, benzaldehyde, butyraldehyde, ethyl propionate, propionaldehyde, isopropyl acetate, ethyl acetate, 2-pentanone were both detected in the fresh samples and preservation agents groups of *Annona squamosa* L., while the control group contained no or very little contents. Therefore, it was found that he preservation agents treatments (exogenous NO and 1-MCP) provided better aroma compounds, compared with the cold stored fruit with no treatment.
Fig. 2 PCA of volatiles compounds in *Annona squamosa* L. treated with different preservation agents

As Fig. 2 shown, different colors represented different treatments of *Annona squamosa* L with or with no preservation agents, in which black indicates fresh samples at harvest, red indicates SNP treated samples, green indicates 1-MCP treated samples, and blue indicates control groups. According to the cluster analysis, the different preservation agents (exogenous NO and 1-MCP) and the control group had significant differences in flavor compounds during postharvest storage, among which the flavor observed in SNP and 1-MCP treated *Annona squamosa* L. fruit were similar, but there was an significant difference in the aroma compounds.

3. Conclusions

*Annona squamosa* L. is a nutrimental fruit and valuable for its anti-oxidation characteristics. It should be given more attention to its storage and transportation after postharvest, due to its climaacteric property, which is highly susceptible to spoilage. Different preservation methods could change the nutritional components, especially the volatile aroma. In this work, the effect of different preservation agents, namely NO and 1-MCP were investigated to extend the shelf life. The changes of volatile compounds in the flesh with different treatments were analyzed by GC-IMS, and the result showed that 1-MCP was the suitable agent for *Annona squamosa* L storage.

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