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The Effect of Pasteurization, Freezing and Prolonged Storage on Volatile Compounds of Mangaba Pulp

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Abstract Mangaba (*Hancornia speciosa* Gomes) is a fruit of the Brazilian Cerrado. Mangaba is valued for its high nutritional value and bioactive compounds, as well as the attractive and peculiar sensorial characteristics of its flavor and aroma. Considering possible changes in the natural flavor of mango fruit derivatives during processing and storage, here we aimed to evaluate the volatile compounds of mango pulp, submitted to pasteurization processes, freezing methods, and prolonged storage. Two freezing methods (static air and forced air) and five frozen storage times (0, 3, 6, 9 and 12 months) (-18°C) were evaluated for fruit and pulp submitted to two levels of pasteurization (without pasteurization and pasteurized). The extraction and analysis of the volatile compounds were performed using the SPME technique coupled to the mass spectrometer. Twenty-five volatile compounds were identified in the fruit and mangaba pulp, with the esters predominating. The 4-Pentenyl acetate and isopentyl acetate esters were predominant in the fruit, whereas in the pulps ethanol was predominant from three months of storage onwards. Pasteurization favors the retention of the aroma compounds of the mangaba pulp, independent of the freezing method. Storage, from 9 months onwards, favors the development or accumulation of compounds responsible for aroma degradation, such as ethanol, ethyl acetate, and acetic acid.

Keywords: *Hancornia speciosa Gomes, SPME-GC-MS, esters, aroma, food conservation*

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1. Introduction

The Cerrado, the second largest biome in South America, is an immeasurable heritage of renewable natural resources, with an emphasis on fruit species whose fruits have pleasant and exotic sensorial characteristics, such as color, taste, and aroma [1]. These fruits are still little known and usually of regional importance, but the demand for new and exotic flavors has attracted the attention of the flavor industries to characterize the volatile compounds of these fruits [2]. In addition to this, recent research has demonstrated the potential role of volatile compounds for human health, including antioxidant, anti-inflammatory, anticancer, and anti-obesity action [3,4,5]. However, the compound of interest must withstand processing; depending on the time and temperature applied, it can be either volatilized or become inactive [6].

Considering that the development of food products using volatile compounds seems to be a future trend due to its potential expanding market, it is suggested that research addresses, among other aspects, the stability of these compounds to processing and storage for their use and retention in products [6].

The mangaba (*Hancornia speciosa* Gomes), belonging to the Apocinacea family, stands out and has great potential for economic exploitation, due to its high nutritional and functional value, as well as intense and peculiar flavor and aroma [7].

However, it is extremely perishable when mature and demands the application of preservation techniques to ensure its commercialization with safety and quality. Among these techniques, freezing is efficient for the long-term preservation of the flavor and aroma of fruits and derivatives, since the freezing temperature crystallizes 85–90% of the fruit water, reducing water activity, biochemical changes, and microbial growth [8]. Associated with freezing, pasteurization can be employed because it prolongs pulp life by destroying enzymes and microorganisms, although some changes may occur, such as the loss of volatile compounds during processing. In contrast, other aromas are revealed or formed by the action of heat [9].

The few published works on volatile compounds of the mangaba identified esters and alcohols as predominant compounds [10,11,12] and only Lima et al. [12] evaluated the effect of storage on fruit quality using refrigeration over 20 days.

The effect of processing on the volatile compounds of fruits and derivatives has been reported. Modise [13] evaluated the storage of frozen strawberries for one week and identified increased concentration of most esters. Hyperbaric storage avoided changes in the key compounds of the strawberry juice aroma, [14] while Gonçalves et al. [15] concluded that the storage time is decisive in modifying the original aroma profile of strawberry pulps. Pasteurization caused a decrease of most alcohols, terpenes, esters, aldehydes, ketones, and sesquiterpenes, and a significant increase of monoterpenes in volatile orange juice compounds, whereas storage for four months induced an increase of monoterpenes and sesquiterpenes and reduction of esters [16]. The freezing and storage process for twelve months did not significantly affect the flavor profile of four raspberry cultivars [17].

Although pasteurization and freezing of fruits and derivatives are well-established conservation techniques, no study has addressed the volatile characterization of mangaba when subjected to prolonged processing and storage. Thus, this research aims to evaluate the volatile compounds of mangaba pulp submitted to pasteurization processes, freezing methods, and storage for twelve months.

2. Material and Methods

2.1. Obtaining and Sample Preparation

Mangabas (*Hancornia speciosa* Gomes), of Curvelo City, Minas Gerais, Brazil (latitude 18° 45 '23"S, longitude 44° 25'51"W and altitude 632 m), were harvested in November 2013 and used as raw material. The fruits were prewashed, sanitized in sodium hypochlorite solution (100 mg L^{-1} for 15 min) and pulped in a horizontal pulper (Bonina, model 0.25 Df). The pulp was packed in low-density polyethylene bags (100 g per package), using a wrapper/doser (Hubber, model DMM20 manual), and sealed with Termosolder pedal sealer (R. Baião, model 3138). Half of the packages obtained were subjected to pasteurization (85°C for 5 min) and immediately cooled in an ice bath. Pulps without pasteurization proceeded directly to freezing. The two types of pasteurized (P) and unpasteurized (UP) pulp were divided into two batches and frozen by forced air (FA) (forced air freezing chamber, the air velocity was measured at different locations of the chamber using an anemometer Of TSI 9535-USA hot wire, the average air velocity was 1.78 ± 0.08 m/s, and air cooling temperature was -25 ± 3°C for 10 h) or by static air (SA) (-18°C). The pulps were stored in a horizontal freezer (Consul, model CHA31C) at -18°C for 12 months. The volatile compounds were analyzed in fresh fruit and pulps that had been stored frozen for 0, 3, 6, 9 and 12 months. Samples were thawed in tap water.

2.2. Extraction

Volatile compounds were extracted by solid phase microextraction (SPME) technique. Polydimethylsiloxane/divinylbenzene fiber (PDMS DVB, 65 µm, Supelco) was used for the separation of the volatile compounds present in the sample. Four grams of pulp was transferred to a 10 mL flask. The samples were then shaken at a constant rate of 1,400 × g and heated at 40°C for 30 min. The fiber was exposed to the free space of the flask, containing the sample. After 15 min of fiber exposure at room temperature, the syringe was immediately taken to the chromatographic injector, where the volatile compounds were desorbed at 220°C for 2 min.

2.3. Identification

The identification of volatile compounds was performed by gas chromatography, associated with mass spectrometry (CG-MS). A Shimadzu CG-2010 Plus (Shimadzu, Japan), equipped with automatic injector for liquids and gases AOC-5000 (Shimadzu, Japan) with a selective mass detector model QP5050A, was used under the following operating conditions: SLBTM column (5% phenyl- 95% dimethylsiloxane) 30 m × 0.25 mm × 0.25 µm thick, stationary phase 5% diphenyl and 95% polydimethylsiloxane (DB5); injector temperature 220°C; initial column temperature 40°C, increasing at 3°C per min to 240°C; helium carrier gas, at a flow rate of 1.8 mL min^{-1} in the column; ratio of division = 1:8; volume injected, 1 µL; and an initial pressure of 100 KPa column.

The conditions of the mass spectrometer were: selective mass detector operating by electronic impact and impact energy of 70 eV; operating speed 1000 m/z s^{-1}; scanning range 0.5 fragments/s and detected fragments of 29 and 600 Da. Each component was tentatively identified by comparing its retention indices with respect to co-injection of a standard solution of n-alkanes (C8-C20, Sigma- Aldrich, St. Louis, USA) and by comparing the mass spectra of the Wiley library database (Wiley 8. FFNSC, 1.2, lib and LIB) and the literature [18]. The retention indices were and the retention indices of the literature [18] were used for assignments. The concentrations of the constituents present in the volatile fraction were expressed by the percentage area of the total ion chromatogram (area normalized in percentage).

2.4. Statistical Analysis

Data were presented as the mean ± standard deviation. A chemometric approach, principal component analysis (PCA), and hierarchical cluster analysis (HCA) were applied using statistical software R version 3.3.1 (06-26-2916), [19] to analyze the (Unpasteurized = UP and pasteurized = P), two storage method levels (forced air = FA and static air = SA), and storage time (zero = T0 , 3 = T3, 6 = T6, 9 = T9, and 12 = T12 months). Before Chemometrics, all variables were self-staggered as to the statistical significance of all responses. PCA was applied to separate the pulps (n = 19) according to the values of the variables, based on linear correlations. HCA was performed to evaluate similarities between the pulps according to the analyzed variables. In this sense, the similarities of the samples were calculated based on the Euclidean metric, and the Ward method was used to form and to suggest groups of similar samples. The dendrogram imposes a hierarchy by similarity so that it is possible to have a two-dimensional view of the whole set of samples.

3. Results and Discussion

Twenty-five volatile compounds were tentatively identified, 12 of which were in the fruit and 24 in the pulps, corresponding to the average 63.05% of the volatile compounds in the fruit and 79.28% in the pulps. In the fruit, the predominant classes were esters (46.12%), hydrocarbons (13.61%) and alcohols (3.27%), whereas in the pulps esters (46.77%) and alcohols (29.40 %) there predominant (Table 1 and Table 2).

The volatile compounds of mangaba were previously evaluated, and the esters were also identified as the predominant compounds by Assumpção et al. [20] (68.11%), Sampaio and Nogueira [10] (40.9%), and Narain et al. [11] (35.48%).

The esters identified in the fruit and mangaba pulps over the storage time are presented in Table 1. In the fruit, we detected 4-Pentenyl acetate (28.69%), isopentyl acetate (11.34%) and prenyl acetate (5.57%). The isopentyl acetate and prenyl acetate esters have already been identified among the major compounds in mangaba [10,20,21]. Hexyl acetate and ethyl acetate were also previously identified in the fruit [10,12] although hexyl acetate was identified in this study only from the ninth month of storage. The literature describes these esters as having a strong, sweet, fruity aroma, similar to pineapple, banana and tropical fruits [22,23,24]. According to Oliveira et al., [20] mangaba puree has a fruity and tropical aroma due to the relatively large amount of isopentyl acetate and 4-pentenyl acetate, and the complexity of the aroma is attributed to the additional esters.

At time zero (immediately after processing), the esters present in the fruit presented different behavior when submitted to processing and pasteurization. While ethyl acetate and isopentyl acetate decreased their area percentages with processing and pasteurization, 4-pentenyl acetate and prenyl acetate increased with processing but reduced with pasteurization. Throughout the storage time, ethyl acetate and prenyl acetate, in general, tended to be elevated independently of pasteurization and freezing method. The accumulation of ethyl acetate is associated with the development of *off-flavors* and chemical aroma [25, 26]. Different from these results, Sádecká et al. [16] identified a significant reduction of esters, among them ethyl acetate, when evaluating the stability of volatile compounds of pasteurized orange juice stored refrigerated for 4 months. Isopentyl acetate and 4-pentenyl acetate showed some stability in both pasteurized (P) and unpasteurized UP pulps in the two freezing methods. Only the hexyl acetate ester was identified with small percentages of the area from the ninth month of storage, independent of pasteurization and freezing method; indicating that this compound was formed after prolonged storage. However, as it has a pleasant fruity aroma and pear odor [27], its presence does not compromise the aroma of stored pulp.

Table 2 shows the fruit alcohols and mangaba pulps. In the fruit, the 3-methyl-3-buten-1-ol was predominant (2.56%). The 3-methyl-3-buten-1-ol, 1-Butanol (3-methyl), 2,3-butanediol, ethanol, and hexanol alcohols identified in this paper have been previously identified in mangaba [20].

Table 1. Percentage of area of esters tentatively identified in mangaba fruit and pulps

			Esters				
	Time (months)	**Samples**	Ethyl acetate	Isopentyl acetate	4-Pentenyl acetate	Prenyl acetate	Hexyl acetate
			LRI* 819	881	918	874	1071
% Area* **	**0**	**F**	0,52 ± 0,60	11,34 ± 0,76	28,69 ± 6,36	5,57 ± 6,29	nd**
		UP	0,33 ± 0,14	7,61 ± 0,48	50,29 ± 11,26	6,23 ± 3,56	nd
		P	0,37 ± 0,20	6,52 ± 2,96	44,11 ± 18,20	3,38 ± 0,73	nd
	3	**UPSA**	0,21 ± 0,02	18,69 ± 1,77	25,02 ± 0,49	10,05 ± 3,39	nd
		UPFA	0,31 ± 0,20	15,18 ± 0,20	30,79 ± 13,39	6,41 ± 2,86	nd
		PSA	0,33 ± 0,21	15,86 ± 1,56	23,91 ± 1,41	3,17 ± 4,48	nd
		PFA	0,30 ± 0,19	18,54 ± 0,95	25,38 ± 4,52	nd	nd
	6	**UPSA**	0,51 ± 0,12	11,17 ± 2,40	29,59 ± 11,29	7,57 ± 3,02	nd
		UPFA	2,10 ± 0,60	16,05 ± 1,90	25,00 ± 3,74	5,97 ± 1,38	nd
		PSA	0,09 ± 0,04	5,85 ± 0,23	21,83 ± 10,24	nd	nd
		PFA	0,10 ± 0,01	8,72 ± 0,69	28,45 ± 9,40	nd	nd
	9	**UPSA**	6,86 ± 2,25	13,67 ± 10,88	15,22 ± 7,50	9,79 ± 5,04	0,1 ± 0,08
		UPFA	2,94 ± 0,03	4,58 ± 3,29	20,92 ± 5,01	9,48 ± 7,55	0,14 ± 0,02
		PSA	5,40 ± 2,22	15,11 ± 11,17	15,68 ± 9,30	8,97 ± 6,72	0,10 ± 0,10
		PFA	5,05 ± 3,08	12,99 ± 9,38	21,50 ± 18,60	9,99 ± 5,01	0,13 ± 0,01
	12	**UPSA**	1,83 ± 0,22	10,75 ± 12,24	7,88 ± 4,48	9,33 ± 8,92	0,06 ± 0,04
		UPFA	5,13 ± 2,42	13,36 ± 7,67	13,53 ± 7,67	8,68 ± 4,91	0,10 ± 0,06
		PSA	5,79 ± 3,15	13,02 ± 5,94	17,06 ± 2,20	5,41 ± 5,71	0,11 ± 0,03
		PFA	3,18 ± 1,10	4,21 ± 0,78	31,91 ± 9,43	12,16 ± 3,61	0,11 ± 0,01

*LRI (Wiley-NIST): Linear retention indices matching with the Wiley 7th Edition and NIST 05 Mass Spectra Libraries. **nd: not detected. ***Mean values from two repetitions ± Standard deviation. Acronyms: F (fruit), SP (unpasteurized SPAE (unpasteurized frozen by static air), SPAF (unpasteurized frozen by forced air), PSA (pasteurized frozen by static air) and PFA (pasteurized frozen by forced air)), P (pasteurized).

Table 2. Percentage of area of alcohols tentatively identified in fruits and mangaba pulps

	Time (months)	Samples	Ethanol	Butanol	1-Butanol <3-methyl->	3-methyl-3-buten-1-ol	2-Buten-1-ol, 3-methyl-	2,3-Hexanediol	2,3-Butanediol	Hexanol
			LRI* 930	907	747	746	1245	906	804	891
% Area***	0	F	0,77 ± 0,95	nd**	nd	2,56 ± 2,95	nd	nd	nd	nd
		SP	2,76 ± 0,43	nd	7,54 ± 1,39	1,10 ± 1,55	nd	nd	nd	nd
		P	3,33 ± 3,34	nd	nd	3,84 ± 5,42	nd	nd	nd	nd
	3	UPSA	20,76 ± 2,98	nd	8,33 ± 0,92	2,59 ± 0,75	nd	nd	nd	nd
		UPFA	16,52 ± 2,81	nd	2,69 ± 3,80	2,72 ± 1,03	nd	nd	nd	nd
		PSA	15,51 ± 4,50	nd	1,60 ± 1.21	4,54 ± 1,25	nd	nd	nd	nd
		PFA	14,75 ± 3,89	nd	1,72 ± 2,43	1,98 ± 0,03	nd	nd	nd	nd
	6	UPSA	15,17 ± 3,51	nd	8,69 ± 0,68	6,46 ± 0,90	nd	nd	nd	0,05 ± 0,06
		UPFA	16,78 ± 1,65	nd	8,09 ± 0,46	5,05 ± 4,19	nd	nd	nd	0,12 ± 0,01
		PSA	13,45 ± 5,48	nd	1,18 ± 0,20	4,01 ± 5,67	nd	nd	nd	0,05 ± 0,06
		PFA	15,90 ± 0,65	nd	1,18 ± 0,21	6,53 ± 0,54	nd	nd	nd	0,07 ± 0,09
	9	UPSA	21,31 ± 17,06	0,13 ± 0,03	4,90 ± 1,27	9,33 ± 2,45	1,03 ± 0,04	0,05 ± 0,04	2,45 ± 1,86	0,15 ± 0,09
		UPFA	20,54 ± 11,05	0,11 ± 0,01	1,44 ± 0,92	5,64 ± 2,14	1,26 ± 0,34	0,69 ± 0,76	7,10 ± 4,89	0,12 ± 0,04
		PSA	20,13 ± 14,85	0,00 ± 0,00	6,57 ± 2,67	10,85 ± 6,68	1,16 ± 0,63	0,09 ± 0,01	1,44 ± 0,78	0,10 ± 0,03
		PFA	18,54 ± 14,15	0,00 ± 0,00	2,74 ± 2,23	5,24 ± 1,34	1,35 ± 0,30	0,18 ± 0,06	5,57 ± 6,39	0,09 ± 0,13
	12	UPSA	25,43 ± 11,12	0,16 ± 0,05	2,12 ± 2,55	9,59 ± 6,44	1,17 ± 1,48	0,19 ± 0,26	5,87 ± 5,59	1,10 ± 1,45
		UPFA	19,98 ± 10,70	0,13 ± 0,02	6,58 ± 2,56	10,94 ± 5,44	1,55 ± 0,80	0,11 ± 0,03	5,57 ± 2,67	0,20 ± 0,11
		PSA	13,38 ± 6,87	0,05 ± 0,04	3,37 ± 1,22	5,12 ± 1,13	0,58 ± 0,04	0,10 ± 0,01	5,83 ± 4,72	0,10 ± 0,02
		PFA	13,34 ± 5,06	0,06 ± 0,01	1,69 ± 0,33	6,45 ± 0,93	0,69 ± 0,47	0,33 ± 0,02	7,32 ± 2,03	0,09 ± 0,01

Ethanol, 1-Butanol 3-methyl, and 3-methyl-3-buten-1-ol are identified at all times and treatments except for 1-Butanol 3-methyl, which is not identified in the fruit or pulp of SP (without pasteurization) at time zero. This indicates that these alcohols are common constituents of mangaba pulps. These alcohols have an alcoholic aroma, fruity, fresh and floral notes [24,28,29,30].

The ethanol present in the fruit increased as a percentage with the processing (+358.44% with the pulp and +432.46% with the pasteurization). This increase was even more significant with increasing storage time (Table 2) with similar behavior in both the P and SP pulps in the two freezing methods. Although the alcohols are common constituents of mangaba and other fruits, they contribute little to the flavor and are irrelevant as volatile impact compounds [14]. However, the literature indicates that the accumulation of some alcohols, such as ethanol, is associated with changes in the fruit aroma profile due to an increase in the production of ethyl esters in relation to other alkyl esters [31, 43]. It has been described as having chemical and penetrating aromas [24], a very mature fruit and an *off-flavor*, suggesting a lower preference for flavor [32]. Increased ethanol over 12 months of frozen storage in strawberry pulps was also recently identified [15].

Thus, we detected an increase in area percentages and the generation of different types of alcohols during long-term storage (butanol, 2-buten-1-ol-3-methyl, 2-3 hexanediol, 2-3 butanediol and hexanol) of both the P pulps and in the SP pulps and independent of the freezing method. This might compromise the flavor quality of the mangaba pulp since these alcohols are described as having intoxicating, alcoholic, spicy, green, herbaceous, fresh and fruity aromas.

Identification of such alcohols, even when the pulp has been frozen, indicates that volatile synthesis enzymes can be retained during frozen storage and subsequently activated during thawing. In addition, as water does not pass into the crystalline state, the occurrence of chemical and enzymatic reactions may continue, although at lower speeds [33].

Table 3. Percentage of area of tentatively identified hydrocarbons in mangaba fruit and pulp

	Time (months)	Samples	Undecane	Dodecane	Pentadecane	Hexadecane	Heptadecane	Octadecane
			LRI* 1100	1200	1500	1628	1678	1724
% Area***	0	F	0,51 ± 0,35	4,90 ± 6,63	1,33 ± 0,50	4,98 ± 3,43	1,50 ± 0,29	0,40 ± 0,42
		UP	0,45 ± 0,13	nd**	0,93 ± 0,71	0,32 ± 0,12	0,64 ± 0,33	1,25 ± 0,45
		P	0,43 ± 0,12	nd	0,81 ± 0,43	1,38 ± 0,05	0,76 ± 0,37	1,15 ± 0,38
	3, 6, 9 e 12	UPSA	nd	nd	nd	nd	nd	nd
		UPFA	nd	nd	nd	nd	nd	nd
		PSA	nd	nd	nd	nd	nd	nd
		PFA	nd	nd	nd	nd	nd	nd

Table 3 shows the aliphatic hydrocarbons (C11-C18 alkanes) tentatively identified in the mangaba and pulp samples submitted to the treatments. The hexadecane (4.98%) and dodecane (4.90%) were predominant in the fruit. Among the n-alkanes shown in Table 3, pentadecane, hexadecane, heptadecane, and octadecane were previously reported in mangabas [10,12].

All of the hydrocarbons were identified only at time zero, in the fruit and the pulps SP and P. Dodecane was only identified in the fruit, and the others decreased with processing. It is believed that n-alkanes are endogenous and formed from the decarboxylation of long chain fatty acids present in plants [34]. Hydrocarbons typically have relatively high odor detection thresholds and probably have little contribution to aroma [35], and need to be present at high concentrations to be perceived. As they presented low percentages of the area, even at time zero, especially after processing and pasteurization, it can be suggested that their absence from the 3-month stored sample would not compromise the aroma of mangaba pulps.

The aldehyde, terpene, ketone, and acid class compounds are shown in Table 4. Pentanal and nonanal aldehydes, terpenes linalool and ocimene, butane-2-one-hydroxy ketone, and acetic acid have been tentatively identified. All of these compounds were identified from the 6-month (linalool) and 9-months frozen samples, presenting similar behavior in both P and SP pulps, regardless of the freezing method. The nonanal and linalool were identified in mangaba stored at different temperatures (0–24°C) and storage times (0–20 days) [12] and also at different stages of maturation [10,11] Lima et al. [12] have identified 3-hydroxy-> Butan-2-one in mangabas after 5 days of storage (24°C).

Other studies have identified the increase of linalool in strawberries and by-products submitted to freezing/thawing and prolonged storage [13,15,25].

Although many of the flavors of cooked and processed foods come from modest concentrations of aldehydes and ketones [36], they are the main volatile compounds of autoxidation, which can cause odor of paint, grease, metal, and candle in food, and pentanal is used to evaluate food stability, as it favors undesirable aromas [37] and its quantification is a useful method of measuring oxidation Lipid. The pentanal is described as a green scent and pungent [38], whereas the nonanal has a greasy floral aroma [23]. Thus, the presence of these aldehydes from the ninth month in the mangaba pulp may indicate flavor degradation independent of pasteurization (UP or P) and the freezing method (SA or FA) with increasing storage time, even though they presented low percentages of the area in all the treatments.

The linalool and ocimene terpenes provide floral [24] and herbaceous and mushroom aromas [39], respectively. The increase in the content of monoterpenes with thermal treatment of spices was attributed to the increase in the thermal isomerization of some terpenes [40,41]. In the case of this study, the detection of linalool (third month) and ocimene (ninth month) was independent of the pasteurization or freezing method, suggesting that the time factor may be more important. This is likely because enzyme activities are paused but not eliminated when frozen [9].

In the present study, the use of butan-2-one <3-hydroxy->, which was previously identified in stored mangaba[12], is associated with creamy, buttery and lactic odors [23,24,27]. Its presence with percentages of the area ranging from 2.52% to 11.42% from the ninth month of storage in all treatments may be associated with aroma degradation with increased storage.

The acetic acid, also identified from the ninth month, has a strong odor [27], of vinegar [24,42] and therefore is unpleasant indicating degradation of the aroma of mango pulps when stored for long periods.

Table 4. Percentage of area of aldehydes, terpenes, ketone and acid tentatively identified in mangaba fruit and pulps

			Aldehydes		Terpenes		Ketone	Acid
	Time (months)	**Samples**	Pentanal	Nonanal	Linalool	Ocimene	Butan-2-one <3-hydroxy->	Acetic Acid
			LRI* 1007	1163	1157	1041	779	968
% Area* **	**0**	**F**	nd**	nd	nd	nd	nd	nd
		UP	nd	nd	nd	nd	nd	nd
		P	nd	nd	nd	nd	nd	nd
	3	**UPSA**	nd	nd	nd	nd	nd	nd
		UPFA	nd	nd	nd	nd	nd	nd
		PSA	nd	nd	nd	nd	nd	nd
		PFA	nd	nd	nd	nd	nd	nd
	6	**UPSA**	nd	nd	0,37 ± 0,42	nd	nd	nd
		UPFA	nd	nd	0,31 ± 0,35	nd	nd	nd
		PSA	nd	nd	0,61 ± 0,86	nd	nd	nd
		PFA	nd	nd	0,56 ± 0,57	nd	nd	nd
	9	**UPSA**	0,50 ± 0,45	0,08 ± 0,11	0,07 ± 0,02	0,08 ± 0,02	8,42 ± 5,69	1,13 ± 1,26
		UPFA	0,57 ± 0,66	0,08 ± 0,1	0,10 ± 0,05	0,09 ± 0,05	11,43 ± 0,70	4,84 ± 3,97
		PSA	1,43 ± 1,24	0,07 ± 0,03	0,24 ± 0,11	0,07 ± 0,03	2,52 ± 1,44	0,50 ± 0,03
		PFA	2,02 ± 0,22	0,12 ± 0,04	0,19 ± 0,08	0,12 ± 0,06	4,72 ± 6,68	1,28 ± 1,20
	12	**UPSA**	0,76 ± 0,04	0,11 ± 0,00	0,17 ± 0,08	0,07 ± 0,01	8,07 ± 9,96	3,37 ± 4,64
		UPFA	0,89 ± 0,04	0,10 ± 0,01	0,04 ± 0,01	0,06 ± 0,03	4,97 ± 1,43	0,12 ± 0,16
		PSA	0,14 ± 0,18	0,15 ± 0,00	0,33 ± 0,08	0,11 ± 0,04	7,85 ± 9,84	1,02 ± 1,44
		PFA	1,42 ± 1,56	0,21 ± 0,08	0,22 ± 0,11	0,11 ± 0,02	11,34 ± 7,21	1,95 ± 0,18

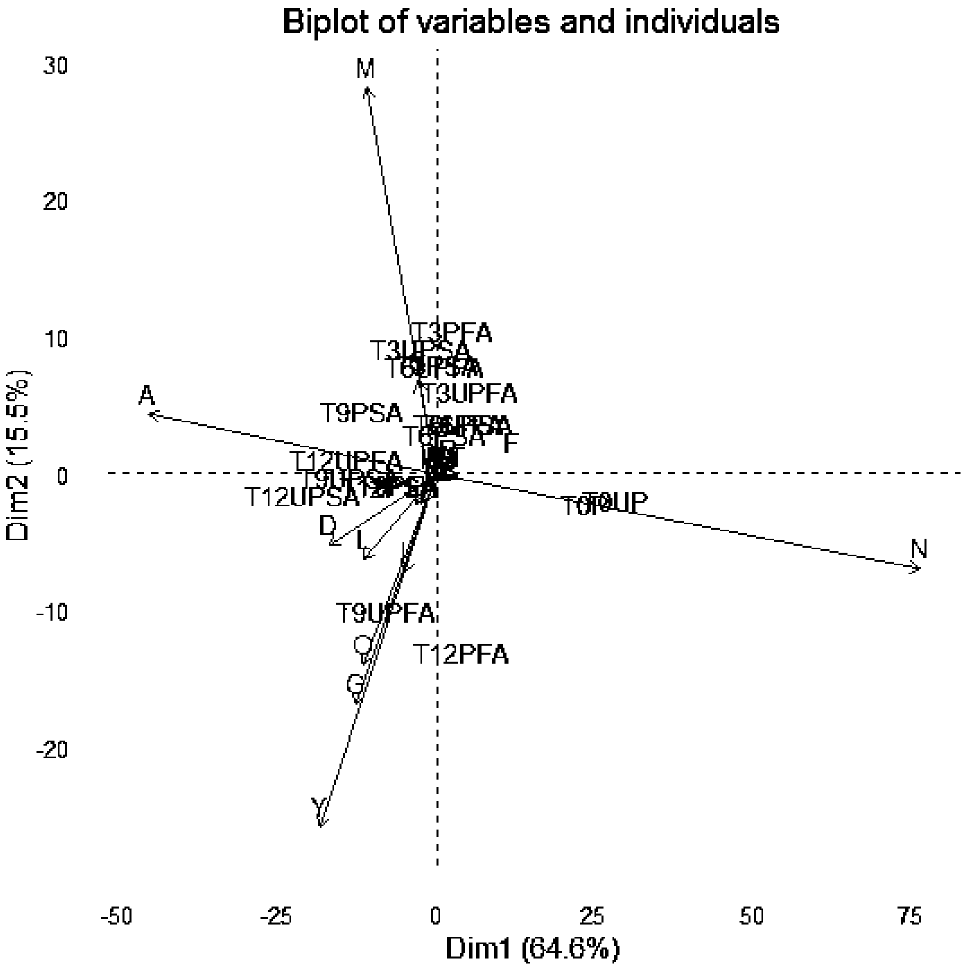

Figure 1. PCA of the volatile compounds of mangaba pulps. T0 = zero time, T3 = 3 months, T6 = 6 months, T9 = 9 months and T12 = 12 months of storage. Unpasteurized froze by static air (UPSA); unpasteurized frozen by forced air (UPFA); pasteurized frozen static air (PSA); and pasteurized frozen by forced air (PFA). Compounds: ethanol (A); butanol (B); 1-Butanol 3-methyl- (C); 3-methyl-3-buten-1-ol (D); 2-Buten-1-ol, 3 (E); 2,3-Hexanediol (F); 2,3-Butanediol (G); hexanol (H); acetic acid (I); pentanal (J); nonanal (K); ethyl acetate (L); isopentyl acetate (M); 4-Pentenyl acetate (N); prenyl acetate (O); hexyl acetate (P); undecane (Q); dodecane (R); pentadecane (S); hexadecane (T); heptadecane (U); octadecane (V); linalool (W); ocimene (X); and butan-2-one <3-hydroxy-> (Y)

In the PCA (Figure 1) the two major components cluster together, explaining 80.1% of the variability between the samples. In the PCA, the without pasteurization and zero storage time (T0UP) and pasteurized and zero storage time(T0P) samples differed from the others and were characterized mainly by the high percentage of the area of 4-Pentenyl acetate (N) ester, which was identified with the highest percentage of area in the fruit (Table 1). 4-Pentenyl acetate has a fruity aroma. The grouping of these samples at time zero indicates that, even after processing and pasteurization, the pulps retained a similar aroma to that of the fresh fruit, since as discussed earlier, the mangaba flavor is due to the relatively large amount of 4- Pentenyl acetate and isopentyl acetate, in addition to other additional esters [21].

The samples unpasteurized by static air with twelve months of storage (T12UPSA), unpasteurized frozen by forced air with twelve months of storage (T12UPFA), pasteurized frozen by static air with twelve months of storage (T12PSA), unpasteurized frozen by static air with nine months of storage (T9UPSA), unpasteurized frozen by forced air with nine months of storage (T9UPFA), and pasteurized frozen by static air with nine months of storage (T9PSA) were grouped by ethanol (A), 3-Methyl-3-Buten-1-ol (D), 2-Buten-1-ol, 3-methyl- (E), 2,3-Butanediol (G), acetic acid (I), Ethyl acetate (L), Prenyl acetate (O), and Butan-2-one <3-hydroxy- (Y). This group is represented mostly by samples without pasteurization and samples stored for a longer period. While this group is characterized by pleasant aromas of esters, alcohols and ketones, the high percentages of ethanol and ethyl acetate area may indicate aroma degradation, since the accumulation of these compounds is related to the development of off-flavors [25], which is reinforced by the presence of 2,3-Butanediol and acetic acid in this group. Thus, the absence of pasteurization and the increase in storage time, indicate that the pasteurization of pulps may compromise the flavor quality of mangaba. The T3PSA, T3PFA, T6PSA, T6PFA and fruit, samples were characterized by the esters prenyl acetate (O) and hexyl acetate (P). This group is composed of the fruit and by pasteurized samples that were stored for up to six months, suggesting that pasteurization, independent of the freezing method (AE or AF) and a shorter storage time, favor the maintenance of the aroma similar to fresh fruit, as the esters that identify this group attribute a pleasant, sweet fruity aroma of pear, banana, pineapple and tropical fruits [22,26,27,28].

The T3UPSA, T3UPFA, T6UPSA, T6UPFA, T9PFA, and T12PSA samples were grouped by a large percentage of the area of the alcohol 1-butanol (3-methyl-> (C) and isopentyl acetate ester [M]). They are samples without pasteurization or pasteurized and stored for nine and twelve months. While such compounds are associated with pleasant aromas, high percentages of the area may indicate some degradation of the aroma, by providing a very intense aroma of the compound over the perception of other substances important for the harmony of the aroma. However, as discussed earlier, the accumulation of alcohols is related to undesirable changes in the aroma profile [31,43].

The similarity of the samples was evaluated using hierarchical cluster analysis (HCA), which seeks to group the samples into classes, based on the principle that spatially closer samples are similar and, therefore, can be considered belonging to the same class or group [44]. The HCA analysis is represented as a dendrogram (Figure 2) for volatile compounds from the mangaba pulps of the 19 samples. By this approach, we detected four clusters with groupings defined according to the Ward method, which confirm the groupings identified by PCA.

Cluster one is composed of the UP and P samples at time zero, indicating that these samples are similar. Cluster two included the T12UPSA, T12UPFA, T12PSA, T9UPSA, T9PSA and T9UPFA samples, which have mostly been stored for a longer period of time and not submitted to pasteurization. Cluster three includes the T3PSA, T3PFA, T6PSA, T6PFA and the fruit samples, which had been stored for a shorter period, including fruit submitted to pasteurization. The fourth cluster consists of the T3UPSA, T3UPFA, T6UPSA, T6UPFA, T9PFA, and T12PSA samples, which were mostly not pasteurized and had been stored for a short period or were pasteurized and stored for a longer period.

The results showed significant differences in the volatile compounds with the applied treatments, especially with pasteurization and storage time. In findings of the present study were similar to those reported in the literature (Table 1). Studies with frozen strawberry and pulp identified a significant increase in volatile compounds after thawing[13] and subjected to high pressure. The latter authors attributed this increase to β-glucosidase activity during storage, since this enzyme acts on the release of volatiles into fruits. On the other hand, De Ancos et al. [8] did not identify significant differences in the aroma profile of different frozen raspberry cultivars stored for 12 months.

To preserve the volatile compounds responsible for the aroma, we recommend the pasteurization of mangaba pulp before freezing. This effect, however, is observed only for six months of storage, because pulps stored for periods of six months or longer, independent of the freezing method, tended to be grouped and characterized by compounds normally associated with aroma degradation. Based on our findings, frozen storage may cause loss of the compounds responsible for the aroma and also the accumulation of undesirable products and indicators of the development of off-flavors [15,45].

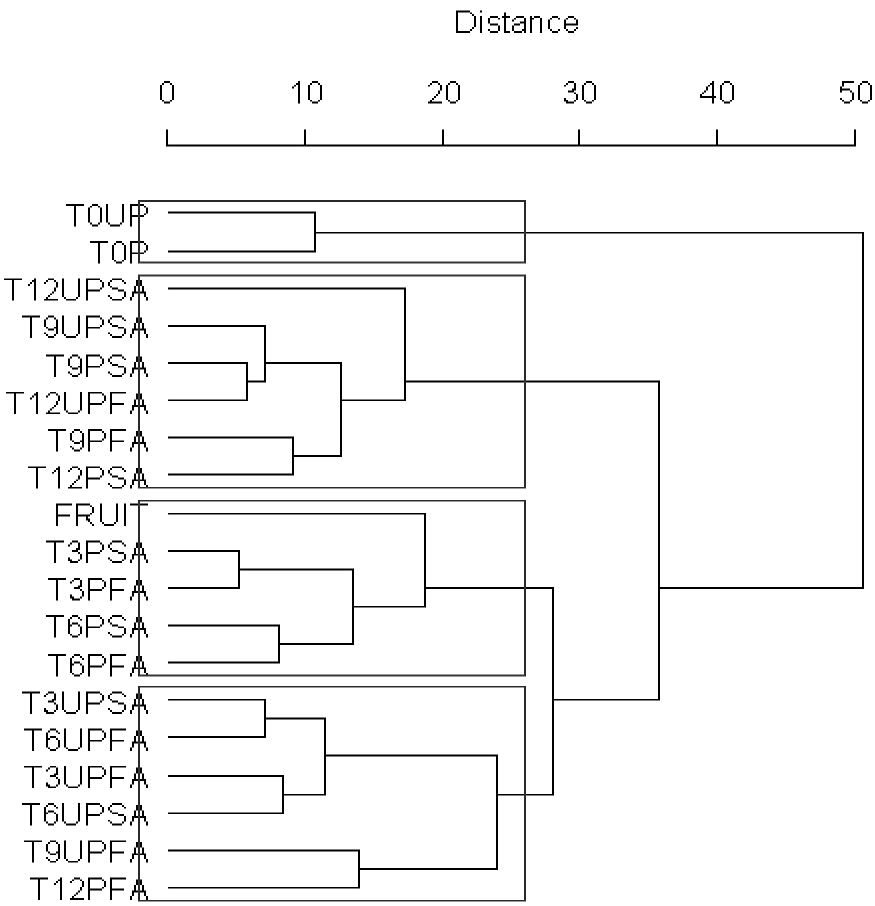

Figure 2. A hierarchical cluster analysis based on the volatile compounds of mangaba pulps. Codes used: T0 = zero time, T3 = 3 months, T6 = 6 months, T9 = 9 months and T12 = 12 months of storage. Unpasteurized frozen by static air (UPSA); unpasteurized frozen by forced air (UPFA); pasteurized frozen by static air (PSA); and pasteurized frozen by forced air (PFA)

4. Conclusion

Twenty-five volatile compounds were tentatively identified in the fruit and pulp of mangaba. Esters predominated in both the fruit and pulps, with a predominance of 4-pentenyl acetate and isopentyl acetate, whereas ethanol predominance was observed after three months of storage.

The pasteurization favors the preservation of aroma compounds of the mangaba pulp, independent of freezing. Frozen storage from nine months favors the development or accumulation of compounds responsible for aroma degradation, such as ethanol, ethyl acetate, and acetic acid.

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Statement of Competing Interests

The authors have no competing interests.

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