Evaluation of *Hancornia speciosa* Gomes Lyophilization at Different Stages of Maturation

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Abstract-Mangabeira (Hancornia speciosa Gomes), a native plant in Brazil, is found growing spontaneously in various regions of the country. The high perishability of tropical fruits such as mangaba, causes it to be necessary to use technologies that promote conservation, aiming to increase the shelf life of this fruit and add value. The objective of this study was to compare the mangabas lyophilization curves behaviors with different sizes and maturation stages. The fruits were freeze-dried for a period of approximately 45 hours at lyophilizer Liotop brand, model L -108. It has been considered large the fruits between 38 and 58 mm diameter and small, between 23 and 28 mm diameter and the two states of maturation, intermediate and mature. Large size mangabas drying curves in both states of maturation were linear behavior at all process, while the kinetic drying curves related to small fruits, independent of maturation state, had a typical behavior of drying, with all the welldefined steps. With these results it was noted that the time of lyophilization was suitable for small mangabas, a fact that did not happen with the larger one. This may indicate that the large mangabas require a longer time to freeze until reaches the equilibrium level, as it happens with the small fruits, going to have constant moisture at the end of the process. For both types of fruit were analyzed water activity, acidity, protein, lipid, and vitamin C before and after the process.

Keywords—Freeze dryer, mangaba, conservation, chemical characteristics.

I. INTRODUCTION

OVER the time, the tropical fruits have been winning their market space, because they possess an exotic flavor different from other fruits, besides being good nutritional sources. Among these fruits is *Hancornia speciosa* Gomes, commonly known as "mangaba", a plant species found in Brazil, especially in the North and Northeast, which has great potential for exploitation, mainly in agribusiness. The fruit has great flavor and is used mainly in the production of jams, squashes, compotes, ice creams and juices, with industrial use

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becoming more widespread due to the wide acceptance [1].

In Sergipe, mangaba is one of the fruits most abundant and sought after in the free fairs, reaching price higher than of grapes and other noble fruits [2]. Generally, is explored in extractive. According to [3], the fruit of mangabeira is an important source of nutrients and it is easily digestible, which the high demand for fresh consumption and its derivatives suggest studies on the composition and quality.

The fruit is classified as a berry type, with rounded or ellipsoid shape, reaching up to 6.5cm. The color of the peel varies from light green to yellowish, with grooves yellowish or reddish. The different shapes and colors can be associated with the variety or progeny. These and other features such as variability in fruit size and productivity, demonstrated the need for selection and evaluation for commercial purposes [1]-[4].

The fruit is fully utilized. Besides the use of fruit pulp, the peel is used in combating skin disorders, diabetes and obesity [5]. The latex, beyond to heal fractures and blows, it is used against cramp pulmonary and for produce rubber balls by native children. Its leaf is used against menstrual colic. The greenish yellow fruit is very aromatic [5]-[7].

After removal from the mother plant, the fruit continues with their metabolic processes, reducing the shelf life. Thus, it is necessary to use techniques for maintaining postharvest quality of fruits, as a process of dehydration, extremely common for this purpose. In addition to being used as a method of preservation, preventing the deterioration and loss of commercial value, the method also results in a product transformation, adding value and giving rise to a new alternative in the market [7].

Freeze-drying is a very important separation process involving a moving sublimation interface and fundamental mechanisms of heat and mass transfer, with use widespread in the fine chemicals, food, pharmaceutical, and biotechnology industries [8], [9]. It consists of three steps: freezing, primary drying and secondary drying [10]. During the freezing step, the liquid formulation is cooled until ice starts to nucleate, which is followed by ice growth. This results in the separation of most of the water into ice crystals from a matrix of glassy and/or crystalline solutes [11], [12]. In the primary drying, the crystalline ice formed during freezing is removed by sublimation. Therefore, the chamber pressure is reduced well below the vapor pressure of ice and the shelf temperature is raised to supply the heat removed by ice sublimation [13]. At the completion of primary drying, the product can still contain approximately 15-20% of unfrozen water, which is, then, desorbed during the secondary drying stage, usually at

elevated temperature and low pressure, to finally allow the desired low moisture content to be achieved. Such as others fresh fruit pulps, the mangaba submitted to freeze-dried treatment may be intended for the same purposes, which are preparations of juice, frozen sweets, popsicles, among other products. However, the dehydrated have the advantage of enabling the expansion of the mangaba consumption to areas where it were not native; increase its lifespan, because it is a seasonal and highly perishable fruit, in addition to offer a value-added product, with nutritional characteristics close to natural [14].

Lyophilizing is divided into three main stages: freezing, sublimation and desorption, differentiating itself. from other drying techniques because the product can be reconstituted easily, due to the pore structure formed resembles a beehive, which generates a good permeability of the product; operating conditions do not provide protein denaturation, the loss of volatile compounds (taste and aroma) and thermosensitive vitamins, as well as hindering the proliferation of microorganisms, shrinkage is minimal and does not occur besides the formation of hard and impermeable layer ("case-hardening") [15].

This study aimed to compare the behavior of lyophilizing curves of mangaba in different sizes and in two stages of maturation, intermediate and mature, analyzing the behavior of some characteristics of the fruit after the drying process.

II. MATERIALS AND METHODS

This work was conducted at the Laboratory of Processing Products from Vegetal Origin, located in the Department of Food Technology, at Universidade Federal de Sergipe(UFS), and Bromatology Laboratory at Instituto de Tecnologia e Pesquisa do Estado de Sergipe(ITPS) . The fruits used in the experiments were purchased in Abaís beach, located in Estância-SE and transported to the laboratory, cooled in ice buckets.

The mangabas were selected manually, eliminating the fruits which showed non-conformities (injury, disease caused by pests, green fruits or fruit in a state of senescence, etc.). It was used two maturation stages, which were identified based on peel color and texture of the fruit [16]. For this paper, the yellow-green peel's color indicated the intermediate stage and the yellow color, mature fruit.

As for the choice of mangabas of different diameters, the following criterion was used for characterization: small mangabas were considered those that have a diameter less than 30mm and for large the fruit diameter greater than 38mm. As a result, in the proposed study were lyophilized mangabas large (between 38 and 58mm diameter) and small (between 23 and 28mm in diameter).

The selected material was sanitized in active chlorine solution of 200 ppm for 10 minutes and then washed in potable water. After sanitization, the fruits were frozen and freeze-dried for a period of 45 hours to analyze the kinetics of drying and subsequent chemical composition of fresh mangabas (*in nature*) and lyophilized to verify the influence of the drying process on the parameters in study.

A. Lyophilization

The lyophilization was performed with fresh fruits, in different diameters, frozen at -20°C in a conventional freezer. For lyophilization, it was used the freeze dryer of Liotop mark model L-108, at -50°C and a partial vacuum of 38 μmHg for 45 hours. After the end of the process, the samples were stored in polyethylene packets laminated.

B. Physicochemical Analysis

Analysis of water activity, protein, total acidity and vitamin C with freeze-dried and fresh mangabas, were performed in triplicate, according to the methods described by Instituto Adolfo Lutz manual [33].

C. Statistical Analysis

The experimental data on the physicochemical characterization of freeze dried and fresh mangaba were statistically analyzed using the program STATISTICA $^{\otimes}$, version 11. The comparison between means was performed using the Tukey test at 5% probability.

III. RESULTS AND DISCUSSION

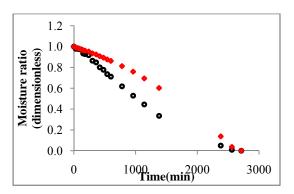
It was studied the kinetics of drying mangabas entire with different diameters and two stages of maturation, intermediate (also called "de vez") and mature, which behavior analyzes of the curves of freeze drying, after 45h of lyophilization, beyond the physicochemical characterization of fresh fruit and lyophilized.

From the results of dry basis moisture content, it was calculated the dimensionless moisture ratio, plotted as a function of lyophilization time in Fig. 1 (a) to large mangabas and in Fig. 1 (b) to small fruits.

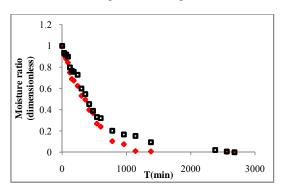
From Fig. 1, it was observed that the graphical representations of the curves are similar, in the first 100 minutes of drying, where the accommodation of drying conditions occurs, with no significant loss of moisture. The curves represent the time required for the fruit adapts to conditions of dehydration and the temperature reaches a constant value.

It was visible the period in which the drying rate is constant for small mangabas, that has not been achieved with great mangabas the same range of process nor after. At this stage, the movement of moisture within the fruit is fast enough to maintain a saturation condition on its surface, with a constant rate controlled by diffusion mechanism of water vapor through the air interface. During this period the sublimation occurs, since the moisture is not linked to the molecular structure of the fruit. This process was finished when all the free water is sublimated.

The beginning of the drying rate constant only for small mangabas occurs at 120 minutes. From this instant the water in the food was easily removed due to the formation of a continuous film of water on the surface of the solid. Because it is a food non-porous and high moisture content, this phase was well defined for all curves.



(a) circle: mangabas large in intermediate stage; lozenge: mangabas large in mature stage



(b) square: mangabas small in intermediate stage; lozenge: mangabas small in mature stage

Fig. 1 Mangabas drying curves at different stages of maturation and diameters

The critical moisture correspond the point where the change occurs in the period the rate constant for the decreasing rate. At this time, the water in the food was removed with difficulty, since movement of the liquid interior to the surface was minimal [17]. According to Fig. 1, it was estimated the critical moisture content for fruits studied, equal to 0.27 for small mature mangaba, 0.33 for small mangaba in the intermediate stage, 0.44 for large mature mangaba and 0, 53 for large mangaba in intermediate stage.

Then, there was the phase in which the rate was decreasing in resistance due to the mass and heat transfer from the dependence of the thermal conductivity of the dry matrix and decreased of moisture concentration. However, it appears that the larger mangabas require a longer drying time curve for the present behave similarly to the lower mangabas.

The values obtained with the mangaba physico-chemical analyze, in intermediate and mature stages, in fresh and lyophilized fruits were presented in Table I.

TABLE I
PHYSICAL-CHEMICAL CHARACTERISTICS (MEAN*±STANDARD DEVIATION) IN
THE INTERMEDIATE AND MATURE STAGES OF FRESH AND LYOPHILIZED
MANGABAS

	Samples			
Parameter	Intermediate stage		Mature stage	
	Fresh	Lyophilized	Fresh	Lyophilized
Water activity	0.97°±0.00	$0.52^a \pm 0.26$	0.98°±0.00	$0.44^{b} \pm 0.01$
Acidity (%)	$6.62^{b} \pm 0.81$	$11.72^{a}\pm1.69$	$6.90^{b} \pm 0.66$	$10.60^a \pm 0.31$
Protein (%)	$12.19^{a}\pm1.00$	$8.30^{b} \pm 0.77$	$11.08^a \pm 0.96$	$7.46^{b} \pm 0.14$
Vitamin C (mg of ascorbic acid.50g ⁻¹ of	119.75 ^b ±15.7	198.13 ^a ±20.22	189.45°±5.07	94.36 ^b ± 11.89
sample)				

^{*} Means in the same line that have the same letter do not differ by Tukey test at 5% probability.

According to the data obtained, it is possible to perceive changes in the values of the parameters analyzed.

After lyophilization, it was observed a reduction in water activity of the fruit due to the drying process. According to [18] for a dry product guarantees stability it is necessary that the water activity is between 0.20 and 0.40 since no decrease in speed of browning reactions, hydrolytic, oxidation, rust liquid, self-oxidation and enzymatic activity. Although the values obtained were not within the range presented, they were considered satisfactory by the proximity in absolute terms.

The levels of acidity, which represents the content of organic acids present in mangaba, had an increase after lyophilization due to concentration by removal of water from the fruit. The same results were obtained in other drying processes, with mango, presenting on the solar-osmotic and fresh dehydration, 0.61 and 1.40%, respectively [19]. As well in drying banana osmotic pretreatment, stored under vacuum, 0.71 to 1.01% citric acid, after drying. [20]

The protein content of fresh mangaba was superior when compared to acerola pulp, 1.27% [21]. Similar values were obtained in lyophilized açaí pulp, 8.13 g .100 g⁻¹ [22].

There was a decrease of the protein content in all samples of mangaba lyophilized compared with fresh samples. According [23], the stability of proteins is influenced by changes in pH. During the freezing of buffer solutions, the concentration of buffer salts will rise, increasing the ionic concentration and possibly changing the pH [23]. This will change the environment and probably the structure and activity level of the protein [24]. Many proteins are stable only in a narrow pH range, such as urokinase with low molecular weight (LMW-UK) at pH 6-7. In extreme pH values, increased electrostatic repulsion between similar loads tend to cause unfolding or denaturing of the protein [23].

When making a comparison with fruits, it is possible that the biochemical processes occurring during lyophilization because the level of acidity increased in all samples after treatment, causing the pH decrease, thus causing denaturation of the proteins, although the type of drying used not involve high temperatures.

The vitamin C content of fresh mangabas, in the intermediate and mature stages, were higher than other fresh fruits such as pineapple, guava, mango and papaya [25]. Also it was verified that the mangaba has a high content of this vitamin. Higher values were presented by [26], between 250 and 300mg of vitamin C.100 g⁻¹ of fresh material in the study of post-harvest conservation of mangaba, and similar values were found by [27] with 190 ± 1.91 mg vitamin C. $100g^{-1}$ of pulp and [28] in mangaba's clones 164.77 to 188.75 54 mg of ascorbic acid. $100 g^{-1}$ of pulp, when compared to mature mangaba. The difference in the values found was due to the C vitamin content vary depending on the soil, climate, maturity stage and even the position of fruit on the tree [29].

After lyophilization, the content of vitamin C of mangaba in the intermediate stage, as seen in freeze-dried fresh fruits of ubaia, was 43.72 mg. 100 g⁻¹ and 112.41 mg. 100 g⁻¹ for lyophilized [30]. However, there was a reduction of approximately 50% of vitamin C for the mature mangaba. As well, they found themselves lost 33.47% in lyophilized powder acerola green while the dry kiln was found 49.52%. [31].

Ascorbic acid is one of the vitamins that can be altered more in food processing, due to the fact that it is water soluble, the action of heat from light, oxygen, alkalis, ascorbic acid oxidase, as well as traces of copper and iron , besides, its conservation is favored in acidic [32] . And as shown in Table I, the vitamin C content of the lyophilized mangaba intermediate stage is higher than mature.

IV. CONCLUSION

The results obtained in the drying kinetics of fruits analyzed allow concluding that the small mangabas showed typical behavior of drying, which did not occur with the largest, that obtained a linear behavior, require a longer freeze time to reach the equilibrium of moisture content. This result is related to the critical moisture which proved to be smaller in reduced diameters of mangabas.

It was noted that after the lyophilization process reduction on water activity and protein content. A total acidity presented an increase in the two states of maturation due to the concentration of the acid after the drying process. It could be observed that mangaba has a high content of vitamin C, where the fruit in the intermidiate stage got an increase and the mature mangaba an reduction in relation to fresh fruit.

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