Vitamin C Content of Freeze-Dried Tropical Fruits

Luanda G. Marques[a], Manoel M. Prado[a]; José T. Freire[b]

[a] *Department of Chemical Engineering, Federal University of Sergipe, São Cristóvão, Brazil (luanda_gimeno@yahoo.com.br)*
[b] *Department of Chemical Engineering, Federal University of São Carlos, São Carlos, Brazil (freire@power.ufscar.br)*

ABSTRACT

Brazil is among the largest producers of tropical fruits in the world. Commercialization of dried fruits has gained importance worldly due to the search of consumers for practicability and products of great nutritional value. The application of the freeze-drying technique in fruits conservation is the key for a successful of their commercialization. Freeze-drying is a technique that preserves the flavor, color and nutrients in the final product. Therefore, the aim of this work was to analyze the vitamin C content in fresh and freeze-dried guava, mango, papaya and pineapple. As the freezing is the first stage of freeze-drying process, it was also evaluated the influence of type of freezing, such as conventional freezer and cryogenic, in the final product. In addition it was carried out a comparative study between freeze-drying and convective drying techniques. The ascorbic acid content of "in nature", freeze-dried and hot air dried pulps was determined using the 2.6 dichlorophenolindophenol titration. Vitamin C content was utilized as the quality parameter. It was observed losses of 37.47 to 3.05% for freeze-dried guava, mango, papaya and pineapple, whereas these losses were of 49.3% after convective drying. The freezing using conventional freezer resulted in highest vitamin C losses.

Keywords: Ascorbic acid; guava; mango; papaya; pineapple

INTRODUCTION

Tropical fruits such as guava, mango, papaya and pineapple have a characteristic smell, diversified flavors and succulent pulps although sweet and acid. They are excellent source of carotenoids (β-carotene, α-carotene, α-cryptoxanthin and lycopene), vitamins (A, C and complex B) and minerals. In recent years, increasing attention has been paid to the role of diet in human health. Among antioxidant vitamins, vitamin C has many biological activities in human body reducing levels of C-reactive protein (CRP), a marker of inflammation and possibly a predictor of heart disease [1], the risk of arteriosclerosis and some forms of cancer [2].

It knows more than 90% of the vitamin C in human diets is supplied by fruits and vegetables [2]. However, the high moisture contents of fruits, approximately 87%, can cause rapid deterioration after cropping. Thus, the dehydration is used to improve fruits stability by decreasing the water activity and microbiological activity to minimize physical and chemical reactions that may occur during storage. Besides aggregating commercial value to the fruits, drying reduces wastes and post -harvest losses, and might allow their commercialization for extended periods of time, with minor dependence on seasonal conditions [3]. The dehydration techniques commonly employed to preserve fruits are: solar drying; hot air drying, microwave drying, osmotic dehydration, foam-mat, fluidized bed drying, spray-drying, and freeze-drying [4].

The high temperature convective drying required for removing water from fruits can cause serious damages to their flavor, texture and color and it also can result in nutrients degradation in the dried product [5, 6]. This technique provides products with longer shelf-life. Nevertheless, the quality of the dried product is inferior if compared to the original product [7].

Among the drying techniques, freeze-drying is a technique that results in high-quality dehydrated products due to the absence of liquid water and the low temperatures required in the process. The solid state of water during freeze-drying protects the primary structure and minimizes changes in the shape of the product, with minimal reduction of volume. In addition, it contributes to preserve constituents as minerals and vitamins, as well as to retain original flavor and aroma [3].

Nutritional characteristics of dehydrated fruits are also evaluated as quality parameters. Ascorbic acid content is usually adopted as the quality index of nutrients in food processing and storage [6]. Authors assume that if a significant portion of vitamin C content is retained after processing, other nutrients are also likely to be preserved because the ascorbic acid is extremely unstable to heat, oxygen, light, pH, moisture content, and heavy metallic ions (Cu^{2+}, Ag^{+} e Fe^{3+}) [2, 5].

In general, quick drying retains larger quantity of ascorbic acid (vitamin C) than slow drying. Therefore, the vitamin C content of vegetable tissue is greatly reduced during the sun and hot air drying, whereas during freeze-drying and spray-drying this loss is reduced [8].

Shadle et al. [9] determined the vitamin C contents of carrots after convective and freeze-drying and observed losses of 81.3% and 60.8% in the dried samples for the first and second techniques, respectively. Yang & Atallah [10] compared the effects of freeze drying, forced air, vacuum micro-convection and oven methods on the quality of lowbush blueberries at intermediate moisture (16-25%). Higher vitamin C and soluble solids retention were observed in the freeze-dried products.

Considering the importance of freeze-drying process to fruits preservation, and the high quality of dried fruits that must be offered to the consumers, the aim of this work was to determine the vitamin C content of fresh and freeze-dried guava, mango, papaya and pineapple, to evaluate the influence of freezing on the vitamin C retention in freeze-dried fruits and to compare the freeze-drying and convective drying using the vitamin C content as the quality parameter.

MATERIALS & METHODS

Fresh fruits (guava, mango, papaya and pineapple) were purchased from local market in the city of São Carlos-SP, Brazil. The cores of the mango and pineapple samples and the seeds of papaya were removed. The fruits were cut into slices of 5 mm thickness and placed in a circular tray with a diameter of 125 mm and height of 15 mm and subsequently were frozen in liquid N_2. The frozen fruits were dehydrated in a laboratorial scale freeze-dryer, manufactured by Edwards, L4KR model.

Freeze-drying tests were performed with total pressure and temperature inside the vacuum chamber of 1.3×10^{-1} mbar and –30ºC, respectively. One thermocouple probe was used to control and monitor the product temperature near to the tray bottom during drying. The sublimation heat was supplied by a heating plate through the tray and the frozen product. The final product temperature during the secondary drying was about 38ºC. The convective drying was performed in forced air oven at 45ºC, 0.6 m/s air velocity, and 42% relative humidity. Moisture content at a given time was calculated by the ratio between the mass of evaporated water and the bone dry mass, which was determined at the end of each experiment by the oven method at (105 ± 3)^{o}C for 24 hours.

The ascorbic acid content of “in nature”, freeze-dried and hot air dried pulps was determined using the 2.6 dichlorophenolindophenol titration. About 4.0 g of “in nature” sample and 1.2 g of dried sample were homogenized with 50 ml of extraction solution (oxalic acid 2%) in a blender for approximately 2 min [11]. An aliquot of 10 ml was taken for titration with 2.6 dichlorophenolindophenol. The titration end point was detected visually and the procedure was repeated ten times for four different samples. Ascorbic acid content was then determined using the following:

$$Aa = \frac{(V_T)(0{,}5/V_t)(V)(100)}{(V_a)(m)} \tag{1}$$

where A_a is the ascorbic acid content (mg/100g), V_T is titration volume (mL), V_t is volume titrationed in standardization (mL), V is checking volume (mL), V_a volume aliquot (mL), and m the sample mass (g).

RESULTS & DISCUSSION

Figure 1 shows the vitamin C content determined for “in nature” tropical fruits and the values found in the literature. Initially it was verified that “in nature” guava and papaya show vitamin C content lower than those mentioned in the literature, while the values obtained for pineapple and mango were higher and similar, respectively, as it can be seen in Figure 1. Regarding this analysis it is necessary to consider the geographic localization differences from the literature data, EUA, and the fruits studied in this work, Brazil. Nelson et al. [12] found a range from 19.3 to 71.5 mg/100g AA in six strawberry cultivars from four locations. In addition, the vitamin C content in fruits can also be influenced by various factors such as genotype differences, climatic conditions, soil state, maturity at harvest and harvesting methods [1, 2]. The higher the intensity of light during the growing season, the greater is vitamin C content in plant tissue [2].

After freeze-drying the moisture content was equal to 5, 4, 2 and 7% (wet basis) for guava, mango, papaya and pineapple, respectively. Figure 2 presents the vitamin C content determined for "in nature" and freeze-dried tropical fruits. It can be observed after the process vitamin C losses of 37.47, 3.05; 6.91, and 27.31% for guava, mango, papaya and pineapple, respectively. The low residual moisture content, inferior than 10% (w.b.), in freeze-dried fruit, allied with the thermal process employed, it may have favored the low vitamin losses, since the degradation reactions rates of ascorbic acid are decreased in dehydrated products with lower moisture content [13].

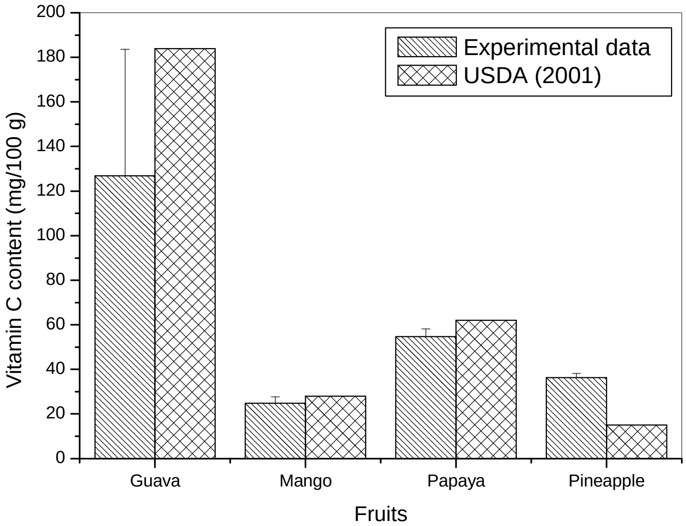

Figure 1. Experimental and literature values of vitamin C content for fresh tropical fruits.

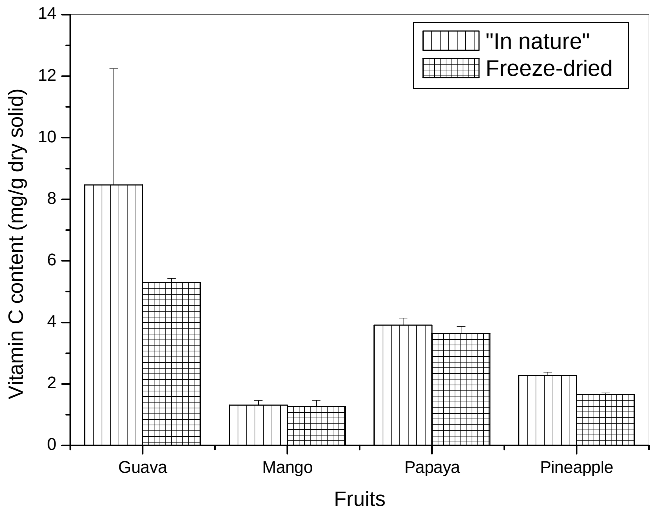

Figure 2. Vitamin C content for the fresh and freeze-dried tropical fruits.

Ascorbic acid oxidation is greatly favored by the presence of heavy metal ions, especially Cu^{2+}, Ag^{+} e Fe^{3+}, alkaline pH, high temperature [2], the salt and sugar concentration and a presence of same enzyme [14]. Thus, the difference in ascorbic acid content of freeze-dried fruits can be explained by the differences between the physical and chemical properties of morphological structures of each fruit.

The results shown in Figure 2 are in agreement with those obtained by Chang et al. [15] who reported a loss of ascorbic acid of 8 and 10%, respectively, in the SN and ITH varieties of tomatoes. LIN et al. [5] found no significant loss of vitamin C in freeze-dried carrots. The stability of ascorbic acid in freeze-dried acerola was studied by Leme et al. [16]. The authors verified an average loss of vitamin C of 5.0% after drying and a loss of 1.0% during storage for 4-9 months at ambient temperature. Marques et al. [3] determined the vitamin C content in freeze-dried acerola for three different ripening stages. It was observed that the smaller loss of vitamin C was of 13% for the intermediate stage (yellow-reddish fruits), while the greater loss was of 69.3% for the green fruit. The vitamin C losses for freeze-dried fruits are considerable smaller when compared the vitamin C losses caused to others drying methods.

Cutting and slicing fruits may induce a rapid enzymatic depletion due to the cellular disruption which allows contacts of substrates and enzymes [1]. Thus, the vitamin C losses can be due not only to primary and secondary drying of freeze-drying (thermal processing), but also by the operations before drying such as cutting, slicing and freezing (first stage of freeze-drying). Ascorbate oxidase has been proposed to be the major enzyme responsible for enzymatic degradation of ascorbic acid. Other plant enzymes, including plenolase, cytochrome oxidase and peroxidase, are indirectly responsible for ascorbic acid loss [2].

Lee & Kader [2] have shown that freezing also results in reduction of the vitamin C content. Thus, a study to verify the influence of freezing on vitamin C content in lyophilized fruits was also performed. Figures 4 and 5 show the vitamin C content for freeze-dried acerola and papaya, respectively, using different types of freezing before lyophilization. Concerning to acerola, there was a loss of 55% using freezing in the freezer, and 53 and 54% using N_2 (l) and N_2 (v). Therefore, for acerola the type of freezing did not influence the vitamin C content in the freeze-dried product. However, for the papaya frozen in the conventional freezer there was a reduction in vitamin C content of 13%, while for samples frozen in N_2 (l) and N_2 (v) the reduction was of 5%. This result was expected, since the degradation of ascorbic acid is greater when material is exposed for long time periods to low temperature ambients.

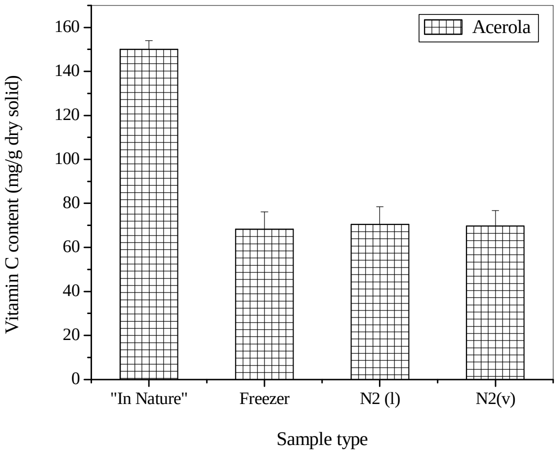

Figure 4. Vitamin C content for “in nature” acerola and freeze-dried samples after three types of freezing: (IN) $X_{d.b.}$ = 10.00; (Freezer) $X_{d.b.}$ = 0.16; (N_2(l)) $X_{d.b.}$ = 0.13; (N_2(v)) $X_{d.b.}$ = 0.16.

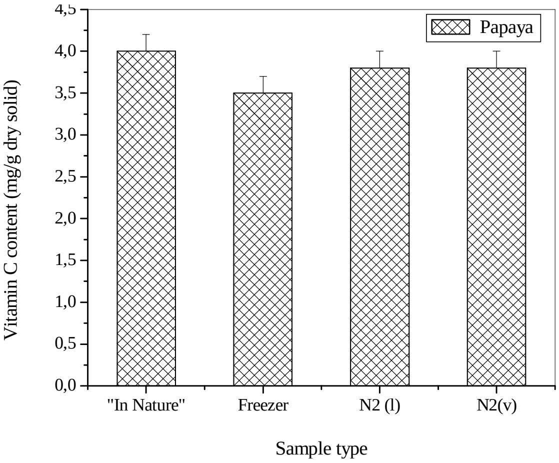

Figure 5. Vitamin C content for “in nature” papaya and freeze-dried samples after three types of freezing: (IN) $X_{d.b.}$ = 7.33; (Freezer) $X_{d.b.}$ = 0.14; (N_2(l)) $X_{d.b.}$ = 0.089; (N_2(v)) $X_{d.b.}$ = 0.082.

The retention of ascorbic acid can be used as an indicator for the quality of dehydrated products, since this vitamin is very heat-sensitive and easily degraded, as discussed earlier. Thus, if vitamin C is well retained in the dry material, other nutrients are probably also preserved [5]. Therefore, it can be seen in Figure 2 that the ascorbic acid content retained in the freeze-dried guava, mango, papaya and pineapple characterizes these products as a valuable source of vitamin C. In Brazil, the Recommended Daily Intake (RDI) for adults is 60 mg. However, a high recommendation of 100-200 mg/day has been suggested, since stress in modern life is known to increase the requirement for vitamin C [2].

The small vitamin C losses in freeze-dried guava, mango, papaya and pineapple are attributed to the low temperatures and to the use of vacuum in the process. In addition, the final structure of freeze-dried tropical fruits, which were neither collapsed nor sticky, probably contributed for the preservation of vitamin C in the product. It must be pointed out that, due to the highly porous structure of freeze-dried products [4], an inadequate storage may cause oxidative reactions, leading to additional losses of vitamin C in the final product. Then, to ensure the quality of the lyophilized products, metal packaging, polyethylene and polyethylene double layer must be used to storage.

In order to corroborate that the freeze-drying is the best method for drying fruits, a comparative study between freeze-drying and convective drying of papaya and pineapple was carried out. The quality of the final product was evaluated in terms of the vitamin C retention.

Initially, it was verified significant differences in the drying times required by each technique. While in freeze-drying it took 24 h for drying papaya (85%) and pineapple (84%), with final moisture contents of 2.3 and 2.8%, respectively, 4 days were required to reach final moisture contents of 4.3% for papaya and 5.5% for pineapple in hot air drying. These results are attributed to the low drying rate conditions used in the convective drying (T=45ºC, v= 0.6 m/s, UR= 42%), order to minimize the ascorbic acid degradation, hardening and collapse of the material.

Figure 6 shows the values of vitamin C content determined in this work for fresh, freeze-dried (FD) and air dried (CD) papaya and pineapple. It can be noticed that vitamin C content in the freeze-dried fruits was higher than the fruits dehydrated conventionally. This result agrees with those reported in literature by Lin et al. [5], who verified that the total loss of vitamin C during air drying of carrot was 62.0%, while the loss for the freeze-dried samples was negligible. Similar results were observed by Shadle et al. [9] and Yang and Atallah [10].

Visually it was possible to note that the product obtained after convective drying displayed a darker appearance when compared with the freeze-dried papaya and pineapple.

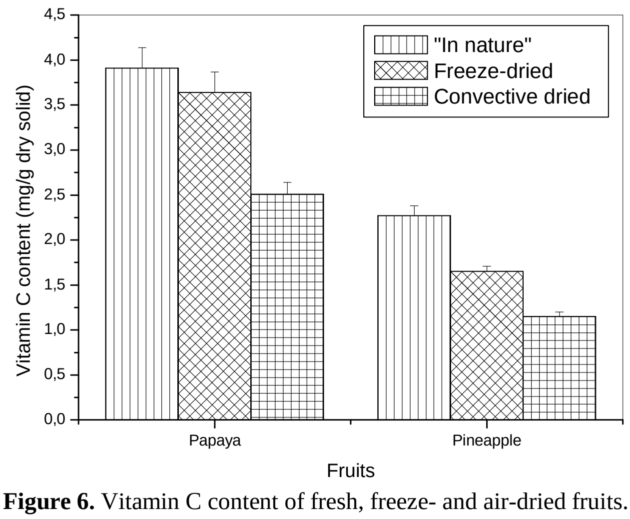

Figure 6. Vitamin C content of fresh, freeze- and air-dried fruits.

The significant losses of vitamin C, 49.3 and 31.0%, for pineapple and papaya, respectively, during the convective drying is related with oxidation of ascorbic acid due at long drying time and the glass transition temperature (Tg). When the process temperature is larger than Tg of materials transition from glassy state to rubbery state occurs. The rubbery state of material is characterized by high mobility of the matrix, which contributes for its deformation and changes such as stickiness, collapse and crystallization, resulting in increasing rates of deteriorative changes, such as enzymatic reactions, non-enzymatic browning and oxidation [17]. The probable collapse and consequent stickiness of air-dried samples contributed for the loss of vitamin C in final product. The stickiness can cause the over-heating of heat-sensitive products resulting in degradation and undesirable sensorial characteristics [18, 19]. No significant loss of vitamin C occurred during freeze-drying because of the very low temperature and depletion of oxygen offered by vacuum during process.

CONCLUSION

The vitamin C content of both fresh and freeze-dried guava, mango, papaya and pineapple was determined. Although losses have occurred during the process, the ascorbic acid content retained in the freeze-dried guava, mango, papaya and pineapple characterizes these products as a valuable source of vitamin C. Concerning to papaya, the use of conventional freezing led to higher vitamin C loss when compared with the cryogenic freezing.

ACKNOWLEDGEMENTS

The authors are grateful to the Brazilian research supporting foundations FAPESP, Proc. 05/54624-9 and CNPq/PRONEX for their financial support.

REFERENCES

[1] Podsedek, A. 2007. Natural antioxidants and antioxidant capacity of Brassica vegetables: A review. LWT-Food Science and Technology, 40, 1-11.

[2] Lee, S. K. & Kader, A. A. 2000. Preharvest and postharvest factors influencing vitamin C content of horticultural crops. Postharvest Biology and Technology, 20, 207-220.

[3] Marques, L. G.; Ferreira, M. C. & Freire, J. T. 2007. Freeze-drying of acerola (Malpighia glabra L.). Chemical Engineering and Processing, 46, 451–457.

[4] Marques, L. G.; Silveira, A. M. & Freire, J. T. 2006. Freeze-drying characteristics of tropical fruits. Drying Technology, 24(4), 457-463.

[5] Lin, T. M.; Durance, T. D. & Scaman, C. H. 1998. Characterization of vacuum microwave, air and freeze-dried carrot slices. Food Research International, 31(2), 111-117.

[6] Marfil, P. H. M.; Santos, E. M. & Telis, V. R. N. 2008. Ascorbic acid degradation kinetics in tomatoes at different drying conditions. LWT-Food Science and Technology, 1-6.

[7] Ratti, C. 2001. Hot air and freeze-drying of high-values foods: A review. Journal Food Engineering, 49, 311-319.

[8] Jayaraman, K. S., & Das Gupta, D. K. 1995. Drying of fruits and vegetables. In: Mujumdar, A. S. (Ed.). Handbook of Industrial Drying. Inc. Marcel Dekker, New York, USA, 643-689.

[9] Shadle, E. R.; Burns, E.E. & Talley, L. J. 1983. Forced air drying of partially freeze-dried compressed carrot bars. Journal of Food Science, 48(1), 193.

[10] Yang, C. S. T. & Atallah, W. A. 1985. Effect of four drying methods on quality of intermediate moisture lowbush blueberries. Journal of Food Science, 1233-1237.

[11] Benassi, M. T. & Antunes, A. J. 1988. A comparison of metaphosphoric and oxalic acids as extractants solutions for the determination of vitamin C in selected vegetables. Arq. Biol. Technol., 31(4), 507-513.

[12] Nelson, J. W.; Barritt, B. H. & Wolford, E. R. 1972. Influence of location and cultivar on color and chemical composition of strawberry fruit. Wash. Agric. Exp. Stn. Tech. Bull, 74, 1-7.

[13] Karel, M. & Nickerson, J. T. R. 1964. Effects of relative humidity, air and vacuum on browning of dehydrated orange juice. Food Technology.

[14] Righetto, A. M. 2003. Caracterização físico-química e estabilidade de suco de acerola verde microencapsulado por atomização e liofilização, Tese de Doutorado, FEA/UNICAMP, 176 p.

[15] Chang, C.; Lin, H.; Chang, C.; Liu, Y. 2006. Comparisons on the antioxidant properties of fresh, freeze-dried and hot-air dried tomatoes. Journal of Food Engineering, 77, 478-485.

[16] Leme, Jr., Fonseca, H. & Nogueira, J. N. 1973. Variação do teor de ácido ascórbico e beta-caroteno em cereja-das-antilhas (Malpighia punicifolia L.) liofilizada. Archivos Latinoamericanos de Nutricion, 23(2), 207-215.

[17] Roos, Y. H. 1993. Water activity and physical state effects on amorphous food stability. Journal of Food Processing and Preservation, 16, 433-447.

[18] Papadakis, S. E. & Bahu, R. E. (1992). The sticky tissues of drying. Drying Technology, 10(4), 817-837.

[19] Chuy, L. E. & Labuza, T. P. 1994. Caking and stickiness of dairy-based food powders as related to glass transition. Journal of Food Science, 59(1), 43-46.