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POST-HARVEST QUALITY OF PEQUI (*Caryocar brasiliense* CAMB.) COLLECTED FROM THE PLANT OR AFTER NATURALLY FALLING OFF AND SUBJECTED TO SLOW AND QUICK FREEZING[1]

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ABSTRACT- Soluble solids (SS), titratable acidity (TA), SS/TA ratio, pH, moisture, soluble sugars (SSU), total reducing sugars (RSU), and non-reducing sugars (NRS) were assessed in the pulp of pequi fruits collected at three ripening stages: from the plant, from the ground after naturally falling off, and collected from the ground three days after naturally falling off. The evaluation was performed after six months of freezer storage both for fruits subjected to quick freezing (liquid nitrogen followed by freezer) and slow freezing (straight into the freezer). The variables assessed were not influenced by the freezing method. The SS, TA, and RSU contents increased with the ripening stage, suggesting that the fruits collected from the plant are still immature and have lower quality than those collected after naturally falling off. Although considered mature when they fall off, fruits consumed three days after naturally falling off have better quality.
Index terms: Extractivism; management, pulp chemical composition, fruit development stage, handling.

QUALIDADE PÓS-COLHEITA DO PEQUI (*Caryocar brasiliense* CAMB.) COLETADO NA PLANTA OU APÓS A QUEDA NATURAL E SUBMETIDO AO CONGELAMENTO LENTO OU RÁPIDO

RESUMO - Foram avaliados os teores de sólidos solúveis (SS), acidez titulável (AT), relação SS/AT, pH, teor de umidade, açúcares solúveis (AS), açúcares redutores (AR) e açúcares não redutores (ANR) em polpa de frutos de pequi coletados na planta, coletados no chão após a queda natural e coletados no chão três dias após a queda natural (caracterizando três estágios de maturação), e mantidos por seis meses em freezer após submetidos a congelamento rápido (nitrogênio líquido seguido de freezer) e lento (diretamente em freezer). As variáveis avaliadas não foram influenciadas pelo método de congelamento. Os teores de SS, AT, e AR foram crescentes com o avanço no estágio de maturação dos frutos, indicando que frutos coletados na planta encontram-se imaturos e apresentam qualidade inferior aos coletados após a queda natural. Embora considerados maduros quando caem da planta, um intervalo de três dias entre a coleta após a queda natural e o consumo favorece a qualidade dos frutos.
Termos para indexação: Extrativismo, composição química, congelamento, estágios de desenvolvimento do fruto, manejo.

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INTRODUCTION

Pequi (*C. brasiliense* Camb.) is one of the most marketed fruits from the Cerrado bioma and is important to keep peasant families in rural areas, especially in the north of Minas Gerais state, Brazil, and has a substantial ecological impact on the country as well. The fruits, which have very high oil, protein, and carotenoid contents (FARIA-MACHADO et al. 2015), are cooked for consumption and serve as ingredients for liqueurs, oils, flours, creams, preserved nut and pulp, syrups, ice creams, sweets, and soaps. Traditionally is regarded as a very rich source of vitamin A, whose deficiency is a public health problem in some areas of Brazil (FERREIRA et al. 2013). The pulp oil is traditionally used as tonic agent in popular medicine due to its natural antioxidants. The fat, fiber and carotenoid composition from *Caryocar brasiliense* pulp points out this exotic fruit as a potential cardio protective food (TEIXEIRA et al. 2013). Because of its nutritional and functional characteristics, most studies with *C. brasiliense* are related to the chemical composition and postharvest technologies of conservation and performance (SANTANA et al. 2014; PLÁCIDO et al. 2015).

Despite some experimental farming, pequi fruits are typically explored through extractivism and are collected from the ground as soon as they ripen and fall off the plant. In case they are not collected immediately after falling off, the fruits become soft and quickly start rotting. When the market price of the fruit is high, or when the supply needs to be increased to middlemen/buyers from other states, the fruit is often picked from the plant, a practice popularly known as “pequi on the rod.” This practice, besides injuring the plant mainly by breaking its branches and consequently harming future production, risks collecting fruits that have not reached their full development. The content of many chemical components varies with the stage of fruits development. Oliveira et al. (2006) related nutritional and texture aspects of the pulp with the ripening stages and found that fruits picked from the plant have a lower carotenoid content, leading to a fairer colored pulp, which is less desirable by consumers. According to Parra-Coronado (2014), fruits harvested before their full physiological development on the plant may be stored for long periods, but will never reach ideal conditions for consumption.

In the north of Minas Gerais state, pequi collection begins in November or December and lasts until February or March, depending on the region, with effectively three months of collection. In face of the seasonality of the fruit’s supply, pequi is commonly frozen for storage so it can be marketed in the inter-harvest period, an increasingly important practice for the product’s economy. An estimated 50% of the pequi production is lost after harvest due to poor classification, transport, and storage (GONÇALVES et al. 2010). Freezing may effectively guarantee marketing in the inter-harvest period and is able to preserve post-harvest quality (GONÇALVES et al. 2010). In the traditional processing, during the harvest season, the fruits are peeled and the putamens (or pyrenes, i.e., pulp or inner mesocarp + seed) are placed in polyethylene bags and freezer-stored for consumption in the inter-harvest period. A few have assessed the changes caused by different freezing methods (temperature and freezing speed) and the freezer-storage period of processed and/or *in natura* pequi studies (OLIVEIRA et al. 2006; GONÇALVES et al. 2010; ALVES et al. 2010; VILAS BOAS et al. 2013).

Characterizing the main changes in the pulp at different development stages is essential to defining the time of harvest and post-harvest handling of the fruit. Given that the ripening stage at harvest impacts the post-harvest characteristics of pequi, the present study assessed the components of pequi pulp grown in the north of Minas Gerais state and collected from the plant, collected from the ground immediately after naturally falling off, and collected from the ground three days after naturally falling off, which were stored in a freezer for six months after either quick freezing (liquid nitrogen followed by freezer) or slow freezing (straight into the freezer).

MATERIAL AND METHODS

The pequi (*C. brasiliense* Camb.) fruits came from an area of Cerrado from the Center of Alternative Agriculture of the North of Minas Gerais (Centro de Agricultura Alternativa do Norte de Minas - CAA/NM), 40 km away from Montes Claros, MG, Brazil. Between five and eight fruits were obtained from each of eight randomly chosen trees. The fruits were collected between December and January, at three development stages (collection sites) in an attempt to simulate the usual handling adopted by the rural populations: 1) Fruits collected straight from the tree before naturally falling off (CP), that simulates the practice known as “pequi on the rod,” which means dropping the fruit while still attached to the plant; 2) fruits collected from the ground immediately after naturally falling off (CG), which is the usual and recommended practice since the fruit is considered ripe; 3) fruits collected from the ground after naturally falling off and kept for three days at ambient conditions on the laboratory bench (CG3), which simulates the typical time between collection and consumption.

After being collected at the different ripening stages, the fruits were peeled while avoiding contact with the putamens, which then were disinfected with 1% sodium hypochlorite for 5 min. For each ripening stage, the putamens, selected so that they had no defects and were of similar size, were sorted into two groups. One group was frozen with liquid nitrogen at -196 °C (quick freezing), placed in polyethylene bags, and then stored in a freezer at -18 °C. The second group was placed in polyethylene bags and stored straight in the freezer (slow freezing). Freezer storage for six months, which simulates the time during which pequi is usually frozen for inter-harvest consumption, and CG, for being the usual and recommended practice, will be considered the reference treatment.

After six months of freezer storage, the putamens were taken to the Fruit Biochemistry Laboratory of the Department of Food Sciences of the Federal University of Lavras, where the pulp (mesocarp) was removed and subjected to the following assessments according to the laboratory's routine methodologies: Total soluble sugars (SS), reducing sugars (RSU), and non-reducing sugars (NRS) according to Lane-Enyon, cited by the AOAC (1992), and determined through the Somogyi technique adapted by (Nelson 1944); soluble solids (SS) through refractometry according to the AOAC (1992) guidelines using an ABBE refractometer 2WAJ; titratable acidity (TA) through the technique recommended by the AOAC (1992) and expressed as percentage of citric acid; SS/TA ratio; pH, determined by glass-electrode potentiometry according to the AOAC (1992) technique; and moisture content, determined by gravimetry with an forced-ventilation drying oven at 105 °C until constant weight, according to the AOAC (1992). Pequi pulp from another batch, but also frozen for six months, underwent testing with lugol to detect starch.

The experiment followed a completely randomized 3x2 factorial design with three development stages (CP, CG, and CG3) and two freezing methods (freezer and liquid nitrogen followed by freezer). Three repetitions with ten putamens were used for each treatment. Analysis of variance (ANOVA) was applied to interpret the results and the treatment means were compared with Tukey's test at 5% probability.

RESULTS AND DISCUSSION

The freezing method – quick freezing with liquid nitrogen followed by freezer storage or slow with both freezing and storage in the freezer – did not influence the variables assessed. Therefore, the data presented in each fruit development stage represent the average between the two treatments of freezing. The results match the study by Tavares et al. (1998), who found no effect of the freezing method (slow or quick) on the same variables for acerola. According to Gonçalves et al. (2010), the time of freezer storage is more relevant for pequi pulp's chemical characteristics than the freezing method.

Moisture content, pH, soluble sugars, and reducing sugars were significantly ($p<0.05$) affected by the fruits' ripening stage (Table 1). pH values were lower in CG3. In general, pH variation in fruit pulp has no defined response as a function of the ripening stage. While in some fruits pH increases with ripening (DANTAS et al. 2016), it decreases (STAFENELLO et al. 2010) or remains stable in others (OLIVEIRA JÚNIOR et al. 2004).

pH of pequi pulp frozen for six months ranged from 5.4 to 6.2, which is similar to the values reported by other authors (OLIVEIRA et al. 2011; SOUSA et al. 2012; VILAS BOAS et al. 2013), but less than the found by Plácido et al. (2015) in freshly picked fruit. Pequi differs from most tropical fruit with industrial use for having a pH that classifies it as a low-acidity food (pH above 4.5), which favors microorganism development and quick rotting (OLIVEIRA et al. 2011; SOUSA et al. 2013). That requires greater care in processing and storage conditions of this fruit. It is recommended that the pulp be acidified when it is to be used in commercial products (OLIVEIRA et al. 2011). Therefore, pH values lower in stage CG3, three day after naturally falling off, when the fruits were more mature, may represent an advantage in industrial processing. Besides the pulp's high pH (5.4 to 6.2) and moisture content (53.8 to 61.4% - Table 1), the fruit's high respiratory rate (RODRIGUES et al. 2013; RODRIGUES et al. 2015) contribute to pequi's short post-harvest life. Moisture content is within the range reported by Gonçalves et al. (2010), and decreased with the ripening stage, a response that was expected due to natural dehydration.

Reducing sugars contentes were higher ($p<0.05$) in CG3 compared to CP and CG (Table 1). Reducing sugars (glucose and fructose) content normally rises at the same time that non-reducing sugars content (mainly saccharose) decreases due to the sugars conversion (MORAIS et al. 2002). The highest reducing sugars contents found at the most advanced ripening stage, without a corresponding reduction in non-reducing sugars content may indicate hydrolysis of starch, a carbohydrate stored during the development of certain fruits, such as wolf apple (*Solanum lycocarpum*) (OLIVEIRA et al. 2011) and mango (MORAIS et al. 2002). During the ripening of sugar-apple (*Annona squamosa*), soursop (*Annona muricata*), and atemoya *(Annona atemoya*), starch degrades into glucose, which can be used to synthesize saccharose (ALVES and SILVA 2005). In this case, both reducing sugars and non-reducing sugars increase during ripening. Although there is no reference in the literature of starch being present in pequi pulp, the treatment with lugol showed its presence. Moreover, the solubilization of pectins (OLIVEIRA et al. 2006; VILAS BOAS et al. 2013) and the decrease in the pulp's moisture content may have contributed to the accumulation of sugars as the pequi fruits ripened.

The soluble solids (SS) and titratable acidity (TA) contents and the SS/TA ratio were impacted by the effect of the fruits' ripening stage (Table 2). SS and TA increased with pequi ripening stage (Table 2), as is the case with most fruits (RODRIGUES et al. 2009; DANTAS et al. 2016). SS represents the content of sugars, organic acids, and other smaller constituents, but mainly glucose, fructose and saccharose, which suggests a direct relation with the fruit's sweetness. In the industry, analyzing °Brix (soluble solids) is highly important in controlling the ingredients to be added to the product and in the final quality since the higher the SS content the lower the need to add sugars and the lower the time for water to evaporate. That reduces production costs and increases the yield and quality of the product (COSTA et al. 2004). Thus, the industrial use of pequi fruits collected from the plant may lead to lower product yield and quality.

The mean values of SS (between 8 and 10 °Brix) and TA (between 0.15 and 0.23%) are within the range found in other studies with *C. brasiliense* (VILAS BOAS et al. 2012; RODRIGUES et al. 2015). Rodrigues et al (2015) found TA 0.26% in fruits 28 days after flowering and 0.6% in mature fruits collected at the plant (84 days after anthesis). In *C. coriaceum*, TA (1.5%) is higher and SS (4.5 °Brix) is lower (OLIVEIRA et al. 2010; SOUSA et al. 2012) than the values found for *C. brasiliense*.

TA is calculated based on the citric and malic acids, which are the main components responsible for acidity in most fruits. The content of these acids usually decrease with ripening as they are consumed in the respiratory process by being converted into sugars and/or aroma components. However, in pequi pulp, as in pineapple (THÉ et al. 2001), soursop (LIMA et al. 2007), wolf apple (OLIVEIRA JÚNIOR et al. 2004), and cocona (*Solanum sessiliflorum*) (STEFANELLO et al. 2010), TA rises with the ripening stage (Table 2). In the present study, TA was calculated based on citric acid (citric acid equivalents/100 g pulp). A possible reason for the increase in TA with ripening may be that this acid is not the most prevalent in pequi pulp as is the case with *Eugenia stipitata*, in which malic acid prevails (HERNÁNDEZ et al. 2007). There may also be a reduced use of organic acids in the regular oxidative pathways, which favor accumulation, such as in soursop (LIMA et al. 2007). On the other hand, the post-harvest increase in TA in fruits can be explained by the generation of acid radicals (galacturonic acids) from the hydrolysis of cell-wall components, especially pectins. In pequi, cell-wall pectin hydrolysis gradually increases with the fruits' ripening stage (OLIVEIRA et al. 2006).

The SS/TA ratio is one of the most widely used indices to determine ripening stage and is one of the best ways of assessing flavor since it reflects the balance between sugars and acids. In pequi, the SS/TA ratio varied between CP and CG, and was lower in CG3 (Table 2). Overall, the SS/TA ratio increases with the ripening stage due to a reduction in acidity (RODRIGUES et al 2015; DANTAS et al. 2016). As SS and TA in pequi increased with the ripening stage (Table 2), the lower SS/TA ratio in the fruits from CG3 (more advanced ripening stage) may be related to a proportionally greater increase in TA (30.4%) compared to the increase in SS content (5%) after the fruits naturally fall off.

The results of the present work allow stating that collecting pequi from the plant is harmful to the product's quality, as shown by the lower SS, TA, and RSU values found in the pulp of fruits from CP compared to those CG. These results complement those from Oliveira et al. (2006), who found a lower nutritional quality in pequi fruits collected from the plant. Therefore, fruits collected from the plant have lower quality than those collected after naturally falling off regarding both nutritionally and flavor since ripening is incomplete and this process continues after the fruits naturally fall off, which confirms the climacteric character found by Rodrigues et al. (2015). Although the fruits are considered ripe when they fall off the plant, a three-day period between collection after naturally falling off and consumption was shown to improve quality. Nonetheless, since the fruit perishes quickly, the time after the fruits naturally fall off during which pulp quality is maintained must still be assessed.

TABLE 1 - Effect of the fruits' ripening stage on the pH, moisture content (%), total reducing sugars (g/100 g), non--reducing sugars (g/100 g) and total sugars contents (g/100 g) in *C. brasiliense* pulp stored for six months in a freezer.

Fruit ripening stage	pH	Moisture	Reducing sugars	Non-reducing sugars	Total soluble sugars
Collection from the tree	6.04A	61,48A	1.97B	1.18A	5.81AB
Collection from the ground after naturally falling off	6.22A	56,20B	2.13B	1.17A	6.15A
Collection from the ground 3 days after naturally falling off	5.44B	53,87C	3.23A	1.12A	5.55B

Means followed by the same letter in the columns indicate that the fruits' ripening stage do not differ statistically according to Tukey's test ($p<0.05$).

TABLE 2 - Effect of the fruits' ripening stage on the soluble solids contents (°Brix), tiratable acidity (%) and soluble solids/titratable acidity ratio (SS/TA) on *C. brasiliense* pulp stored for six months in a freezer.

Fruit ripening stage	Soluble solids	Titratable acidity	SS/TA
Collection from the tree	8,16B	0,15B	58,48A
Collection from the ground after naturally falling off	9,33A	0,16B	55,99B
Collection from the ground 3 days after naturally falling off	9,83A	0,23A	53,67C

Means followed by the same letter in the columns indicate that the fruits' ripening stage do not differ statistically according to Tukey's test ($p<0.05$).

CONCLUSIONS

- Overall, it can be said that slow or quick freezing do not impact pequi quality regarding flavor-related components;
- Reducing sugars, soluble solids and tritatable acidity increased with the fruits' ripening stage, suggesting that pequi fruits collected before naturally falling off have lower quality than those collected after naturally falling off since the former are not fully ripe;
- Although considered mature when they fall off, fruit quality is higher three days after they naturally fall off, which is favorable in the handling between collection and consumption;
- Although the three-day period after the fruits naturally fall off has led to better fruit quality, the time after pequi fruits naturally fall off while still maintaining pulp quality must be assessed.

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