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Chemical composition and nutritional of pequi fruits (*Caryocar brasiliense* Camb.) with and without thorns at the endocarp

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Abstract
The present study analyzed the centesimal composition (proteins, lipids, ash, and total carbohydrates), chemical quantification (vitamin C, beta-carotene, lycopene, chlorophyll-a, chlorophyll-b, and total phenolics), energy value (kcal / kj), and physical-chemical properties (pH, titratable total acidity, moisture and yield of fresh pulp) of pequi (*Caryocar brasiliense*) with and without thorns at the endocarp. The chemical-bromatological profile of pequi without thorns was carried out for the first time and can serve as a basis for further studies. The analyzes were performed on the peel (external mesocarp), pulp (internal mesocarp) and almonds of the fruits. The analyzes were performed on the shell (external mesocarp), pulp (internal mesocarp) and fruit almonds. The samples were composed by a bulk of 10 fruits with thorns and 10 fruits without thorns in the endocarp. The data were submitted to analysis of variance, and the means were compared by the Tukey's test at 95% confidence level, using GENES Software. In fruits of pequi with and without thorns in the endocarp, the physical-chemical characteristics presented significant differences (Test t, $p \leq 0.05$) only for the pH of the peel. For the nutritional analysis, significant differences ($p \leq 0.05$) were observed only in carbohydrate content on the peel; carbohydrates, phenolic compounds and ashes in the pulp, and carbohydrates in the almond. High concentrations of β-carotene in pequi pulps were found, especially in fruits with thorns on the endocarp, whose average was 21.50 mg/ 100g, significantly higher (Test t, $p \leq 0.05$) on endocarp fruits without thorns (8.70 mg/ 100g).

Keywords: cerrado fruits, nutritional, chemistry, caryocaraceae, biometry, quantitative traits

1. Introduction

Caryocar brasiliense Camb. (Caryocaraceae), grows naturally in Brazilian savanna (Cerrado) of Central West and South Eastern Region of Brazil [1]. Ecologically, the specie *C. brasiliense* present a significant role on the Cerrado composition. Considered as a specie of extractivist, its fruits feeds many families and utilized as an income alternative, mainly for the rural environment [2]. The pequi fruits and seeds are over-exploited due to their wide range of uses, and questions have been raised about whether the intensive exploitation poses any threat to the conservation of the species [1]. The *C. brasiliense* present many applications like energy matrix, food, prospecting molecules with pharmacological effects, reforestation, and another else. The leaves and the fruit oil are used in the folk medicine of the Brazilian Cerrado region to treat cold, cough, bronchitis, edema and burns, and the seeds are considered aphrodisiacs [3].

Pequi trees and fruits are important sources of different biological compounds that can be used in pharmacological and nutritional bioprospecting. Substances like oleanolic acid, β-sitosterol, stigmasterol, ellagic acid, and oleanolic acid are founding in the species [4]. Other substances like anthocyanin, saponins, tannins, flavonoids, steroids, triterpenes and reducing glycosides were identified in leaves and flower buds. The protein and lipid content of pequi stands out in relation to other native species of Cerrado, presenting 2.64% of protein, and up to 20% of lipids [5]. The oil contains myristic acid, palmitic, stearic, oleic and linoleic acid [6], vitamin A, and carotenoids [7]. The pulp presents from 36% to 66% of oil [8] with high levels of carotenoids and triacylglycerols [9]. The major triacylglycerols present in the pulp oil are 3-dipalmitoyl-2-oleoyl-glycerol, 1,2-dioleyl-3-palmitoylglycerol and palmitoyl-oleoyl-stearoyl-glycerol [7, 10].

Studies shown that *C. brasiliense* has a high concentration of phenols, such as flavonoid, quercetin and quercetin-3-O-arabinose, as well as acid components such as gallic acid and quinic acid in fruit and peel [6, 11, 12]. The fruits presented β-carotene, z-carotene, cryptoflavine, β-cryptoxanthin, antheraxanthin (79.14 mg/g), zeaxanthin and mutatexanthin. Among the volatile chemical components are then some hydrocarbons, fatty acids and terpenoids, ethyl hexanoate, ethyl octanoate, acyclic monoterpene β-oxygen and acid [13].

It has been shown to be a highly nutritious and low-cost food [14]. It has a toning action, an appetite stimulant, a source of vitamins and several other nutrients. It is widely used in typical dishes in some regions of Brazil [5,12].

The extensive supply period of the pequi fruits, together with the heterogeneity of the producing regions, leads to the existence of differences between their physical and nutritional attributes [15]. Bromatological analysis are essential for the knowledge of the nutritional and chemical composition of a given food. Considering the economic, social, cultural and nutritional importance of pequi, the aim of the present study is to determine the centesimal composition, pigment concentration, total phenolic compounds and physical attributes of pequi fruits with and without thorns at the endocarp. The analysis of these fruits will helpful in future studies like environmental conservation and genetic improvement of this species.

2. Materials and methods

2.1 Samples

The analyzes were carried out on fruits of *C. brasiliense*, with and without thorns at the endocarp, cultivated on the Água Limpa Experimental Station, Federal University of Uberlândia (UFU) (19º 05' 57,92" S e 48º 20' 49,79" W), on Uberlândia city, Minas Gerais, Brazil. The fruits were collected in January 2018, in a stage of complete maturation. For the preparation of the samples, the fruits were sanitized, peeled and pulped manually with the help of a stainless-steel knife. The samples were composed by bulk of 10 fruits with thorns and 10 fruits without thorns at the endocarp. Aliquots of peel (external mesocarp), pulp (internal mesocarp) and pequis almonds were prepared with and without thorns at the endocarp, which were kept frozen until the beginning of the analyzes.

2.2. Physical-chemical profile

2.2.1 Ph

The measurements of the hydrogen ionic potential (pH) were carried out on the peel and fruit pulp with and without thorns by means of a pHmeter (Tecnopon - MPA - 210). The pH was measured by direct immersion of the electrodes in the sample [16].

2.2.2 Titratable total acidity (TTA)

The titratable total acidity of the pulp and almond samples of the pequi with and without thorns was determined by standard titration in 0.1N sodium hydroxide solution until obtaining a pink color [16]. The titratable acidity was expressed in grams of acid per 100 g of sample, by the following equation 1:

$$AAT = \frac{n \times N \times Eq}{10 \times P} \quad (1)$$

n: volume of the sodium hydroxide solution is used in titration (mL); N: normality of the sodium hydroxide solution; Eq: gram-equivalent of acid; P: mass of the sample (g);

2.2.3 Dry matter (DM)

1.0 g of the sample pequi fruit were placed in the laboratory oven at 105 °C for 24 hours. After this period of time, plates with samples were placed in the desiccator until reaching room temperature. Samples were weighed again. DM analysis was performed in triplicate [16].

2.2.4 Yield fresh pulp (YFP)

For the analysis of the yield of fresh pulp, the pequis with and without thorns were weighed in semi analytic scale (BK-4000) to obtain the total gross mass (TGM). Then the internal mesocarp was removed with the aid of a stainless-steel knife and weighed. The yield of fresh pulp was obtained by the relation between mass of the fresh pulp (MFP) and the total gross mass, with subsequent conversion to percentage, according by equation 2:

$$YFP = \left(\frac{MFP}{TGM}\right) * 100 \quad (2)$$

2.3 Phenolic compounds

2.3.1 Preparation of Phenolic Extract

To obtain the phenolic fraction from epicarp, mesocarp and seeds, 1.0 g of each fresh and crushed sample was used, to which were added 40 mL ethanol at 95%, remaining under orbital magnetic shaking for 2 hours. After this period of time, samples were allowed to rest for 48 hours. The extraction of phenolic content was run in triplicate.

2.3.2 Determination of total phenolic content

Phenolic content of pequi extracts was determined using the Folin - Ciocalteu colorimetric method, based in the formation of a blue complex produced by the reduction of the reagent caused by phenolic compounds present in samples [17]. Briefly, 0.5 mL of each extract prepared in ethanol 95% was collected and placed in test tubes, to which were added 2.5 mL of 10% (v/v) Folin - Ciocalteu solution and 2 mL 4% (w/v) Na_2CO_3. The mixture was kept in water bath at a temperature of 50 ºC for 5 minutes. Samples were allowed to rest at room temperature, and then the absorbance was measured at 760 nm in a spectrophotometer. Total phenolic content of extracts was carried out in triplicate and results were expressed by mg of gallic acid equivalents (eq GA) per 100 g of sample. For the calibration curve, a stock solution of 100 mg/L gallic acid was prepared. From the stock solution, standard curve points were prepared (0, 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 mg/L). Samples were allowed to rest at room temperature and then the absorbance was measured at 760 nm in a spectrophotometer.

2.4. Bromatological profile

2.4.1 Crude Protein (CP)

Kjeldahl method [18] was used to determine total nitrogen on the organic matter, including protein nitrogen. 0.5 g of fresh samples were placed into a digestion tube. 2.0 g of a digester mixture [H_2SO_4 and $CuSO_4$ (1:10)] plus 5 mL H_2SO_4 concentrated was used to start the digestion process at low temperature. Maximal temperature of 350 ºC was reached and samples were let to rest for 30 minutes until the lightening of the solution. After cooling the samples, a little portion of distilled water was added until complete dissolution. Digester tubes containing the samples were transferred to the distillation apparatus to which were added 5 mL NaOH at 0.2 N. Fifty milliliters of distilled water plus 50 mL of 4% H_3BO_3 and the mixed indicator were added to an Erlenmeyer. Distillation was performed by samples dragging, keeping the condenser terminal inside the receptor solution that was present in the Erlenmeyer flask until all ammonia was released in a volume of approximately 100 mL. By withdrawing the flask, the tip of the condenser was

washed with distilled water and titrated with standard HCl at 0.1N to turn the mixed indicator. A blank test was conducted in order to eliminate interference of reagents. For the determination of the crude protein present in the peel, pulp and almond of the pequis with and without thorns in the endocarp, the factor of 5.75 of conversion of nitrogen in protein was taken into account, which allowed its determination by the Kjeldahl method. Considering the HCl conversion factor of 1.013 and the normality of 0.1, the result was transformed into crude protein using the equation 3:

$$\%PB = \frac{[(V'-V)* Fc* N* 5.75* 0.014]}{P} *100 \quad (3)$$

V': volume of HCl 0.1 N spent on the titration; V: volume of HCl 0.1 N spent in the blank; Fc: Correction factor of 0.1N HCl; N: normality; P: weight of the sample (g); 5.75: Nitrogen conversion factor to protein (for plant proteins); 0.014: milliequivalent-gram of nitrogen.

2.4.2 Lipids (L)

For the quantification of the lipid content in pequis with and without thorns in the endocarp, the methodology described by Bligh and Dyer [19] with some modifications was used. Initially 1.0 g of each sample (pericarp, mesocarp and seeds) was weighed in an analytical balance. 100 mL of methanol and 50 mL of chloroform were added to each sample, forming a single phase, which was stirred on a magnetic stirrer for 10 minutes. After the stirring period, 50 mL of chloroform and 50 mL of water were added to each sample to form two phases, one of chloroform containing the lipids and another of the non-lipid containing hydro methanol. The chloroform phase with the fat was isolated and, after evaporation of the chloroform, the amount of fat per gravimetry was obtained. The analyzes were performed in triplicate.

2.4.3 Carbohydrate

The quantification of total carbohydrates was done by the phenol-sulfuric method [20]. For the standard glucose curve, a stock solution of D-glucose at 200 mg/L was prepared. From this stock solution, the curve points (0, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75 and 80 mg/L). For each concentration of the standard curve, 1.0 mL aliquots of the glucose solution were added and 1.0 mL of 5% phenol (C_6H_5OH) and 5.0 mL of concentrated sulfuric acid (H_2SO_4) were added. Subsequently, the samples were naturally cooled to room temperature (25 ºC) before measuring their absorbance at 490 nm in a spectrophotometer (UV 340G - Gehaka). For the quantification of total carbohydrate present in the peel, pulp and almond of pequi with and without thorns in the endocarp, 1.0 g of each sample was weighed in analytical balance, directly in 250 mL beaker. The samples were diluted in 100 mL of distilled water and filtered on 125 mm quantitative filter paper. 250 µL of the filtered sample was transferred to a test tube containing 750 µL of distilled water and 1 mL of C_6H_5OH at 5%. The solution was homogenized and 5 mL of concentrated H_2SO_4 was added to the exhaust hood. Once the reaction is exothermic, the samples were naturally cooled to room temperature (25 °C) before reading the absorbance at 490 nm in spectrophotometer (UV 340G - Gehaka). The analyzes were performed in triplicates.

2.4.4 Ash

Porcelain crucibles were placed in a drying oven at 105 ºC for 2 hours and cooled sequentially in a desiccator for 1 hour. Two grams of each corn sample were weighed and subjected to burning in a muffle furnace for 6 hours after the temperature reached 600 ºC to obtain a light ash [16]. After this period, the furnace was turned off and the crucibles were cooled at a temperature lower than 250 ºC. At the end of the process, the crucibles with the samples were cooled to room temperature in a desiccator and the weight was recorded.

2.4.5 Ascorbic acid

The levels of ascorbic acid were quantified by the methodology based on the oxidation of ascorbic acid ($C_6H_8O_6$) with potassium iodate (KIO_3) [16]. For the determination of the vitamin C content in fruits of pequi tree with and without thorns in the endocarp, 2.0 g of samples of external peel (exocarp), internal peel (external mesocarp), pulp (internal mesocarp) and almonds, directly into 100 mL beaker. The samples were homogenized, 50 mL of distilled water added, which were kept under magnetic stirring for 5 minutes. After the agitation period, a 10 mL aliquot was placed in 250 mL Erlenmeyer flask. 10 mL of 20% H_2SO_4 solution and 1 mL of the 10% (w / v) potassium iodide (KI) solution and 1 mL of the 1% starch solution (w / v) were titrated and titrated with iodate solution of potassium (KIO_3) 0.002 mol/L to blue coloration. The analyzes were performed in triplicate.

2.4.5 Total energy value

The total energy value (TEV) was calculated by summing the calories provided by carbohydrates, lipids and proteins by multiplying their values in grams by the factors of Atwater 4 Kcal / g, 9 Kcal / g and 4 Kcal / g. The energy in kilojoules (kJ) was determined by multiplying the energy in kcal by factor 4.2.

2.5 Pigments

The pigments analyzed were β-carotene, lycopene, chlorophyll-a and chlorophyll-b, after extraction with acetone and hexane, using the spectrophotometric method described by Nagata and Yamashita [21]. 1.0 g of peel, pulp and pequis almonds were weighed with and without thorns in the endocarp. Each sample was added in light-protected test tubes with sheets of foil. An extraction solution containing acetone: hexane (4: 6) was placed over each sample. The tubes with the sample and the extractive solution were shaken vigorously and then held for 1 hour, out of the light. After the resting period, the samples were homogenized and the optical density of the supernatant was measured in spectrophotometer (UV 340G - Gehaka) at wavelengths 663 nm, 645 nm, 505 nm and 453 nm. The levels of chlorophyll a, chlorophyll b, lycopene and β-carotene were estimated in mg/ 100 mL by the following equations:

$$\text{chlorophyll a} = 0{,}999A_{663} - 0{,}0989A_{645} \quad (4)$$

$$\text{chlorophyll b} = 0{,}328A_{663} + 1{,}77A_{645} \quad (5)$$

$$\text{Lycopene} = -0{,}0458A_{663} + 0{,}204A_{645} + 0{,}372A_{505} - 0{,}0806A_{453} \quad (6)$$

$$\beta\text{-carotene} = 0{,}216A_{663} - 1{,}22A_{645} - 0{,}304A_{505} + 0{,}452A_{453} \quad (7)$$

2.6. Statistical Analysis

The data were submitted to analysis of variance (ANOVA), and the means of the treatments were compared statistically by the Tukey's test at 95% confidence level. The Student t-test, with a 95% confidence level, was used for comparison between mean values obtained by analysis and those reported on the products labels. Statistical analysis was performed using a GENES Software [22].

3. Results & Discussion

3.1 Physical chemical and nutritional analysis

The physical chemical analysis was related to pH, total titratable acidity and humidity. The pH and total titratable acidity were determined to evaluate the quality of foods of plant origin to industrial processing. Humidity is related to microbiological quality in storage processes. Fruits of *C. brasiliense* with and without thorns at the endocarp, the physical-chemical characteristics presented significant differences (Test t, $p \leq 0.05$) only to pH of the peel (Table 1). The other parameters evaluated didn't present significant differences between the groups with and without thorns.

Table 1: Physical-chemical analysis of peel, pulp and almonds in pequi with and without thorns at the endocarp. Água Limpa Experimental Station - UFU, Uberlândia – MG, 2017-2018.

	With thorns		without thorns		
Physical parameters	**CV (%)**	**Mean**	**CV (%)**	**Mean**	**t_{cal}**
----------Pericarp----------					
pH	0,13	4,70±0,36	0,09	4,11±0,30	5,08*
Dry matter	2,76	83,88±1,72	2,17	85,30±1,56	2,02 ^{NS}
TTA	0,008	2,76±0,09	0,003	2,78±0,05	0,33 ^{NS}
----------Mesocarp----------					
pH	0,08	7,03±0,29	0,034	7,00±0,18	0,30^{NS}
Dry matter	54,96	55,48±8,50	36,02	61,65±5,86	2,04^{NS}
TTA	0,01	0,65±0,11	0,00	0,75±0,00	1,63^{NS}
---------- Almonds----------					
Dry matter	2,11	49,04±1,44	4,20	50,04±2,41	1,26^{NS}
TTA	0,04	0,98±0,21	0,01281	1,24±0,11	1,87 ^{NS}

ATT: Titratable total acidity, CV: Coefficient of variation; *: significant at 5% by the t test, ^{NS}: Not significant by the t test.

The pH of the peel was 4.70 for pequis with thorns, and 4.11 for pequis without thorns (Table 1). The peel was considered of medium acidity, results close to that reported by Costa *et al.* [23] that verified a pH value of 4.25. pH values determined for the pulp in both groups of fruits are in accordance with that described by Paz *et al.* [24], for fruits with thorns at the endocarp. The percentage of moisture found for the peel, in both groups, of 83.88% and 85.30% for fruits with and without thorns at the endocarp (Table 1), respectively, are close to that determined by Costa *et al.* [23] that obtained 88.60% humidity. The humidity of fruit pulp with spiked endocarp (Table 1) was close to that reported by Vera *et al.* [25] and Paz *et al.* [24] which verified moisture contents of 54.4% and 52.4% in fruits with thorns at the endocarp. For the almond, the humidity values of 49.04% and 50.04% for fruits with and without thorns in the endocarp, respectively, were higher to that described by Damiani *et al.* [26] and Lima [27], which reported, respectively, 25.1% and 8.68% moisture in fruits with thorns. Due to the moisture content of the fruits of *C. brasiliense*, both with thorns and without thorns at the endocarp, are high (Table 1), the character must be evaluated when considering technologies of storage and processing of the fruits in order to guarantee their stability. Considering the humidity an important parameter, high concentrations of water in the food result in the reduction of the shelf life and the compromise of its quality [28].

Determination of the total acidity in foods is important because it can provide data for the evaluation of the processing and the state of conservation of the food, while humidity of the plant samples is related to the physical, chemical and microbiological stabilities [29]. The total acidity values (Table 1) found in fruits of *C. brasiliense* with and without thorns at the endocarp were relatively close to that determined by Paz *et al.* [24] for pulp (0.70) of pequis with thorns.

The pequi as a source of nutrients is important for food. However, the period of fruit supply and the different maturation periods associated with the variability of the environmental conditions, especially the temperature and relative humidity of the Cerrado region, give the fruits different physical and chemical properties [15,25]. Therefore, the nutritional content of the peel, pulp and almonds of the pequi with and without thorns at the endocarp of this region was evaluated. Significant differences ($p \leq 0.05$) were observed for the t-test only for the carbohydrate content in the rind; carbohydrates, phenolic compounds and ashes in the pulp and carbohydrates in the almond (Table 2).

Table 2: Nutritional composition of peel, pulp and almonds in fruits of the *C. brasiliense* with and without thorns at the endocarp, in wet basis. Água Limpa Experimental Station - UFU, Uberlândia - MG, 2017-2018

Nutritional composition	**with thorns**	**without thorns**	
	Mean	**Mean**	**t_{cal}**
----------Pericarp----------			
Carbohydrates (%)	21,10±19,04	31,06±14,63	5,40*
phenolic content (eq GA)	602,30±37,31	531,68±62,85	1,35 ^{NS}
Lipids (%)	0,54±0,38	0,48±0,43	0,19 ^{NS}

Ash (%)	0,76±0,79			0,54±0,08		0,49 ^{NS}
Proteins (%)	1,50±0,05			1,14±0,37		1,68 ^{NS}
----------Mesocarp----------						
Carbohydrates (%)	21,10±3,14			42,95±2,92		8,81*
phenolic content (eq GA)	902,12±15,52			566,59±74,67		7,62*
Lipids (%)	37,90±10,6			56,51,25		1,35 ^{NS}
Ash (%)	0,55±0,06			1,27±0,14		8,17*
Proteins (%)	5,01±0,37			4,55±0,40		1,45 ^{NS}
Vitamin C (mg.100g^{-1})	12,04±4,17			17,25±4,27		1,51 ^{NS}
----------Almonds----------						
Carbohydrates (%)	7,74±1,87			19,99±3,02		5,97*
Lipids (%)	49,31±3,19			49,34±2,26		0,013^{NS}
Ash (%)	5,10±1,21			6,00±1,47		0,79 ^{NS}
Proteins (%)	26,59±6,99			30,88±1,73		1,02 ^{NS}
Vitamin C (mg.100g^{-1})	22,57±4,88			19,41±4,80		0,80 ^{NS}
Energetic	pequi with thorns			pequi without thorns		
Value	Mesocarp	Epicarp	Seeds	Mesocarp	Epicarp	Seeds
TEV $^{(Kcal)/100g}$	445,62	105,93	581,13	698,60	79,71	647,51
TEV $^{(KJ)/100g}$	1864,47	443,22	2431,46	2922,95	333,54	2709,20

tcal: Calculated T-value (5%); VET: Total energy value; *: Significant at 5% by the T test, ^{NS}: Not significant by the t test; GAE: gallic acid equivalent

The amount of carbohydrates found at the pequis pulp without thorns was approximately two times higher than at the pequi pulp with thorns (Table 2). The results found for carbohydrates in pequi pulp (21.10%) are in agreement with those obtained by Macedo *et al.* [30] that determined 19.8% in peach pulp with thorns at the endocarp, by the same method used (phenol-sulfuric) in this research. However, these same authors obtained 23.8% of carbohydrates per difference. Paz *et al*. [24] obtained a 3.4% carbohydrate (by difference) and 9.4% (sulfuric phenol) in wet basis, and 7.2% (by difference) and 19.8% (sulfuric phenol method) on a dry basis, in pequi pulp with thorns.

Fruits of *C. brasiliense*, both fruits with thorns endocarp and those without thorns, presented large amounts of total phenolic compounds. In the pulps, 902.12 mg eq GA/ 100 g of sample were obtained in fruits with thorns and 566.59 mg eq GA/ 100 g in fruits without thorns. The lowest concentrations of phenolic compounds were obtained at the peel, with 21.10 mg eq GA/ 100 g in fruits with thorns and 31.06 mg eq GA/ 100 g in fruits with no thorns at the endocarp (Table 2). Lima [27] found a significant amount of phenolic compounds at the fruit (209.0 mg/ 100g) and Paz *et al.* [24] found a quantity of 531.5 mg/ 100g.

The lipid content at the pequis pulp with (37.90%) and without (56.51%) thorns did not show significant differences, by the t-test, at 5% of probability (Table 2), however the values obtained were higher than those described by Macedo *et al.* [30] and Paz *et al.* [24] in fruits with thorns, 29.7% and 31.5%, on wet basis. Pequi oil is a chemical component that is present in large quantities and, due to its chemical properties and antioxidant action, makes it a raw material for the cosmetic industry.

The high ash content on the almonds of the pequis with (5.10%) and without thorns (6.0%) were superior to those described by Ramos e Souza [31] for almonds of *Caryocar coriaceum* (2.44%). The ash content was 0.5% and 1.2% for pequis with and without thorns, respectively. A similar value to that obtained by Macedo *et al.* [30] and Paz *et al*. [24], which obtained 0.5% and 0.7% of mineral matter in pequi pulp with thorns. The peel showed 0.7% and 0.5% of ash content, respectively, in fruits with and without thorns, values close to those reported by Costa *et al.* [23] of 0.43%.

Minerals were found predominantly on the almonds (Table 2), attention to their use in human nutrition is important. The ash content represents the amount of minerals essential for plant formation. In addition, they may represent possible contaminations with inorganic impurities, such as metals and silica [29].

The values of proteins on the pulp of fruits with and without thorns were 5.01% and 4.55%, respectively (Table 2). The protein concentration was slightly higher than those described by Paz *et al.* [24] they analyzed pequi pulp with thorns and found, respectively, 2.6% and 2.4%. The almonds, both of the pequis with thorns and of the pequis without thorns, showed high concentrations of proteins, being 26.59% (with thorns) and 30.88% (without thorns) (Table 2).

Levels of vitamin C were obtained in the pulp and in almonds. In the pulp were found 12.04 mg/ 100g in pequis with thorns and 17.25 mg/ 100g in pequi without thorns (Table 2). These values are lower than those obtained by Paz *et al.* [24], who found 45.0 mg/ 100g in pequi pulp with thorns on the endocarp, on a wet basis.

The pequi is considered an important source of nutrients and energy value (Table 2). When considering an adult human diet of 2,000 Kcal, 100 g of pequi pulp with or without thorns can provide, respectively, 22.28% and 34.93% of daily energy recommendations. The results of this research show that the energy contribution of pequi fruit pulp was 4.22% of carbohydrates, 17.05% of lipids and 1.00% of proteins in fruits with thorns and pequi pulp without thorns 8, 59% correspond to carbohydrates, 25.43% to lipids and 0.91% to proteins.

Almonds of fruits with and without thorns are also important sources of energy, providing 19.05% and 28.37% of the total energy value, respectively. In the almonds of pequi with thorns 1,53% corresponds to carbohydrates, 22,19% to lipids and 5,32% to proteins and in almonds of pequi without thorns, 0,89% of carbohydrates, 22,20% of lipids and 17% protein. The peel of the fruits are residues

that, for the most part, are discarded without any use. The peel corresponds to most of the total mass of the fruits and, due to its nutritional composition, can be used for processing in value-added products, for example, flour production for the complementation or replacement of ingredients in bread making, animal feed or plant fertilizers.

3.2 Pigments

The color of the pequi pulp varies from light yellow to intense orange, with preference being given to the fruits with darker coloring. The pigments responsible for the color of pequi pulp are carotenoids [32]. In this study it was noticed that there is difference of color between the two groups of pequis, being the fruits without thorns presents light yellow coloration whereas the fruits with thorns have orange color.

On the pequi, in addition to the size and thickness of the pyrenes, the coloration of the pulp is used as criterion for selecting the most attractive fruits. Pigments are substances with different chemical structures, which are present in the form of pigments of porphyrin, carotenoids, anthocyanins and flavones [33]. Among the carotenoids identified in fruits and vegetables, β-carotene is the most popular. High concentrations of β-carotene in pequi pulps were found, especially in fruits with thorns endocarp, whose average was 21.50 mg/ 100g, significantly higher (Test t, $p \leq 0.05$) on endocarp fruits without thorns (8.70 mg/ 100g) (Table 3). The other characters evaluated did not present a significant difference between the groups of pequis with and without thorns in the endocarp.

Table 3: Concentration of the pigments found in pequi fruits (*C. brasiliense*) with and without thorns at the endocarp at full maturation stage. Água Limpa Experimental Station - UFU, Uberlândia - MG, 2017-2018

	With thorns		Without thorns		
Characters	**Variance**	**Mean**	**Variance**	**Mean**	t_{cal}
----------Pulp----------					
β-carotene	42,74	21,50	8,70	9,17	2,97*
Lycopene	9,49	9,59	--	--	
----------Pericarp----------					
β-carotene	1,36	1,34	0,60	1,95	$0,094^{NS}$
Chlorophyll-a	0.17	0,92	0.02	0.95	1.09^{NS}
----------External Mesocarp----------					
β-carotene	0,21	1,65	1,15	3,52	$0,76^{NS}$
Chlorophyll-a	25.84	19.30	2.37	32.89	1.62^{NS}
Chlorophyll -b	31.30	22.50	34.08	39.46	0.88^{NS}

*: significative at 5% by t-teste, ^{NS}: no significative, --: unquantified

Boas *et al.* [34] found concentrations of 3.0 mg/ 100g and Paz *et al.* [24] 5.4 mg/ 100g of β-carotene in pequi pulp with spiked endocarp, lower than the one reported in the present study. β-carotene is a precursor antioxidant of vitamin A, it is abundantly present in yellow-orange colored foods, as in the fruits of pequi trees. Both the inner peel (external mesocarp) and the outer peel (pericarp) showed the presence of small amount of β-carotene. Lycopene contents were found only in fruit pulp with thorns endocarp, which averaged 9.59 mg/ 100g (Table 3). Oliveira *et al.* [32] found β-carotene concentrations varying from 6.26 mg/ 100g to 11.4 mg/ 100g and lycopene from 1.12 mg/ 100g to 2.08 mg/ 100g in thorns in the endocarp.

Chlorophylls are the most abundant natural pigments present in plants and occur in chloroplasts of leaves and other plant tissues, such in the peel of pequi, and are responsible for their coloration. Chlorophyll-a is present in all organisms that perform photosynthesis, while chlorophyll-b is an accessory pigment that assists in the absorption of light and the transfer of energy to the reaction centers [35].

Table 3 shows the chlorophyll levels (a and b) in the outer and inner peel of the fruits, with chlorophyll-b present only in the outer peel. A practical application of chlorophylls is their use as a natural dye in both food and pharmaceutical products and food supplements [36,37]. From the biological point of view, studies have shown that chlorophylls present anti-mutagenic, antigenotoxic properties [38,39] and antioxidants [40,41], and the chlorophylls have the ability to induce cytoprotective genes, which protect cells against oxidative damage caused by free radicals [42].

4. Conclusion

This paper describes for the first time the nutritional composition of pequi fruits without spines in the endocarp. We found significant differences in the chemical and bromatological profile of pequi fruits with and without spikes in the endocarp. The consumption of pequi provides appreciable amounts of nutrients, thus meeting the needs of consumers. However, it is necessary to analyze fruits from other sites and in different crops to evaluate the nutritional diversity of the fruits of *Caryocar brasiliense*.

Declarations of interest: none

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