Chemical characterization and antioxidant potential of native fruits of the Cerrado of northern Minas Gerais

O objetivo deste estudo foi caracterizar quimicamente as polpas das frutas tropicais araticum (Annona crassiflora), buriti (Mauritia flexuosa), coquinho-azedo (Butia capitata), cagaita (Eugenia dysenterica), e cajá (Spondias mombin), com foco no potencial antioxidante e nos microminerais. O nível de cálcio na polpa de Araticum foi de 9,35 mg/100 g e o teor de ferro foi de 4,78 mg/100 g. Na polpa de cagaita, o teor de cálcio foi de 15,35 mg/100 g e o de magnésio, 66,00 mg/100 g. O teor de ferro presente na polpa de coquinho foi de 11,47 mg/100 g e na polpa de cagaita foi de 11,53 mg/100 g. Os extratos com os maiores teores de compostos fenólicos totais foram araticum (433,80 mg GAE/g) e coquinho (173,5 mg GAE/g). Araticum pulp had the highest antioxidant potential because it had the lowest EC50 (0,04 mg/mL). The results presented here demonstrate the great potential of the fruits of the Cerrado in terms of rich mineral nutrients and bioactive compounds.

Keywords: Bioactive compounds; Micronutrients; Fruit pulp; Araticum; Buriti; Coquinho-azedo; Cagaita; Cajá.

Palavras-chave: Compostos bioativos; Micronutrientes; Polpa de fruta; Araticum; Buriti; Coquinho-azedo; Cagaita; Cajá.
1 Introduction

The Cerrado is an ecoregion with specific characteristics and great diversity. The richness of native fruit species and a large amount of edible fruit makes the Cerrado the most diversified tropical savanna in the world (Klink & Machado, 2005; Schiassi et al., 2018).

The greatness of this savannah indicates the importance of studies aimed at the conservation and management of its biodiversity. Fruits are the plant species of the Cerrado, which stand out for their potential for sustainable use.

In addition to its environmental importance, the Cerrado is also a major center for the production of food, fiber, and other products, helping to integrate sustainable development and guaranteeing the quality of life for the population (Avidos & Ferreira, 2000; Vieira et al., 2006). The native fruits of the Cerrado have great nutritional potential with considerable amounts of protein, fiber, energy content, vitamins, calcium, phosphorus, and fatty acids (Vieira et al., 2006). Data regarding the physicochemical characteristics as well as the nutritional and functional value of the fruits of the Cerrado are essential for boosting the consumption and production of new products with added value (Silva et al., 2008; Morzelle et al., 2015).

Fruits are rich sources of antioxidant compounds, and some studies suggest that the daily intake of antioxidants can effectively protect against oxidative processes (Chen et al., 2014; Lima et al., 2015; Siriamornpun & Kaewseejan, 2017; Brabo de Sousa et al., 2018). Free radicals and oxidants derive from both internal sources, including metabolism, and external sources (pollution, cigarette smoke, and radiation, among others). Accumulation of these substances can trigger chronic diseases such as cancer, autoimmune diseases, aging processes, cataracts, rheumatoid arthritis, and cardiovascular diseases. Antioxidants are substances that bind radicals, preventing the attacks on lipids, amino acids of proteins and DNA bases, preventing the formation of lesions and the loss of cellular integrity (Van Breda et al., 2008; Suzuki-Sugihara et al., 2016; Melo et al., 2018).

Phenolic compounds are antioxidants derived from benzoic and cinnamic acids that interact with radical species and are consumed during the reaction; these compounds also act as blockers of chain reactions. They are widely distributed in nature (Moreira & Mancini-Filho, 2004; Dutra et al., 2017).

Mineral nutrients also play a vital role in the development and proper physiological function, and fruits are considered the main sources of minerals required in human diets. Although quantitatively they represent a small fraction of the total mineral content of the human body, microelements, and trace elements such as zinc, copper manganese, and iron play important roles in several metabolic pathways (Hardisson et al., 2001; Trindade, 2005).

Therefore, the present study was designed to chemically characterize the pulp of araticum, buriti, coquinho azedo, cagaita, and cajá with a focus on their antioxidant potential, their content of phenolic compounds, macronutrients, and minerals.

2 Materials and methods

The fruits araticum (*Annona crassiflora*), buriti (*Mauritia flexuosa*), coquinho azedo (*Butia capitata*), cagaita (*Eugenia dysenterica*), and cajá (*Spondias mombin L.*), in complete maturation stage, were acquired in cooperative in the city of Montes Claros of the state of Minas Gerais, Brazil (Figure 1) during the harvesting of the year 2018. All analyses were performed in triplicate with 3 replicates. All solvents and reagents used were of analytical grade.
2.1 Physicochemical analyses

After extraction of the pulps from the fruits, the moisture (method No. 967.08), ash (method No. 942.05), lipid (method No. 2003.06), and protein (method No. 988.05) contents were determined according to methodologies proposed by the Association of Official Analytical Chemists (AOAC) (Association of Official Analytical Chemists, 2005). The carbohydrate levels were calculated using the following formula: 100 − (moisture + ash + lipid + protein). The total energy value of the pulp was estimated using the conversion factors of 4 kcal/g for protein and carbohydrate and 9 kcal/g for lipid.

Acidity was determined by titration according to Association of Official Analytical Chemists (2005) (method No. 920.124) and was expressed as grams of citric acid per 100 g of sample. The pH was determined using a potentiometer (Even model PHS 3E).

Soluble solids were determined using a refractometer (Ávila científica model Biobrix). The color determination was performed using a colorimeter (Konica Miolta model KM- CR-400) by reading the coordinates L*, a*, and b*. The parameters of hue (h*) and saturation (C*) were calculated from values of a* and b*, according to Equations 1 and 2, respectively.

\[
h^* = \arctan\left(\frac{b^*}{a^*}\right)
\]

\[
c^* = \sqrt{a^{*2} + b^{*2}}
\]

2.2 Analysis of mineral nutrients

The samples were digested according to the procedure described by Sobukola et al. (2010). The digestion was carried out with 0.5 g of dry sample (105 °C for 24 hours), 2.5 mL of HCl, 1 mL of H2SO4, and 10 mL of HNO3 on a heating plate for 30 min at 180 °C.

Calcium (Ca), magnesium (Mg), iron (Fe), manganese (Mn), copper (Cu), and zinc (Zn) were analyzed by atomic absorbance spectroscopy (Varian, model AAS 240 FS). Sodium (Na) was analyzed by flame photometry.

2.3 Preparation of the methanolic-acetanolic extracts

For the analysis of total phenolic compounds and total antioxidant activity, we obtained extracts of fruit pulp according to a method adapted from Rufino et al. (2007). Five grams of each sample was diluted in 10 mL of 50% methanol. After standing for 1 hour, it was centrifuged at 4000 rpm for 30 minutes (Kacil centrifuge model CEO1). The supernatant was transferred to a 25 mL flask. To the precipitate, we added
10 mL of 70% acetone and homogenized again. After 1 hour of standing it was centrifuged again at 4000 rpm for 30 minutes. The supernatant was transferred to the flask and the volume was brought to 25 mL.

2.4 Total phenolic compounds

Analysis of total phenolic compounds was adapted from Singleton & Rossi (1965). For the reaction, 0.5 mL of sample extract, 2.5 mL of Folin-Ciocalteu solution (10%), and 2 mL of sodium carbonate solution (4%) were used. After 2 hours, a spectrophotometer (Nova model 1600UV) reading at 750 nm was performed. The phenolic content was calculated using a standard curve prepared with gallic acid and expressed in mg of gallic acid equivalent (GAE)/100 g.

2.5 Antioxidant capacity

For the determination of the antioxidant capacity (AC) we used a methodology described by Re et al. (1999), with adaptations. This methodology proposes that the stable radical purple DPPH decolorizes in reactions with antioxidants present in the sample, thus the higher the antioxidant capacity of the sample, the greater the loss of DPPH reagent staining with a consequent decrease in absorbance reading.

To prepare the curves for each fruit, 0.1 mL of the extract of the samples described in section 2.3 at various dilutions and 3.9 mL of DPPH solution were used. The reading was made after 1 hour and 30 minutes of reaction. This time was determined after preliminary tests of the stabilization of the spectrophotometer (Nova model 1600UV) readings.

The EC50 calculation for the percentage of radical oxidation inhibition was calculated using Equation 3.

\[
\% \text{ Inhibition} = \left( \frac{Abs_{\text{DPPH}} - Abs_{\text{Extr}}}{Abs_{\text{DPPH}}} \right) \times 100
\]

where AbsDPPH represents the absorbance obtained from the DPPH solution (60 μM) and AbsExtr is the absorbance of the extract from each sample.

2.6 Statistical analysis

The results were subjected to analysis of variance (ANOVA) and the mean values were compared to the confidence level of 95% \((p < 0.05)\) by the Tukey test. We used the statistical software package SAS, Statistical Analysis System, version 9.1.

The correlation between TAC and the total phenolic compound content was calculated using the statistical package Bioestat, version 5.3, at a 5% significance level.

3 Results and discussion

The centesimal composition and caloric value of the analyzed fruit pulps are presented in Table 1.

| Fruit pulps | Moisture (% m/m) | Protein (% m/m) | Ash (% m/m) | Lipids (% m/m) | Total carbohydrates (% m/m) | Caloric value (kcal/100 g) |
|-------------|-----------------|----------------|------------|----------------|-----------------------------|---------------------------|
| Araticum    | 71.42 ± 0.39\(^d\) | 1.51 ± 0.22\(^a\) | 0.54 ± 0.02\(^a\) | 3.11 ± 0.04\(^b\) | 23.42 ± 0.20\(^a\) | 127.71 ± 1.75\(^b\) |
| Buriti      | 70.65 ± 0.19\(^e\) | 1.26 ± 0.37\(^ab\) | 0.56 ± 0.03\(^a\) | 11.29 ± 0.08\(^a\) | 16.24 ± 0.39\(^b\) | 171.61 ± 1.20\(^a\) |
| Cagaita     | 92.44 ± 0.27\(^a\) | 1.14 ± 0.29\(^b\) | 0.04 ± 0.01\(^c\) | 0.05 ± 0.01\(^d\) | 6.33 ± 0.46\(^d\) | 30.33 ± 1.04\(^c\) |
| Caja        | 84.87 ± 0.35\(^c\) | 0.86 ± 0.20\(^ab\) | 0.17 ± 0.05\(^b\) | 0.03 ± 0.02\(^d\) | 14.07 ± 0.34\(^c\) | 59.99 ± 1.29\(^a\) |
| Coquinho    | 90.00 ± 0.06\(^d\) | 0.83 ± 0.07\(^b\) | 0.54 ± 0.07\(^a\) | 2.62 ± 0.14\(^c\) | 6.01 ± 0.12\(^d\) | 50.94 ± 1.08\(^d\) |

Legend: mean ± standard deviation \((n = 3)\). The averages with the same letters in the column do not differ by the Tukey test \((p > 0.05)\).
We observed that all the analyzed pulps had high levels of moisture varying from 70.65% for buriti to 92.44% for cagaita. The pulp that presented the highest protein content was araticum (1.51%) and the lowest was coquinho (0.83%). The value found for buriti pulp (1.26%) was below the value found by Manhães & Sabaa-Srur (2011), which was 2.10% for buriti in the region of Pará-BR. In general, these differences in composition can be the result of several factors, including the place of cultivation, temperature, degree of maturity, etc. The pulps with the highest ash contents were araticum (0.54%), buriti (0.56%), and coquinho (0.54%). The lowest ash value was found in cagaita pulp (0.04%).

The highest lipid content was found for buriti (11.29%). This fruit is naturally oily and is exploited for this characteristic in oil production. The high lipid content of buriti gives this pulp a characteristically higher caloric value among the analyzed pulps. Cajá (0.03%) and cagaita (0.05%) were the pulps with the lowest lipid content.

The pulps were rich in water and total carbohydrates, including fibers and sugars. They all had low caloric value, except for buriti (171.61 kcal/100 g) which stands out for its richness in lipids. Araticum also had a high caloric value (127.71 kcal/100 g), because it had a high total carbohydrate content compared to other analyzed pulps.

The differences between our results regarding chemical composition and values reported in studies of other authors are due to variations of factors such as degree of maturity, harvest season, location, and climate (Ferrão et al., 2013; Siriamornpun & Kaewseejan, 2017). Table 2 shows the results of soluble solids, pH, acidity, and color.

For soluble solids, the sample with the highest value was araticum (17.37 °Brix) value less than the value reported by Cardoso et al. (2013) (22.54 °Brix), but higher than the value reported by Souza et al. (2012) (11.33 °Brix). These differences can occur due to several factors including place of cultivation, climate, time of harvest, and degree of maturation. The pulp with the highest acidity was cajá, with 1.21 g/100 g.

The values of pH varied between 2.49 and 4.17 for cajá and buriti, respectively. The pH values for cagaita (4.02) and araticum (3.07) differed from those reported by Roesler et al. (2007), which were 2.8 and 4.8, respectively.

Table 2. Physicochemical properties of fruit pulps from the Cerrado of northern Minas Gerais.

| Fruit pulps | Soluble solids (°Brix) | pH | Titratable acidity (g/100 g) | L* | C* | h* |
|-------------|------------------------|----|-----------------------------|----|----|----|
| Araticum    | 17.37 ± 0.58a          | 4.02 ± 0.02a | 0.45 ± 0.02a | 58.19 ± 0.95a | 8.41 ± 0.06b | 75.45 ± 0.01b |
| Buriti      | 2.17 ± 0.29d           | 4.17 ± 0.26d | 0.73 ± 0.09b | 38.50 ± 1.01d | 8.58 ± 0.14b | 68.63 ± 0.02c |
| Cagaita     | 5.40 ± 0.36c           | 3.07 ± 0.06c | 0.31 ± 0.01d | 50.62 ± 0.35b | 6.59 ± 0.68c | -79.73 ± 0.02c |
| Cajá        | 15.17 ± 0.14b          | 2.49 ± 0.01d | 1.21 ± 0.01a | 42.60 ± 0.10d | 6.79 ± 0.05c | -86.87 ± 0.00d |
| Coquinho    | 5.75 ± 0.00c           | 3.41 ± 0.01b | 1.16 ± 0.01a | 56.53 ± 0.10a | 10.65 ± 0.01a | 81.94 ± 0.00b |

Legend: L* (Luminosity); C* (Saturation); h* (Tonalità). Mean ± Standard Deviation (n = 3). The averages with the same letters in the column do not differ by the Tukey test (p ≥ 0.05).

The Normative Instruction No. 37, of October 1, 2018, from the Ministry of Agriculture, Livestock and Supply, provided parameters for quality and identity of various fruit pulps including buriti and cajá. According to this Normative Instruction (Brasil, 2018), the minimum values for soluble solids in buriti pulp were 4.5 °Brix, pH 3.5, and total acids 2.2 g/100 g. The values we reported for buriti samples would therefore be characterized as non-standard. For the pulp of the cajá, the minimum values were soluble solids 9.0 °Brix, pH 2.2, and total acids 0.9 g/100 g. Therefore, our cajá sample analyzed met all parameters. The other pulps studied did not have parameters of quality and identity foreseen in the Brazilian legislation (Brasil, 2018).

The values of luminosity (L*) showed that the pulps with the darkest coloration were those of buriti (38.50) and cajá (42.60) with the lowest values of L*. Saturation values (C*) varied from 0 to 100 with higher values...
indicating a more intense color. The values presented by the analyzed pulps are considered low, suggesting that they are not pure colors but rather were a mixture of shades. The parameter tonality (h*) shows that the pulp of araticum and coquinho tended to be yellow, the pulps of cagaita and cajá demonstrated green shades and the pulp of buriti tended toward red tones. However, because the values of C* were low, these colors are not pure, i.e., they showed tendencies toward these tones.

Table 3 shows the results of the mineral analysis of the pulps of the fruits studied. For each fruit and mineral, the Dietary Reference Intake (DRI) for a healthy male adult was calculated. For calcium, magnesium, and zinc, the FAO/WHO reference values (Food and Agriculture Organization of the United Nations, 2001) were used, and the reference values of the Institute of Medicine (2001) were used for copper and manganese.

Magnesium was the element with the greatest concentration among the analyzed elements in the pulps studied. The pulp of cagaita had the highest magnesium content (66.00 mg/100 g) representing about 25% of the recommended daily intake.

In addition to calcium being an important metal in the development and maintenance of bones and teeth, is also necessary for processes that carry ions through cell membranes and for the regulation of cardiac muscle function. Buriti (36.93 mg/100 g) and coquinho (31.64 mg/100 g) had the highest content of calcium. Schiassi et al. (2018) reported similar values for buriti (37.83 mg/100 g). However, the value obtained was well below that found by Manhães & Sabaa-Srur (2011) for buriti in the region of Pará-BR (80.49 mg/100 g). As previously mentioned, these results demonstrate that the composition of these fruits varies considerably depending on the region of cultivation.
0.79 mg/100 g, while in the present study the value found for zinc in araticum was 0.35 mg/100 g. The pulps with the lowest zinc content were cajá (0.06 mg/100 g) and araticum (0.35 mg/100 g).

The pulps of cagaita and coquinho had the highest contents of iron at 11.53 mg/100 g and 11.47 mg/100 g, respectively. These values represent about 82% of the recommended daily intake. Coquinho pulp also had the highest copper (0.69 mg/100 g). Cajá pulp had the lowest copper content (0.24 mg/100 g).

Buriti pulp had the highest manganese content (4.69 mg/100 g). This value was higher than that reported by Manhães & Sabaa-Srur (2011) (1.79 mg/100 g). The value found for manganese in buriti was above the recommended value for daily intake of this mineral, however, the maximum tolerable levels of intake of this mineral are 11 mg per day (Institute of Medicine, 2001).

The results of analyses of phenolic compound content and antioxidant capacity are shown in Table 4.

The extracts with the highest values of total phenolic compounds were those of araticum (433.80 mg GAE/g). Cajá (58.27 mg GAE/g) and buriti (90.24 mg GAE/g) had the lowest content of phenolic compounds.

The pulps of araticum, coquinho, and cagaita presented high phenolic contents when compared to other traditional fruit pulps such as tamarind (23.57 mg GAE/g), caju (201.61 mg GAE/g), and goiaba (104.79 mg GAE/g) reported by Vieira et al. (2011). For cajá, this same researcher found 70.92 mg GAE/g. This value was higher than the value we reported in the present study (58.3 mg GAE/g). The content of phenolic compounds in fruits varies widely with the species of the crop, the local the time of the harvest, and season of the year. In general, the high total phenolic content observed in the present study demonstrates the great potential in bioactive compounds presented by the fruits of the Cerrado of northern Minas Gerais.

Table 4. Total phenolic content and antioxidant capacity of native fruits of the Cerrado of northern Minas Gerais.

| Fruit pulp | Total phenolics (mg GAE/100 g) | EC50 (mg/mL) |
|------------|---------------------------------|--------------|
| Araticum   | 433.75 ± 0.07\textsuperscript{a}  | 0.04 ± 0.04\textsuperscript{d} |
| Buriti     | 90.24 ± 0.01\textsuperscript{c}  | 3.27 ± 0.25\textsuperscript{b} |
| Cagaita    | 143.81 ± 0.03\textsuperscript{b} | 0.73 ± 0.08\textsuperscript{c} |
| Cajá       | 58.27 ± 0.01\textsuperscript{c}  | 4.68 ± 0.06\textsuperscript{a} |
| Coquinho   | 173.49 ± 0.06\textsuperscript{b} | 0.77 ± 0.12\textsuperscript{c} |

Legend: GAE: Gallic acid equivalent; Total phenolics per 100 grams of fruit pulp. Antioxidant capacity (AC) expressed in EC\textsubscript{50}. Mean ± Standard Deviation (n = 3). The averages with the same letters in the column do not differ by the Tukey test (p ≥ 0.05).

The analysis was used for AC determination based on the transfer of electrons between antioxidants in the sample and the stable radical DPPH. This reaction discolors the purple DPPH reagent, causing a decrease in absorbance with increasing antioxidant potential. Therefore, samples with the lowest content of EC\textsubscript{50} were those that presented the highest AC (Table 4).

Araticum pulp had the lowest EC\textsubscript{50} value (0.04 mg/mL) and, consequently, the highest antioxidant potential. Cajá pulp had the highest EC\textsubscript{50} value (4.68 mg/mL), and therefore the lowest antioxidant potential.

Roesler et al. (2007) found that araticum pulp had an EC\textsubscript{50} value of 0.14882 mg/mL, higher than the value obtained in the present study (0.04 mg/mL). For cagaita, this same researcher found EC\textsubscript{50} of 0.387 mg/mL, slightly lower than the value presented in this study (0.73 mg/mL).

The correlation found between AC and total phenolic compounds content was negative and of high magnitude, but was not significant (r = -0.7343; p = 0.3751), that is, as the content of phenolic compounds increases, antioxidant activity increases. However, when the correlation was tested without the data obtained for the araticum pulp, the correlation increased (r = -0.9717; p = 0.6833). The antioxidant capacity of the
araticum pulp is probably linked to other groups such as carotenoids, chlorophyll, and vitamins, among others.

4 Conclusion

Cerrado fruit pulps were high in water and carbohydrates. Buriti pulp had the highest lipid content. In general, caloric values were highest for buriti and araticum. The highest iron content in the pulps was found in coquinho and cagaita. Araticum and cagaita had the highest antioxidant capacity. The pulps with the highest content of phenolic compounds were araticum and coquinho.

This study provides important information regarding these Cerrado fruit pulps. We highlighted their great nutritional and bioactive potential that can be exploited by industry to add value to products and to add value to their origin, the Cerrado.

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