

PROPERTIES OF DIFFERENT VARIETIES OF *MARANTA ARUNDINACEA*'S STARCH

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ABSTRACT: The objective of this study was to analyze and compare arrowroot starch in the "seta" (AS) and "redonda" (AR) varieties by assessing their chemical, morphological, rheological, structural and thermal characteristics, and to suggest possible applications in the food industry. The analyzes of proximal composition, infrared spectroscopy, scanning electron microscopy, determination of paste clarity and properties, X-ray diffraction, and thermal properties have been conducted. The extracted starches present high purity, with the carbohydrate level above 97%. The two types of arrowroot starches have exhibited vulnerability to high temperatures, lower resistance to dissociation of hydrogen bonds, and high final viscosity (357.63 RVU to AR and 432.46 RVU to AS). The characteristic size of the starch granules is in the range of 8 μm to 45 μm . In this study, there was a predominance of granules of approximately 30 μm , for both AR and AS, which can be considered large for granules. The granules predominant geometric shapes are oval and ellipsoid. Starches exhibited type-C crystallinity and initial, peak, and final temperature values for gelatinization well below the temperatures found in literature. The two starches exhibited potential for use in the industry of instant foods, breakfast cereals, infant food, meat products, and bakery products. However, studies applying these starches in the matrices need to be carried out to prove its use.

KEY-WORDS: Arrowroot; Gelatinization; Paste properties; Paste clarity; Thermal properties.

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1. INTRODUCTION

2.

Starch is the main energy reserve carbohydrate in plants, and it is found in great amounts, especially in roots, tubercles and cereals. Beyond being a complement in man's diet, starch is also used as an ingredient or additive (Gutiérrez, Hernion-Julien, Álvarez & Alvarez, 2018) to enhance product production, presentation, and conservation in several industrial areas. In the food industry, starch is used to modify or control product characteristics through its use as texturizer, thickener, stabilizer, moisture retainer, and gelatinizer (Agama-Acevedo, Flores-Silva & Bello-Perez, 2019; Mendes, Bora, & Ribeiro, 2012).

The main conventional and commercial starch sources with several uses are maize (52%), cassava (34%), potatoes (7%), and wheat (5%), as well as other conventional and unconventional sources (2%) (Agama-Acevedo et al., 2019; Felipe, Alves & Vieira, 2013). However, the use of starch in its native form is limited by some of its natural characteristics such as its low solubility, thermal resistance, and its high tendency to retrograde (Haq et al., 2019). Thus, over the years, there have been attempts to modify these properties of starch, and methods to make them better suitable for industrial food processes have been studied.

There are several methods to carry out the modification of starch. Among them, the chemical, physical, and enzymatic techniques stand out. They can be applied individually or combined. The type of modification and the agent to be used is chosen accordingly to the application given to the modified product obtained since the different types of modification reflect in the obtaining of starches with different properties (Almeida et al., 2019; Palavecino; Penci; Ribotta, 2019).

Countries located in tropical regions, such as Brazil, possess a great variety in starch-rich vegetables, such as taro (*Colocasia esculenta*), yam (*Dioscorea* sp.), "mangarito" (*Xanthosoma riedelianum*) and arrowroot or maranta (*Maranta arundinacea* L.), which could be used in their native form, dismissing modifications (Andrade, Barbosa & Pereira, 2017; Martins, Souza, Botrel, Resende & Pereira, 2020; Nogueira, Fakhouri & Oliveira, 2018; Souza et al., 2019).

The arrowroot (*Maranta arundinacea* L.) belongs to Marantaceae family, and it produces rhizomes that store starch with unparalleled characteristics. This vegetable is a plant originated in Latin America that has aroused interest in the food industry due to its high starch content with differentiated characteristics and high commercial value. (Souza et al., 2019). Despite the affordable commercial price reached by its starch, and its widespread use in Brazilian cuisine, the arrowroot is not among the traditionally cultivated vegetables, simply because its consumption is limited to just a few regions of the country. Its world production is also low, and there are only a few studies on this species, with scarce production data.

According to Valencia et al. (2015), the arrowroot starch (without specifying the variety) has granules with spherical and elongated geometries with an average size of 56.60 μm . Its granules also have type B crystallinity, and a gelatinization temperature of 65.5 $^{\circ}\text{C}$. This type of starch is very digestible, has high gelling capacity, and presents special physicochemical characteristics such as high amylose content, in addition to being gluten-free (Charles et al., 2016). In general, the maranta starch could have numerous applications in the food industry, with promising potential formation of strong polymeric matrices for the preparation of edible coating and film applications, due to the high amylose content (Valencia et al. 2015).

In view of the potential use of this polysaccharide, studies that further investigate its properties are necessary to assess its capacity for industrial application. In addition to the study of starch as an unconventional vegetable, it is interesting to investigate its varieties, especially the arrowroot starches in the varieties "seta" and "redonda". Thus, the objective of this study was to analyze and compare arrowroot starch in the "seta" (AS) and "redonda" (AR) varieties by assessing their chemical, morphological, rheological, structural, and thermal characteristics as well as verifying their possible applicability in the food industry.

2. MATERIAL AND METHODS

2.1 STARCH EXTRACTION

Redonda and Seta arrowroot rhizomes were supplied by the Brazilian Agricultural Research Corporation (Embrapa). The planting of both types of arrowroot was simultaneous, carried out in mid-October 2013, and harvested in early June 2014. The work was conducted at Embrapa Hortaliças, Brasília, DF (15°56'S, 48°08'W, altitude of 997 m), in an open field. No pesticides were used due to its rusticity.

The redonda (AR) and seta (AS) arrowroot varieties rhizomes were selected according to the lack of injuries and deformities. Afterwards, they were weighted with their peels and washed in running water. After washing, they were immersed in sodium hypochlorite solution (0.150 mL L^{-1}), for a 15 min period, for sanitation. Next, they were manually peeled with a stainless-steel knife, and, once again, washed, and weighted. The rhizomes were cut into 0.5 cm thick slices and immersed in sodium metabisulphite solution (2 mg kg^{-1}) for 15 minutes to avoid darkening.

To extract the starch, the arrowroot rhizomes were crushed in a industrial blender (Lucre, model C4, Brazil) in the proportion of 1:1 with distilled water, and, then, filtered in polyester mesh. The suspension was left to rest (± 16 hours) in a refrigerated environment ($\pm 5 \text{ }^\circ\text{C}$). The supernatant was discarded, and the precipitated starch was resuspended with distilled water to be decanted again. This procedure of starch suspension and decantation was repeated until the product presented color and texture that are characteristic for starch. The material was then dried in forced air circulation oven at $45 \text{ }^\circ\text{C}$ until reaching constant weight, cooled at room temperature, then reduced to powder using mortar and pestle, and sieved through 0.350 mm sieve, and, finally, conditioned in bottles until its later use, according to methodology quoted by Daiuto and Cereda (2003). Subsequently, characterization analyzes were carried out on AR and AS starches.

2.2 CHEMICAL ANALYSIS AND INFRARED SPECTRUM

The moisture, ether extract, crude protein, ash and carbohydrate fraction contents, were determined according to the AOAC (2010). Crude fiber content was determined using the method of Van de Kamer and Van Ginkel (1952). This method is gravimetric, and it uses reflux with acetic, trichloroacetic, and nitric acids as well as subsequent filtration and drying in an oven.

The ART-FTIR (Infrared Analysis with Attenuated Total Reflectance) specter was collected through a spectrometer (IRAffinity-1) equipped with an accessory for Attenuated Total Reflectance (ATR) with ZnSe crystal. The specter was acquired with 64 scans and resolution of 4 cm^{-1} , in the range of $4,400 \text{ cm}^{-1}$ to 600 cm^{-1} according to the methodology proposed by Chen et al. (2018), with modifications.

2.3 MORPHOLOGICAL PROPERTIES - SCANNING ELECTRON MICROSCOPE (SEM)

After drying and grinding, the powder samples of AR and AS were deposited on a double-sided carbon tape, placed on racks covered with aluminum foil, and sputter-coated with gold (Balzers Sputter Coater SCD 050). At the end of this procedure, the samples were examined under a scanning electron microscope. The generated images were scanned at varying magnifications at 20.00 kV, and work distance between 8.0 and 9.0 mm (Andrade, Barbosa & Pereira, 2017). Approximately 10 starch scanning electromicrographs of each arrowroot variety were taken at 830x magnification and 20 μm scale.

2.4 DETERMINATION OF PASTE CLARITY AND PROPERTIES

The paste clarity was determined as described by Craig, Maningat, Seib, and Hosene (1989) using starch suspensions ($1\% \text{ w v}^{-1}$) in deionized water. The suspension was gelatinized and placed in a water bath of boiling water for 30 minutes, with agitation for 30 seconds every 5 minutes. The solution was agitated and cooled down to room temperature, and the transmittance (percentage) was determined at 650 nm (wavelength) using a spectrophotometer (Varian Indústria e Comércio Ltda., Inc., model Cary 50, Brazil) and a computer system.

Paste viscosity analyzes were conducted using the fast viscosity analyzer (Rapid Visco Analyser – RVA; Newport Scientific) to set the starches viscosity profile, following the methodology proposed by Diniz (2006). At first, the paste viscosity was set at 50°C for four minutes. Later, the gel was heated to a temperature of $95 \text{ }^\circ\text{C}$, for 3 minutes. Cooling was carried out to 50°C , and then the gels were kept at this temperature for another 4 minutes. In this analysis, the values of paste temperature, as well as maximum, minimum and final viscosities, viscosity drop (difference between maximum and minimum viscosity), and tendency to retrograde (difference between final and minimum viscosity) were obtained.

2.5 X-RAY DIFFRACTION (XRD)

The starches were also characterized using the X-Ray diffraction (XRD) powder method with

PANalytical equipment, model X'Pert Pro, a 2θ angular variation of 4° to 70° , $\text{CoK}\alpha$ radiation and a scanning rate of 5° min^{-1} . The spacing d was calculated using the Bragg equations ($n\lambda = 2d\sin\theta$, where d is the spacing, $n = 1$, and $\lambda = 1.7889 \text{ \AA}$). From the recorded diffractogram, the crystallinity index (CI) was calculated (Andrade, Barbosa & Pereira, 2017).

2.6 THERMAL PROPERTIES – TGA, DTGA, DTA AND DSC

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were performed according to the methodology proposed by Pan et al. (2019), with modifications, in a DTG-60H thermogravimetric analyzer (Shimadzu) at temperatures ranging from 30° C to 600° C and scanning rates of $10^\circ \text{ C min}^{-1}$. The analyzes were also run under N_2 atmosphere with a flow rate of 50 mL min^{-1} . Derived thermogravimetry (DTGA) is a mathematical resource that provides the first derivative of the TGA curve as a function of time or temperature. The peak area under the DTGA curve is proportional to the loss of mass during a thermal event. The calculation peak area was performed in the present work.

The differential scanning calorimetry (DSC) analysis was conducted in a DSC Q200 differential scanning calorimeter (TA Instruments, New Castle, USA), according to the methodology (Fakirov et al., 1997). The sample was prepared in suspension with distilled water, in the proportion of 3:1, and kept at rest for 30 minutes at 5° C . The instrument was calibrated using indium as a standard. In order to determine the starch gelatinization temperature, approximately 5.0 mg of a known moisture sample were placed in a hermetically sealed aluminum crucible. Heating up to 120° C was used as the scanning profile, with a heating rate of $10^\circ \text{ C min}^{-1}$, under a flow of 50 mL of nitrogen min^{-1} . The gelatinization enthalpy was calculated using the Universal Analysis software version 4.3A.

3. RESULTS AND DISCUSSION

3.1 CHEMICAL COMPOSITION AND INFRARED SPECTRUM (ATR-FTIR)

Table 1 shows the values for the proximal composition (moisture, ether extract, crude protein, crude fiber, ashes, and carbohydrate fraction) from starches AR and AS.

Table 1 Chemical components and paste properties of AR and AS starches.

Chemical components ($\text{g } 100\text{g}^{-1}$)	Starches	
	AR	AS
Moisture	$10,56 \pm 0,03$	$10,12 \pm 0,02$
Ether Extract*	$0,35 \pm 0,03$	$0,48 \pm 0,08$
Crude Protein*	$0,85 \pm 0,01$	$0,85 \pm 0,01$
Crude Fiber*	$1,63 \pm 0,18$	$1,06 \pm 0,07$
Ashes*	$0,03 \pm 0,00$	$0,12 \pm 0,01$
Carbohydrate Fraction*	$97,14 \pm 0,00$	$97,49 \pm 0,00$
Parameters (RVA)**	AR	AS
Temperature initial paste ($^\circ \text{C}$)	69.85	68.95
Maximum viscosity (RVU)	563.15	481.55
Maximum viscosity temperature ($^\circ \text{C}$)	78.05	84.60
Minimum viscosity (RVU)	184.35	221.98
Minimum viscosity temperature ($^\circ \text{C}$)	89.90	91.50
Final viscosity (RVU)	357.63	432.46
Breakdown (RVU)	378.79	259.57
Set back (RVU)	173.28	210.47

*Dry basis; **Each value represents the average of two determinations; AR = Arrowroot Redonda and AS = Arrowroot Seta.

The moisture for AR and AS starches were $10.56 \pm 0.03 \text{ g } 100\text{g}^{-1}$ and $10.12 \pm 0.02 \text{ g } 100\text{g}^{-1}$, respectively. The level of arrowroot starch present in the work of Nogueira et al. (2018) was higher, approximately $15 \text{ g } 100\text{g}^{-1}$. The moisture contents were less than $14 \text{ g } 100 \text{ g}^{-1}$, which is generally acceptable for dry products and, consequently, a longer life cycle for the product (Andrade et al., 2017).

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It can be observed that the levels of ether extract, proteins, ash, and crude fiber were low, therefore having a high purity level in the starches obtained. Also, high levels of carbohydrate fraction were obtained. Souza et al. (2019) also obtained a high content of glycidic fraction (greater than $93.98 \text{ g } 100\text{g}^{-1}$) in the extraction of arrowroot starch grown under different agronomic managements.

Gordillo, Valencia, Zapata, and Henao (2014) also found low values for the components of ash, crude protein, lipids, and crude fiber in arrowroot starch used to produce glycerol membranes, showing efficiency in extraction, like the present work.

Starches were evaluated by ATR-FTIR spectra to determine the presence of functional groups by bands, which explain their structure (Figure 1).

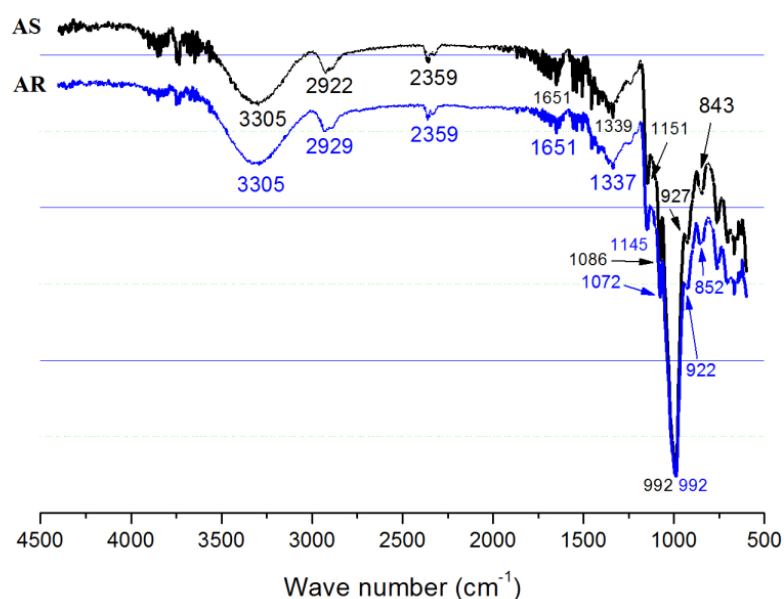


Figure 1 ATR-FTIR spectra for the arrowroot redonda (AR) and arrowroot seta (AS) starches

The ATR-FTIR specters represent a typical starch behavior, as described in the literature. Thus, it is not possible to observe many differences between the samples in absorption bands, with only small changes in their transmittances.

The specters show a broad band between $3,400 \text{ cm}^{-1}$ and $3,200 \text{ cm}^{-1}$ which corresponds to the axis deformation of hydroxyl groups ($-\text{OH}$) in the inter-molecular hydrogen bonds of alcohols commonly found in polysaccharides, confirming the presence of carbohydrates (Andrade, Silva, Nundes & Pereira, 2020; Saikia & Konwar, 2012), in the present case, starch.

The bands at $2,929 \text{ cm}^{-1}$ and 2922 cm^{-1} are attributed to the axis deformation of the C-H bond found in the region between $3,000 \text{ cm}^{-1}$ and $2,840 \text{ cm}^{-1}$ (Zeng, Liu & Liu, 2014). Meanwhile, the bands at $2,359 \text{ cm}^{-1}$ are attributed to the CO_2 absorbed from the environment (Andrade et al., 2020).

Absorption bands at $1,651 \text{ cm}^{-1}$ correspond to bound water in the amorphous region in starch granules. As this band is related to crystallinity of each starch, its variations have the potential of affecting this band (Kizil, Irudayaraj & Seetharaman, 2002). In the present study, the bands at $1,651 \text{ cm}^{-1}$ in two arrowroot starches do not present different intensities, which may indicate that the crystallinity patterns of AS and AR starches do not differ significantly (Andrade et al., 2017). The absorptions in $1,339\text{-}1,337 \text{ cm}^{-1}$ have been related to deformations of C-OH groups or vibrational bands (bending and deformation) related to C and H atoms (Andrade et al., 2020; Andrade et al., 2017).

The bands at $1,151 \text{ cm}^{-1}$ and $1,145 \text{ cm}^{-1}$ correspond to the coupling of the C-O and C-C

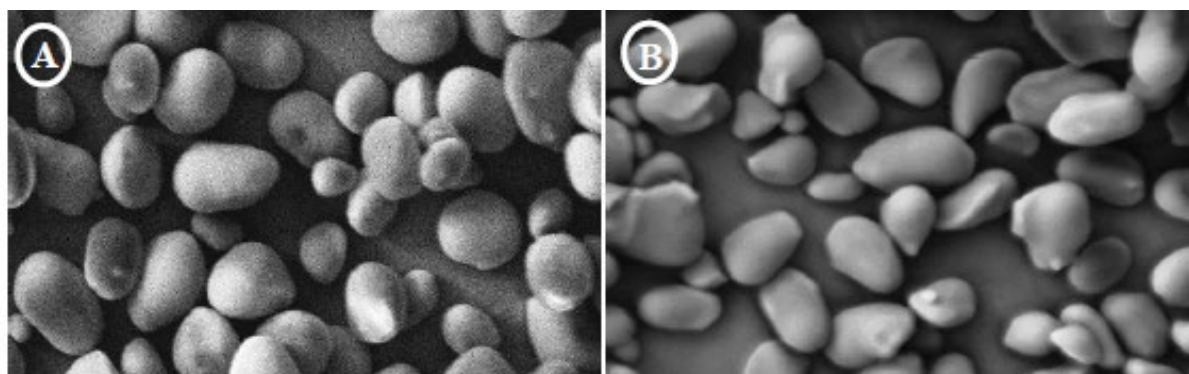
stretching mode (Andrade et al., 2017). Thus, the infrared spectra prove the structure of a polysaccharide with C-O-C bonds, characteristic to carbohydrates (like starch) between $1,200\text{ cm}^{-1}$ and 900 cm^{-1} , confirming the bond between the polymer forming monomers, as observed by Andrade et al. (2020). According to Zeng et al. (2014), who studied the taro starch cultivated in China, the bands at $1,081\text{ cm}^{-1}$ and $1,019\text{ cm}^{-1}$ are characteristic of the O-C stretching associated with anhydrous glucose, which can be observed at $1,072\text{ cm}^{-1}$ for AR and at 1086 cm^{-1} for AS.

The bands at 927 cm^{-1} and 922 cm^{-1} correspond to the water sensitivity and indicates the presence of this molecule in the starch structure (Deepika, Jayaram Kumar & Anima, 2013; Andrade et al., 2017), as evidenced by the moisture analysis (Table 1).

3.2 MORPHOLOGICAL PROPERTIES

The size and shape of the arrowroot starch granules are shown in the Figure 2. It is possible to see that the predominant geometric shapes of the starch granules of the two arrowroot varieties are oval and ellipsoid. The characteristic size is in the range of $8\text{ }\mu\text{m}$ to $45\text{ }\mu\text{m}$, with a predominance of granules of approximately $30\text{ }\mu\text{m}$, for both AR and AS. Therefore, they can be considered large granules (ten granules were measured in order to best represent the average of their size). It can also be observed that the surface of the granules is quite smooth, without irregularities or superficial porosity, which shows intact and undamaged granules, similar to the ones in work of Nogueira et al. (2018).

The average size found for arrowroot in the work of Valencia et al. (2015) was approximately $56.60\text{ }\mu\text{m}$, a higher value than those found in the present study. This difference may be due to the difference in the variety of arrowroot used for the extraction of starch. However, the work cited does



not specify the variety used.

Figure 2 Scanning electromicrographs of AR starch (A) and AS starch (B), with 830x magnification and $20\text{ }\mu\text{m}$ scale.

3.3 PASTE CLARITY AND PROPERTIES

AR and AS starches showed a low percentage of transmittance, 6.99% and 3.92%, respectively, thus forming opaque pastes. According to Craig et al. (1989), the clarity of the paste and the tendency to retrograde influence the technological quality of the starch. Starches used as a thickener in pie fillings, in food topping, or as edible films should preferably be transparent, while starches used in salad dressings, and in the preparation of puddings and ready-made desserts must be opaque, like the starch pastes analyzed in the present work.

The rheological profile of AR and AS starches was analyzed by RVA and their results are shown in Table 1. It is verified that the AR starch presented paste temperature of $69.85\text{ }^{\circ}\text{C}$, and maximum viscosity of 563.15 RVU. The values for paste temperature and maximum viscosity for the AS starch were, respectively, $68.95\text{ }^{\circ}\text{C}$ and 481.55 RVU. The two temperatures are low, which may indicate a smaller resistance to dissociation of intramolecular hydrogen bonds, and greater starch ability for expansion. Because they produce viscous pastes more rapidly, these starches may be potentially useful for their use in instant-preparation food, such as soups and puddings, and, due to their high viscosity, they can be used as thickeners.

Paste temperatures for the starches of the two arrowroot varieties were close to the ones found by Barroso and Mastro (2019), which were of 67.2°C for arrowroot starch. As for the viscosity

peaks, they were higher than all the starches from different vegetables (sweet potato, peruvian carrot, cassava, maize, and waxy maize) analyzed by Shirai et al. (2007), except the potato starch.

The AR starch breakdown presented itself to be higher (378.79 RVU) than AS' (259.57 RVU), which characterizes greater fragility when cooked in water, and lower resistance to hot agitation. When compared to the values observed by Shirai et al. (2007), the potato starch, once again, obtained greater values while the peruvian carrot starch presented a breakdown value that is only higher than the arrowroot seta starch.

The AS starch setback was of 210.47 RVU, higher than the setback for AR starch, which was 173.28 RVU. This higher tendency to starch setback for the two arrowroot varieties indicates lower granule stability to mechanical work and higher capability of amylose recrystallization. When compared to studies in which the arrowroot starch was analyzed, these values are higher (Barroso & Mastro, 2019, Leonel, Sarmento & Cereda, 2002; Ferrari, Leonel & Sarmento, 2005), as well as for the starches in potato, sweet potato, Peruvian carrot, cassava, maize, and waxy maize, in the study by Shirai et al. (2007).

Both the AR starch (357.63 RVU) and the AS starch (432.46 RVU) presented high final viscosities. In the study of Barroso and Mastro (2019), the final viscosity value in the starch arrowroot was 57.2 RVU, which is different from the values found in the present study. Final viscosity is an important parameter in starch use in food because it corresponds to the product's viscosity after cooling, in this case, at 50 °C. Pie fillings demand higher viscosity, which would avoid overflowing during transportation.

The AR sample presented higher paste temperature, as well as maximum viscosity and breakdown while the AS sample presented higher minimum viscosity, higher final viscosity, and higher setback. All the differences among the analyzed results for arrowroot starches, both among the varieties here analyzed and among other authors' starches, can occur, partially, due to variations observed in the composition (amylose and lipid content), in the starch granule size (Ferrari et al., 2005), and in the physiological maturity stage of rhizomes. The phosphor and lipid contents, in high amounts, could influence the paste characteristics.

The elevated values for viscosity peak, viscosity breaking, and setback tendency for the arrowroot starch samples enable their use in fortified breakfast cereals, infant food, or as ingredients for their formulation, as well as meat products and bakery products (Maia, Wang, Ascheri, Cabral, & Fernandes, 1999).

3.4 X-RAY DIFFRACTION (XRD)

X-ray diffractometry reveals the characteristics of crystalline structure of starch granules (Figure 3). It is possible to observe in Figure 3 that the starches in AR and AS presented pattern type-C, confirming the result observed in work of Nogueira et al. (2018). It was observed in the work of Andrade et al. (2017) type-C crystallinity for the yam tuber starch, a vegetable from underground parts of the plant, such as arrowroot rhizomes.

The crystallinity index (CI), determined from the total areas and peaks of the X-ray diffractograms, is an important parameter that influences the physical, mechanical, and technological properties of starch (Martins et al., 2020). The CI found for AR and AS starches was of 40.79% and 39.17%, respectively, considered high, but within the range suggested by Miranda, Carvalho, Vieira and Castro (2019), between 15 and 45% for native starches. As observed by the infrared spectrum in the band intensity at 1651 cm^{-1} , there is no great difference in the crystallinity of the two starches studied.

According to Pepe (2011), the X-ray diffractogram of the native arrowroot starch showed a very mild peak, around 5.6°, peaks at 17°, 18°, and 23°, indicating that these starches had a type C crystalline pattern. In the work of Salgado et al. (2005), there is the influence of the maturation stage, with green bean starch within pattern C and mature beans within pattern A, showing differences in the three-dimensional organization of structures, which may be related to the size of the amylopectin chain (Freitas, 2002). Therefore, the advanced maturation of arrowroots studied in this work may have altered their crystalline structure since they do not a peak at 5.6°, for example.

As for the degree of crystallinity being studied, it is possible to observe that the intensity values for the peaks in the diffractogram were similar, suggesting approximate values for the internal bonding forces in the molecules as well as association degrees among the starch chains.

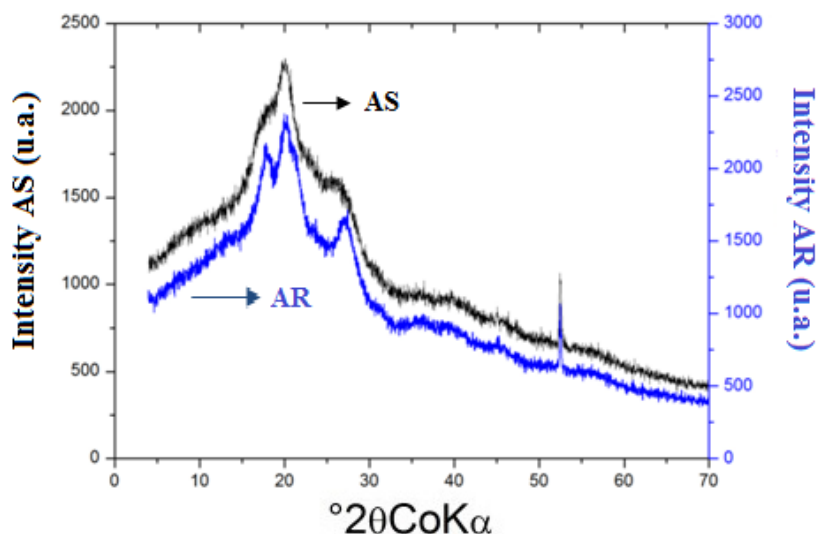


Figure 3 X-Ray diffractograms for starch of arrowroot redonda (AR) and starch of arrowroot seta (AS)

3.5 THERMAL PROPERTIES

Through the thermogravimetric technique, it is possible to measure the mass variation of a substance in function of the temperature, and the results are obtained through curves that show the conclusions regarding stoichiometry, thermal stability, and composition of the analyzed samples. In the starch, the thermogravimetry (TGA/DTGA) is used to assist in the studies of thermal degradation of starch material whereas it is important for the material. However, it should not be used in heating conditions under which degradation, or any undesirable alteration might happen to its properties. Therefore, knowing the temperature and the degradation parameters for the starch material, it is essential in its application. Figures 4a and 4b show the TGA/DTGA/DTA curves for AR and AS starches, respectively.

In the AR starch (Figure 4a) two thermal events of weight loss were observed through the TGA curve. The first, which corresponds to weight loss of 14%, was attributed to evaporation of volatile materials (majorly, the water absorbed by the starch material), and occurred between 24 °C and 112 °C. The second event is related to the stage of thermal degradation for major starch constituents, and minor constituents as well, such as proteins and lipids, with initial degradation temperature (T_{onset}) at 299°C and final (T_{endset}) at 326°C, and weight loss at 49%.

In the AS starch sample (Figure 4b), the two thermal events were also observed. The first, weight loss of 13%, happened between 21°C and 107 °C while, in the second thermal event, there was a weight loss of 52%, and T_{onset} at 293 °C and T_{endset} at 326°C. The results were similar between the two samples.

Percentage values of the first mass loss in TGA by both starches are slightly higher than the moisture content (Table 1). It can be concluded that in addition to water, there may be, in small quantities, other volatile substances.

From the obtainment of the derived thermogram curve (DTGA), it was possible to determinate the temperatures at which the degradation velocity is maximum to each of the samples in the two weight loss events, which are 53.12 °C, when the maximum volatiles loss happens, and 313.51 °C, which is when the maximum degradation happens for the AR starch, and, respectively, 55.02 °C and 309.41°C for the AS starch.

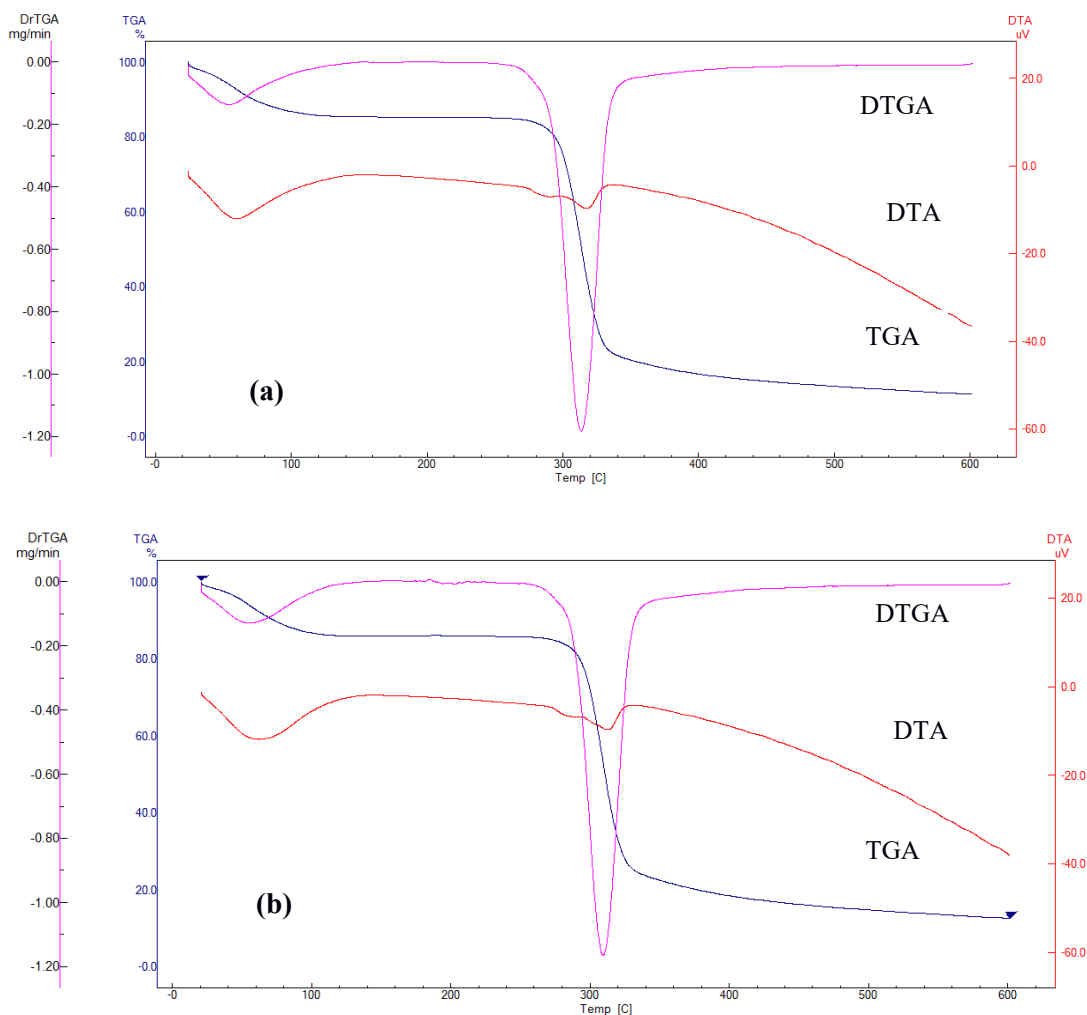


Figure 4 TGA/DTGA/DTA curves for starch in arrowroot redonda (a) and for starch in arrowroot seta (b)

From the thermogravimetric analysis, it is possible to determine the content of inorganic substances in the samples (Araújo et al., 2006). However, the analysis carried out under a controlled atmosphere of N_2 did not provide data compatible with the ash content values obtained in the chemical composition (Table 1) as the impurities present remain as residue after sample volatilization and decompose differently in atmosphere of air or nitrogen (BERNAL et al., 2002). For the arrowroot redonda, this value was 11%, while for the arrowhead seta it was 12.29%, a difference that was already expected since the ash content in the arrowroot redonda is higher than in the arrowroot seta.

The second well-defined peak for DTGA for both studied starches suggest the possibility of a simple degradation mechanism involving amylose and amylopectin as observed by Franklin et al. (2017) for the *Curcuma angustifolia* starch. The same occurs in the work of Nogueira et al. (2018) with arrowroot starch. Given these results, it is possible to affirm that the arrowroot starch is thermally stable, and has desirable characteristics to produce biodegradable, and edible packaging or films (Nogueira et al., 2018).

For all thermal events, the DTA curves showed endothermic processes, that is, they absorb energy for mass losses to occur. In the study of yam and taro starches by Andrade et al. (2017), all mass loss processes were endothermic, being like the present work even though they are starches from different plant sources.

To better understand arrowroot starches, we investigated the heat flow signals of DSC starches gelatinization that revealed significant variation in their gelatinization transition. The parameters of gelatinization temperature [start (T_o), peak temperature (T_p), conclusion (T_c)], gelatinization temperature range ($\Delta T = T_c - T_o$), and gelatinization enthalpy (ΔH) on a dry starch basis are presented in Table 2. It can be verified that the AR starch gelatinization occurred at the temperature of 57.61 °C while AS starch gelatinized occurred at a slightly lower temperature, at 55.39 °C, demonstrating the same behavior observed in the pasta properties analysis.

Table 2 Thermal properties for gelatinization of AR and AS starches

Starches	T _o (°C)	T _p (°C)	T _c (°C)	ΔT (°C)	ΔH (J g ⁻¹)
Arrowroot redonda (AR)	45.87	57.61	61.37	15.50	12.56
Arrowroot seta (AS)	46.83	55.39	62.10	15.27	15.73

T_o, T_p, T_c = initial temperature or onset, peak temperature and final or conclusion temperature, respectively; ΔT = temperature variation; ΔH = enthalpy variation.

The results obtained in the gelatinization enthalpy determination demonstrated that the AR starch demands less energy in order to make the tumescence happen through water absorption and temperature elevation (gelatinization) than the AS starch.

The initial, peak, and final temperature values for gelatinization were well below the temperatures found in the literature. In the study of Barroso and Mastro (2019), the value found for initial temperature was 63.9 °C, and 81.3 °C for final temperature. In the work of Charles et al. (2016), the values of T_o, T_c, and T_p for arrowroot starch were 76 °C, 86 °C, and 80 °C, values also higher than the ones in the present study. The enthalpy of the work mentioned above was closer to the AR and AS starches, 11.0 J g⁻¹, but different from the work of Barroso and Mastro (2019), which has an enthalpy of only 4.2 J g⁻¹. This difference may be due to the possible difference in arrowroot cultivars among the vegetables studied.

The initial gelatinization temperatures of the samples of the two starches obtained by the DSC were lower than those presented by the RVA because, according to Jane et al. (1999) and Pérez, Breene and Bahnassey (1998), the paste temperature obtained from the RVA is related to the sensitivity of the device in detecting the first increases in the paste viscosity of starches, differently from the initial gelatinization temperature, which is detected when the starches first granules begin to disorganize. The values obtained in DSC are, therefore, more accurate, while those obtained in RVA correspond to a specific temperature range. Another important fact is that the RVA analysis started at a temperature of 50 °C, which is higher than the one found by the DSC.

The size of the granules can also influence gelatinization temperatures (T_o and T_p), and smaller granules provide higher gelatinization temperatures (initial, peak, and final). Gelatinization and enthalpy temperatures are altered by the shape and composition of the granule (crystalline and amorphous zones), distribution of small and large granules, and by the sources of starches that may contain different amounts of amylose, amylopectin, and phosphorus (Yonemoto; Calori- Domingues; Franco, 2008). The crystallinity indices of the studied starches were close (approximately 40%). Therefore, it was not the factor that caused the difference between the ΔH found.

According to Charles et al. (2016), flours and/or starches composed of root and tuber can meet industrial requirements of carbohydrate-based food products since they gelatinize at relatively low temperatures and exhibit a high viscosity profile when compared to cereal starches, as occurred in the present study for arrowroot rhizomes of two varieties.

4. CONCLUSIONS

1. The extracted starches present a high purity level, with low levels of lipids, crude protein, crude fiber, and ash. The infrared spectra have characteristics of carbohydrates.
2. The predominant geometric shapes in AR and AS starches are oval and ellipsoid with sizes ranging from 8 μm to 45 μm.
2. Starches (AR and AS) have low paste clarity and can be used in salad dressings as well as in the preparation of puddings and ready-made desserts.
3. The starches presented relatively high maximum viscosity, being the highest value found in AR, and both were not stable at high temperatures and agitation, tending to regression, which was higher for AS – these characteristics suggest the use of these starches in the instant food industry and in fortified breakfast cereals industry, infant food, meat products, and bakery products.
4. The starches of both arrowroot varieties presented type-C crystalline structure, and CI according to literature, approximately 40%.
5. The characterization through thermogravimetry allowed the determination of the average initial temperature for degradation, and the DTGA obtainment provided the values under which the dehydration phenomenon and the polysaccharide degradation events occur, similarly in both starches.
6. The paste temperatures were shown to be lower than the gelatinization temperatures obtained by the DSC, and were smaller for the arrowroot seta starch, which presented higher ΔH.

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6. REFERENCES

AGAMA-ACEVEDO, E.; FLORES-SILVA, C. P.; BELLO-PEREZ, A. L. Cereal starch production for food applications. In: **Starches for Food Application**. Academic Press, p. 71-102, 2019.

ALMEIDA, R. L. J.; PEREIRA, S.T.; FREIRE, A. V.; SANTIAGO, M. A.; OLIVEIRA, L. M. H.; CONRADO, S. L.; GUSMÃO, P. R. Influence of enzymatic hydrolysis on the properties of red rice starch. **International journal of biological macromolecules**, v. 141, p. 1210-1219, 2019.

ANDRADE, A. L.; SILVA, O. A. D.; NUNES, A. C.; PEREIRA, J. Experimental techniques for the extraction of taro mucilage with enhanced emulsifier properties using chemical characterization. **Food Chemistry**, v. 327, p. 127095, 2020.

ANDRADE, A. L.; BARBOSA, A. N.; PEREIRA, J. Extraction and properties of starches from the non-traditional vegetables Yam and Taro. **Polímeros**, v. 27, p. 151-157, 2017.

ARAÚJO, A. A. S.; MERCURI, L. P.; SEIXAS, S. R. S.; STORPIRTIS, S.; MATOS, J. R. Determination of humidity and ash content of guarana commercial samples using conventional method and thermal analysis. **Brazilian Journal of Pharmaceutical Science**, v. 42, n. 2, p. 269-277, 2006.

ASSOCIATION OF OFFICIAL ANALYTICAL CHEMISTS. **Official methods of analysis**. 18th ed. Washington, 2010. 1094 p.

BARROSO, G. A.; DEL MASTRO, N. L. Physicochemical characterization of irradiated arrowroot starch. **Radiation Physics and Chemistry**, v. 158, p. 194-198, 2019.

BERNAL, C.; COUTO, A. B.; BREVIGLIERI, S. T.; CAVALHEIRO, E. T. G. Influência de alguns parâmetros experimentais nos resultados de análises calorimétricas diferenciais - DSC. **Química Nova**, v. 25, p. 849-855, 2002.

CHARLES, A. L.; CATO K.; HUANG, T. C.; HUANG, T. C.; CHANG, Y, H.; CIOU, J. Y.; CHANG, J. S.; LIN, H. H. Functional properties of arrowroot starch in cassava and sweet potato composite starches. **Food Hydrocolloids**, v. 53, p. 187-191, 2016.

CHEN, L.; TIAN, Y.; SUN, B.; CAR, C.; MA, R., JIN, Z. Measurement and characterization of external oil in the fried waxy maize starch granules using ATR-FTIR and XRD. **Food chemistry**, v. 242, p. 131-138, 2018.

CRAIG, S. A. S.; MANINGAT, C. C.; SEIB, P. A.; HOSENEY, R. C. Starch paste clarity. **Cereal chemistry**, v. 66, n. 3, p. 173-182, 1989.

DAIÚTO, E. R.; CEREDA, M. P. Amido como suporte na desidratação por atomização e em microencapsulamento. In: CEREDA, M. P.; VILPOUX, O. F. **Tecnologias, usos e potencialidades de tuberosas amiláceas Latino Americanas**. São Paulo: Fundação Cargill, 2003. v. 3. cap. 16, p. 449-474. (Série: Culturas de tuberosas amiláceas Latino Americanas).

DEEPIKA, V.; KUMAR, K. J.; ANIMA, P. Isolation and physicochemical characterization of sustained releasing starches from Dioscorea of Jharkhand. **International journal of biological**

macromolecules, v. 55, p. 193-200, 2013.

DINIZ, I. P. Caracterização tecnológica do polvilho azedo produzido em diferentes regiões do estado de Minas Gerais. (**Dissertação de Mestrado**). Programa de pós-graduação em Ciência e Tecnologia de Alimentos, Universidade Federal de Viçosa, Viçosa. (2006).

FAKIROV, S.; SARAC, Z.; ANBAR, T.; BOZ, B.; BAHAR, I.; EVSTATIEV, M.; APOSTOLOV, A. A.; MARK, J. E.; KLOCZKOWSKI, A. Mechanical properties and transition temperatures of crosslinked-oriented gelatin. **Colloid and Polymer Science**, v. 275, n. 4, p. 307-314, 1997.

FERRARI, T. B.; LEONEL, M.; SARMENTO, S. B. S. Características dos rizomas e do amido de araruta (*Maranta arundinacea*) em diferentes estádios de desenvolvimento da planta. **Brazilian Journal of Food Technology**, v. 8, n. 2, p. 93-98, 2005.

FELIPE, F. I.; ALVES, L. R. A.; VIEIRA, R. M. Fécula de mandioca, produção na Tailândia versus Brasil. **Mercado & Negócios, Agroanalysis**, 2013.

FRANKLIN, M. E. E.; PUSHPADASS, H. A.; KUMAR, B.; KULKARNI, S.; MUTHURAYAPPA, M.; KANDASAMY, R.; VENKATACHALAM, P.; VELLINGIRI, P. Physicochemical, thermal, pasting and microstructural characterization of commercial *Curcuma angustifolia* starch. **Food hydrocolloids**, v. 67, p. 27-36, 2017.

FREITAS, M. C. J. Amido resistente: propriedades funcionais. **Nutrição Brasil**, v. 1, p. 40-48, 2002.

GORDILLO, C. A. S.; VALENCIA, G. A.; ZAPATA, R. A. V.; HENAO, A. C. A L. Physicochemical characterization of arrowroot starch (*Maranta arundinacea* Linn) and glycerol/arrowroot starch membranes. **International Journal of Food Engineering**, v. 10, n. 4, p. 727-735, 2014.

GUTIÉRREZ, T. J.; SUNIAGA, J.; MONSALVE, A.; GARCÍA, N. L. Influence of beet flour on the relationship surface-properties of edible and intelligent films made from native and modified plantain flour. **Food Hydrocolloids**, v. 54, p. 234-244, 2016.

HAQ, F.; YU, H.; WANG, L.; TENG, L.; HAROON, M.; KHAN, R. U.; MEHMOOD, S.; AMIN, U. I. B.; ULLAH, S. R.; KHAN, A.; NAZIR, A. Advances in chemical modifications of starches and their applications. **Carbohydrate research**, v. 476, p. 12-35, 2019.

JANE, J.; CHEN, Y. Y.; LEE, L. F.; MCPHERSON, A. E.; WONG, K. S.; RADOSAVLJEVIC, M.; KASEMSUWAN, T. Effects of amylopectin branch chain length and amylose content on the gelatinization and pasting properties of starch. **Cereal chemistry**, v. 76, n. 5, p. 629-637, 1999.

KIZIL, R.; IRUDAYARAJ, J.; SEETHARAMAN, K. Characterization of irradiated starches by using FT-Raman and FTIR spectroscopy. **Journal of agricultural and food chemistry**, v. 50, n. 14, p. 3912-3918, 2002.

LEONEL, M.; CEREDA, M. P.; SARMENTO, S. B. S. Processamento de araruta (*Maranta arundinacea*) para extração e caracterização da fração amilácea. **Brazilian Journal of Food Technology**, v. 5, n. 93, p. 151-155, 2002.

MAIA, L. H.; WANG, S. H.; ASCHERI, J. L. R.; CABRAL, L. C.; FERNANDES, M. S. Viscosidade de pasta, absorção de água e índice de solubilidade em água dos mingaus desidratados de arroz e soja. **Food Science and Technology**, v. 19, p. 391-396, 1999.

MARTINS, M. M. M.; SOUZA, D. C.; BOTREL, N.; RESENDE, L. V.; PEREIRA, J. Xanthosoma riedelianum starch for use in the food industry. **Pesquisa Agropecuária Brasileira**, v. 55, 2020.

MENDES, M. L. M.; BORA, S. P.; RIBEIRO, L. A. P. Propriedades morfológicas e funcionais e outras características da pasta do amido nativo e oxidado da amêndoa do caroço de manga (*Mangifera indica* L.), variedade Tommy Atkins. **Revista do Instituto Adolfo Lutz (Impresso)**, v. 71, n. 1, p. 76-84, 2012.

MIRANDA, T. J. A.; CARVALHO, J. M. L.; VIEIRA, M. A. C.; CASTRO, M. I. Scanning Electron Microscopy and Crystallinity of starches granules from cowpea, black and carioca beans in raw and cooked forms. **Food Science and Technology**, v. 39, p. 718-724, 2019.

NOGUEIRA, F. G.; FAKHOURI, M. F.; OLIVEIRA, A. R. Extraction and characterization of arrowroot (*Maranta arundinaceae* L.) starch and its application in edible films. **Carbohydrate Polymers**, v. 186, p. 64-72, 2018.

PALAVECINO, M. P; PENCI, C. M; RIBOTTA, P. D. Impact of chemical modifications in pilot-scale isolated sorghum starch and commercial cassava starch. **International journal of biological macromolecules**, v. 135, p. 521-529, 2019.

PAN, J.; LI, M., ZHANG, S., JIANG, Y., LV, Y., LIU, J.; LIU, Q.; ZHU, Y., ZHANG, H. Effect of epigallocatechin gallate on the gelatinisation and retrogradation of wheat starch. **Food chemistry**, v. 294, p. 209-215, 2019.

PEPE, L. S. Impacto do tratamento térmico com baixa umidade sobre as características físico-químicas e reológicas de amidos de mandioca, araruta e mandioquinha-salsa. **(Dissertação de Mestrado)** Programa de pós-graduação em Engenharia e Ciência de Alimentos, Universidade Estadual Paulista "Júlio de Mesquita Filho", São José do Rio Preto, 2011.

PÉREZ, E. E.; BREENE, M. W.; BAHNASSEY, A. Y. Ariations in the gelatinization profiles of cassava, Sagu and arrowroot native starches as measured with different thermal and mechanical methods. **Starch-Stärke**, v. 50, n. 2-3, p. 70-72, 1998.

SAIKIA, P. J.; KONWAR, B. K. Physicochemical properties of starch from aroids of North East India. **International journal of food properties**, v. 15, n. 6, p. 1247-1261, 2012.

SALGADO, S. M.; GUERRA, N.B.; ANDRADE, S. A. C.; LIVERA, A. V. S. Caracterização físico-química do grândulo do amido do feijão caupi. **Food Science and Technology**, v. 25, p. 525-530, 2005.

SHIRAI, A. M.; Haas, A.; Ferreira, G. F.; Matsuguma, L. S.; Franco, C. M. L.; Demiate, I. M. Características físico-químicas e utilização em alimentos de amidos modificados por tratamento oxidativo. **Food Science and Technology**, v. 27, p. 239-247, 2007.

SOUZA, D. C.; SILVA, R. J.; GUERRA, T. S.; SILVA, L. F. L.; RESENDE, L. V.; PEREIRA, J. Characterization of arrowroot starch in different agronomic managements¹. **Revista Ceres**, v. 66, p. 323-332, 2019.

VALENCIA, A. G.; MORAES, I. C. F.; LOURENÇO, R. V.; BITTANTE, A. M. B.; SOBRAL, P. J. A. Physicochemical properties of *Maranta* (*Maranta arundinacea* L.) starch. **International Journal of Food Properties**, v. 18, n. 9, p. 1990-2001, 2015.

VAN DE KAMER, J. H.; Van Ginkel, L. Rapid determination of crude fiber in cereals. **Cereal Chemistry**, v. 29, p. 239-251, 1952.

YONEMOTO, P.G.; CALORI-DOMINGUES, M. A.; FRANCO, C. M. L. Efeito do tamanho dos grânulos nas características estruturais e físico-químicas do amido de trigo. **Food Science and Technology**, v. 27, n. 4, p. 761-771, 2007.

ZENG, F.; LIU, H.; LIU, G. Physicochemical properties of starch extracted from *Colocasia esculenta* (L.) Schott (Bun-long taro) grown in Hunan, China. **Starch-Stärke**, v. 66, n. 1-2, p. 142-148, 2014.