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RESEARCH ARTICLE

Characterization and in vitro digestibility of non-conventional starches from guinea arrowroot and La Armuña lentils as potential food sources for special diet regimens

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Starches from guinea arrowroot (*Calathea allouia*) and La Armuña lentils (*Lens culinaris* var. La Armuña; certificate of origin La Armuña, Salamanca, Spain) were characterized and their in vitro digestibility investigated. This with the aim to compare the functional properties of starches from two different crops: Guinea arrowroot, which originated from the Amazon, and La Armuña lentils, an extremely well known species, but poorly studied as a starch source. To achieve this, proximate analysis, water activity, color parameters, microstructural analysis, X-ray diffraction, thermogravimetric analysis, rheological characterization, differential scanning calorimetry, resistant starch (RS), and in vitro digestibility assays were carried out. The study revealed that guinea arrowroot starch has some exceptional properties that "could" be promising for the development of functional foods, especially for those suffering from obesity and diabetes. In addition, the high purity of the guinea arrowroot starch compared to the La Armuña lentil starch enabled the preparation of whiter and more thermally resistant starches that could be used in sauces, ice creams and pasteurized juices. Finally, the guinea arrowroot starch (higher amylose content, 17.97%) showed a higher percent crystallinity (25%) than the La Armuña lentil starch (lower amylose content 15.94%, and crystallinity 14%). This was attributed to the formation of an amylose–lipid complex in the guinea arrowroot starch.

Keywords:
Digestibility / Functional starches / Nutritional aspects / Resistant starch

1 Introduction

Non-conventional starches have generated great interest worldwide for their numerous properties potentially beneficial for human health. Venezuela is a country rich in starch sources, due to the plant diversity found in the Amazon basin. Among these are the tubers of the guinea arrowroot (*Calathea allouia*). This species is called "agua bendita" or "cocurito" in Venezuela and is also known by the following common names: *English:* guinea arrowroot, sweet corn root topeetampo, topitamboo, topinambour (Caribbean); *Spanish:* dale dale (Perú – Amazonia), lerenes (Puerto Rico), topitambo or tambu (West Indies), topinambur (Antilles); *Portuguese:* aria (Brazil – Amazonia), láirem (Brazil); *French*: touple nambours (Santa Lucía), alleluia, curcuma d'Amérique (France) [1].

Guinea arrowroot belongs to the Marantaceae family, and is an oleiferous species that has been known and cultivated for a long time by the indigenous peoples of tropical America. It is considered to be native to Brazil, Colombia, Cuba, Ecuador, Guyana, Haití, Perú, Puerto Rico, Surinam, the Lesser Antilles, Trinidad and Tobago, and Venezuela. It has also been introduced into Jamaica as well as, on a limited scale, several other tropical regions around the world [1].

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Abbreviations: DSC, differential scanning calorimetry; **FESEM,** field-emission scanning electron microscopy; **GI,** glycemic index; **RS,** resistant starch.

Colour online: See the article online to view Fig. 4 in color.

Guinea arrowroot is grown on a small scale by traditional growers in their gardens. It is, however, now rare to find a grower who still grows guinea arrowroot in rural communities in the Amazon, except for indigenous populations, who still continue to cultivate the species for cultural reasons. Its increasing abandonment seems to have been caused by two main factors: A very long vegetative cycle (10–12 months) and its replacement by other types of food (sweet potato, yam, or industrialized products such as wheat biscuits and bread) in the diet of small rural producers [1]. Even in its region of origin, where its cultivation dates back to 1000 years, the tuberous roots of guinea arrowroot are currently used only in subsistence farming by traditional growers and indigenous populations. It has thus been classified as a nonconventional crop by the FAO [1]. However, it is precisely these types of little-known species that may have properties potentially beneficial to human health.

Another important crop that has been poorly studied is the lentil. Almost all the pulses (peas, chickpeas, lentils, beans) represent important sources of proteins and fibers, while being generally low in fat [2] (exceptions include soybeans that are fat rich [3]). Interest in the utilization of pulses as an alternative source of protein has increased, as they are nutritionally of a higher quality than meat products. Pulses contain proteins of high nutritional value (multiple essential amino-acids) whilst being low in saturated fatty acids, which have been shown to have a negative effect on health [4, 5]. For this reason, the 68th UN General Assembly declared 2016 the International Year of Pulses (IYP) (A/RES/68/231) [6]. The IYP 2016 aims to heighten public awareness of the nutritional benefits of pulses as part of a drive toward sustainable food production aimed at increasing food security and nutrition levels. In this regard, lentils (*Lens culinaris*, M.) are one of the most important crops in the Leguminoseae family. Lentil seeds contain about 69% carbohydrates most of which are present in the form of starch [7]. This is mainly distributed in the protein matrix of the cotyledons and exists in granular form. The current world production of lentils is about 4.6 million metric tons per year [8]. They are exclusively used as a human food and are mainly produced in Asia and the Middle East, although Canada has now become the largest lentil producer in North America and the largest lentil exporter in the world. Lentils are well-suited to the growing conditions in western Canada (responsible for approximately 30% of global production) and are also an emerging specialty crop in both the Pacific Northwest and the Midwest of the United States [9].

Lentils are exported as a raw material after primary processing, and there are thus many opportunities for the development of value added products. However, lentil starches have not yet been used in food formulations due to the paucity of information about their physicochemical properties [10]. Specifically, La Armuña lentil starch has not yet been characterized. A greater understanding of the physicochemical characteristics of La Armuña lentil starch which is the major constituent is thus essential in order to provide a sound scientific basis for new products.

The supramolecular arrangement of starch, percentage of crystallinity, and retrogradation have been identified as the main determinants of the extent of starch digestion and absorption in the small intestine [11]. In addition, differences in the nutritional properties of starch-containing foodstuffs are related to the bioavailability of the polymer [12].

Amylose in starch also has an effect on the extent of starch digestion in the small intestine. An increase in amylose levels appears to lower the rate of glucose delivery to the blood, resulting in a lower glycemic index (GI) [13]. The long-term consumption of high amylose starch thus has a positive effect on human health by reducing glucose and insulin responses. This results in lower triglyceride concentrations compared to high-amylopectin starches in healthy and hyperinsulinemic humans [13]. Würsch et al. [14] reported that pea starch was digested more slowly than starches from other sources such as rice starch due to its high amylose content. Because of all this the utilization of pulse components as new ingredients in the food industry has drawn the attention of researchers [15].

From a nutritional point of view, starch has been classified into three groups: Rapidly digestible, slowly digestible, and indigestible or resistant starch (RS) [16]. According to Asp [17], RS is defined as the sum of the starch plus starch degradation products not absorbed in the small intestines of healthy individuals.

RS content is an important parameter from a nutritional point of view as it escapes digestion in the small intestine of healthy individuals. It is thus considered a type of dietary fiber as it can deliver some of the benefits of both insoluble and soluble fiber [18].

According to Jenkins et al. [19] lentils induce a low-glycemic response attributable the high resistance of lentil starch to hydrolysis. The high concentrations of RS in lentils compared to other crops is a function of many contributing factors such as: Intact tissues and cells, a high amylose concentration (20–40% of total starch), a high soluble fiber content, the presence of antinutrients and strong interactions between the amylose chains [20–24].

In addition, new concepts in the starch technology are emerging as a result of continued advances in science. In this context, historically, modified starches with altered physicochemical properties were known as functional starches. Currently, however, these types of starches are better called functionalized and modified starches, in order to avoid confusion with the concept of functional foods. In this paper, functional starches are defined as native or modified (or functionalized) starches that can or could impart some kind of health benefit to consumers.

The aims of this study were firstly, to evaluate the rheological, morphological, thermal, and nutritional

properties of two starches obtained from a pulse and a tuber, for their potential use in the food industry as sources of functional starch; secondly, to reduce the knowledge gap between traditional starches, which have been extensively studied, and non-conventional starches; and thirdly, to highlight the nutritional advantages of the starches obtained compared to the properties reported in the literature for conventional starches. With this in mind, this paper aims to demonstrate the importance of pulses and tubers as functional starches rather than focusing on their more well-known characteristics, such as for example, lentils as a good source of plant protein [25].

Finally, this article provides new knowledge as regards the characterization and nutritional properties of these two starches, which have been scarcely studied. The advantages of these starches for the development of mass consumption food products as regards health benefits and the increase of food and nutritional security of the population are also discussed.

2 Materials and Methods

2.1 Materials

Native starch from guinea arrowroot (*C. allouia*) tubers was obtained from a harvested crop in Amazonas state, Venezuela, near the riverbanks of the Orinoco River. Native lentil starch was obtained from *Lens culinaris* var. La Armuña lentils (International Feed N° 5-02-506); certificate of origin, that is, protected geographical indication La Armuña lentils (La Armuña, Salamanca, Spain) on sale at a local market in Caracas, Venezuela.

2.2 Starch extraction

Native starches from guinea arrowroot tubers and La Armuña lentils were isolated and purified using the procedure suggested by Pérez et al. [26] with some modifications. The raw materials were peeled and the edible portions sliced. Around 0.5 kg of the resulting materials were then mixed for 2 min in a blender with twice the volume of distilled water. This procedure was repeated six times to process approximately 3 kg, and the collected homogenate was passed through a 200-mesh sieve. The mixing and sieving operations were then repeated four more times. The resulting slurry was centrifuged at 1500 rpm for 15 min at room temperature (25°C) to facilitate separation of the starch from the viscous mucilage. After carefully removing the remaining mucilaginous layer, the sediment was washed several times by suspending in distilled water and centrifuging until it appeared free of non-starch material. The sediment was then dried in a ventilated oven (Mitchell dehydrator – Model 645 159) for 24 h at 45°C. Starches were blended, passed through a 60-mesh sieve and stored at room temperature in sealed plastic bags inside hermetic glass containers until their subsequent analysis.

2.3 Characterization of starches

2.3.1 Proximate composition

Moisture, ash, fat, and crude protein content ($N \times 6.25$) (obtained by the micro-Kjeldahl method) were calculated using the official methods [27]. Total amylose content was determined by the differential scanning calorimetry (DSC) method described by Pérez et al. [28], which is based on the energy of the amylose/lyso-phospholipid complex formation. All procedures were performed in triplicate.

2.3.2 Water activity (a_w)

The water activity (a_w) of the starches was determined using a psychrometric a_w meter Aqualab Cx-2 (Decagon Devices, Pullman, USA) previously calibrated with water at 25°C. All readings were carried out in triplicate.

2.3.3 Color parameters

The color parameters of the starches were measured using the CIE-$L^*a^*b^*$ coordinates with the aid of a Macbeth® colorimeter (Color-Eye 2445 model) in reflectance mode. Illuminant D65 and a 10° observer angle were used. Hunter scale values were expressed as $L^* = 0$ (black) to $L^* = 100$ (white), $-a^*$ (greenness) to $+a^*$ (redness), $-b^*$ (blueness) to $+b^*$ (yellowness) [29]. The instrument was calibrated using a white standard plate ($L^* = 93.52$, $a^* = -0.81$ and $b^* = 1.58$). Color differences (ΔE^*) were calculated according to Eq. (1) described by Gennadios et al. [30]:

$$\Delta E = \left(\Delta a^2 + \Delta b^2 + \Delta L^2\right)^{0.5} \quad (1)$$

where $\Delta L = L^*_{\text{standard}} - L^*_{\text{sample}}$, $\Delta a = a^*_{\text{standard}} - a^*_{\text{sample}}$, and $b^*_{\text{standard}} - b^*_{\text{sample}}$.

The whiteness index (WI) was calculated according to Atarés et al. [31] and the yellowness index (YI) following ASTM D-1925 [32, 33] using the CIE-$L^*a^*b^*$ coordinates. Three readings were taken for each replicate.

2.3.4 Morphology

The morphology of the starch granules was observed using optical microscopy [34] and by field-emission scanning electron microscopy (FESEM). FESEM images of starch granules of each raw material were then analyzed using a FEI INSPECT F50 model for FESEM (Oberkochen, Germany) at an acceleration voltage of 10 kV. For FESEM analysis samples of both starches were mounted on bronze stubs and sputter

coated with a thin layer of gold for 35 s. The average size of the starch particles was determined using the well-known image processing software ImageJ by randomly choosing at least 5 FESEM images.

2.3.5 X-ray diffraction (XRD)

A PAN analytical X'Pert PRO diffractometer (Netherlands) equipped with a monochromatic Cu K_α radiation source ($\lambda = 1.5406$ Å) operating at 40 kV and 40 mA at a scanning rate of 1° per min was used to obtain the X-ray diffractograms of the starches. Samples were scanned in a 2θ range, varying from 3 to 33°. The crystalline fraction was estimated in each case by the area above the smooth curve drawn using the main peaks (main *d*-spacings) [35]. The distances between the planes of the crystals d (Å) were calculated from the diffraction angles (°) measured from the X-ray pattern, according to Bragg's law:

$$d = \frac{n\lambda}{2\sin\theta} \quad (2)$$

where λ is the wavelength of radiation Cu K_α and n is the order of reflection. For all calculations, n was taken as 1.

2.3.6 Thermogravimetric analysis (TGA)

Thermogravimetric assays (TGA) of starches were carried out with a TA instrument TGA Q500 (Hüllhorst, Germany). Samples were heated at a constant rate of 10°C/min from room temperature (~25°C) to 600°C, under a nitrogen atmosphere (gas flow 30 mL/min). The characteristic decomposition temperature of each starch was then determined from the thermogravimetric *DTGA* (TGA derivative) curves obtained.

2.3.7 Rheological properties

The rheological properties of the starches were determined by interpreting the data obtained from a Brabender® Rapid-Visco-Analyser (RVA), (Micro Visco-Amylo-Graph model, Duisbur's, Germany), executed under the Viscograph (Version 2.4.9) program. A 100 mL suspension of 7% starch solids (dry basis to 14% moisture) was prepared, and gradually heated from 30 to 90°C at a constant rate (6°C/min), left to cool from 90 to 50 °C, and finally further cooled at the same rate (6°C/min). The start of gelatinization (A), maximum viscosity (B), stability "Breakdown" (breakdown = maximum viscosity − viscosity at the end of the heating period at 90°C), settling "Setback" (setback = viscosity at the start of the cooling period at 50°C − maximum viscosity) and consistency (consistency = viscosity at the start of cooling period at 50°C − viscosity at the end of heating period at 90°C), were then calculated [34, 36]. Results were reported using the mean values ± SD of two determinations.

2.3.8 Differential scanning calorimetry (DSC)

The heat flow curves for the starches under study were determined using a Pyris 1 Perkin Elmer differential scanning calorimeter (Waltham, MA, USA). A sample weight of approximately 10 mg was packed and sealed in a high pressure aluminum pan. The reference was an empty aluminum pan. Samples were then heated from 20 to 120°C at a constant rate of 10°C/min. The gelatinization temperature ($T_{\text{gelatinization}}$) was obtained from the middle temperature of the relaxation range of the heat flow curves, and the gelatinization enthalpy (ΔH_g) was estimated as the area below the gelatinization peak. This test was performed for two samples of each starch.

2.3.9 Determination of resistant starch (RS)

The resistant starch (RS) content was measured [37] as follows: Individual starch samples, weighing 0.20 g each, were put into 125-mL Erlenmeyer flasks and dispersed in 0.08 M phosphate buffer (20 mL, pH 6.0). To each flask 0.05 mL of porcine pancreatic α-amylase (Enzyme Commission (EC) Number 3.2.1.1) (68 300 U/mL) (Aldrich, product code: A3176, USA) was added and the flask was covered with aluminum foil and placed in a water bath at 95°C for 15 min, agitating gently at 5-min intervals. After cooling to room temperature, the solution was adjusted to pH 7.5 ± 0.2 by the addition of 0.275 N aqueous NaOH solution and protease from *Bacillus licheniformis* (EC 3.4.21.62) (Aldrich, product code: P3910, USA) (0.02 mL, 50 mg/mL solution of protease in phosphate buffer). The blend was then placed in a shaking incubator for 30 min at 60°C before cooling to room temperature and adjusting to pH 4.3 ± 0.2 by adding 0.325 N aqueous HCl solution. Then, 0.02 mL of amyloglucosidase (10,863 U/mL; A9913) was added and the blend placed once more in a shaking incubator at 60°C for 30 min. Four volumes of 95% ethanol (10 mL each) were then added and the mixture was allowed to stand overnight at room temperature for complete precipitation. The insoluble residue was collected using a Whatman #2 filter paper, washed twice with 15 mL of absolute ethanol and once with 10 mL acetone, and then dried in an oven at 40°C overnight. The yield of RS was determined as:

$$\text{RS}(\%) = \frac{\text{Residue mass (g)}}{\text{Sample mass (g)}} \times 100 \text{ (dry weight basis)} \quad (3)$$

2.3.10 In vitro digestibility tests − starch hydrolysis index

In vitro starch availability for the gelatinized starch suspension was analyzed as follows [38]: A α-amylase (1200 UI/mg and 27 mg of proteins/mL) from a porcine pancreas preparation was used (A3176, Sigma Chemical Co.,

St. Louis, MO, USA). About 700 mg of dry starch was suspended into 50 mL of a sodium and potassium phosphate buffer (0.5 M pH 6.9) and homogenized. Approximately 4 mg/mL of the α-amylase solution diluted in the phosphate buffer was then mixed into the starch suspensions and incubated at 37°C for an hour. Sampling was carried out in triplicate at various times post-incubation (5, 15, 30, and 60 min) in addition to the initial condition where no enzyme was used. A standard curve was prepared using pure dry maltose in the 0–2 mg/mL range in addition to the use of a control made from pure potato starch. The 3,5-dinitrosalicylic acid method (DNS) was used: 0.2 mL sample and 0.8 mL of distilled water were added to 1 mL DNS solution in boiling water for 10 min, before cooling to room temperature and reading at 540 nm against a DNS blank. The extent of the hydrolysis was computed as the percentage of hydrolyzed dry starch (mg of maltose/100 mg of pure starch).

2.4 Statistical analysis

OriginPro 8 (Version 8.5, OriginLab, Northampton, MA, USA) was used to analyze the resulting data. The data corresponding to the different properties of the starches were initially evaluated by analysis of variance (ANOVA), and significant results were then further analyzed using Tukey's multiple range tests ($p < 0.05$) to compare mean values.

3 Results and discussion

3.1 Proximate composition

The chemical composition of the starches is given in Table 1. Moisture, proteins, lipids, and ash were present in very small quantities, showing that these components were extensively removed during starch extraction. Similar results were reported by Pelissari et al. [39]. Moisture typically equilibrates to about 12% in starch powder, and the moisture contents of the starches evaluated in this study are comparable to this value (approx. 15%) thus giving them an appropriately long shelf life [40, 41]. The two starches isolated contained low or trace amounts of ash: 0.15–0.25% (Table 1), which is similar to that reported in the literature [41]. However, there were statistically significant differences in ash content between the guinea arrowroot and La Armuña lentil starch. The crude protein content was low in both the starches investigated, varying from 0.28 to 0.35% (Table 1), demonstrating that the purification process was efficient. The guinea arrowroot starch showed a lower crude protein content than the La Armuña lentil starch. The level of lipids in the starches was generally between 0.09 and 0.12% [40, 42]. Although a small amount of fatty material can influence the gelatinization temperature, the most remarkable effect it has is on the flavor profile of starches [34]. Starch purity values were very high in this study, corroborating that the isolation process was carried out successfully. Similar results were reported by Gutiérrez et al. [34] for cassava and cush-cush yam starches. The total amylose contents of the guinea arrowroot and La Armuña lentil starches were 17.97 and 15.94%, respectively. Amylose content is a valuable parameter to be considered, as it has an influence on the properties of starch or starch containing products.

Table 1. Chemical composition on dry basis of the guinea arrowroot and La Armuña lentil starches

Parameter	Guinea arrowroot (%)	La Armuña lentil (%)
Moisture	16 ± 3^{a}	15.2 ± 0.4^{a}
Crude protein	0.28 ± 0.01^{b}	0.35 ± 0.02^{a}
Crude fat	0.09 ± 0.01^{a}	0.12 ± 0.01^{b}
Ash	0.15 ± 0.02^{a}	0.25 ± 0.07^{a}
Starch purity	99.48 ± 0.02^{b}	99.28 ± 0.07^{a}
Total amylose	17.97 ± 0.01^{b}	15.94 ± 0.01^{a}

Similar superscript letters in the same row indicate no statistically significant difference ($p \leq 0.05$).

3.2 Water activity (a_w)

Table 2 shows the water activity (a_w) values for the starches analyzed. As can be seen, low a_w values were obtained for both starches, and no significant differences ($p \geq 0.05$) were found between them. Similar a_w values were reported by Gutiérrez et al. [43] for native and modified plantain flour. It is thus unlikely that either of these two starches would suffer significant microbiological growth.

3.3 Color parameters

Table 2 shows the results of the color parameters of the starches studied. The guinea arrowroot starch showed the highest L^* value, indicating that it tends to be whiter than the La Armuña lentil starch, a property possibly related to its greater purity (Table 1) [34]. This is consistent with the

Table 2. Water activity (a_w) and color parameters of the guinea arrowroot and La Armuña lentil starches

Parameter	Guinea arrowroot	La Armuña lentil
a_w	0.532 ± 0.007^{a}	0.533 ± 0.007^{a}
L^*	99.38 ± 0.01^{b}	97.69 ± 0.01^{a}
a^*	-0.03 ± 0.01^{a}	0.50 ± 0.01^{b}
b^*	-0.15 ± 0.01^{a}	6.30 ± 0.01^{b}
Color difference (ΔE)	6.14 ± 0.01^{a}	6.42 ± 0.01^{b}
Whiteness index (WI)	99.37 ± 0.01^{b}	93.28 ± 0.01^{a}
Yellow index (YI)	-0.29 ± 0.01^{a}	11.89 ± 0.02^{b}

The values are the average of three determinations, similar letters in the same row indicates non-significant differences ($n = 3$, $p \leq 0.05$).

results of the whiteness index (WI) and color difference (ΔE). Based on the values of the latter, guinea arrowroot starch can be recommended for its use in products requiring a uniform color (*e.g.*, candies, ice creams, juices), whereas La Armuña lentil starch would be more appropriate for foods that do not require whiteness values as high as sauces.

With regard to the a^* color parameter, both starches showed values of around zero. Nevertheless, the starch derived from guinea arrowroot showed a slight bias toward negative values, indicating that it tended toward a green color.

The parameter b^* indicates a tendency toward a blue coloration. This effect was more marked in the guinea arrowroot (negative b^* value). In contrast, the La Armuña lentil starch was yellower (positive b^* value). This fits well with the higher yellowness index (Yl) value obtained for this material.

In addition, the guinea arrowroot starch showed a lower pigment content than the La Armuña lentil starch, confirmed by the higher WI value and lower a^* and b^* values.

3.4 Morphology

Granule size distribution is an important characteristic that can be considered as a functional property of starch, and one that has a direct influence on other material properties such as reactivity or dissolution rate, stability in suspension, delivery efficiency, texture and feeling, appearance, flow ability, handling, viscosity, packing density, and porosity. In the food industry starch granule size affects the properties related to processing (*e.g.*, gelatinization, solubility, and the absorption of water and reagents), and the nutritional value (*e.g.*, starch digestion rate) of foods and feeds [44].

The native La Armuña lentil starch granules were essentially ellipsoidal, kidney, or boat-shaped with a width between 10 and 15 μm and a length between 20 and 25 μm, without evidence of compound granulation (Fig. 1B). Similar sizes and shapes have been reported previously for lentil starch granules [10, 45]. In contrast, the guinea arrowroot starch granules were oval shaped, elongated (Fig. 1A), and approximately 1.6 times larger than those of the La Armuña lentil starch. In addition, some starch granules of both types showed slight damage on their surfaces, probably due to the extraction method used.

Optical micrographs of the starches showed that they exhibited a tendency to agglomerate into clusters. This was more evident in the smaller starch granules (La Armuña lentil starch). The hilum was also observed in both the starches studied.

3.5 X-ray diffraction (XRD)

Figure 2 shows the X-ray diffraction patterns of the two starches. As can be seen, the guinea arrowroot starch showed a curve with diffraction peaks corresponding to the following $2\theta = 11.4°$, 15.1°, 17.0°, 18.1°, 23.1°, and 26.5°, associated with the *d*-spacings $\cong$ 7.8 Å, 5.9 Å, 5.2 Å, 4.9 Å, 3.9 Å, and 3.4 Å, respectively. In general, the guinea arrowroot starch displayed a B-type crystalline structure [46–48]. In contrast, the La Armuña lentil starch presented diffraction peaks corresponding to the following $2\theta = 15.1°$, 17.0°, 18.1°, and 23.1°, associated with the *d*-spacings $\cong$ 5.9 Å, 5.2 Å, 4.9 Å, and 3.9 Å, respectively, and showed a C-type crystalline pattern. This type of diffraction pattern is intermediate between A (cereal) and B (tuber) type diffraction patterns and is common in legume starches [7, 49]. According to Thielemans et al. [50] and Primo-Martin et al. [51] the A-type crystalline pattern can occur due to a local order generated by the amylopectin chains. This type of rearrangement was observed in the La Armuña lentil starch.

Biliaderis and Galloway [52] and Cova et al. [53] reported two types of amylose–lipid complexes. Type I is a lipid complex with randomly distributed lateral helix chains, and type II is associated with the lipid complex with the V-type starch crystalline structure. The presence of the latter of these complexes was evidenced from the peak located at $2\theta = 19.8°$, corresponding to the *d*-spacing $\cong$ 4.5 Å, and a higher lipid-amylose interaction was observed from the guinea arrowroot starch. Based on the chemical composition of the evaluated starches (Table 1) it seems that the higher occurrence of this type of interactions is related more to a higher amylose content, and not so much to the lipid content, that is, the amylose content represents a limiting reagent for the formation of the amylose–lipid complex.

The differences in the percentage of crystallinity between the starches were correlated with the differences in the diffraction patterns (Fig. 2): The major peaks of the guinea arrowroot starch were more intense than those of the La Armuña lentil starch. The order of crystallinity in the two starches was: La Armuña lentil starch (14%) < guinea arrowroot starch (25%). The percentage of crystallinity of the La Armuña lentil starch coincides with published data [7], and the higher percentage of crystallinity of the guinea arrowroot starch is associated with the formation of the amylose–lipid complex (Table 1). Pérez et al. [54], Tapia et al. [55], and others [56–58] suggested that in the native starch granules, amylose, and the branching points of amylopectin are amorphous. However, the linear branches of amylopectin and some amylose combine in crystalline double helixes that are arranged in parallel to form the V-type structure. This forms an amylose–lipid complex, and results in a more crystalline structure. This would explain how guinea arrowroot starch, with a higher amylose content, was the more crystalline starch.

3.6 Thermogravimetric analysis (TGA)

Figure 3 shows the TGA and DTGA curves for the starches used. A sharper weight loss was observed in the guinea

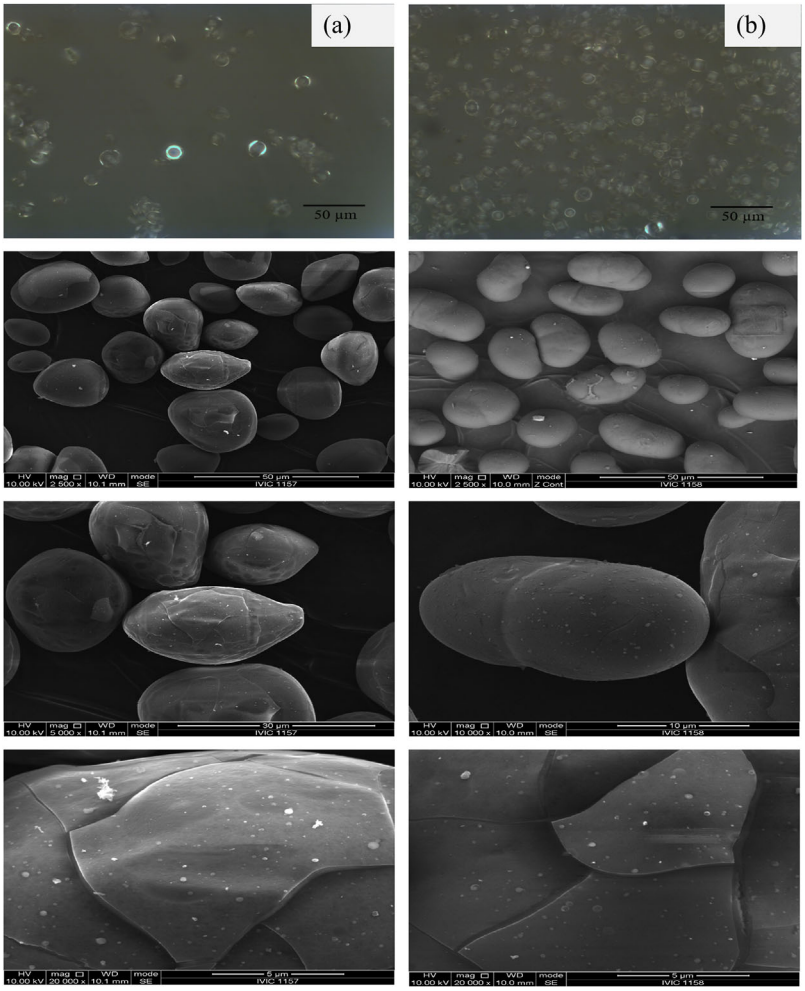

Figure 1. Optical micrographs at 20× and SEM micrographs of the granules of: (a) Guinea arrowroot and (b) La Armuña lentil starch.

arrowroot starch compared to the La Armuña lentil starch, probably due to its greater purity. The slightly higher decomposition temperature of the La Armuña lentil starch can be attributed to impurities contained within it.

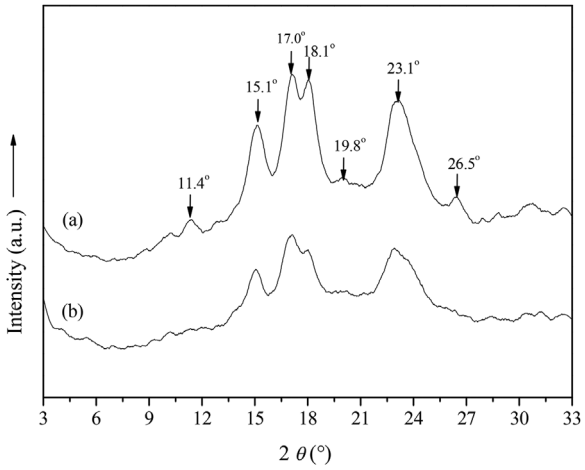

Figure 2. X-ray diffraction patterns of the starches studied: (a) Guinea arrowroot and (b) La Armuña lentil starch.

3.7 Rheological properties

As can be seen from Fig. 4, the pasting profile is quite different between the two starches evaluated. It is noteworthy that the La Armuña lentil starch did not exhibit a peak

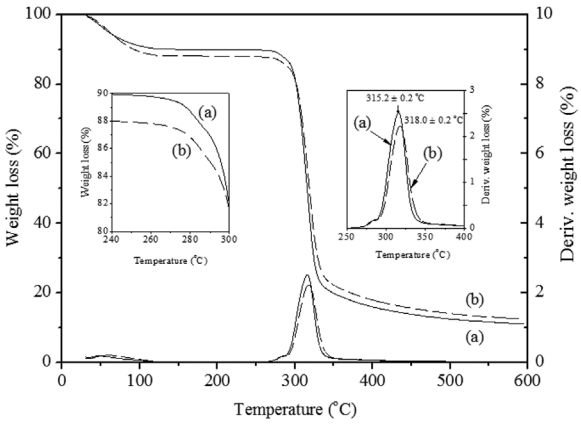

Figure 3. TGA and DTGA curves of the starches studied: (a) Guinea arrowroot and (b) La Armuña lentil starch.

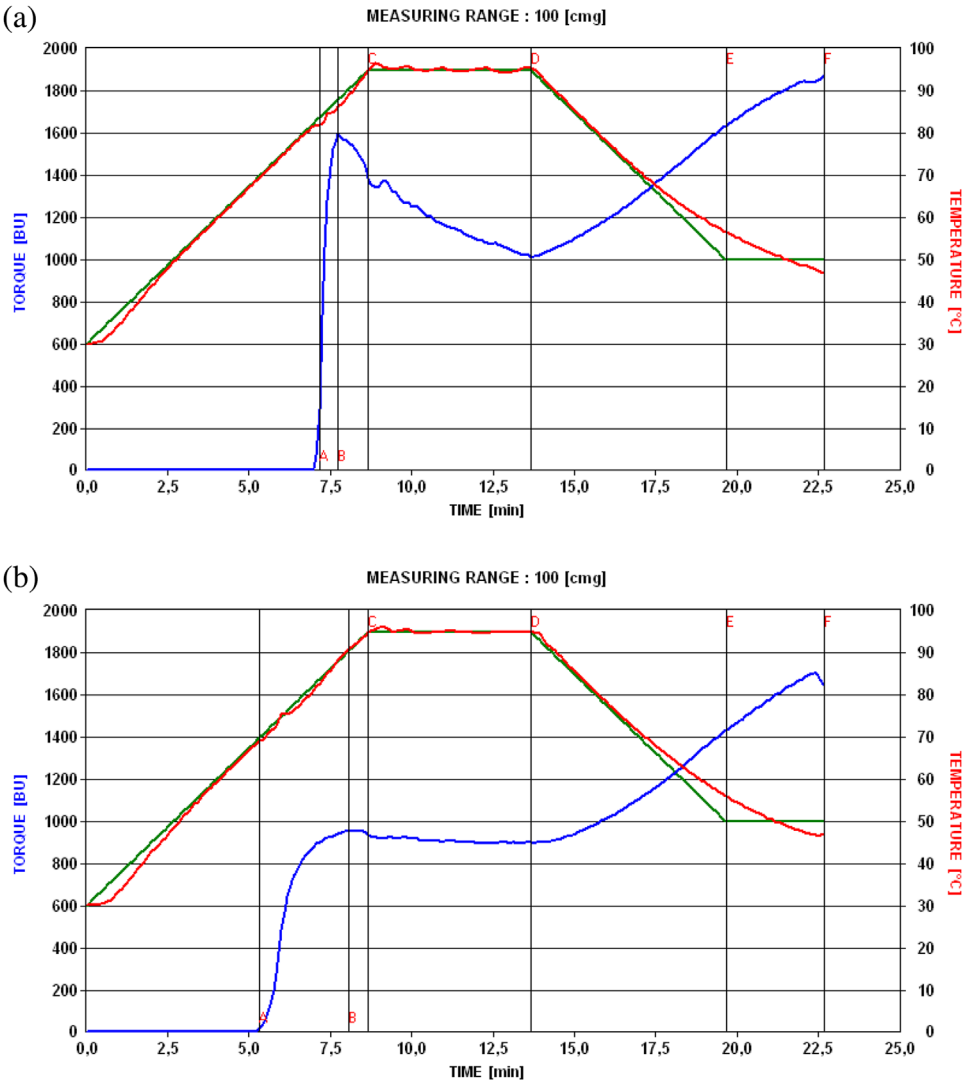

Figure 4. Gelatinization profile of the different starches studied: (a) Guinea arrowroot and (b) La Armuña lentil starch. The letters within the graph represent: A – start of gelatinization, B – maximum viscosity, C – viscosity at the start of constant heating at 90°C, D – viscosity at the end of the heating period at 90°C, E – viscosity at the start of the cooling period at 50°C, and F – viscosity at the end of the cooling period at 50°C.

viscosity, which is normally a characteristic of legume starches [10]. The data corresponding to the rheological properties of the starches are summarized in Table 3. According to Pelissari et al. [39], Rasper [59], Hoseney [60], and Zhou et al. [61], pasting properties are influenced by granular size, the amylose/amylopectin ratio, starch molecular characteristics, the volume fraction of suspended solids, the affinity between the hydroxyl groups of molecules, the molecular weight of amylose leached from the starch granules and the conditions of the thermal process used to induce gelatinization. The gelatinization temperature of the guinea arrowroot starch was higher than that of the La Armuña lentil starch. This is probably due to the larger granules of the former. In addition, the maximum viscosity, breakdown and setback values of the guinea arrowroot starch were noticeably higher than those of the La Armuña lentil starch. According to Harper and Tribelhorn [62] starches with high maximum viscosity values show weak cohesive forces, high swelling and high leaching of amylose into the surrounding medium. This fits well with the results reported here, as the guinea arrowroot starch had a higher amylose content than the La Armuña lentil starch.

Table 3. Pasting properties of the guinea arrowroot and La Armuña lentil starches to 7% solution

Parameters	Guinea arrowroot	La Armuña lentil
Initial gelatinization temperature (°C)	82.1 ± 0.1^{b}	69.2 ± 0.1^{a}
Maximum viscosity (BU)	1594 ± 1^{b}	958 ± 1^{a}
Breakdown (BU)	574 ± 2^{b}	58 ± 1^{a}
Setback (BU)	604 ± 3^{b}	525 ± 1^{a}
Consistency (BU)	40 ± 5^{a}	475 ± 1^{b}

The values are the average of two determinations; similar letters in the same raw indicates no statistically significant difference ($n = 2$, $p \leq 0.05$). BU, Brabender units.

On the other hand, the guinea arrowroot starch was more resistant to mechanical fragmentation than the La Armuña lentil starch. This behavior was confirmed by the breakdown values which represent granule fragmentation. The retrogradation of the guinea arrowroot starch was also higher than the La Armuña lentil starch (setback values in Table 3). This is consistent with the higher amylose content obtained for the guinea arrowroot starch, since it is well known that the retrogradation tendency of starches depends mainly on their amylose content [63].

Finally, the La Armuña lentil starch showed a greater paste consistency than the guinea arrowroot starch. Thus, La Armuña lentil starch could prove useful as a thickener for products requiring stabilization such as sauces and baby foods [64].

3.8 Differential scanning calorimetry (DSC)

The DSC heating curves for the guinea arrowroot and La Armuña lentil starches are shown in Fig. 5. The DSC thermograms show a decrease in heat flow, which can be attributed to the gelatinization process. The La Armuña lentil starch had a significantly lower gelatinization temperature ($T_{gelatinization}$) than the guinea arrowroot starch ($p \leq 0.05$). These results are consistent with those obtained by RVA. In this regard, Osman [65] suggested that lipids can form stable complexes with amylose, and their presence may contribute to increasing $T_{gelatinization}$ values in starches. This is in line with the results obtained from the XRD patterns where a higher lipid-amylose interaction was observed in the guinea arrowroot starch. Another factor that may increase the gelatinization temperature is the presence of proteins in suspension, which may provide a protective effect by preventing the entry of water into the starch granules as noted by Pelissari et al. [39] and Zaidul et al. [66]. Hence, the presence of other components (lipids and proteins) could explain the differences in the thermal properties of the starches.

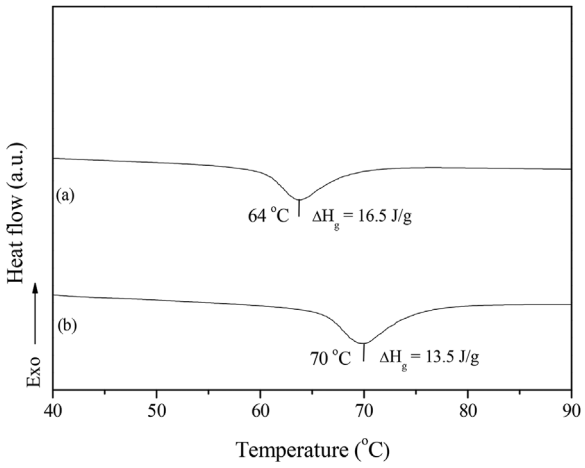

Figure 5. DSC thermograms for the starches studied: (a) Guinea arrowroot and (b) La Armuña lentil starch.

It has also been postulated that the gelatinization enthalpy (ΔH_g) is associated with the proportion of the crystalline region and the type of crystallinity, which is in turn linked to the distribution of amylopectin short chains and the amylose/amylopectin ratio [55, 67]. The ΔH_g is specifically related to the net energy required to carry out physicochemical processes such as swelling and the molecular rearrangement of the starch chains, leading to gelatinization [68]. Tapia et al. [55] reported a positive relationship between the percentage of crystallinity and the ΔH_g of different starches, that is, more energy is required to gelatinize more crystalline starches. The ΔH_g thus reflects the loss of molecular order. This fits well with the results reported here, since the guinea arrowroot starch had a higher percentage of crystallinity (25%), a greater total amylose content (17.97%) and a higher ΔHg (16.5 J/g) than the La Armuña lentil starch (percentage of crystallinity 14%; total amylose content 15.94%; and ΔH_g 13.5 J/g). Chung et al. [69] also observed higher ΔH_g values in starches where the amylose–lipid complex was more evident. This again agrees with the results reported here, since the arrowroot starch with the amylose–lipid complex (see XRD results, Section 3.5) showed a higher ΔH_g value than the Armuña lentil starch.

3.9 Nutritional aspects: Resistant starch (RS) and in vitro digestibility

The results of the RS and in vitro digestibility analyses of the starches studied can be observed in Fig. 6. It is worth noting the relationship between the RS content and starch crystallinity, which suggests that the former could affect the latter. Similar results have been reported by Gutiérrez and Álvarez [70] for plantain flour-based films. In addition, the greater retrogradation tendency of the guinea arrowroot starch as determined from the RVA data (Table 3) suggests that there is a positive relationship between starch retrogradation tendency, the percentage of starch crystallinity and RS content. From this we can infer that RS content, at least type 3 RS which itself is a product of the retrogradation of starch polymers, may increase starch crystallinity [70].

Björck and Asp [12] and García-Alonso and Goñi [71] have indicated that RS can be fermented by a wide variety of bacteria that are found in the human colon producing short fatty acids, and as such has important implications for human health. The higher RS content in guinea arrowroot starch thus means that it has a greater potential as a source of functional foods in the food industry than the La Armuña lentil starch. Similar RS contents have been reported by Hernández et al. [11] for other non-conventional starches (banana and sagu).

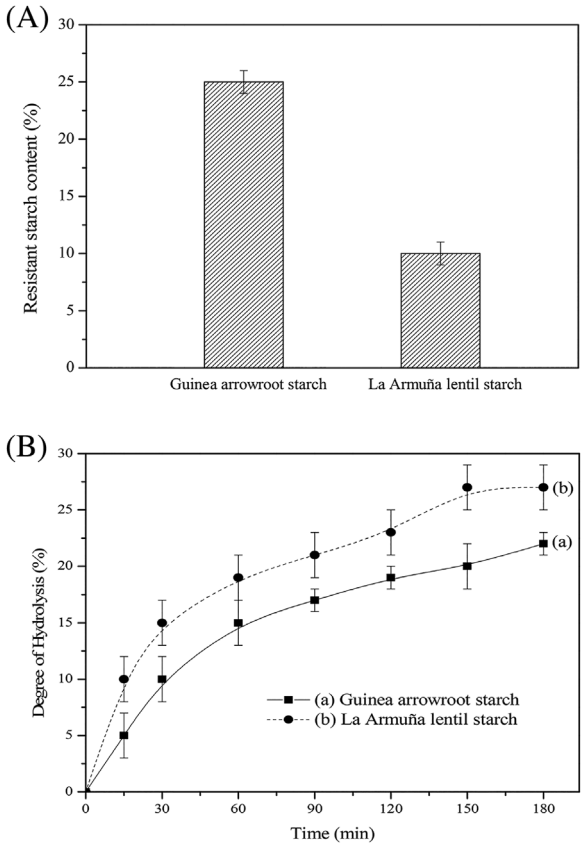

Figure 6. (A) Resistant starch content and (B) in vitro α-amylolysis curves of the different starches studied: (a) Guinea arrowroot and (b) La Armuña lentil starch.

Jenkins et al. [19] indicated that a tool for ranking foods with respect to their blood glucose raising potential is the glycemic index (GI). RS content is a nutritional variable that may be inversely linked to the GI, such that a high RS content is correlated with low-glycemic-index foods. It is worth noting that a lower starch digestion rate can promote a moderated in vivo glycemic response, an important parameter to be considered in the dietary management of diabetics [72]. With this in mind, the FAO [63] has indicated that starch digestibility determines the available energy content, which in turn depends on the hydrolysis of starch by pancreatic enzymes. As can be seen in Fig. 6B, guinea arrowroot starch showed a lower in vitro digestibility rate than La Armuña lentil starch, further indicating the "possible health benefits" of this non-conventional starch from the Venezuelan Amazon. Both the starches studied, however, had lower in vitro digestibility rates than conventional starches such as potato and corn, as reported by Hernández et al. [11].

It is, of course, well known that cooking and other processing methods affect the RS content in starch-based foods, which in turn affects the in vitro digestibility rate and the GI [73]. Nevertheless, these preliminary results suggest that the incorporation of guinea arrowroot starch into foods "could" possibly improve dietary control for diabetics and those suffering from obesity. In contrast, the lower RS content of the La Armuña lentil starch makes it more appropriate for inclusion in the dietary formulas of athletes, vegetarians, vegans, and celiacs since these individuals require a higher caloric intake. In the first case this is due to the physical activities performed, and in the others because they are following special diet regimes that do not permit the consumption of certain food types. The greater caloric contribution of the La Armuña lentil starch is possibly related to its higher thermal degradation temperature (318°C) (see TGA results, Section 3.6).

However, because cooking and processing methods usually decrease the RS content and increase the in vitro digestibility rate and the GI of starch-based food [73] more detailed studies should be performed, for example the incorporation of these non-conventional starches into foods that are then cooked or otherwise processed. This would allow us to confirm the most appropriate consumer group or groups toward whom these non-conventional starches are directed.

According to Chung et al. [69] and Asp and Björck [74] the in vitro digestibility of native starches is a product of the interplay of many factors, such as the amylose/amylopectin ratio, percent crystallinity, the presence of amylose–lipid complexes, and the molecular structure of amylopectin. Specifically, Chung et al. [69] and Guraya et al. [75] observed that the formation of the amylose–lipid complex decreases the in vitro digestibility rate of the starches. This agrees with the results obtained here, since the guinea arrowroot starch had a lower in vitro digestibility rate and more developed amylose–lipid complex than the La Armuña lentil starch (higher in vitro digestibility rate and less developed amylose-lipid complex).

Asp and Björck [74] reported that starches with B-type structures tend to have lower in vitro digestibility rates. This is also in line with the results obtained: The guinea arrowroot starch had a B-type structure and relatively low in vitro digestibility. The La Armuña lentil starch (higher in vitro digestibility rate) however, showed a C-type structure which is intermediate between A (cereals) and B (tubers) type structures

Truswell [13] demonstrated that an increase in amylose levels reduces the in vitro digestibility rate which reduces the glucose administration to the blood. This fits well with the results obtained here. In addition, it seems that a high gelatinization temperature, as was recorded by both the RVA and DSC, is not only related to a higher amylose content, but also to a lower in vitro digestibility rate.

Another important point to note is that the La Armuña lentil starch (smaller starch granules) showed a significantly higher in vitro digestibility rate ($p \leq 0.05$) than the guinea arrowroot starch (larger starch granules). This was probably due to the fact that smaller particles have a greater area-volume ratio than

larger ones giving the La Armuña lentil starch a greater surface area. This would give the digestion enzymes a greater area over which to act thus increasing the in vitro digestibility rate.

4 Conclusions

In this paper two starchy sources, guinea arrowroot and La Armuña lentils, were investigated. Native guinea arrowroot and La Armuña lentil starches were isolated with high levels of purity. The guinea arrowroot starch had a larger particle size, a higher amylose and RS content and greater thermal stability than the La Armuña lentil starch. Both the starches evaluated had a lower in vitro digestibility rate. However, this was significantly more marked in the guinea arrowroot starch. La Armuña lentils had a designation of origin and the properties of starches often change from one variety to another in the same species. Nevertheless, several of the properties of the La Armuña lentil starch were similar to those of other lentil varieties reported in the literature. Based on these results, food products from guinea arrowroot starch "could" enable the development of functional foods aimed at people under special diet regimes such as diabetics and those suffering from obesity. Nevertheless, more exhaustive studies should be carried out since the RS content and in vitro digestibility may be modified after cooking and processing.

5 Novelty statement

In recent years, the interest in functional starches has brought the attention of food scientists and technologists, as it allows better the nutritional quality of food products. In addition, they could be used in the diets of people with special regimens, namely: Diabetics and obese. The originality of this work is based on the use of non-conventional starches such as guinea arrowroot starch obtained from the Venezuelan Amazons or starch from a pulse such as La Armuña lentils. In both, none of the starches has been previously characterized in the literature. It is worth noting that in the case of lentil starch other varieties have been characterized and analyzed by different authors. However, starch obtained from the La Armuña lentil variety has not been reported. In addition, due to the denomination of origin that possesses the La Armuña lentil it is of interest determine what are the unique characteristics that differentiate this lentil variety in relation to others reported; at least in terms of the characterization of their starches, since in terms of the composition of polyphenol compounds has been recently published [76].

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The author declares no conflict of interest.

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