Research Article

# *Pachyrhizus ahipa* roots and starches: Composition and functional properties related to their food uses

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Chemical composition of two accessions (N° 11 and Local) of *Pachyrhizus ahipa* was evaluated and their starches were characterized from a technological and nutritional point of view. Ahipa roots were characterized by their high protein (8–9%) level compared to other roots and tubers. Accession 11 exhibited higher starch content than Local accession. Compared to cassava, ahipa starch showed lower gelatinization temperature, exhibiting accession 11 the lowest value. Ahipa starch digestibility was similar to that of other leguminous plants. Accession 11 showed higher rapidly digestible (RD), resistant (RS) and lower slowly digestible (SD) starch than cassava. Rotational rheological assays indicated that gelatinized ahipa starch suspensions present a pseudoplastic thixotropic behavior and under dynamic assays they behaved as a weak gel. Finally, ahipa can be considered a very good source of starch and might be used as a functional food, contributing to increase the RD and SD fractions.

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## 1 Introduction

America Andean region is an important center of biodiversity and domestication of plants in the world, including at least nine native Andean R&T crops that hold economic and nutritional significance for subsistence farmers. “Ahipa” or “Andean yam bean” is the vernacular name for *Pachyrhizus ahipa* (Wedd.) Parodi. The genus *Pachyrhizus* (yam beans), from the Fabaceae botanical family is native to Southern and Central America. *P. ahipa* is found at the Andes of Peru, Bolivia, and Northern Argentina [1–3]. This species is characterized by the starch accumulation of industrial interest in its tuberous root. The crisp root is almost exclusively consumed raw or even cooked and it is very similar to that of its close relative, jicama (*P. erosus*); the root skin lifts off quite easily from the internal portion, fleshy and mostly white [4]. The plants produce one enlarged root weighing between 0.5 and 0.8 kg which is the only edible part of the plant [5].

Extensive work has been conducted on the structure and functional properties of native starches obtained from grains (mainly corn, wheat and rice), R&T (particularly potato, sweet potato and cassava) due to their ready availability and their wide use in food and non-food applications [6–9]. Nevertheless, there are few works referred to the properties of the starch obtained from *P. ahipa* and particularly those concerning different ahipa accessions.

The understanding of the structural characteristics of starches is greatly important in order to suggest possible applications. Related to botanical source, properties such as amylose content, granule shape and size distribution, and molecular structure have great incidence in the main physicochemical and functional properties of starches, i.e., gelatinization, retrogradation, solubility, swelling power, water-binding capacity, rheological behavior, and pasting properties [8].

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**Abbreviations: DSC,** differential scanning calorimetry; **GI,** glycemic index; **RDS,** rapidly digested starch; **RS,** resistant starch; **R&T,** roots and tubers; **SDS,** slowly digested starch

 

According to their functional properties, native starches from novel plant sources could potentially replace chemically modified starches [10, 11] and contribute to the new developments in the food and pharmaceutical industries. There is growing interest in finding new sources of starch with novel and distinctive properties that could potentially replace chemically modified starches in different applications [12].

Starch is mostly responsible for the technological properties that characterize many processed food products, having diverse industrial applications as a thickener, colloidal stabilizer, gelling agent, and volume enhancer [13, 14]. During food processing, starch undergoes variable shear rates and heating–cooling cycles, which affect the texture, form, size, and color of the final products [11]. Thermal and rheological properties are generally discussed on the basis of the microstructure and molecular architecture of starch.

On the other hand, according to its susceptibility to the amylolytic enzymes, starch can be classified as digestible or resistant, being relevant this distinction because of its health benefits [13]. Processing and storage conditions also affect starch digestibility [15, 16]. For example, native potato starch is highly resistant to hydrolysis by pancreatic α-amylase but it is rendered rapidly digestible (RD) after cooked by conventional techniques [17].

The objective of the present work was to characterize the starch obtained from *P. ahipa* roots belonging to two particular accessions (N° 11 and Local accessions) from a technological and nutritional point of view.

## 2 Materials and Methods

### 2.1 Plant material

*P. ahipa* (Wedd.) Parodi plants were grown at the Instituto Nacional de Tecnología Agropecuaria INTA – Montecarlo farm (Misiones, Argentina). For this work, two accessions were used: the Local accession (originally from Perico, Jujuy, Argentina) and the accession N° 11 (originally from Las Cabezas, Sevilla, Spain). Roots were harvested in April 2010 when aerial plant parts began their senescence.

Ahipa samples were received at the laboratory and processed immediately. Selected roots were thoroughly washed with tap water and they were sanitized by immersion in NaClO solution (250 ppm of chlorine, 10 min). Then, roots were dried at room temperature, sliced and dried in an oven at 60°C until constant weight was achieved. They were grinded and kept into hermetically closed jars until analyses were performed. This material corresponds to "partially dehydrated roots."

### 2.2 Starch obtaining procedure

Selected, washed, and sanitized fresh ahipa roots were hand peeled and processed for starch obtaining as described in a previous work [18]. For comparison, cassava roots coming from the same cropping area were processed in the same way. Ahipa and cassava starch yield (% w/w) was calculated through a mass balance, considering the weight of the starch extracted and the initial weight of roots processed.

### 2.3 Analyses

#### 2.3.1 Macrocomponents of ahipa roots

Ahipa samples were analyzed in duplicate for residual water and total ash content using reference methods [19] and following the steps described by Doporto et al. [20] and Dini et al. [21]. Results were expressed as percentage (%) of the initial weight.

For the determination of crude fat content, partially dehydrated ahipa roots (12 g) were extracted with hexane for 2 h in a Soxhlet apparatus. Crude protein content was calculated from total nitrogen quantified by the Kjeldahl method. A Büchi K-435 digestion unit (Flawil, Switzerland) and a Büchi K-350 distillation unit (Flawil, Switzerland) were used. The crude protein content was calculated using the conversion factor 6.25.

To quantify acid detergent fiber (ADF), samples were accurately weighed (1.0 g) in duplicate, and the Van Soest method was followed [22]. Samples were boiled for 1 h in a solution containing sulfuric acid and cetyltrimethylammonium bromide and the residue was quantified gravimetrically. For all determinations, results were expressed as percentage (%) on a dry basis.

Likewise, partially dehydrated ahipa roots (0.10–0.15 g) were analyzed for total starch content by means of the enzymatic kit K-TSTA 05/06 Megazyme© (Ireland) [20, 21]. Results were expressed as percentage (%) on a dry basis.

#### 2.3.2 Starch phosphorus and amylose content

The quantification of phosphorus on ahipa starch samples was carried out by quadruplicate using the vanado-molybdate method [19]. Final results were expressed as mg/100 g. Amylose concentration (%) was determined spectrophotometrically at 635 nm, as described in previous works [18, 23].

#### 2.3.3 Ahipa starch digestion kinetics

According to Juansang et al. [24], for the quantification of the RDS, RS and SDS fractions from gelatinized starches, suspensions (10% w/v) in distilled water were prepared and they were gelatinized at 90°C for 20 min. To each tube, 5 ml maleate buffer (100 mM; pH 6) and 5 ml of an enzymatic solution containing pancreatic α-amylase (20 U $ml^{-1}$) and amyloglucosidase (15 U $ml^{-1}$) (Megazyme, K-RSTAR 05/2008) were added. The tubes were incubated at 37°C with constant shaking (200 rpm). At 20 and 120 min, 0.2 ml aliquots were taken by duplicate; they were added with 4 ml absolute ethanol and centrifuged (10 min at 2300×*g*). Samples of the supernatant (0.1 ml) were transferred onto test tubes and the concentration of released glucose was measured as previously indicated. The starch fraction digested at 20 min, between 20 and 120 min and the remaining non-digested starch after 120 min were classified as rapidly digested starch (RDS); slowly digested starch (SDS); and resistant starch (RS), respectively [24, 25].

The hydrolysis index (HI) of native and gelatinized starches was calculated following the protocol described by Goñi et al. [26], by comparison of the percentage of total starch hydrolyzed obtained from the hydrolysis curve (0–180 min) and that released from white bread over the same hydrolysis period. Starch hydrolysis percentage at each sampling time was calculated from total glucose released. The hydrolysis curves were fitted to Goñi et al. [26] equation as follows:

$$C = C_{\infty}(1 - e^{-kt}) \qquad (1)$$

where $C$ is the concentration at time $t$, $C_{\infty}$ is the equilibrium concentration, $k$ is the kinetic constant, and $t$ is the chosen time.

From HI values, the glycemic index (GI) was then estimated by the equation described by Goñi et al. [26]: $GI = 39.71 + 0.549HI$.

In order to determine the time required for maximum hydrolysis percentage of native starches, the method described by Hung and Morita [27] was followed, with slight modifications. Native starch suspensions (1% w/v) were prepared in sodium maleate buffer (100 mM; pH 6); 120 U ml$^{-1}$ of pancreatic α-amylase (Megazyme, K-RSTAR 05/2008) were added. The mixtures were incubated with continuous shaking (100 rpm) at 37°C. At different incubation times (0; 3; 6; 8; 18; and 20.5 h) aliquots were withdrawn and they were centrifuged (5 min at 5000 × g). From the supernatants, 0.25 ml samples were put in two separate test glass tubes and they were added with 2.25 ml sodium acetate buffer (100 mM; pH 4.5), incubated with 25 μl of amyloglucosidase (Megazyme, K-RSTAR 05/2008; 3300 U ml$^{-1}$) for 30 min at 50°C. To determine the concentration of glucose released in the supernatant, 0.1 ml of the mixture were transferred onto test tubes and 3 ml of the reagent glucose oxidase/peroxidase (GOPOD; Megazyme, K-RSTAR 05/2008) were added. Samples were incubated at 50°C for 20 min. Absorbance of the mixture were read at 510 nm against the reagents' blank. Results were expressed as percentage (%) of hydrolyzed starch.

#### 2.3.4 Thermal properties

Thermal properties of partially dehydrated ahipa root samples as well as ahipa and cassava starches were determined by DSC according to previous works [21, 23] using a Q100 differential scanning calorimeter controlled by a TA 5000 module (TA Instruments, New Castle, DE, USA) with a quench-cooling accessory, under a $N_2$ atmosphere (20 mL/min). The scanning rate was 10°C/min and heating range varied between 10 and 120°C for all samples. Onset ($T_o$, °C), peak ($T_p$, °C), and conclusion temperature ($T_c$, °C) were determined as well as the enthalpy that corresponds to the area under the peak ($\Delta H$, mJ/mg of the dry sample).

#### 2.3.5 Rheological behavior of starch suspensions

Ahipa and cassava starch aqueous suspensions 4% (w/w) were prepared and gelatinized at 90°C for 20 min. A Rheo Stress 600 ThermoHaake (Haake, Germany) rheometer with a plate-plate system PP35 (gap size 1 mm) at controlled temperature (25°C) was used. Rotational mode allowed to investigate time-dependent behavior of gelatinized starch suspensions as described in a previous work [18]. The resulting curves were mathematically modeled as Ostwald de Waele ($\tau = k\gamma^n$) fluids, being $k$ the consistency coefficient and $n$ the flow behavior index.

Viscoelastic behavior of starch pastes were studied by performing dynamic assays. The linear viscoelasticity range, where sample does not suffer structural damage, was determined in a stress sweep (0–20 Pa) assay at constant frequency (1 Hz). This range was extended up to 2 Pa for all starch pastes, so for frequency sweeps 1 Pa was the shear stress value selected.

Then, frequency sweeps (0.01–100 Hz) were performed at constant stress. The storage modulus ($G'$), the loss modulus ($G''$), the tangent of the phase angle ($\tan \delta = G''/G'$) and the complex shear stress ($G^*$) were recorded. Mechanical spectra were obtained by plotting $G'$ and $G''$ versus frequency ($f$) and they were modeled using the following equations (Power law model) [28]:

$$G' = af^b \qquad (2)$$

$$G'' = cf^d \qquad (3)$$

where $f$ is the frequency expressed in Hz and $a$, $b$, $c$, and $d$ are the fitting parameters.

In order to relax the samples before the dynamic shear rheological measurements, samples were allowed to rest at the initial temperature for 5 min. Average of at least three recorded measurements were reported.

### 2.4 Statistical analysis

Determinations were carried out at least by duplicate. Analysis of variance (ANOVA) and comparison of means with the Fisher's least significant difference (LSD) test were conducted, at a significance level $p = 0.05$.

 

## 3 Results and Discussion

### 3.1 Starch yield and dry matter content

Starch yield and dry matter content are important determinants of storage root yield and could be relevant selection criteria in breeding programs [29].

Starch extraction from peeled ahipa roots allowed to the following yields: 9.27 and 9.61% w/w on wet basis for N° 11 and the Local accession, respectively. Cassava roots yielded 20.15% w/w of starch on wet basis. This value is in accordance with those reported by Ebah-Djedji et al. [29] for improved cassava varieties (20.17 ± 2.82%) at 13 months after planting. Starch content for the main R&T crops ranges from 13 to 16% for potato, 19 to 21% for the Aroids, 18 to 28% for yams and sweet potato [30].

Although ahipa starch content is lower than the one yielded by cassava, ahipa roots might constitute an alternative raw material in some periods of the year when cassava is not available, provided that efficient conservation methods for the roots are developed.

Dry matter content of ahipa and cassava extracted starches were 87.8 ± 1.0%, 88.2 ± 0.7% and 87.4 ± 0.3% for N° 11, Local ahipa accession and cassava starches respectively. Rolland-Sabaté et al. [31] reported dry matter content for cassava starch in the range of 84.7–94.8%.

### 3.2 Macrocomponents of ahipa roots

Root water content quantified at 60°C was 79.2 ± 0.9 and 78.4 ± 0.3% for N° 11 and Local ahipa accessions, respectively. Residual water content (quantified at 105°C) was 12.7 ± 0.3% for the accession N° 11 and 13.0 ± 0.3% for the local accession. Water content of ahipa roots were similar to those found in potatoes but higher than those characteristic of other R&T crops such as cassava, with water content ranging from 63 to 65% [32, 33].

Results from the proximate chemical analysis carried out in ahipa roots are shown in Table 1. Ahipa total ash content was 1.3–1.5 times higher than the levels reported for sweet potato [34]; 3.6–4.5 times higher than taro, 3.75–4.1 times higher than yam and 2.9–3.2 times higher than cassava [35].

Ahipa roots outstand for their high protein content in comparison to other R&T crops. Total protein content found in both ahipa accessions was comprised between 7.9 and 9.1% (Table 1). Forsyth and Shewry [3] analyzed total protein content in six ahipa accessions and found that it ranged between 4.80 and 8.40% on a dry basis. Sørensen [36] found higher protein content when analyzing 20 ahipa accessions with a minimum of 8.7% and a maximum of 14.2% on a dry basis. Ahipa protein content is clearly above that present in other common R&T crops [37]. Referring to total starch content, ahipa Local accession had significantly lower content than accession N° 11.

### 3.3 Ahipa starch phosphorus and amylose content

Phosphorus content was measured in ahipa starch, finding 7.7 ± 0.9 and 6.7 ± 0.3 mg/100 g for N° 11 and Local accessions, respectively.

Phosphorus of starches from immature, premature and mature canna segments ranged between 25.1 and 26.4 mg/100 g [38]. Phosphorus, although at low concentration, plays an important role in starch functional properties [39].

Amylose content of ahipa starch was 13.71 ± 0.32% and 12.11 ± 0.43% for accession 11 and Local, respectively. Ahipa starch would be suitable for food processing since low retrogradation tendency is associated to low amylose starches [40].

### 3.4 Thermal properties

Aqueous suspensions of the studied starches exhibited thermograms with a single endothermic transition, typical of the gelatinization process of high water content suspensions. Thermal properties of starches depended on botanical source, being gelatinization temperature significantly ($p<0.05$) different for ahipa and cassava. Besides, significant differences ($p<0.05$) were detected between starch from different ahipa accessions, exhibiting that extracted from ahipa N° 11 the lowest value (Table 2). Nevertheless, gelatinization temperatures of the analyzed starches were lower than cereal and legume starches such as corn, wheat, pea, and mung bean, indicating a better aptitude for cooking [41, 42].

Ahipa starch exhibited a gelatinization range significantly ($p<0.05$) narrower ($T_c - T_o$, Table 2) than that of cassava, which could be related with a highly cooperative process [43] and would be indicative of a narrower amylose and amylopectin size distribution.

**Table 1.** Proximate chemical composition (% w/w) of *Pachyrhizus ahipa* roots from accessions N° 11 and Local

| Sample | Total ash[a)] | Crude fat[a)] | Crude protein | Acid detergent fiber (ADF) | Total starch content[a)] |
|---|---|---|---|---|---|
| Accession N° 11 | $3.70 \pm 0.08^a$ | $0.47 \pm 0.02^a$ | $7.9 \pm 0.2^a$ | $7.56 \pm 0.32^a$ | $64.98 \pm 0.60^a$ |
| Local accession | $3.32 \pm 0.10^a$ | $0.48 \pm 0.01^a$ | $9.1 \pm 0.3^a$ | $7.47 \pm 0.05^a$ | $56.76 \pm 0.87^b$ |

Reported values correspond to the mean ± standard deviation. Results are expressed on dry basis. Different letters in the same column indicate significant differences ($p<0.05$).
a) From [21].

 

**Table 2.** Thermal parameters of *Pachyrhizus ahipa* partially dehydrated roots and starches

| Sample | Onset temperature, $T_o$ (°C) | Peak temperature, $T_p$ (°C) | Conclusion temperature, $T_c$ (°C) | Enthalpy, $\Delta H$ (J/g dry basis) |
|---|---|---|---|---|
| Starch | | | | |
| Ahipa accession 11 | $60.3 \pm 0.6^b$ | $64.8 \pm 0.4^b$ | $74.5 \pm 0.6^b$ | $12.4 \pm 1.2^b$ |
| Ahipa accession Local | $60.0 \pm 0.2^b$ | $65.7 \pm 0.1^a$ | $76.9 \pm 1.0^a$ | $12.6 \pm 1.7^b$ |
| Cassava | $58.8 \pm 0.3^a$ | $67.6 \pm 0.3^c$ | $82.3 \pm 1.0^c$ | $9.7 \pm 0.4^a$ |
| Partially dehydrated roots[a)] | | | | |
| Ahipa accession 11 | $66.1 \pm 0.4^a$ | $71.9 \pm 0.5^a$ | $86.5 \pm 1.4^a$ | $25.4 \pm 0.9^a$ |
| Ahipa accession Local | $66.1 \pm 0.1^a$ | $71.3 \pm 0.4^a$ | $87.9 \pm 0.5^a$ | $24.7 \pm 2.9^a$ |

Reported values correspond to the mean ± standard deviation. Different letters in the same column indicate significant differences ($p<0.05$).
a) From [21].

Peak enthalpy, which is an indicator of the molecular order within the granule, were statistically ($p<0.05$) higher for ahipa starches than that of cassava (Table 2). Gelatinization enthalpy of cassava starch was similar to those informed by Betancur et al. [44]. Several authors have stressed that gelatinization enthalpy is affected by the starch crystallinity degree as well as granule size and shape, phosphorus content and amylopectin chain length [11, 45–48].

In a previous work [21] aqueous partially dehydrated ahipa root suspensions of five accessions were analyzed. Samples exhibited a wide transition with a peak temperature associated higher than that corresponding to the gelatinization temperatures of ahipa starch [21]. This transition was associated to both starch gelatinization and protein denaturalization present in the partially dehydrated root. Likewise, the relatively high sugar content present in ahipa roots [21] contributed to shift of the peak temperature compared with starch gelatinization one. Besides, onset peak temperature and enthalpy corresponding to partially dehydrated roots were higher than those of the derived starches (Table 2). A similar trend was observed comparing thermal parameters of flours and starches from different sources and especially those from ahipa and cassava [18, 20–21, 49]. Likewise, no significant differences were observed between both ahipa accessions.

### 3.5 Starch digestibility

Values corresponding to RDS, SDS, and RS fractions obtained from gelatinized starches digestion are shown in Fig. 1. Ahipa N° 11 showed higher RDS and RS fractions than cassava ($p<0.05$), while both ahipa 11 and Local, exhibited lower SDS fractions than the latter ($p<0.05$), presenting ahipa N° 11 the lowest value among the three starches assayed ($p<0.05$). This RS is classified as RS3, which appertain to the non-hydrolyzed fraction mainly composed of retrograded amylose formed during the cooling process of gelatinized starch pastes.

Figure 2a shows the enzymatic hydrolysis kinetics for ahipa and cassava gelatinized starch suspensions compared to that of white bread digestion. Experimental data were satisfactorily fitted to Goñi et al. [26] model ($r^2>0.9506$). The studied gelatinized starches gave total starch hydrolysis percentages above those corresponding to white bread in all sampling points analyzed. Consequently, HI values of the three gelatinized starches were higher than 100 (Table 3).

The expected GI and the digestibility of starches could be mathematically related. One of those mathematical functions is that proposed by Goñi et al. [26] where the GI in vivo is related to the amount of starch hydrolyzed in vitro after incubation for 180 min. As expected, the GI of gelatinized starches was higher than that of native starches (Table 3), since the disruption of the hydrogen bonds between starch chains during the gelatinization process increases starch chains exposure to the enzymatic attack [50]. No significant ($p>0.05$) differences were observed in the GI of gelatinized starches, neither by botanical origin nor by accession (Table 3). Ingredients with estimated GI values higher than that from white bread, such as hydrothermal treated oat starch [51], could be useful for the formulation of dietary products with high energy contents similar to several cooked natural starchy foods such as rice from cultivar Karaya [52] and potatoes belonging to the varieties Russet Burbank (boiled pieces or baked whole) and Desireed (boiled whole or halved) [53].

As expected, native starches presented estimated GI values lower than those of gelatinized starches, resulting also

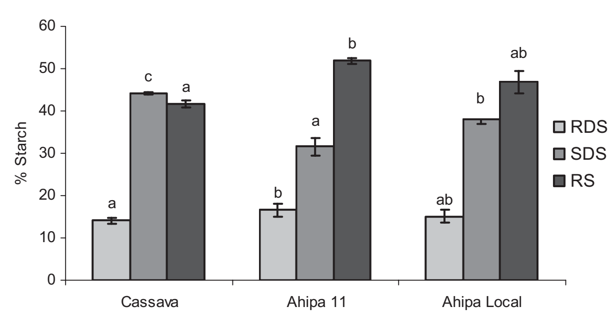


**Figure 1.** Percentage of rapidly digestible starch (RDS), slowly digestible starch (SDS), and resistant starch (RS) from gelatinized ahipa and cassava starches. Different letters within the same starch fraction indicate significant differences ($p<0.05$) between materials.

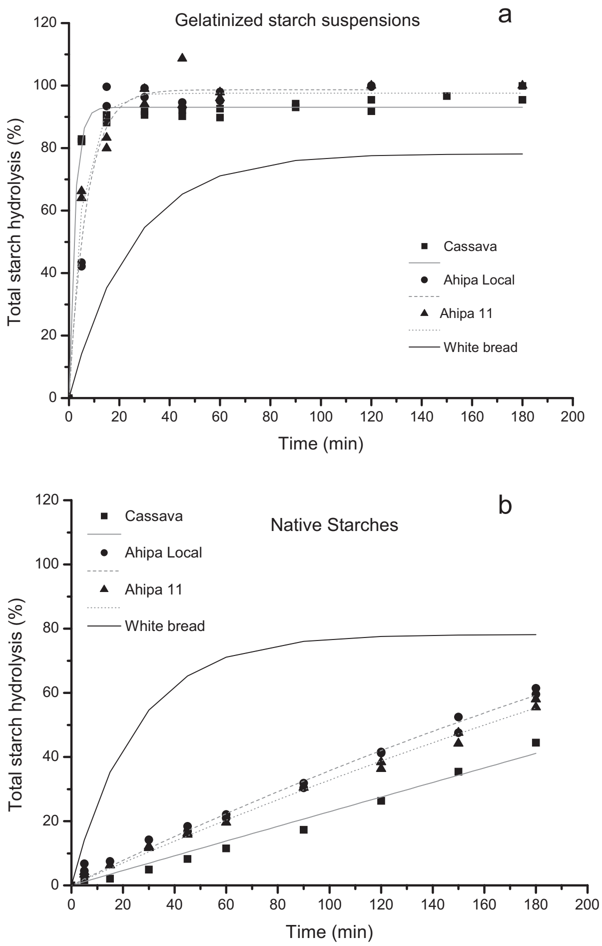


**Figure 2.** Experimental data (indicated by the symbols) of enzymatic hydrolysis kinetic (total starch hydrolysis percentage) of starches from ahipa accession 11, accession Local and cassava and the fitting curve (indicated by the lines) to Goñi et al. (1997) model. a, Gelatinized starch suspensions; b, native starches.

lower than that of white bread (Table 3). Cassava native starch exhibited a lower GI value than those of ahipa starches ($p<0.05$). Kinetics after 3 h of digestion did not achieve a maximum starch hydrolysis percentage (Fig. 2b).

**Table 3.** Hydrolysis index (HI) and estimated glycemic index (GI) for native (N) and gelatinized (G) ahipa and cassava starches

| Source | HI | GI |
|---|---|---|
| White bread[a)] | 100 | 94 |
| A11N | $43.22 \pm 0.12^a$ | $63.43 \pm 0.07^a$ |
| ALN | $47.22 \pm 0.45^a$ | $65.63 \pm 0.25^a$ |
| CN | $30.04 \pm 1.06^b$ | $56.2 \pm 0.58^b$ |
| A11G | $136.12 \pm 2.77^a$ | $114.44 \pm 1.52^a$ |
| ALG | $135.60 \pm 4.40^a$ | $114.16 \pm 2.41^a$ |
| CG | $136.69 \pm 0.16^a$ | $114.75 \pm 0.09^a$ |

A11, ahipa accession 11; AL, ahipa accession Local; C, cassava.
a) White bread data from [29].

Long-term (20.5 h) hydrolysis kinetics of raw native starches with pancreatic α-amylase is shown in Fig. 3. A maximum percentage of enzymatic digestion is observed after 8 h of incubation for the three native starches analyzed, with no significant differences among them ($p>0.05$). The maximum hydrolysis percentage values for cassava and ahipa starches ranged from 84.0 to 87.2%, implying that 12.8–16% corresponded to type II resistant starch (RS2), based on the classification derived from the nutritional characteristics of starch [25].

The maximum digestive percentage obtained for cassava starch in the present work was similar to that reported by Srichuwong et al. [54] who informed a maximum α-amylase digestion rate of 88.4% for type A cassava starch. In general, starches with type B crystalline structure exhibited low in vitro digestibility [55]. In a previous work, crystallinity pattern of ahipa starch was assigned as type C [18], which is a mixture of A- and B-crystalline types and has digestibility values intermediate between A and B types [54].

Although the crystalline form of starch granules has been cited as the most important factor affecting the extent of enzymatic hydrolysis [54], other granule features such as their size or the amylose:amylopectin ratio have also been cited as factors affecting enzyme activity. However, the correlation with enzyme activity varied among the nature of the starch analyzed [56–60].

The analysis of granule size and digestibility of ahipa and cassava starches showed no correlation with the values reported for other edible R&T crops. Lesser yam, for example, which also presents a type C crystalline structure, showed a maximum digestion percentage close to 30%, considerably lower than that of ahipa starches. However, lesser yam starch has a mean particle size that is approximately half of that of ahipa [54, 61] and shows an apparent amylose content (14.2%) higher than that of ahipa starch.

Taking into account that ahipa belongs to the leguminous family, ahipa starch structure and digestibility is in agreement with those from other leguminous plants since most of them present type C starch structure [62]. The RS values reported

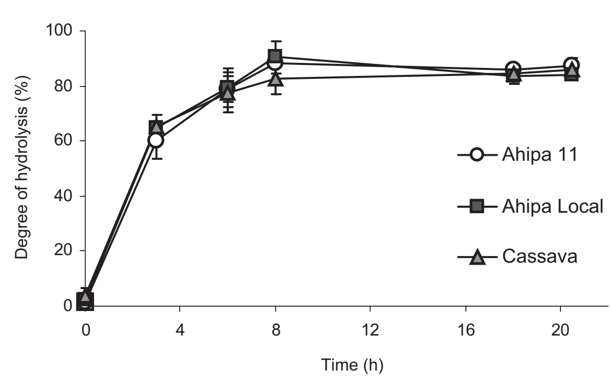


**Figure 3.** Long-term enzymatic hydrolysis kinetics of native starches from ahipa accessions 11 and Local (11 and L) and cassava.

for various legume starches (after 120-min digestion) are within the range 50–79% [62], in the order of the RS values observed for ahipa in this work (~54%).

Thus, ahipa can be considered a very good source of starch and might be used as a functional food, contributing to increase the rapidly and slowly digestible (SD) fraction. Particularly, ahipa starch is a gluten free product [20] which could also be of interest as an ingredient for the elaboration of foods for people with celiac disease.

### 3.6 Rheological behavior

Figure 4 shows the flow curves corresponding to gelatinized starch suspensions from ahipa and cassava. All of them presented a pseudoplastic behavior ($n<1$), which was satisfactorily adjusted by Ostwald de Waele model. This property of gelatinized starch is important in many products since a pseudoplastic material has suspending properties at low shear rates and its viscosity becomes sufficiently low when it is processed at higher shear rates [63].

Besides, gelatinized starch suspensions were characterized as thixotropic ones, indicating that rheological behavior of these systems was time dependent (Fig. 4). Thixotropic systems exhibit decreasing shear stress and apparent viscosity over time at a fixed shear rate. The corresponding thixotropic indexes were calculated as the area between the flux curves. No significant differences ($p>0.05$) were detected between gelatinized ahipa starch suspensions, being the thixotropic indexes 6564 and 6580 Pa/s for Local and 11 ahipa accessions, respectively. Gelatinized cassava starch suspensions exhibited significantly ($p<0.05$) higher thixotropy values (7672 Pa/s) and apparent viscosity values (Table 4) indicating that remaining amylopectin inside starch granules reinforces amylose network.

Figure 5a shows the mechanical spectra obtained from frequency sweeps corresponding to ahipa Local gelatinized pastes. Ahipa and cassava starch gelatinized suspensions presented a typically gel behavior since significantly higher ($p<0.05$) elastic module values than viscous ones ($G'>G''$) were registered over almost all the frequency range, and curves maintained practically parallel (Fig. 5a). Meanwhile, ahipa starch pastes behaved like a weak gel and exhibited $G'$ values significantly lower ($p<0.05$) than those corresponding to cassava. For example, at 1 Hz, $G'$ and $G''$ of cassava starch pastes resulted 68 and 55% higher, respectively, than the values corresponding to ahipa starch pastes (Fig. 5b). Besides, Lee and Yoo [64] also reported a weak gel-like behavior for sweet potato starch pastes.

Dynamic rheological results are in agreement with the apparent viscosities informed previously (Table 4). Differences in rheological properties between ahipa and cassava starches can be attributed to differences in granule size and shape, as was observed in a previous work [65], the presence of phosphate esters and the amylose:amylopectin ratio. It has

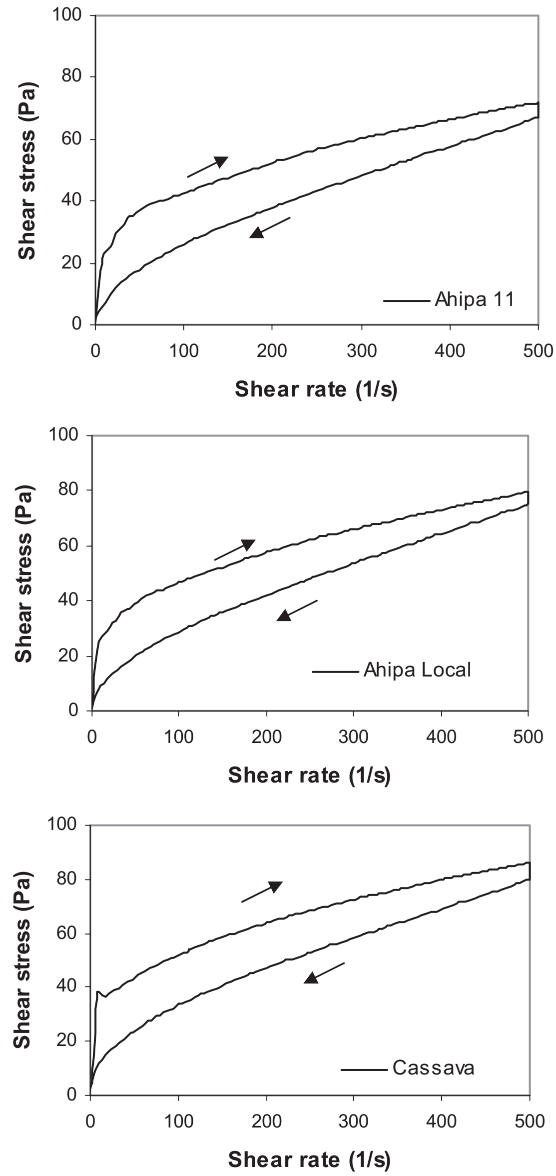


**Figure 4.** Flow curves of ahipa from different accessions and cassava gelatinized suspensions. Arrows indicate the up and down flow curves.

**Table 4.** Parameters corresponding to Ostwald de Waele modeled of flow curves and apparent viscosities at 500 $s^{-1}$ ($\eta$)

| Starch | Ostwald de Waele model | | | |
|---|---|---|---|---|
| | $k$ | $n$ | $r^2$ | $\eta$ (mPa s) |
| Ahipa accession 11 | 11.228$^a$ | 0.304$^a$ | 0.9938 | 145.63 ± 10.65$^a$ |
| Ahipa accession Local | 11.227$^a$ | 0.314$^a$ | 0.9928 | 156.00 ± 3.47$^{ab}$ |
| Cassava | 14.570$^b$ | 0.281$^b$ | 0.9900 | 166.50 ± 5.70$^b$ |

Reported values correspond to the mean ± standard deviation. Different letters in the same column indicate significant differences ($p<0.05$).

 

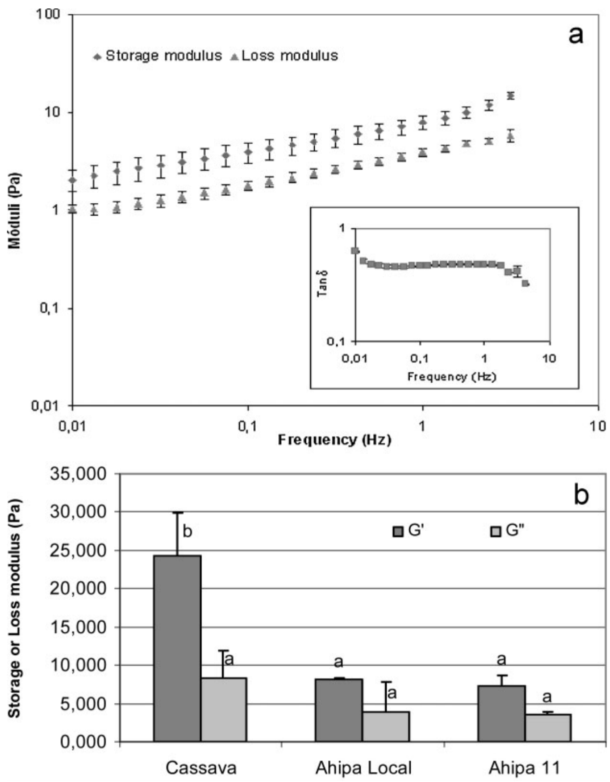


**Figure 5.** a, Mechanical spectra, at constant amplitude = 1 Pa; tan δ curve as a function of frequency is shown as an insert. b, Storage ($G'$) and loss ($G''$) moduli at 1 Hz of gelatinized suspensions of ahipa (N° 11 and Local accessions) and cassava starches. Different letters indicate significant differences ($p<0.05$) between materials for the storage and loss moduli.

been reported that swelling power and temperature govern the viscoelastic properties of gelatinized starch dispersion [66]. In previous works, swelling power as well as water holding capacity of ahipa flours and starches were studied [20, 61].

Likewise, non-significant differences ($p>0.05$) on $G'$ and $G''$ values were observed for ahipa starches from different accessions. A similar trend was observed by Che et al. [63] studying the rheological behavior of the starches from two different cassava cultivars.

The tan δ values of the gelatinized starch suspensions were lower than 1, indicating that the samples are elastic in nature, as it was exemplified for ahipa Local pastes (Fig. 5a).

The proposed equations fitted satisfactorily the variation of both storage and loss moduli with frequency, achieving higher values of the correlation coefficients for ahipa starches. The values of the fitted parameters are shown in Table 5. No significant differences were detected between ahipa accessions while the higher values of the mathematical model parameters were obtained for cassava starch pastes.

## 4 Conclusions

Concerning chemical composition, the outstanding characteristic of ahipa roots was their high protein (8–9%) level. Accession 11 exhibited higher starch content than Local accession, being this result relevant to be considered in a breeding program.

Compared to cassava, ahipa starch showed lower gelatinization temperature, exhibiting accession 11 the lowest value. Ahipa starch digestibility was similar to that of other leguminous plants. Accession 11 showed higher RD and resistant (RS) and lower SD starch than cassava. Starch from ahipa Local accession presented RD and RS values intermediate between accession 11 and cassava. From a nutritional point of view, these results could indicate certain versatility of ahipa starch in order to be used as an ingredient for foods with high energy content.

Rotational rheological assays indicated that gelatinized ahipa starch suspensions presented a pseudoplastic thixotropic behavior and under dynamic assays they behaved as a weak gel.

Based on the chemical composition of ahipa roots and the technological functional properties studied of ahipa starch, they may find suitable applications in the food processing industry. Likewise, rotational and dynamic rheological results suggest that ahipa starch can be a functional native starch thickener that withstands shear conditions associated with food processing. Further research is required to utilize their unique characteristics for novel product developments.

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**Table 5.** Mathematical model parameters of dynamic behavior curves of starch pastes

| | Storage moduli $G'$(Pa), $G' = af^b$ | | | Loss moduli $G''$(Pa), $G'' = cf^d$ | | |
|---|---|---|---|---|---|---|
| Starch | Correlation coefficient ($r^2$) | Parameter *a* (Pa s$^b$) | Parameter *b* | Correlation coefficient ($r^2$) | Parameter *c* (Pa s$^d$) | Parameter *d* |
| Ahipa accession Local | 0.9779 | $3.6 \pm 0.9^a$ | $0.56 \pm 0.01^a$ | 0.9804 | $4.2 \pm 1.1^a$ | $0.41 \pm 0.06^a$ |
| Ahipa accession 11 | 0.9810 | $3.5 \pm 1.0^a$ | $0.550 \pm 0.005^a$ | 0.9723 | $4.0 \pm 1.1^a$ | $0.42 \pm 0.07^a$ |
| Cassava | 0.9681 | $14.3 \pm 4.1^b$ | $1.10 \pm 0.42^b$ | 0.9779 | $15.9 \pm 4.7^b$ | $0.25 \pm 0.02^b$ |

*f* is the frequency expressed in Hz and *a*, *b*, *c*, and *d* are the fitting parameters of Power law model. Different letters in the same column indicate significant differences ($p<0.05$).

 

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## 5 References

[1] Sørensen, M., Døygaard, S., Estrella, J., Kvist, L., Nielsen, P., Status of the South American tuberous legume *Pachyrhizus tuberosus* (Lam.) Spreng.: Field observations, taxonomic analysis, linguistic studies and agronomic data on the diversity of the South American *Pachyrhizus tuberosus* (Lam.) Spreng. complex with special reference to the identification of two new cultivar groups from Ecuador and Peru. *Biodivers. Conserv.* 1997, *6*, 1581–1625.

[2] Zanklan, A. S., Ahouangonou, S., Becker, H. C., Pawelzik, E., Grüneberg, W. J., Evaluation of the storage root-forming legume yam bean (*Pachyrhizus* spp.) under West African conditions. *Crop Sci.* 2007, *47*, 1934–1946.

[3] Forsyth, J. L., Shewry, P. R., Characterization of the major proteins of tubers of yam bean (*Pachyrhizus ahipa*). *J. Agric. Food Chem.* 2002, *50*, 1939–1944.

[4] Milanez, C. R. D., Moraes-Dallaqua, M. A., Ontogênese do sistema subterrâneo de *Pachyrhizus ahipa* (Wedd.) Parodi (Fabaceae). *Rev. Bras. Bot.* 2003, *26*, 415–427.

[5] Sørensen, M., A taxonomic revision of the genus *Pachyrhizus* (Fabaceae–Phaseoleae). *Nord. J. Bot.* 1988, *8*, 167–192.

[6] Kaur, L., Singh, N., Sodhi, N. S., Some properties of potatoes and their starches. II. Morphological, thermal and rheological properties of starches. *Food Chem.* 2002, *79*, 183–192.

[7] Singh, J., Singh, N., Studies on the morphological, thermal and rheological properties of starch separated from some Indian potato cultivars. *Food Chem.* 2001, *75*, 67–77.

[8] Jiang, Q., Gao, W., Li, X., Xia, Y., et al., Characterizations of starches isolated from five different *Dioscorea L*. species. *Food Hydrocolloid.* 2012, *29*, 35–41.

[9] Murniece, I., Karklina, D., Galoburda, R., Santare, D., et al., Nutritional composition of freshly harvested and stored Latvian potato (*Solanum tuberosum* L.) varieties depending on traditional cooking methods. *J. Food Comp. Anal.* 2011, *24*, 699–710.

[10] Kaur, L., Singh, J., Singh, N., Effect of glycerol monostearate on the physico-chemical, thermal, rheological and noodle making properties of corn and potato starches. *Food Hydrocolloid.* 2005, *19*, 839–849.

[11] Singh, J., McCarthy, O. J., Singh, H., Moughan, P. J., Kaur, L., Morphological, thermal and rheological characterization of starch isolated from New Zealand Kamo Kamo (*Cucurbita pepo*) fruit – A novel source. *Carbohydr. Polym.* 2007, *67*, 233–244.

[12] Cisneros, F. H., Zevillanos, R., Cisneros-Zevallos, L., Characterization of starch from two ecotypes of andean achira roots (*Canna edulis*). *J. Agric. Food Chem.* 2009, *57*, 7363–7368.

[13] Vieira Bezerra, C., Amante, E. R., de Oliveira, D. C., Rodrigues, A. M. C., da Silva, L. H. M., Green banana (*Musa cavendishii*) flour obtained in spouted bed – Effect of drying on physico-chemical, functional and morphological characteristics of the starch. *Ind. Crops Prod.* 2013, *41*, 241–249.

[14] Vandeputte, G. E., Vermeylen, R., Geeroms, J., Delcour, J. A., Rice starches. I. Structural aspects provide insight into crystallinity characteristics and gelatinisation behaviour of granular starch. *J. Cereal Sci.* 2003, *38*, 43–52.

[15] Noda, T., Takigawa, S., Matsuura-Endo, C., Suzuki, T., et al., Factors affecting the digestibility of raw and gelatinized potato starches. *Food Chem.* 2008, *110*, 465–470.

[16] Lu, Z. H., Donner, E., Yada, R. Y., Liu, Q., The synergistic effects of amylose and phosphorus on rheological, thermal and nutritional properties of potato starch and gel. *Food Chem.* 2012, *133*, 1214–1221.

[17] Kingman, S. M., Englyst, H. N., The influence of food preparation methods on the in-vitro digestibility of starch in potatoes. *Food Chem.* 1994, *49*, 181–186.

[18] López, O. V., Viña, S. Z., Pachas, A. N. A., Sisterna, M. N., et al., Composition and food properties of *Pachyrhizus ahipa* roots and starch. *Int. J. Food Sci. Technol.* 2010, *45*, 223–233.

[19] AOAC, *Official Methods of Analysis of the Association of Official Analytical Chemists*, Association of Official Analytical Chemists, Arlington, VA 1990.

[20] Doporto, M. C., Mugridge, A., García, M. A., Viña, S. Z., *Pachyrhizus ahipa* (Wedd.) Parodi roots and flour: Biochemical and functional characteristics. *Food Chem.* 2011, *126*, 1670–1678.

[21] Dini, C., Doporto, M. C., García, M. A., Viña, S. Z., Nutritional profile and anti-nutrient analyses of *Pachyrhizus ahipa* roots from different accessions. *Food Res. Int.* 2013, *54*, 255–261.

[22] Van Soest, P. J., Wine, R. H., Use of detergents in the analysis of fibrous feeds. IV. Determination of plant cell wall constituents. *J. Assoc. Off. Agric. Chem.* 1967, *50*, 50–55.

[23] López, O. V., García, M. A., Zaritzky, N. E., Film forming capacity of chemically modified corn starches. *Carbohydr. Polym.* 2008, *73*, 573–581.

[24] Juansang, J., Puttanlek, C., Rungsardthong, V., Puncha-arnon, S., Uttapap, D., Effect of gelatinisation on slowly digestible starch and resistant starch of heat-moisture treated and chemically modified canna starches. *Food Chem.* 2012, *131*, 500–507.

[25] Englyst, H. N., Kingman, S. M., Cummings, J. H., Classification and measurement of nutritionally important starch fractions. *Eur. J. Clin. Nutr.* 1992, *46*, S33–S50.

[26] Goñi, I., Garcia-Alonso, A., Saura-Calixto, F., A starch hydrolysis procedure to estimate glycemic index. *Nutr. Res.* 1997, *17*, 427–437.

[27] Hung, P. V., Morita, N., Physicochemical properties and enzymatic digestibility of starch from edible canna (*Canna edulis*) grown in Vietnam. *Carbohydr. Polym.* 2005, *61*, 314–321.

[28] Steffe, J. F., *Rheological Methods in Food Process Engineering*, Freeman Press, East Lansing, USA 1996.

[29] Ebah-Djedji, B. C., Dje, K. M., N'Zue, B., Zohouri, G. P., Amani, N. G., Effect of harvest period on starch yield dry matter content from the tuberous roots of improved cassava (*Manihot esculenta* Crantz) varieties. *Pak. J. Nutr.* 2012, *11*, 414–418.

[30] Opara, L., in: Dris, R., Niskanen, R., Mohan Jain, S. (Eds.), Crop Management and Postharvest Handling of Horticultural Products, Science Publishers, Inc., Enfield, NH, USA 2003, pp. 381–406.

[31] Rolland-Sabaté, A., Sánchez, T., Buléon, A., Colonna, P., et al., Structural characterization of novel cassava starches

 

with low and high-amylose contents in comparison with other commercial sources. *Food Hydrocolloid.* 2012, *27*, 161–174.

[32] Djazuli, M., Bradbury, J. H., Cyanogen content of cassava roots and flour in Indonesia. *Food Chem.* 1999, *65*, 523–525.

[33] Pandey, A., Soccol, C. R., Nigam, P., Soccol, V. T., et al., Biotechnological potential of agro-industrial residues. II: Cassava bagasse. *Bioresour. Technol.* 2000, *74*, 81–87.

[34] Ahmed, M., Sorifa, A. M., Eun, J. B., Effect of pretreatments and drying temperatures on sweet potato flour. *Int. J. Food Sci. Technol.* 2010, *45*, 726–732.

[35] Leterme, P., Buldgen, A., Estrada, F., Londoño, A. M., Mineral content of tropical fruits and unconventional foods of the Andes and the rain forest of Colombia. *Food Chem.* 2006, *95*, 644–652.

[36] Sørensen, M., *Yam bean, Pachyrhizus DC. Promoting the conservation and use of underutilized and neglected crops*. International Plant Genetic Resources Institute, Rome, Italy 1996, *2*, 141.

[37] Shewry, P. R., Tuber storage proteins. *Ann. Bot.* 2003, *91*, 755–769.

[38] Puncha-arnon, S., Puttanlek, C., Rungsardthong, V., Pathipanawat, W., Uttapap, D., Changes in physicochemical properties and morphology of canna starches during rhizomal development. *Carbohydr. Polym.* 2007, *70*, 206–217.

[39] Jane, J., Kasemsuwan, T., Chen, J. F., Juliano, B. O., Phosphorus in rice and other starches. *Cereal Foods World* 1996, *41*, 827–832.

[40] Forsyth, J. L., Ring, S. G., Noel, T. R., Parker, R., et al., Characterization of starch from tubers of yam bean (*Pachyrhizus ahipa*). *J. Agric. Food Chem.* 2002, *50*, 361–367.

[41] Li, J.-Y., Yeh, A.-I., Relationships between thermal, rheological characteristics swelling power for various starches. *J. Food Eng.* 2001, *50*, 141–148.

[42] Melo, E. A., Stamford, T. L., Silva, M. P., Krieger, N., Stamford, N. P., Functional properties of yam bean (*Pachyrhizus erosus*) starch. *Bioresour. Technol.* 2003, *89*, 103–106.

[43] Huang, C.-C., Physicochemical, pasting thermal properties of tuber starches as modified by guar gum locust bean gum. *Int. J. Food Sci. Technol.* 2009, *44*, 50–57.

[44] Betancur, D. A., Ancona, L. A. C., Guerrero, R. I., Camelo Matos, G., Ortiz, D., Physicochemical functional characterization of baby Lima Bean (*Phaseolus lunatus*) starch. *Starch/Stärke* 2001, *53*, 219–226.

[45] Wang, S., Gao, W., Chen, H., Xiao, P., New starches from *Fritillaria* species medicinal plants. *Carbohydr. Polym.* 2005, *61*, 111–114.

[46] Eliasson, A.-C., Gudmundsson, M., in: Eliasson, A.-C. (Ed.), Carbohydrates in Food, Marcel Dekker, New York, USA 1996, p. 561.

[47] Thirathumthavorn, D., Charoenrein, S., Thermal and pasting properties of native and acid-treated starches derivatized by 1-octenyl succinic anhydride. *Carbohydr. Polym.* 2006, *66*, 258–265.

[48] Noda, T., Takahata, Y., Sato, T., Ikoma, H., Mochida, H., Physicochemical properties of starches from purple and orange fleshed sweet potato roots at two levels of fertilizer. *Starch/Stärke* 1996, *48*, 395–399.

[49] Aboubakar, Njintang, Y. N., Scher, J., Mbofung, C. M. F., Physicochemical, thermal properties and microstructure of six varieties of taro (*Colocasia esculenta* L. Schott) flours and starches. *J. Food Eng.* 2008, *86*, 294–305.

[50] Chung, H.-J., Lim, H. S., Lim, S.-T., Effect of partial gelatinization and retrogradation on the enzymatic digestion of waxy rice starch. *J. Cereal Sci.* 2006, *43*, 353–359.

[51] Ovando-Martínez, M., Whitney, K., Reuhs, B. L., Doehlert, D. C., Simsek, S., Effect of hydrothermal treatment on physicochemical and digestibility properties of oat starch. *Food Res. Int.* 2013, *52*, 17–25.

[52] Frei, M., Siddhuraju, P., Becker, K., Studies on the in vitro starch digestibility and the glycemic index of six different indigenous rice cultivars from the Philippines. *Food Chem.* 2003, *83*, 395–402.

[53] Ek, K. L., Brand-Miller, J., Copeland, L., Glycemic effect of potatoes. *Food Chem.* 2012, *133*, 1230–1240.

[54] Srichuwong, S., Sunarti, T. C., Mishima, T., Isono, N., Hisamatsu, M., Starches from different botanical sources I: Contribution of amylopectin fine structure to thermal properties and enzyme digestibility. *Carbohydr. Polym.* 2005, *60*, 529–538.

[55] Annison, G., Topping, D. L., Nutritional role of resistant starch: Chemical structure vs physiological function. *Annu. Rev. Nutr.* 1994, *14*, 297–320.

[56] Franco, C. M. L., do Rio Preto, S. J., Ciacco, C. F., Factors that affect the enzymatic degradation of natural starch granules – Effect of the size of the granules. *Starch/Stärke* 1992, *44*, 422–426.

[57] Granfeldt, Y., Drews, A., Bjorck, I., Arepas made from high amylose corn flour produce favorably low glucose and insulin responses in healthy humans. *J. Nutr.* 1995, *125*, 459–465.

[58] Sajilata, M. G., Singhal, R. S., Kulkarni, P. R., Resistant starch – A review. *Compr. Rev. Food Sci. Food Saf.* 2006, *5*, 1–17.

[59] Singh, J., Lelane, C., Stewart, R. B., Singh, H., Formation of starch spherulites: Role of amylose content and thermal events. *Food Chem.* 2010, *121*, 980–989.

[60] Man, J., Yang, Y., Zhang, C., Zhou, X., et al., Structural changes of high-amylose rice starch residues following in vitro and in vivo digestion. *J. Agric. Food Chem.* 2012, *60*, 9332–9341.

[61] Doporto, M. C., Dini, C., Mugridge, A., Viña, S. Z., García, M. A., Physicochemical, thermal and sorption properties of nutritionally differentiated flours and starches. *J. Food Eng.* 2012, *113*, 569–576.

[62] Sandhu, K. S., Lim, S.-T., Digestibility of legume starches as influenced by their physical and structural properties. *Carbohydr. Polym.* 2008, *71*, 245–252.

[63] Che, L.-M., Li, D., Wang, L.-J., Özkan, N., et al., Rheological properties of dilute aqueous solutions of cassava starch. *Carbohydr. Polym.* 2008, *74*, 385–389.

[64] Lee, H.-L., Yoo, B., Dynamic rheological and thermal properties of acetylated sweet potato starch. *Starch/Stärke* 2009, *61*, 407–413.

[65] López, O. V., García, M. A., Starch films from a novel (*Pachyrhizus ahipa*) and conventional sources: Development and characterization. *Mater. Sci. Eng. C* 2012, *32*, 1931–1940.

[66] Shon, K.-J., Yoo, B., Effect of acetylation on rheological properties of rice starch. *Starch/Stärke* 2006, *58*, 177–185.

 