

Preparation of Indigestible Pyrodextrins from Different Starch Sources

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Starch-modifying processes, such as pyrodextrinization, are potential ways to alter the nutritional features of this polysaccharide. A widely used method for pyrodextrinizing maize starch was also applied to lentil, sorghum, cocoyam, sagu, and cassava starches, and the *in vitro* digestibility of the products was evaluated. Pyrodextrins were produced by heating starch at 140 °C for 3 h, with catalytic amounts of HCl. The enzymatically available starch content of all preparations decreased by 55–65% after modification. Thus, pyrodextrinization seems to be an effective way to produce indigestible glucans from different starches. Pyrodextrins obtained were complex mixtures of starch derivatives with a wide range of molecular weight as estimated by gel filtration chromatography. Both their molecular weight profiles and contents of indigestible fractions varied with starch source. Experiments with lentil and cassava starches showed that changing dextrinization conditions also affects the susceptibility to enzymatic hydrolysis of the product.

KEYWORDS: Indigestible dextrin; modified starch; pyroconversion; pyrodextrinization; *in vitro* digestibility; resistant starch; *Canna edulis*; *Lens esculenta*; *Sorghum bicolor*; *Xanthosoma sagittifolium*; *Manihot esculenta*; *Zea mays*

INTRODUCTION

Modified starches, for the most part, are native materials that have been submitted to one or more physical, chemical, or enzymatic treatments promoting granular disorganization, polymer degradation, molecular rearrangements, oxidation, or chemical group addition (1). Although the development and uses of modified starches have been mainly based on technological aspects, the appreciable interest in controlling starch digestibility features observed during the past two decades places starch-modifying processes as potential means for altering the physiological utilization of this important dietary component (2, 3).

Pyrodextrinization is perhaps one of the early ways to produce modified starches. A soluble, gummy material obtained from the roasting of starch was used to gum stamps and labels in the 19th century (4). In the food industry, dextrins have been used as sweeteners, additives, binders, and, to a lesser extent, encapsulating agents (5). Pyroconversion involves different chemical reactions: hydrolysis, transglucosidation, and, in some cases, repolymerization of the glucan. After hydrolysis, the new reducing end becomes a glucosyl cation, which can undergo either intramolecular dehydration, producing 1,6-anhydro- β -D-

glucose, or intermolecular bond formation (transglucosidation), leading to the formation of atypical linkages such as 1 \rightarrow 2, 1 \rightarrow 3, 1 \rightarrow 4, and 1 \rightarrow 6 (β -anomers) (4, 6, 7).

In this paper, a widely utilized method for pyrodextrinization of maize starch (8), was applied to different starch sources and the effect of the modification on their *in vitro* digestibility was evaluated. The influence of several pyrodextrinization conditions on the susceptibility of lentil and cassava starches to enzymatic hydrolysis was also investigated.

MATERIALS AND METHODS

Starches. Lentil (*Lens esculenta* Medic., Fabaceae) and dark sorghum [*Sorghum bicolor* (L.) Moench, Gramineae] seeds and cocoyam [*Xanthosoma sagittifolium* (L.) Schott., Araceae] and sagu (*Canna edulis* Kerr, Cannaceae) roots were purchased from the local market in Caracas (Venezuela). Decorticated seeds and roots were used to isolate the starch as described elsewhere (9). Additionally, dark sorghum grains were bleached with sodium hypochlorite before starch isolation (10). Commercial cassava (*Manihot esculenta* Crantz, Euphorbiaceae) and maize (*Zea mays* L., Poaceae) starches were supplied by Alfonzo Rivas & Co., Caracas (Venezuela).

Starch Pyrodextrinization. Twenty-two grams of starch was sprayed with 0.5 mL of 2.2 mol L⁻¹ HCl (final proportion = 1.82 g of acid/kg of starch), mixed thoroughly, and left overnight at room temperature. Then, the mixture was incubated at 140 °C for 3 h, and the pyrodextrinized material was milled to pass a 60 mesh screen (8). In complementary experiments with cassava and lentil starches, several

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incubation times and acid concentrations were used to assess their impact on the properties of the modified material.

Starch Digestibility. Both native and modified starches were assessed for available starch, combining hydrolysis with Termamyl and amyloglucosidase (11). Retrograded resistant starch was also evaluated (12). The *in vitro* rate of hydrolysis was measured using porcine pancreatic α -amylase (13); each assay was run with 0.5 g of available starch.

Depolymerization Degree. Molecular depolymerization was assessed by gel filtration chromatography using a Sepharose CL-4B column equilibrated with 0.1 mol L⁻¹ KOH. Dimethyl sulfoxide or KOH (sagu and sorghum) dispersed samples (10 mg) were seeded into a 1.6 cm \times 85 cm column and eluted at 15 mL h⁻¹ into 2 mL fractions (14). Total carbohydrate in the eluted samples was assessed according to the anthrone-sulfuric acid method (15). Known molecular weight dextrans (Pharmacia Fine Chemicals, Uppsala, Sweden) were used for calibration purposes.

Scanning Electron Microscopy. Granular shape and size were studied by scanning electron microscopy. Starch was sprinkled onto adhesive tape, attached to circular stubs, and coated with a platinum/palladium layer using a Hitachi E102 ion sputterer (Tokyo, Japan). The coated samples were observed at 15 kV and photographed in a Hitachi S-2400 scanning electron microscope. The starch granule diameter was estimated by measuring the larger axis of the visible granules in two photographs (16).

Viscosity Evaluation. Apparent viscosity measurements (17) were evaluated with a Rapid Visco Analyzer (RVA) (Newport Scientific P/L, Warriewood, Australia).

Degree of gelatinization was evaluated by differential scanning calorimetry (DSC) profiles using a Mettler DSC 30 calorimeter (Schwerzenbach, Germany) (18).

Color Measurement. Color of native and pyrodextrinized cassava starches was measured with a 2445 photoelectric colorimeter (Macbeth Color Eye, Windsor, NY). Parameters *L*, *a*, and *b* were recorded for all samples, and color difference (ΔE) between modified and native samples was calculated using eq 1 (19).

$$\Delta E = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{1/2} \quad (1)$$

Statistical Analysis. Data were analyzed by one- or two-way ANOVA followed by Duncan's multiple-range test as post hoc comparison of means ($p < 0.05$). The software Statistica for Windows, version 4 (1993), by StatSoft, Inc. (Tulsa, OK), was employed.

RESULTS AND DISCUSSION

Main Physical Properties of Pyrodextrinized Starches.

After pyrodextrinization, the materials were soluble in water at 80 g L⁻¹, presenting a yellowy-brownish color and low water content (1.3–4%); similar findings have been reported by other authors (4, 20).

The extent of polymer degradation due to pyroconversion was assessed by gel filtration chromatography. Eluted fractions were grouped into four categories based on the main peak elution intervals: those with very high molecular weight (VHMW), gathering molecules eluted with $K_d < 0.21$; high molecular weight (HMW), with MW > 105 kDa; intermediate molecular weight (IMW), with MW between 8 and 105 kDa; and low molecular weight (LMW), with MW < 8 kDa.

The elution profile for maize starch, as an example of a typical chromatographic behavior, is shown in Figure 1. Table 1 shows the percentage distribution of apparent molecular weights for all of the samples. For native samples, a main peak located around $K_d = 0.05$ and finishing by $K_d = 0.21$ (VHMW) was clearly defined, whereas pyrodextrinized starches showed several peaks located after $K_d = 0.58$ (IMW and LMW).

In all of the samples, except for sorghum, between 80 and 89% of the carbohydrates from native starches eluted as VHMW, and >98% eluted in the VHMW plus HMW zone

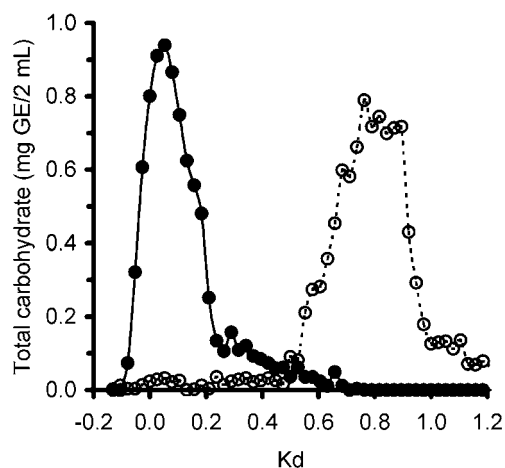


Figure 1. Gel filtration profiles of native (●) and pyrodextrinized (○) maize starch. Samples were eluted using a Sepharose CL-4B column (1.6 cm \times 85 cm) equilibrated with 0.1 mol L⁻¹ KOH. GE, glucose equivalent.

Table 1. Percentage Dose Recovered (PDR) and Percentage Distribution of Apparent Molecular Weight (MW_{app}) of Native and Pyrodextrinized Starches

starch source	PDR	MW_{app}^a			
		VHMW	HMW	IMW	LMW
cassava					
native	91.2	76	8	11	5
pyrodextrinized	99.7	1	10	63	26
cocoyam					
native	81.5	83	14	1	1
pyrodextrinized	75.8	1	8	61	29
lentil					
native	81.4	89	11	0	0
pyrodextrinized	70.7	1	6	52	40
maize					
native	81.3	85	14	1	0
pyrodextrinized	66.9	2	9	57	32
sagu					
native	56.7	87	12	1	1
pyrodextrinized	101.5	0	7	58	35
sorghum					
native	76.7	80	18	1	0
pyrodextrinized, 1st round	89.2	33	39	25	2
pyrodextrinized, 2nd round	99.5	3	11	65	22

^a Values are percentage of recovered carbohydrates. VHMW, very high molecular weight ($kDa \leq 0.21$); HMW, high molecular weight (>105 kDa); IMW, intermediate molecular weight (8–105 kDa); LMW, low molecular weight (<8 kDa).

(Table 1). These fractions must correspond to amylopectin and amylose (21). After the modification, the peak around $K_d = 0.05$ totally disappeared and <10% of the carbohydrate eluted at HMW, whereas a marked increase in the material eluted as IMW and LMW was noted. In fact, most of the carbohydrates (52–63%) eluted at IMW. This is evidence of the extensive depolymerization caused by the pyrodextrinization protocol used.

In an attempt to estimate the degree of gelatinization due to pyroconversion, samples of maize, cocoyam, and lentil pyrodextrinized starches were submitted to DSC. However, no endotherm was detected, supporting the idea of extensive degradation of both amylose and amylopectin, suggested by the gel filtration profiles. Starch depolymerization must have proceeded to such an extent that polymer crystallites responsible for DSC endotherms were eliminated (22). Furthermore, on the basis of RVA analysis, none of the samples developed appreciable viscosity in concentrations up to 80 g L⁻¹, which

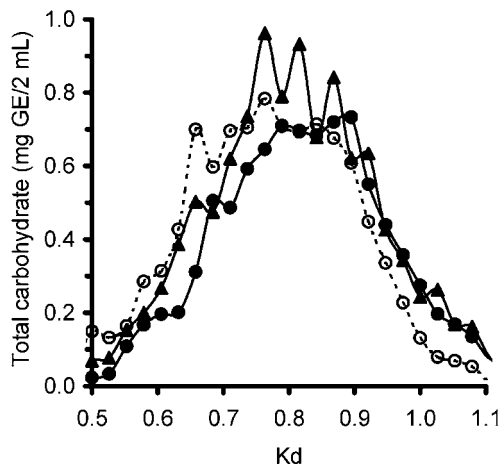


Figure 2. Partial chromatographic profile of pyrodextrinized starches. Intermediate (IMW) and low (LMW) molecular weight regions of pyroconverted lentil (●), cassava (○), and sagu (▲) starches are shown. Samples were eluted using the same conditions as described in **Figure 1**. GE, glucose equivalent.

stresses the drastic molecular degradation produced by the modifying treatment.

A completely different behavior was observed for sorghum starch. After the standard modification, there was still a peak at VHMW representing 33% of the carbohydrates. The rest of the material was distributed evenly along HMW and IMW (**Table 1**). It should be mentioned that the sorghum grains used here to isolate starch were dark brown hulled. They were therefore submitted to a bleaching treatment with alkaline sodium hypochlorite, a reportedly efficient way to obtain light starch from dark sorghum seeds (10), suitable for most food uses. Some reports indicate that chlorine and other halogen derivatives may affect starch structural and reactivity properties (23, 24). Hence, the use of this preisolation phase may have rendered a starch preparation with affected hydrolysis properties. This is noteworthy because hydrolysis is the first reaction to take place during pyrodextrin formation (4, 5). However, further studies are needed to explain fully the low susceptibility observed for sorghum starch. Due to this result, the pyroconverted sorghum starch was submitted to a second modification round using the very same pyroconversion conditions (8). In this case, the peak at VHMW disappeared and almost 90% of the sample eluted in IMW and LMW, which closely resembled the other starches behavior (**Table 1**).

Pyrodextrins produced under the conditions reported by Ghali et al. (8) seemed to consist of a complex mixture of molecules, all with MW below 105 kDa. This was exemplified by the chromatographic behavior of lentil, cassava, and sagu pyroconverted samples (**Figure 2**). Lentil starch exhibited three main peaks at 40, 14, and 5 kDa, whereas cassava starch showed peaks at 49, 19, and 9 kDa. Pyroconverted sagu showed five main peaks at 49, 19, 10, 6, and 4 kDa. Finally, modified maize starch showed four main peaks at 40, 19, 10, and 5 kDa (**Figure 1**).

An interesting feature was found during the microscopy study of the granule morphology. No difference in the size and shape of starch granules was detected between native starch and samples submitted to pyroconversion, even though one of the main changes observed after pyrodextrinization is the increased solubility in cold water (4). In fact, the morphology of cocoyam native granules (**Figure 3a**) was the same as that of the pyrodextrinized ones (**Figure 3b**). Nonetheless, when the pyrodextrinized starch was dissolved in water and subsequently

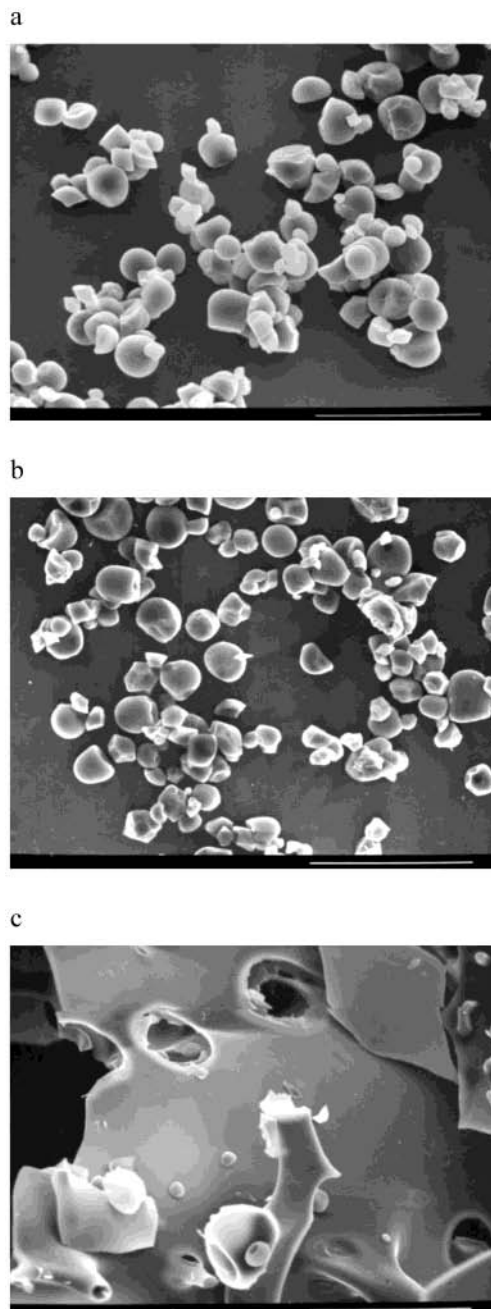


Figure 3. Scanning electron microphotographs of cocoyam starch granules: (a) native starch; (b) pyrodextrinized starch; (c) pyrodextrinized starch suspended in water and freeze-dried. Bar = 50 μm (800 \times).

freeze-dried, there was a total loss of the granule structure and the material appeared as flakes (**Figure 3c**). Similar findings were recorded for lentil and maize starches (data not shown). Hence, the remarkable change in the polymer structure suggested by the physicochemical analyses discussed above was not evident, at first, at the supramolecular level. In other words, the pyroconverted granules stayed like “ghosts” that were disaggregated only after solubilization. To the best of the authors’ knowledge, this is the first documented report of such behavior.

Taken together, these results indicate that the pyrodextrinization protocol proposed by Ghali et al. (8) for the conversion of maize starch is also effective for other starch materials.

Available Starch. The available starch contents of all native samples were similar (**Table 2**); nonetheless, lentil and sagu samples showed a tendency toward lower values. This may be

Table 2. Available Starch Content in both Native and Pyrodextrinized Starches from Several Sources^a

starch source	available starch (% dmb)		fall in AS ^b (%)
	native	pyrodextrinized	
cassava	96.8 ± 1.6 a	42.9 ± 2.0* a	55.7
cocoyam	96.8 ± 0.5 a	38.7 ± 0.6* b	60.0
lentil	94.7 ± 0.5 a	42.5 ± 0.7* c	55.1
maize	96.8 ± 2.7 a	36.6 ± 0.4* d	62.2
sagu	93.6 ± 0.5 a	32.6 ± 0.8* e	65.2
sorghum, 1st round	98.6 ± 1.4 a	88.0 ± 1.3* f	10.8
sorghum, 2nd round		57.4 ± 1.4* g	41.8

^a Values are means ± SD of three independent determinations. * = Significantly different from native starch ($p < 0.05$, Duncan's test). Means in a column with different letters were significantly different ($p < 0.05$, Duncan's test). ^b Fall in available starch (AS) was calculated as $(AS_{\text{native}} - AS_{\text{pyrodextrinized}}) \times 100/AS_{\text{native}}$.

explained by their relatively high content of insoluble proteins and highly hydrated fibers, which settle with the starch during the extraction process (16, 25).

Pyrodextrinization caused a remarkable decrease (55–65%; $p < 0.05$) in the available starch content of all the samples except for sorghum. In this sample, after the combined acid/heat treatment, the available starch decreased by 11% only. Even when it was submitted to a second modification round, the available starch level did not change as much as for the other starches (Table 2). Thus, judged from the product's digestibility viewpoint, sorghum starch seems less susceptible to pyrodextrinization than other starches. This is in accordance with the MW analysis discussed above, and it is probably due to the starch preisolation treatment used for bleaching the sorghum grains.

The drop in apparent starch content is an indication that pyrodextrinization promoted the generation of nondigestible fractions, a change that differed slightly yet significantly ($p < 0.05$) in magnitude depending on the starch substrate. Because the resistant starch due to retrogradation was very low ($< 0.21 \pm 0.01\%$, data not shown) for both native and modified samples, the recorded decrease in enzymatically available starch may be explained by the formation of transglucosidated dextrins resistant to amylolytic attack (26–29). Thus, the difference between the available starch content measured before and after pyrodextrinization represents an estimate of the indigestible fraction produced during the modification process. Although this analytical approach might be less accurate than other methods already explored for the assessment of indigestible chemically altered starches (24, 26, 27, 30), its use appears to be easier and less expensive.

Several modification methods, like drum-drying, extrusion, cross-linking, steam-cooking, and derivatization, have been

shown to produce resistant starch; however, the resistant fraction was not in any case $> 30\%$ (2, 3, 31), which is much smaller than the level of indigestible starch estimated in the pyroconverted samples. Therefore, pyrodextrinization might be proposed as a method to produce resistant starch at an industrial scale. In fact, a process based on pyroconversion has been developed for the production of indigestible dextrins from potato and maize starches (27, 28).

In Vitro Rate of α -Amylolysis. Both initial rate (proportion of starch hydrolyzed at 15 min) and final magnitude (proportion of starch hydrolyzed at 60 min) of starch hydrolysis were measured using porcine pancreatic α -amylase (Table 3). Among raw native starches, the lowest final magnitude was observed for cocoyam, followed by lentil and sagu, and, finally, sorghum, maize, and cassava showed the highest values. Gelatinization of the native starches (by heating at 97 °C for 20 min) led to an increase in both initial rate and final magnitude of hydrolysis for all of the samples, which is a consequence of the granular structure disintegration produced during gelatinization. This increase was more marked for cocoyam and lentil starches (Table 3).

The pyrodextrinizing treatment caused a moderate increase in the degree of hydrolysis of the nongelatinized samples (Table 3), which provides evidence for changes in the granular and molecular structures of the starches. However, the recorded rise in digestion rates after pyroconversion was always notably smaller than that induced by gelatinization of the nonmodified sample (Table 3). This observation may reflect the diminished overall enzymatic availability of the pyroconverted starches (Table 2).

Effect of Acid Catalyst and Incubation Time on Pyrodextrinization. Due to the prospective use of this type of modification as a way to produce man-made resistant starch, it was interesting to study the effect of some process variables on the product characteristics. Using lentil starch as a model, the effect of the acid catalyst on the available starch content was assessed (Table 4). With the standard conditions suggested by Ghali et al. (8) (condition 1) there was a 52% fall ($p < 0.05$) in the enzymatically available starch. Nonetheless, when HCl (condition 2) was omitted and with a 3-fold increase in the incubation period (condition 3), there was a very small decrease in the enzymatically available starch level. These results emphasize the need for an acid catalyst during pyroconversion carried out at temperatures below 200 °C (4, 7) as in the present study. Reactions leading to the formation of 1,6-anhydro- β -D-glucose (intramolecular dehydration) and atypical bonds (transglucosidation) have been documented to occur during the thermal dextrinization of glucans (6, 7, 26). The anhydrous derivative is produced at temperatures > 200 °C, as well as at

Table 3. Initial Rate and Final Magnitude of in Vitro α -Amylolysis (Percent Digested Starch, dmb)^a

starch source	initial rate ^b			final magnitude ^b		
	native and raw	native and gelatinized ^c	pyrodextrinized and raw	native and raw	native and gelatinized ^c	pyrodextrinized and raw
cassava	3.5 ± 0.7	68.0 ± 0.7	18.4 ± 0.7	9.9 ± 1.0	71.6 ± 0.9	24.0 ± 1.7
cocoyam	0.2 ± 0.1	73.6 ± 1.6	17.9 ± 0.3	1.5 ± 0.2	79.3 ± 2.7	27.5 ± 0.5
lentil	1.0 ± 0.1	77.1 ± 0.4	21.3 ± 0.3	5.7 ± 0.6	83.3 ± 0.8	30.4 ± 0.8
maize	1.8 ± 0.2	66.6 ± 1.0	15.4 ± 0.1	8.3 ± 0.5	73.7 ± 1.7	25.2 ± 0.3
sagu	3.0 ± 0.1	68.6 ± 1.8	18.7 ± 0.9	5.7 ± 0.1	73.4 ± 2.3	20.4 ± 0.9
sorghum, 2nd round	3.5 ± 0.1	55.2 ± 0.8	27.7 ± 0.7	8.0 ± 0.1	64.6 ± 3.5	33.9 ± 0.2

^a Values are means ± SD of three independent determinations. ^b Initial rate was determined as the proportion of starch hydrolyzed by α -amylase after the first 15 min, whereas final magnitude was the starch hydrolyzed at 60 min. ^c Gelatinization was carried out by heating (97 °C) the starch suspension for 20 min just before the assay.

Table 4. Effect of HCl Addition and Incubation Time on the Enzymatic Availability of Pyroconverted Lentil Starch

condition	HCl at 1.82 g/kg of starch	incubation time (h)	available starch ^a (% dmb)
control	no	0	94.8 ± 0.5 a
1	yes	3	42.5 ± 0.7 b
2	no	3	93.2 ± 2.2 a
3	no	9	91.3 ± 2.3 a

^a Values are means ± SD of three independent determinations. Means in a column with different letters were significantly different ($p < 0.05$, Duncan's test).

Table 5. Effect of HCl Concentration and Incubation Time on the Available Starch Content and Color Difference (ΔE) of Pyrodextrinized Cassava Starch

condition	HCl (g/kg of starch)	incubation time (h)	available starch ^a (% dmb)	ΔE^a
1	0.99	1.5	39.5 ± 0.5 ab	14.2 ± 0.01 a
2	0.99	3	36.5 ± 1.0 abc	16.3 ± 0.01 b
3	0.99	4.5	37.9 ± 2.0 ab	15.6 ± 0.01 b
4	1.82	1.5	32.2 ± 1.0 bd	27.1 ± 0.01 c
5	1.82	3	42.9 ± 2.0 a	17.6 ± 2.90 b
6	1.82	4.5	2.8 ± 0.2 e	48.8 ± 0.80 d
7	2.65	1.5	29.1 ± 1.3 cd	34.9 ± 0.01 e
8	2.65	3	33.1 ± 0.7 ad	30.0 ± 0.01 f
9	2.65	4.5	2.0 ± 0.4 f	58.4 ± 0.01 g

^a Values are means ± SD of three independent determinations. Means in a column with different letters were significantly different ($p < 0.05$, Duncan's test).

lower temperatures in the presence of catalytic amounts of mineral acids (7). Hence, the present results on starch availability seem to conform to current knowledge about the pyroconversion process, as the formation of indigestible fractions appears to require the presence of an acid catalyst.

In the present study, the influence of incubation time and acid concentration was also evaluated on sample color development, using cassava starch as a model (Table 5). Evidently, the higher the acid catalyst concentration the greater the color difference. This tendency may be explained by the heat sensitive nature of carbohydrate browning reactions (32). However, it is noteworthy that a relatively mild treatment, such as condition 1 (0.99 g of acid/kg of starch and 90 min of heating), had the same impact on starch availability as stronger conditions (1.82 or 2.65 g of acid/kg of starch and 3 h of heating; i.e., conditions 5 and 8, respectively) but yielded markedly lighter products ($p < 0.05$). It is also surprising that a short heating time (1.5 h, conditions 4 and 7) led to greater color differences than longer treatments (3 h, conditions 5 and 8). There is no evident explanation for such a tendency, but it suggests that factors other than temperature/time conditions may also affect the visual properties of pyrodextrins. Although extreme conditions, such as 4.5 h of heating and 1.82 or 2.65 g of acid/kg of starch (conditions 6 and 9), resulted in almost completely indigestible materials, their ΔE indices were also remarkably high. Because the potential commercial application of indigestible pyrodextrins may depend largely on their organoleptic properties, the use of a low acid concentration/short heating time condition appears to be appropriate for preparing indigestible pyroconverted cassava starch. It would be interesting to evaluate the impact of various treatment conditions on both the digestibility and color of pyrodextrins prepared from different sources.

The data presented here confirm pyrodextrinization as an effective alternative method for the production of indigestible

glucans. It can be applied to different starches, although the tendency to form enzyme-resistant fractions may vary significantly with the botanical source. Pyrodextrins seem to consist of a complex mixture of starch derivatives showing a wide range of molecular weights, the *in vitro* indigestible character of which increases with the intensity of the dextrinizing conditions. The possible application of this type of process for adding value to underexploited crops deserves further investigation.

ABBREVIATIONS USED

ΔE , color difference; AS, available starch; dmb, dry matter basis; DSC, differential scanning calorimetry; GE, glucose equivalent; HMW, high molecular weight; IMW, intermediate molecular weight; K_d , coefficient of distribution; LMW, low molecular weight; MW_{app} , apparent molecular weight; PDR, percentage dose recovered; RVA, Rapid Visco Analyzer; VHMW, very high molecular weight.

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