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The low-substituted propylene oxide etherified plantain (*Musa paradisiaca normalis*) starch: Characterization and functional parameters

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ABSTRACT

Starch was isolated from unripe plantain fruit and it was chemically modified where it was hydroxypropylated to improve upon the functional properties of native plantain starch. The yield of the starch was ~19% and molar substitution increased with increase in concentration of propylene oxide. 'C' type X-ray diffraction was shown by native plantain starch and many changes were not noticed after hydroxypropylation. The granules were oval or elliptical in shape with 10–20 μm in width and 15–40 μm in length, modification did not bring about major changes in size and shape except partial erosion of the granules. Hydroxypropylation also improved the swelling capacity from ~20 in native to 90 g/g. Turbidity reduced after hydroxypropylation and increase in molar substitution. Syneresis reduced by 75% with increase in MS. Thermal studies by DSC revealed that all the parameters decreased after this modification. Onset temperature reduced by ~26%, peak temperature reduced by ~9%, endset temperature increased by ~6%, gelatinization temperature range increased by 137%, enthalpy decreased by 38%. Reduction in all parameters were noticed during 3rd and 18th day scan. Enthalpy of retrogradation as well as percentage of retrogradation reduced to a greater extent during the 3rd as well as the 18th day scanning.

1. Introduction

The applications of unmodified starches are often hampered by the extremes of certain conditions such as pH, temperature and shear during processing. Consequently, certain properties of unmodified starches could be inimical to the original concept of the processor's idea of a good product. However, these limitations could be addressed by chemical modification. In recent times, many types of chemically modified starches have been prepared by acid hydrolysis, oxidation, etherification, esterification and cross-linking (Santacruz, Koch, Svensson, Ruales, & Elisson, 2002).

Hydroxypropylation of starch is an etherification process achieved by using propylene oxide as the etherifying reagent. It results in the introduction of hydroxypropyl groups onto the polymeric chain of starch. The reactive nature of propylene oxide is attributed to its highly strained three-membered epoxide ring. Bond angles in the ring average is 60° thus making it a very reactive molecule (Pal, Singhal, & Kulkarni, 2000). In starch etherification, activation is often necessary and alkaline reagents are often used as catalysts to facilitate the formation of nucleophilic starch–O^- alkoxide. This is followed by the reaction of the starch–O^- alkoxide with the propylene oxide leading to a bimolecular substitution to produce hydroxypropyl starch (Tuschoff, 1986). The introduction of hydrophilic hydroxypropyl groups reduces gelatinization temperature of the starches. In addition, the reaction takes place under strong alkaline condition. As a result of these, the reaction has to be carried out with a swelling inhibiting salt such as Na_2SO_4 to prevent starch gelatinization. A measure of the number of propylene oxide moles substituted on an anhydroglucose unit (AGU) is the molar substitution (MS). An AGU is limited to only three hydroxyl groups; hence the maximum MS possible is 3. However, if the substituent groups are able to react further with reagent, it is possible to form oligomeric substituents.

In food applications, hydroxypropylation of starches is used to impart extended shelf-life, freeze–thaw stability and cold storage stability to starch-based food products. Hydroxypropylation prevents retrogradation, resulting in more fluid paste with improved paste clarity. This modification also imparts desired textural properties to the product (Tuschoff, 1986). In addition, enzymatic digestibility of starches improves after hydroxypropylation (Liu, Ramsden, & Corke, 1999).

In the literature, preparation of hydroxypropyl starch using different starch sources have been reported for starches of maize

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(Azemi & Wootton, 1994; Gray & BeMiller, 2005; Liu et al., 1999; Wootton & Haryadi, 1992), rice (Islam & Azemi, 1997; Seow & Thevamalar, 1993; Yeh & Yeh, 1993), wheat (Wootton & Haryadi, 1992; Wootton & Mahdar, 1993), potato (Lammers, Stanhuis, & Beenackers, 1993; Perera & Hoover, 1998; Perera, Hoover, & Martin, 1997; Vorwerg, Dijksterhuis, Borghuis, & Kröger, 2004), amaranth (Pal, Singhal, & Kulkarni, 2000, 2002).

The challenges of the burgeoning biomaterials industries necessitates the need to investigate and report on alternative sources of starch apart from conventional sources such as maize, potato, rice and wheat. This becomes imperative because the aforementioned sources of starch are also major staple foods. In developing countries, occasional price increases occur as a result of large demand for these crops in the production of starch for industrial uses. This development has stimulated research activities on new sources of starch, particularly from underutilized resources such as mucuna beans (Adebowale & Lawal, 2003a, 2003b), jack bean (Lawal & Adebowale, 2005) bambarra groundnut (Adebowale, Afolabi, & Lawal, 2002; Adebowale & Lawal, 2002), new cocoyam (Lawal, 2004; Lawal, Lechner, Hartmann, & Kulicke, 2007), sago (Cui & Oates, 1999), pigeon pea (Akintayo, Oshodi, & Esuoso, 1999), yambean (Agunbiade & Longe, 1999), field pea (Ratnayake, Hoover, Shahidi, Perera, & Jane, 2001) and lentil (Hoover & Manuel, 1996).

Plantain starch that is investigated in this work belongs to the class of underutilized sources of starch. The plantain fruit (*Musa paradisiaca*) is considered to be one of the most important sources of carbohydrate for people living in the humid regions of Latin America, Africa and South Asia (Johnson & Brennan, 2000). It is a seasonal and highly perishable crop. Many attempts have been made to produce stable and storable products from the plantain fruit. These are usually in the form of dried composite flour and chips (Gwanfogbe, Cherry, Simmons, & James, 1988; Ogazi & Jones, 1981). Starch could be isolated from unripe plantain particularly when it is surplus, thereby eliminating or reducing the wastage of this bioresource. However, information about isolation of starch from plantain is very scarce. In addition, the author is not aware of any previous publication detailing isolation and hydroxypropylation of plantain starch. Therefore, the objective of this investigation was to isolate starch from plantain and modify it as means of improving its properties using hydroxypropylation method. The long term objective is that a valuable source of starch which often perishes as a result of lack of storage technology, particularly in Africa would be brought to full industrial utilizations.

2. Materials and methods

2.1. Materials

Unripe commercial plantain fruits were obtained at Awa-Ijebu, Nigeria. The plantain fruits were identified at International Institute for Tropical Agriculture, Ibadan, Nigeria. Propylene oxide, sodium hydroxide, anhydrous sodium sulfate (all analytical grade) were obtained from Merck Schuchardt, Germany. All other reagents used in this work were analytical grade.

2.2. Methods

2.2.1. Isolation of plantain starch

The unripe plantain fruits were peeled and they were dissected into two equal halves longitudinally to remove the seeds inside the fruit. The dissected fruits (1 kg) were then cut into pieces (approximately 2 cm long) and were rinsed thoroughly with distilled water, following which they were ground with blender (Philips HR2094). The resultant slurry was dispersed in distilled water (10 L). It was sieved with 100 mesh screen and the dispersion was allowed to settle for 4 h, after which the supernatant was decanted off. The starch slurry was redispersed in distilled water again and the process was repeated four times until a clean supernatant was obtained. The starch obtained was air-dried at 30 ± 2 °C for 48 h. Starch (128.6 g) was obtained from 1 kg peeled raw plantain.

2.2.2. Proximate composition

The moisture content was determined with a moisture analyzer, Sartorius MA 40 (Sartorius, Edgewood, NJ, USA). The moisture analyzer uses infrared ray as the heating source. After calibration, approximately 5 g of starch was spread evenly on the disposable sample dish and the moisture content was indicated by the analyzer at the end the measurement. Ash, crude protein, crude fiber and lipid were determined according to AACC (1984) procedures. Amylose content was determined using improved colorimetric method described by Chrastil (1987).

2.2.3. Preparation of hydroxypropyl starch

Plantain starch (100 g, d.b.) was weighed inside 500 mL screw cap jars and distilled water (200 mL) was added, followed by the addition of 20 g of (anhydrous sodium sulfate) Na_2SO_4. The slurry was mixed for 30 min and the pH was adjusted to 11.15 with 1 M NaOH. Propylene oxide (10, 20, 30 and 40 mL) was added and the suspension was mixed thoroughly with jars closed. The reaction was maintained at 40 °C for 24 h. The starch suspensions were neutralized with dilute HCl (0.1 M). The slurry was centrifuged for 15 min at 10,000 rpm. The starch cakes obtained were washed with distilled water until its sulfate content was negative with $BaCl_2$. The HPS were dried in the oven to ~10% moisture content.

2.2.4. Determination of molar substitution

The method described by the Joint FAO/WHO Expert Committee on Food Additives (2001) was used for the determination of the hydroxypropyl groups. Hydroxypropylated starch (100 mg, d.b.) were weighed into a 100 mL volumetric flask and sulfuric acid (25 mL; 0.5 M) was added. The mixture was heated in a boiling water bath until a clear solution was obtained. The resulting clear solution was cooled and it was made up to 100 mL with distilled water. The solution (1 mL) was pipetted into 25 mL graduated test tubes, immersed in cold water and 8 mL of concentrated sulfuric acid was added dropwise to the tube. After thorough shaking, the tubes were placed in boiling water bath for 20 min. The tubes were allowed to cool down and they were placed in ice bath until the solution chilled. Ninhydrin reagent (3% ninhydrin in 5% $Na_2S_2O_5$, 0.6 mL) was added and the tubes were shaken well before placing in 25 °C water bath for 1 h. The solutions were then made up to 25 mL with concentrated sulfuric acid and thoroughly mixed. It was transferred to 1-cm cells, and after 10 min, the absorbance was measured at 590 nm. The starch blank was used as reference. A calibration curve was prepared with an aliquot (1 mL) of standard aqueous solutions, containing 10, 20, 30, 40 and 50 μg of propylene glycol per mL.

The propylene glycol concentration in the starch was calculated from the standard curve, converted to equivalent hydroxypropyl groups from each molar solution using the following equation:

$$\mathrm{MS} = 162W/100M - (M-1)W,$$

where MS = molar substitution; W = equivalent hydroxypropyl group in 100 mg of starch; M = molecular weight of C_3H_6O.

2.2.5. Wide angle X-ray diffractometry

The X-ray diffraction pattern of NPS and the HPS were recorded with X′Pert pro X-ray diffractometer equipped with X′celerator as detector. The diffractograms were registered at Bragg angle (2θ) = 5°–60°. The operating conditions were: target voltage

40 kV, target current 100 mA, aging time 5 min; scan speed 2 deg/min; step time 4.55, divergence slit width 1.00; scatter slit width 1.00 and receiving slit width 0.6.

2.2.6. Granule morphology

Starch granule morphology was examined with a Leo 1550 ultra scanning electron microscope. The samples were mounted on studs, sputter-coated with gold (Balzers, SCD-040; Norderstedt, Germany) and examined under the scanning electron microscope.

2.2.7. Determination of swelling capacity

Free swelling capacities (FSC) of the NPS and the hydroxypropyl starches were determined using the teabag method. Starch (0.4 g, d.b.) was weighed and packed inside teabag (TeaGschwendner, Meckenheim, Germany). It was soaked inside distilled deionized water in double jacketed glass bottle (300 mL) connected to a thermostat in which the water was circulated at specific temperature. The temperature range for the study was 30–90 °C. After 1 h, the sample was removed from water and it was allowed to drain for 5 min to ensure uniformity. The swollen starch inside the teabag was weighed. The weight of empty teabag and amount of water absorbed by the empty teabag were predetermined. The FSC was determined as follows:

$$\mathrm{FSC} = \frac{W_{SS}}{W_{CS}},$$

$$W_{SS} = W_4 - W_2 - W_1,$$

$$W_{CS} = \left[W_3 - \frac{W_3 \times M_t}{100}\right],$$

where W_{CS} = corrected weight of starch; W_{SS} = weight of swollen starch; M_t = % moisture content of the starch; W_1 = weight of dry teabag; W_2 = weight of water absorbed by empty teabag; W_3 = weight of starch taken; W_4 = total weight after swelling.

2.2.8. Turbidity and paste clarity

Turbidity of the NPS and the HPS were determined with 2% (w/v) gelatinized starch solution using HACH 2100 AN Turbidimeter (HACH Company, Colorado, USA). Gelatinization of starches was carried out by heating starch solutions at 100 °C for 1 h. To monitor starch retrogradation, gelatinized starch samples were stored for varying number of days (1–30 days). The turbidimeter uses a Tungsten filament lamp as a light source and the values were recorded as NTU (Nephelometric Turbidity Unit).

2.2.9. Freeze–thaw stability

Freeze–thaw stability of gelatinized starch was measured by the method of Kaur, Singh, and Singh (2004) with some modifications. Aqueous suspension of starch (5%, w/w) was heated at 95 °C under constant agitation for 1 h. The paste was weighed (exactly 20 g each) into previously weighed polypropylene centrifuge tubes, and was capped tightly. It was centrifuged at 1000*g* for 10 min to remove free water. The free water (supernatant) was decanted and the tubes containing starch paste were subjected to freeze–thaw cycles, followed by centrifugation at 4000 rpm for 30 min. Alternate freezing and thawing was performed by freezing for 24 h at −18 °C and thawing for 4 h at 30 °C. Eight freeze–thaw cycles were performed. The percentage of water separated after each freeze–thaw cycles was measured. The weight of water was taken and the extent of syneresis was expressed as the percentage of water separated:

$$\mathrm{Syneresis}(\%) = \frac{\mathrm{Water\ separated(g)} \times 100}{\mathrm{Total\ weight\ of\ sample(g)}}.$$

2.2.10. Differential scanning calorimetry and retrogradation studies

Gelatinization and retrogradation of starches were measured using a DSC 821e (Mettler Toledo, Germany). The device was calibrated with indium (T_m = 156.6 °C), cyclopentane (T_m = −93.9 °C) and water (T_m = 0.0 °C). Distilled water (5.0 μL) was added to 2.0 mg of starch in DSC pans (ME-26763). It was sealed, reweighed and kept at 30 ± 2 °C for 24 h to ensure equilibration of the starch sample and water. The samples were scanned from 30 °C to 130 °C at 10 °C/min using empty pans as reference. The heated pans were then cooled immediately and kept at 4 °C inside a refrigerator for 24 h, following which they were kept for 2 or 17 days at 30 ± 2 °C, to make complete storage days of 3 and 18, respectively. At the end of these periods of storage, the samples were scanned under the same condition with the first scanning. Onset temperature (T_o), peak temperature (T_p), endset temperature (T_e) and enthalpy (ΔH, J/g) for gelatinization and retrogradation were determined. The enthalpy (ΔH) was estimated by integrating the area between the thermogram and the base line under the peak.

3. Results and discussion

3.1. Proximate analysis and chemical composition

In Table 1, yield of starch was ~19% (dry basis) and this depends on the variety of plantain, higher and lower yields have been reported in the literature (Bello-Perez, Agama-Acevedo, Sanchez-Hernandez, & Paredes-Lopez 1999; Perez-Sira, 1997; Waliszewski, Aparicio, Bello, & Monroy, 2003). The yield also depends on the time of harvest. Ripe plantain fruit contains more sugar than starch and the starch content decreases progressively as the days of storage increases after harvest (Marriott, Robinson, & Karikari, 1981). The moisture content (9.26%) is consistent with 9.87% reported in the literature (Perez-Sira, 1997). Moisture content depends on the drying method, extent of drying and humidity in the surrounding atmosphere and it influences the flow and other mechanical properties of the starch. The ash content (0.12%) is lower than 0.27–0.34% reported for plantain starches (Eggleston, Swennen, & Akoni, 1992). Ash, lipid, protein and fiber contents are consistent with values reported previously for plantain starches (Eggleston et al., 1992; Perez-Sira, 1997). The fiber content depends on the maturity of the fruit at the time of harvest. Amylose contents observed in the present investigation were 13.61%, 12.46% and 8.45% for total amylose, apparent amylose and lipids-complexed amylose. In comparison with potato starch 25.6%, 21.3% and 16.8% were reported for the total amylose, apparent amylose and lipids-complexed amylose (Perera et al., 1997). It has been reported that during hydroxypropylation, the hydroxypropyl groups in the starch chains are mainly introduced in the amorphous regions which composed

Table 1
Proximate analysis and chemical composition of native plantain starch

Parameter	Composition[a] (%)
Yield[b]	19.3 ± 0.56
Moisture	9.26 ± 0.31
Ash	0.12 ± 0.04
Lipid	0.14 ± 0.04
Crude fiber	0.14 ± 0.02
Crude protein	0.62 ± 0.05
Total amylose[c]	13.61 ± 0.80
Apparent amylose[d]	12.46 ± 0.60
Lipids-complexed amylose[e]	8.45

[a] Means of triplicate determinations are reported.
[b] Based on dry weight.
[c] Total amylose determined after removal of lipids.
[d] Amylose determined before removal of lipids.
[e] $\frac{\text{Total amylose} - \text{Apparent amylose}}{\text{Total amylose}} \times 100$.

primarily of amylose and amylose is modified to a greater extent than amylopectin (Blanshard, 1987; Kavitha & BeMiller, 1998; Shi & BeMiller, 2000).

3.2. Effect of propylene oxide concentration on molar substitution

Corresponding increases were observed in MS as the volume of the propylene oxide added to the reaction mixture increased from 10 to 40 mL (Table 2). Other parameters were kept constant based on previous experiments conducted in our laboratory to optimize the hydroxypropylation of plantain starch. The increases observed in the MS is a result of greater availability of propylene oxide at higher concentrations in the proximity of the starch granules. In a previous work, when other parameters were kept constant, increasing the volume of propylene oxide added to corn starch and amaranth starch produced progressive increases in MS (Pal et al., 2000). This observation is also consistent with increases in MS with corresponding increases in volume of propylene oxide in the hydroxypropylation of canna and maize starches (Chuenkamol, Puttanlek, Rungsardthong, & Uttapap, 2007; Wooton & Manatsathit, 1983). The highest MS observed in the present investigation is 0.18 and that still falls within the limit allowed for the use of hydroxypropylated starched in food applications by the FDA which stipulates that hydroxypropyl group should not be more than 7.0%, i.e. MS = 0.2 (Dias, Tekchandani, & Mehta, 1997).

3.3. Wide angle X-ray diffraction pattern

The wide angle X-ray diffraction pattern of native and hydroxypropylated plantain starches is shown in Fig 1. The figure shows that hydroxypropylation does not alter the diffraction pattern of the native starch. Both NPS and hydroxypropylated starches show the 'C' pattern of diffraction characterized by prominent peaks around $2\theta = 15°$, 17° and 23°. A similar observation was reported for banana starch with similar peaks at $2\theta = 15.3°$, 17.2° and a broad peak at 22°–24° (Waliszewski et al., 2003). However, slight increase in X-ray intensity has been reported for canna starch after hydroxypropylation (Chuenkamol et al., 2007). 'C' crystalline polymorphs of starches is not a true crystalline polymorph but mixtures of 'A' and 'B' polymorphs observed in cereals and tuber starches, respectively (Gernat, Radosta, Damaschun, & Schierbaum, 1990). Both 'A' and 'B' type starches are based on the parallel stranded double helices, in which the double helices are closely packed in the 'A' type starch but loosely packed in the 'B' type starch. Hizukuri (1986) and Hizukuri, Kanebo, and Takeda (1983) have shown that starches with amylopectin of short chain length (<20 residues) exhibit 'A' type of crystallinity, whereas those with amylopectin of longer average chain length show the 'B' pattern.

Table 2
Conditions of preparation of hydroxypropylated plantain starch and the MS of the hydroxypropyl groups

Sample	Starch (g)	Na_2SO_4 (g)	Propylene oxide (mL)	Temperature (°C)	pH	Time (h)	MS
$HPPS_{10}$	100	20	10	40	11.5	24	0.07
$HPPS_{20}$	100	20	20	40	11.5	24	0.15
$HPPS_{30}$	100	20	30	40	11.5	24	0.17
$HPPS_{40}$	100	20	30	40	11.5	24	0.18

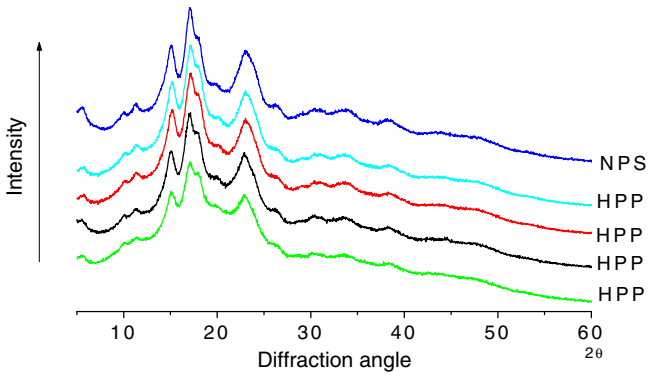

Fig. 1. Wide angle X-ray diffraction pattern of native and hydroxypropyl plantain starch. NMS, native plantain starch; $HPPS_{10–40}$, hyroxypropyl plantain starches with MS 0.07, 0.15, 0.17 and 0.18, respectively. The reaction conditions of preparation are given in Table 2.

3.4. Granule morphology

Scanning electron micrographs of the NPS and $HPPS_{40}$ are shown in Figs. 2 and 3, respectively. Micrograph of only one derivatized starch is presented because no pronounced differences were observed among the micrographs of the hydroxypropylated starches. The starch granules were mainly oval or elliptical in shape with sizes ranging from 10 to 20 μm in width and 15 to 40 μm in length. The surfaces of the native starch granules appeared smooth and no pronounced damage was observed among the granules, suggesting that the method of extraction did not cause significant damage to the starch. Similar observations have been reported for banana starch (Kayisu, Hood, & Vansoest, 1981). Irregular shape with elongated and spheroid forms having 14–88 μm width and 21–108 μm length has also been reported for banana starch (Waliszewski et al., 2003). Oval to round shape granules with 12–20 and 2–8 μm sizes were reported for wheat starch (Hung & Morita, 2005). In addition, oval and round shape with heterogeneous sizes for width, 12–30 and 12–34 mm for length were reported for Jack bean starch (Lawal & Adebowale, 2005). Following hydroxypropylation, the granules were not altered in shape but the surface appeared partly degraded. Changes in appearance of starch granules after hydroxypropylation have been reported for potato starches (Kaur et al., 2004; Kim, Hermansson, & Eriksson, 1992). However, no change in surface and shape characteristics of the granules was reported for canna starches in a previous work (Chuenkamol et al., 2007). These variations could be attributed to the different morphologies of the native starches as well as the various conditions of preparation of the hydroxypropyl starch derivatives.

3.5. Free swelling capacity

The free swelling capacity (FSC) of the NPS and the hydroxypropyl derivatives at various temperatures is presented in Fig. 4. Within the temperature range studied (30–90 °C). The study shows that hydroxypropylation improved starch swelling and swelling of all the hydroxypropyl derivatives were higher than the swelling of the native starch at all temperatures. It is noteworthy that swelling capacities increased with increase in the MS of the hydroxypropyl starch derivatives. It is instructive that above 60 °C the swelling pattern of both native and hydroxypropylated starches changed tremendously, indicating the changes below and above the gelatinization temperature. A similar observation has been reported for wheat starch, banana starch and potato starch after hydroxypropylation (Hung & Morita, 2005; Kaur et al., 2004; Waliszewski et al., 2003). It is reasonable that in the amorphous region of the starch where most of the swelling takes place, introduction of hydrophilic hydroxypropyl groups enhanced water percolation into the granules thereby causing expansion and increase in swelling. Increases observed as the temperature increased is because water pene-

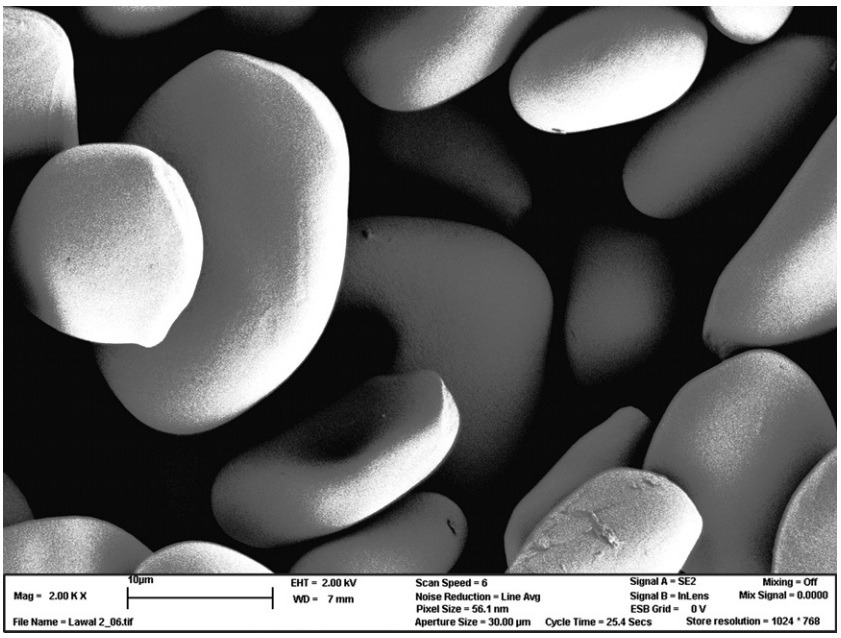

Fig. 2. Scanning electron micrographs of native plantain starches. Magnification 2000×.

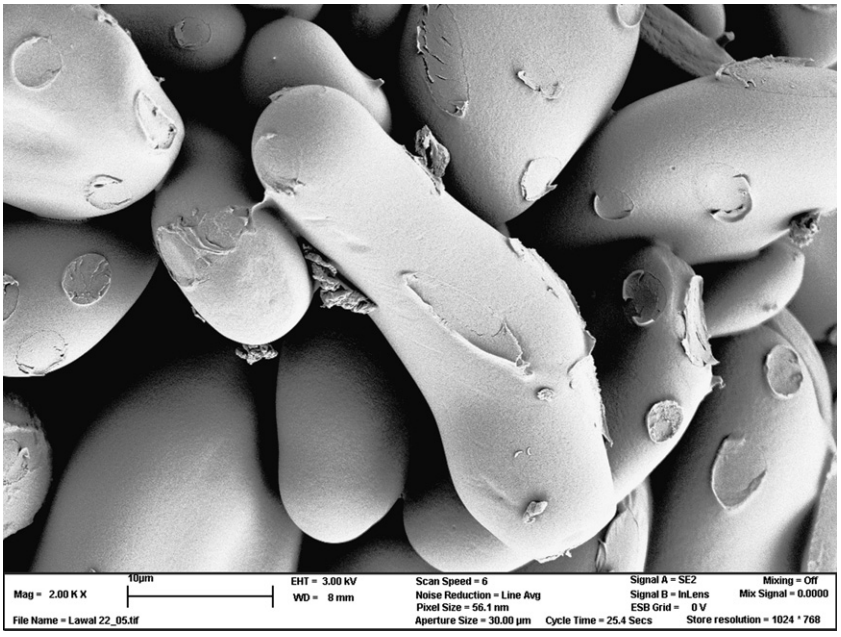

Fig. 3. Scanning electron micrograph of hydroxypropyl plantain starches. Magnification 2000×.

trated into the more amorphous region of the starch granule and as the temperature increases to the point of gelatinization, the swelling of the amorphous phase accelerates the disruption of the crystalline region leading to enhanced swelling. This suggests that in starch applications such as food thickening and hydrogels, hydroxypropyl plantain starches would be relevant.

3.6. Turbidity and paste clarity

Studies were conducted to investigate development of turbidity of the starch pastes on storage as means of investigating paste clarity (Table 3). As indicated, remarkable reductions in turbidity was observed after hydroxypropylation. The ΔT after 30 days in NPS was 951 NTU compared with 2.7 NTU observed for $HPPS_{40}$. Turbidity of the native starch increased progressively with starch storage. It is also noteworthy that turbidity reduced with increase in MS of the hydroxypropyl starches. In the literature, light transmittance of potato starch, corn and amaranth starch increased after hydroxypropylation (Kaur et al., 2004; Pal et al., 2002) suggesting increase in paste clarity. In addition, paste clarity of normal, ae, and wx maize starches increased after hydroxypropylation (Liu et al., 1999). It is reasonable that the hydroxypropyl substituents caused steric hindrance and prevented close association of chains which led to a restriction in the formation of inter-chain hydrogen bonds. This development facilitated improvement of paste clarity after hydroxypropylation.

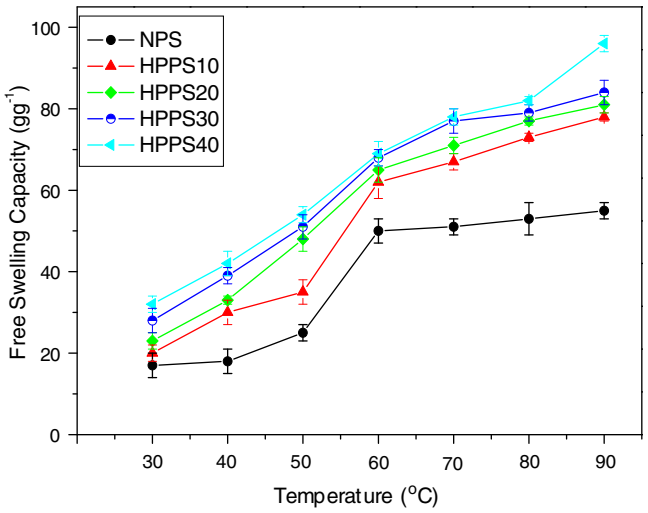

Fig. 4. Effect temperature on swelling capacity of native and hydroxypropyl plantain starch. NMS, native plantain starch; $HPPS_{10–40}$, hyroxypropyl plantain starches with MS 0.07, 0.15, 0.17 and 0.18, respectively. The reaction conditions of preparation are given in Table 2.

3.7. Freeze–thaw stability

The Freeze–thaw stability of native and hydroxypropylated starch derivatives is presented in Table 4. NPS showed syneresis from the first cycle while hydroxypropyl starches started showing syneresis from the fourth cycle. It is noteworthy that $HPPS_{30}$ and $HPPS_{40}$ showed syneresis only from sixth cycle. Remarkably, syneresis reduced after starch hydroxypropylation and reductions in syneresis were observed as the MS of the hydroxypropyl starches increased. Similar observations have been reported for hydroxypropyl corn and amaranth starches (Pal et al., 2002), hydroxypropyl potato starches (Kaur et al., 2004). The poor stability in freeze–thaw of NPS indicates that extensive retrogradation occurs during the frozen storage and this could be reduced remarkably with hydroxypropylation. It is reasonable that the hydrophilic hydroxypropyl groups prevented the water in the starch paste from separation.

3.8. Differential scanning calorimetry and retrogradation properties

Thermal and retrogradation properties of native and hydroxypropylated plantain starches are presented in Table 5. The onset gelatinization temperature (T_o) of native plantain starch is 82.7 °C and this reduced after hydroxypropylation. It was observed that T_o reduced as MS increased among the hydroxypropyl starches. Similar observations were recorded for peak temperature (T_p) and enthalpy of gelatinization (ΔH). In addition, hydroxypropylation increased the gelatinization temperature range and increases were observed as MS of the starch derivatives increased. Increases in gelatinization temperature range are attributed to inhomogeneity of the starches after hydroxypropylation. Also, introduction of the bulky hydroxypropyl groups on the polymer backbone facilitates structural flexibility leading to reduction in gelatinization temperature. The enhanced structural flexibility also accounts for reduced enthalpy of gelatinization of the starch after hydroxypropylation. The reduction in gelatinization temperature could also be due to a reduction in the glass transition temperature, leading to a decrease in hydrogen bonding. This observation is also consistent with previous report on hydroxypropylated potato starch (Kaur et al., 2004). When the starch pastes were stored for 3 and 18 days, it was observed that gelatinization temperature range increased for all starches but shifted to lower values. The enthalpy of regelatinization after 3rd day (ΔH_{R3}) and 18th day (ΔH_{R18}) also reduced. Starch molecule recrystallization occurs in a less ordered manner in stored gels than in native starches. It is reasonable that less heat would be needed to regelatinize stored gels (Morikawa & Nishinari, 2000). Most important, the percentage retrogradation reduced considerably after modification and consistent reductions in percentage retrogradation were observed as MS of the hydroxypropyl starches increased. Reasonably, the introduction of bulky hydroxypropyl groups limited the rearrangement of molecular chains to the ordered structure after gelatinization and

Table 3
Effect of days of storage on turbidity of native and hydroxypropyl plantain starch pastes

Sample	MS	Days of storage of starch paste								
		D1	D2	D3	D4	D5	D6	D7	D30	ΔT
NPS	–	134 ± 3.0	303 ± 2.0	332 ± 4.0	373 ± 3.0	387 ± 4.0	412 ± 2.0	512 ± 2.0	1085 ± 3.0	951
$HPPS_{10}$	0.07	20.7 ± 0.1	21.5 ± 0.7	22.1 ± 1.3	23.6 ± 1.5	32.7 ± 1.2	31.6 ± 1.1	31.4 ± 1.2	32.4 ± 1.5	11.7
$HPPS_{20}$	0.15	22.0 ± 0.3	22.4 ± 0.2	23.9 ± 1.1	23.5 ± 0.9	23.4 ± 1.1	23.5 ± 1.2	23.5 ± 0.7	27.5 ± 1.6	5.5
$HPPS_{30}$	0.17	20.1 ± 0.2	21.1 ± 1.0	21.1 ± 1.1	22.7 ± 0.8	21.7 ± 1.0	21.9 ± 1.0	22.3 ± 1.1	24.3 ± 1.3	4.2
$HPPS_{40}$	0.18	17.8 ± 1.1	17.7 ± 1.2	17.8 ± 1.2	18.1 ± 1.2	18.6 ± 1.0	18.6 ± 1.2	18.5 ± 1.2	20.5 ± 0.9	2.7

Values are means ± standard deviations of three replicate determinations.
Turbidity values are given as NTU; NTU, Nephelometric Turbidity Units.
ΔT, change in turbidity = D30 − D1.
The conditions of preparation are given in Table 2.

Table 4
Effect of hydroxypropylation on the freeze–thaw stability of native and hydroxypropyl plantain starch

Sample	MS	Percentage syneresis[a]							
		1st cycle	2nd cycle	3rd cycle	4th cycle	5th cycle	6th cycle	7th cycle	8th cycle
NDS	–	7.31 ± 0.31	8.71 ± 0.33	9.22 ± 1.24	9.52 ± 1.75	10.43 ± 0.15	10.71 ± 1.12	11.78 ± 1.11	12.67 ± 1.22
$HPPS_{10}$	0.07	Nil	Nil	Nil	3.21 ± 0.01	3.23 ± 1.24	5.13 ± 0.02	6.11 ± 0.24	7.35 ± 1.13
$HPPS_{20}$	0.15	Nil	Nil	Nil	1.74 ± 0.01	2.00 ± 0.02	2.55 ± 0.09	4.71 ± 0.08	5.67 ± 1.29
$HPPS_{30}$	0.17	Nil	Nil	Nil	Nil	Nil	2.51 ± 0.02	4.12 ± 0.04	5.16 ± 0.47
$HPPS_{40}$	0.18	Nil	Nil	Nil	Nil	Nil	2.11 ± 0.03	3.51 ± 0.08	3.23 ± 1.73

The conditions of preparation are given in Table 2.
[a] Values are means ± standard deviations of three replicate determinations.

Table 5
Thermal properties associated with gelatinization and retrogradation properties of native and hydroxypropyl plantain starch

Sample	1st day scan				3rd day scan					18th day scan				
	T_o (°C)	T_p (°C)	T_e (°C)	$T_e - T_o$ (°C)	ΔH (J/g)	T_o (°C)	T_p (°C)	T_e (°C)	$T_e - T_o$ (°C)	ΔH_{R3} (J/g)	R_3 (%)	T_o (°C)	T_p (°C)	T_e (°C)	$T_e - T_o$ (°C)	ΔH_{R18} (J/g)	R_{18} (%)
Native	82.7	98.6	102.4	19.7	16.4	31.9	54.1	64.4	32.5	5.2	31.7	56.7	71.3	82.9	26.2	10.4	63.4
$HPPS_{10}$	76.4	96.1	104.4	28.0	11.4	21.3	41.6	67.3	46.0	2.2	19.2	26.8	54.1	58.0	31.2	2.8	24.6
$HPPS_{20}$	65.6	93.5	107.2	41.6	11.0	20.2	41.6	68.9	48.7	1.6	16.0	23.4	53.6	55.8	32.4	2.6	23.6
$HPPS_{30}$	64.2	90.1	107.4	43.2	9.6	19.4	38.4	69.9	50.5	1.3	13.5	21.6	52.2	54.7	33.1	2.1	21.8
$HPPS_{40}$	61.5	90.0	108.1	46.6	9.1	19.0	37.9	72.7	53.7	1.2	13.1	20.1	51.7	53.9	33.8	1.8	19.8

Sample 1st day scan 3rd day scan 18th day scan.
T_o: Onset of gelatinization temperature; T_p: Peak of gelatinization temperature; T_e: Endset of gelatinization.
Temperature; ΔH: Enthalpy of first scanning; ΔH_{R3}: Enthalpy of retrogradation after 3 days of storage.
ΔH_{R18}: Enthalpy of retrogradation after 18 days of storage; R_3: Percentage retrogradation after 3 days of storage.
R_{18}: Percentage retrogradation after 18 days of storage.

this explains the efficiency of hydroxypropyl starch derivative in reduction of retrogradation even at low level of molar substitution.

4. Conclusion

Starch was isolated from unripe plantain and it was subjected to etherification with hydroxypropylation. Changes in the functional parameters after hydroxypropylation were investigated. The swelling capacity was improved after modification. Other relevant indices that could make the starch derivative useful in the industries such as paste clarity, reduction in syneresis and retrogradation improved after modification. The study also revealed that storage of starch paste could be improved with hydroxypropylation. With the intention of broadening the scope of its applications, the modifications were tailored within the confines of the limits allowed by appropriate regulation agencies for food application. Apart from food, the derivatives would also be relevant in other applications such pharmaceuticals and adhesives. In view of these, the potentials of a relatively new, cheap, underutilized but abundant starch resource are underscored in this work, with a view to bringing it to full industrial utilization.

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References

AACC (1984). Approved methods of the AACC (8th ed.). St. Paul, MN: American Association of Cereal Chemists.

Adebowale, K. O., & Lawal, O. S. (2002). Effect of annealing and heat moisture conditioning on the physicochemical characteristics of bambarra groundnut starch. *Nahrung/Food, 46*, 311–316.

Adebowale, K. O., & Lawal, O. S. (2003a). Functional properties and retrogradation behaviour of native and chemically modified starch of mucuna bean (*Mucuna pruriens*). *Journal of the Science of Food and Agriculture, 83*, 1541–1546.

Adebowale, K. O., & Lawal, O. S. (2003b). Microstructure, physicochemical properties and retrogradation behaviour of mucuna bean (*Mucuna pruriens*) starch on heat moisture treatment. *Food Hydrocolloids, 17*, 265–272.

Adebowale, K. O., Afolabi, T. A., & Lawal, O. S. (2002). Isolation, chemical modification and physicochemical characterisation of bambarra groundnut (*Voandzeia subterranean*) starch and flour. *Food Chemistry, 78*, 305–311.

Agunbiade, S. O., & Longe, O. G. (1999). The physico-functional characteristics of starches from cowpea (*Vigna unguiculata*). Pigeon pea (*Cjanus cajan*) and yambean (*Sphenostylis stenocarpa*). *Food Chemistry, 65*, 469–474.

Akintayo, E. T., Oshodi, A. A., & Esuoso, K. (1999). Effects of NaCl, ionic strength and pH on the foaming and gelation of pigeon pea (*Cjanus cajan*) protein concentrates. *Food Chemistry, 66*, 51–56.

Azemi, B. M. N. M., & Wootton, M. (1994). Distribution of partial digestion products of hydroxypropyl derivatives of maize and high amylose maize starches. *Starch, 46*, 440–443.

Bello-Perez, L. A., Agama-Acevedo, E., Sanchez-Hernandez, L., & Paredes-Lopez, O. (1999). Isolation and partial characterization of banana starches. *Journal of Agricultural and Food Chemistry, 47*, 854–857.

Blanshard, J. M. V. (1987). In T. Galliard (Ed.). *Starch: Properties and potential* (pp. 16). New York: Wiley.

Chrastil, J. (1987). Improved colorimetric determination of amylose in starches or flours. *Carbohydrate Research, 159*, 154–158.

Chuenkamol, B., Puttanlek, C., Rungsardthong, V., & Uttapap, D. (2007). Characterization of low-substituted hydroxypropylated canna starch. *Food Hydrocolloids, 21*, 1123–1132.

Cui, R., & Oates, C. G. (1999). The effects of amylose–lipid complex formation on enzyme susceptibility of sago starch. *Food Chemistry, 65*, 417–425.

Dias, F. F., Tekchandani, H. K., & Mehta, D. (1997). Modified starches and their use by food industries. *Indian Food Industry, 16*(4), 33–39.

Eggleston, G., Swennen, R., & Akoni, S. (1992). Physicochemical studies on starches isolated from plantain cultivars, plantain hybrids and cooking bananas. *Starch/Starke, 44*, 121–128.

Gernat, Ch., Radosta, S., Damaschun, G., & Schierbaum, F. (1990). Supramolecular structure of legume starches revealed by X-ray scattering. *Starch, 42*, 175–178.
Gray, J. A., & BeMiller, J. N. (2005). Influence of reaction conditions on the location of reactions in waxy maize starch granules reacted with a propylene oxide analog at low substitution levels. *Carbohydrate Polymers, 60*, 147–162.
Gwanfogbe, P. N., Cherry, J. P., Simmons, J. G., & James, C. (1988). Functionality and nutritive value of composite flours. *Tropical Science, 28*, 51–66.
Hizukuri, S. (1986). Polymodal distribution of the chain lengths of amylopectin and its significance. *Carbohydrate Research, 147*, 342–347.
Hizukuri, S., Kanebo, T., & Takeda, Y. (1983). Measurement of the chain length of amylopectin and its relevance of the origin of crystalline polymorphism of starch granules. *Biochemica et Biophysica Acta, 760*, 188–191.
Hoover, R., & Manuel, H. (1996). The effect of heat–moisture treatment on the structure and physicochemical properties of normal maize, waxy maize, dull waxy maize and amylomaize V starches. *Journal of Cereal Science, 23*, 153–162.
Hung, P. V., & Morita, N. (2005). Physicochemical properties of hydroxypropylated and cross-linked starches from A-type and B-type wheat starch granules – Review. *Carbohydrate Polymers, 59*, 239–246.
Islam, N., & Azemi, B. M. N. M. (1997). Rheological properties of calcium treated hydroxypropyl rice starches. *Starch, 49*, 136–141.
Johnson, P. N. T., & Brennan, J. G. (2000). Moisture sorption isotherm characteristics of plantain (*Musa*, AAB). *Journal of Food Engineering, 44*, 79–84.
Joint FAO/WHO Expert Committee on Food Additives (2001). In compedium of food additive specifications. Hydroxypropyl Starch, INS No. 1440. FAO Food and Nutrition Paper, Vol. 52, Add. 9. Geneva.
Kaur, L., Singh, N., & Singh, J. (2004). Factors influencing the properties of hydroxypropylated potato starches. *Carbohydrate Polymers, 55*, 211–223.
Kavitha, R., & BeMiller, J. N. (1998). Characterisation of hydroxypropylated potato starch. *Carbohydrate Polymers, 73*, 115–121.
Kayisu, K., Hood, L. F., & Vansoest, P. J. (1981). Characterization of starch and fiber of banana fruit. *Journal of Food Science, 46*, 1885–1890.
Kim, H. R., Hermansson, A. M., & Eriksson, C. E. (1992). Structural characteristics of hydroxypropyl potato starch granules depending on their molar substitution. *Starch, 44*, 111–116.
Lammers, G., Stanhuis, E. J., & Beenackers, A. A. C. M. (1993). Kinetics of the hydroxypropylation of potato starch in aqueous solution. *Starch, 45*, 227–232.
Lawal, O. S. (2004). Composition, physicochemical properties and retrogradation characteristics of native, oxidised, acetylated and acid thinned new cocoyam (*Xanthosoma sagittifolium*) starch. *Food Chemistry, 87*, 205–218.
Lawal, O. S., & Adebowale, K. O. (2005). An assessment of changes in thermal and physico-chemical parameters of jack bean (*Canavalia ensiformis*) starch following hydrothermal modifications. *European Food Research and Technology, 221*, 631–638.
Lawal, O. S., Lechner, M. D., Hartmann, B., & Kulicke, W. M. (2007). Carboxymethyl cocoyam starch: Synthesis, characterisation and influence of reaction parameters. *Starch, 59*, 224–233.
Liu, H. J., Ramsden, L., & Corke, H. (1999). Physical properties and enzymatic digestibility of hydroxypropylated ae, wx, and normal maize starches. *Carbohydrate Polymers, 40*, 175–182.
Marriott, J., Robinson, M., & Karikari, S. K. (1981). Starch and sugar transformation during the ripening of plantains and bananas. *Journal of the Science of Food and Agriculture, 32*, 1021–1026.
Morikawa, K., & Nishinari, K. (2000). Effect of concentration dependence of retrogradation behaviour of dispersions for native and chemically modified potato starch. *Food Hydrocolloids, 14*, 395–401.
Ogazi, P. O., & Jones, M. C. (1981). Plantain flour: Production and potential. *Paradiasca, 5*, 25.
Pal, J., Singhal, R. S., & Kulkarni, P. R. (2000). A comparative account of conditions of synthesis of hydroxypropyl derivative from corn and amaranth starch. *Carbohydrate Polymers, 43*, 155–162.
Pal, J., Singhal, R. S., & Kulkarni, P. R. (2002). Physicochemical properties of hydroxypropyl derivative from corn and amaranth starch. *Carbohydrate Polymers, 48*, 49–53.
Perera, C., & Hoover, R. (1998). The reactivity of porcine pancreatic alpha amylase towards native, defatted and heat–moisture treated potato starches before and after hydroxypropylation. *Starch, 50*, 206–213.
Perera, C., Hoover, R., & Martin, A. M. (1997). The effect of hydroxypropylation on the structure and physicochemical properties of native, defatted and heat–moisture treated potato starches. *Food Research International, 30*, 235–247.
Perez-Sira, E. (1997). Characterisation of starch isolated from plantain. *Starch, 2*, 43–45.
Ratnayake, W. S., Hoover, R., Shahidi, F., Perera, C., & Jane, J. (2001). Composition molecular structure, and physicochemical properties of starches from four field pea (*Pisum* sativum L.) Cultivars. *Food Chemistry, 74*, 189–202.
Santacruz, S., Koch, K., Svensson, E., Ruales, J., & Elisson, A. C. (2002). Three underutilised sources of starch from the Andean region in Ecuador: Part I. Physico-chemical characterisation. *Carbohydrate Polymers, 49*, 63–70.
Seow, C. C., & Thevamalar, K. (1993). Internal plasticization of granular rice starch by hydroxypropylation: Effects of phase transitions associated with gelatinization. *Starch, 45*, 85–88.
Shi, X., & BeMiller, J. N. (2000). Effect of sulphate and citrate salts on derivatization of amylose and amylopectin during hydroxypropylation of corn starch. *Carbohydrate Polymers, 43*, 327–333.
Tuschoff, J. V. (1986). Hydroxypropylated starches. In O. B. Wurzburg (Ed.), *Modified starches: Properties and uses* (pp. 90–95). Boca Raton, FL: CRC Press.
Vorwerg, W., Dijksterhuis, J., Borghuis, J., & Kröger, A. (2004). Film properties of hydroxypropyl starch. *Starch, 56*, 297–306.
Waliszewski, K. N., Aparicio, M. A., Bello, L. A., & Monroy, J. A. (2003). Changes of banana starch by chemical and physical modification. *Carbohydrate Polymers, 52*, 237–242.
Wooton, M., & Manatsathit, A. (1983). The influence of molar substitution on the water binding capacity of hydroxypropyl maize starches. *Starch, 35*, 92–94.
Wootton, M., & Haryadi, X. (1992). Effect of starch type and preparation conditions on substituent distribution in hydroxypropyl starches. *Journal of Cereal Science, 15*, 181–184.
Wootton, M., & Mahdar, D. (1993). Properties of starches from Australian wheats: Part 3. In vitro digestibility and hydroxypropyl derivatives. *Starch, 45*, 337–341.
Yeh, A., & Yeh, S. (1993). Some characteristics of hydroxypropylated and cross-linked rice starch. *Cereal Chemistry, 70*, 596–601.