

Starches from different botanical sources I: Contribution of amylopectin fine structure to thermal properties and enzyme digestibility

Sathaporn Srichuwong^a, Titi Candra Sunarti^b, Takashi Mishima^c,
Naoto Isono^a, Makoto Hisamatsu^{a,*}

^aDepartment of Sustainable Resource Sciences, Faculty of Bioresources, Mie University, 1515 Kamihama, Tsu 514-8507, Japan

^bDepartment of Agro-industrial Technology, Faculty of Agricultural Technology, Bogor Agricultural University, 220, Bogor 16002, Indonesia

^cField Science Center of Kii-Kuroshio Life Area, Faculty of Bioresources, Mie University, 2072-2 Takanoo, Tsu 514-2221, Japan

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Abstract

Fifteen starches from different botanical sources were selected to study the influence of structural features on thermal properties and enzyme digestibility. Morphological appearance, X-ray diffraction pattern, apparent amylose content, unit-chain length distribution of amylopectin, thermal properties and enzyme digestibility of starch varied with botanical source. It was demonstrated that the distribution of unit-chains of amylopectin significantly correlated with functional properties of the starches. Gelatinization temperature of native and retrograded starches decreased and increased with a relative abundance of unit-chains with an approximate degree of polymerization (DP) of 8–12 and 16–26, respectively ($P < 0.01$). Similar unit-chain lengths also affected the enzyme digestibility of starch granules ($P < 0.01$). © 2005 Elsevier Ltd. All rights reserved.

Keywords: Starch; Amylopectin; Degree of polymerization; Gelatinization; Retrogradation; Enzyme digestibility

1. Introduction

Normal starch consists of two types of polysaccharide. Amylose is fundamentally a linear molecule of α -1,4-linked glucan and occupies approximately 15–30% of starch, while amylopectin, the major component (70–85%), is a larger molecule with highly α -1,6 branched chains. Starch granules are thought to have alternative layers of crystalline and amorphous regions constructed by amylopectin and amylose. External chains of amylopectin are organized into double helices and some form crystalline structures (Wang, Bogracheva, & Hedley, 1998). When starch is heated in the presence of sufficient water, granules swell and the crystalline regions are disrupted. Molecular disordering, that is, gelatinization, is generally observed by differential scanning calorimetry (DSC) (Wang et al., 1998). The endothermic peak in DSC reflects the loss of double helices in amylopectin; a higher temperature and larger total energy

reflect stronger crystalline structures or more molecular orders (Cooke & Gidley, 1992). After gelatinization, the aggregation of starch molecules occurs; this is known as retrogradation. The recrystallization during long storage is attributed to the amylopectin fraction (Eliasson, 1985). It is well known that the gelatinization and retrogradation properties of starch reflect individual characteristics. In starches from the same botanical source, the gelatinization and retrogradation properties measured by DSC have been widely reported to be correlated with unit-chain length distribution of amylopectin (Matsuki, Yasui, Kohyama, & Sasaki, 2003; Nakamura et al., 2002; Noda et al., 1998; Shi & Seib, 1992, 1995; Vandeputte, Vermeylen, Geeroms, & Delcour, 2003a, b; Wong et al., 2003), but only a few studies have focused on starches isolated from different botanical sources (Silverio, Fredriksson, Andersson, Eliasson, & Aman, 2000).

The susceptibility of starch to hydrolysis by α -amylase has been shown to vary with botanical origin; nevertheless, it is not clear what structural features affect the degree of digestion. Extent of digestibility is known to be related to crystalline polymorphic forms, and it is accepted that starch with 'A' type X-ray diffraction is more susceptible to amylolysis than that with a 'B' type pattern

* Corresponding author. Tel.: +81 59 231 9614; fax: +81 59 231 9613.
E-mail address: hisamatsu@bio.mie-u.ac.jp (M. Hisamatsu).

(Jane, Wong, & McPherson, 1997; Planchot, Colonna, Buleon, & Gallent, 1997; Valetudie, Colonna, Bouchet, & Gallant, 1993). The inferior crystallites composing linked branch points and the shorter double helices of A-type starch would be more readily digested by α -amylase (Jane et al., 1997). In addition to the crystalline polymorphic form, the fraction of crystalline structures in the starch (Planchot et al., 1997), molecular associations between starch components (Dreher, Berry, & Dreher, 1984), amylose content (Fuwa, Nakajima, Hamada, & Glover, 1977; Noda et al., 2002), granule size (Snow & O'Dea, 1981; Valetudie et al., 1993), granule shape (Valetudie et al., 1993) and surface pores (Jane et al., 1997) have all been mentioned in enzyme digestibility. Among these factors, granular structure is considered to be the most important in defining the rate and extent of enzymatic hydrolysis (Zhang & Oates, 1999). Electron microscopy studies have shown that α -amylase attacks the granule surface before penetrating through internal channels then hydrolyzing the granule from inside out (Li, Vasanthan, Hoover, & Rossnagel, 2004). External chains of amylopectin that construct the crystalline structures of starch granules likely affect the rate of hydrolysis; nevertheless, information concerning the contribution of amylopectin unit-chain length distribution to the enzyme digestibility of various starches has not been reported.

The crystalline structures of starch are expected to be different among botanical sources. In the present work, the structural characteristics, thermal properties and enzyme digestibilities of 15 starches from different plant origins were studied. The relationships between amylopectin unit-chain length distribution and functional properties were also discussed.

2. Materials and methods

2.1. Materials

Tubers of elephant yam (*Amorphophallus paeoniifolius*), new cocoyam (*Xanthosoma sagittifolium*), taro (*Colocasia esculenta*), water yam (*Dioscorea alata*) and lesser yam (*Dioscorea esculenta*), and roots of edible canna (*Canna edulis*) were collected from an experimental farm in Java, Indonesia. Roots of arrowroot (*Maranta arundinacea*) and tubers of yam bean (*Pachyrhizus erosus*) were obtained from local farms in Nakonrachasima and Chiang Mai, Thailand, respectively. Starches of sweet potato (*Ipomoea batatas*) and kudzu (*Pueraria lobata*) were purchased from a local market in Tsu, Japan. Starches of sago (*Metroxylon sagu*), cassava (*Manihot esculenta*), corn (*Zea mays*), rice (*Oryza sativa*) and potato (*Solanum tuberosum*) were a gift from Nihon Shokuhin Kako Co., Ltd (Tokyo, Japan).

Porcine pancreas α -amylase (EC 3.2.1.1) was purchased from Sigma-Aldrich Co. (St Louis, MO, USA) and isoamylase (EC 3.2.1.68) from *Pseudomonas amyloclavata* was purchased from Hayashibara Biochemical Laboratories, Inc. (Okayama, Japan).

2.2. Starch preparation

Tubers and roots were washed with water, peeled then cut into small pieces. The pieces were suspended in deionized water (1:4 w/v) and homogenized in a blender then the homogenate was filtered through two layers of muslin cloth. The filtrate was filtered through a net with a 125- μ m mesh width and allowed to settle. The supernatant was discarded and the precipitate was resuspended in distilled water and centrifuged at $240 \times g$ and 5 °C for 15 min. The supernatant was discarded together with brown material on the surface of the precipitate and the starch layer was resuspended in distilled water. The centrifugation and resuspension steps were repeated five times and the final material was dried in a convection oven at 40 °C for 24 h. Defatted starch was prepared according to Sunarti, Yoshio, and Hisamatsu (2001).

2.3. Scanning electron microscopy (SEM)

Starch granules were fixed onto a circular specimen stub with double-sided tape, coated with gold using an E-1010 ion sputter (Hitachi Science Systems, Ltd, Hitachinaka, Japan) then observed using an S-4000 scanning electron microscope (SEM) (Hitachi Science Systems, Ltd, Hitachinaka, Japan) with an accelerating voltage of 3 kV.

2.4. Starch granule size

Starch granules were fully suspended in water, and then the particle size distribution was examined by a particle size analyzer (Horiba, Ltd, CAPA-700, Kyoto, Japan).

2.5. X-ray diffraction pattern

The X-ray diffraction patterns of starch were obtained using a Miniflex X-ray diffractometer (Rigaku denki Co., Ltd, Tokyo, Japan). The instrument was operated at 10 mA and 30 kV and the scanning regions of the diffraction angle (2θ) were 4–30°. Relative crystallinity was calculated according to Cheetnam and Tao (1998).

2.6. Apparent amylose content

The iodine affinity of defatted starch was determined according to Takeda, Hizukuri, and Juliano (1987). Apparent amylose content was calculated by dividing the iodine affinity value of defatted starch by 20%.

2.7. Branch chain-length distribution

Unit-chains of amylopectin between degree of polymerization (DP) 6 and 30 were analyzed by fluorophore-assisted capillary electrophoresis essentially as described by Morell, Samuel, and O'Shea (1998). Starch was debranched with isoamylase and labeled with 8-amino-1,3,6-pyrenetrisulfonic

acid (APTS) according to Edwards et al. (1999). The labeled sample was diluted with distilled water and electrophoresis was conducted on an ABI PRISM 3100 Genetic Analyzer (Applied Biosystems, Foster City, CA, USA). The POP-6 polymer and 36-cm capillary (Applied Biosystems) were used. Electrophoresis was performed with Genetic Analyzer Buffer (Applied Biosystems) at 15 kV for 2 h, then data were collected and analyzed using Genescan 3.7 software (Applied Biosystems).

2.8. Differential scanning calorimetry (DSC)

The gelatinization properties of starch were analyzed using a differential scanning calorimeter (DSC 100P; Seiko instruments, Inc., Chiba, Japan). Starch (6 mg, dry starch basis) was weighed in an aluminium pan then 12 μ l of water was added. The pan was sealed and allowed to stand at room temperature for 12 h. An empty sealed pan was used as a reference. The scanning temperature range and heating rate were 15–120 °C and 2 °C/min, respectively. Onset (T_o), peak (T_p) and conclusion (T_c) temperatures (°C), and enthalpy change (ΔH , J/g of dry starch) were determined. To study the retrogradation of starch, gelatinized starch was stored at 4 °C for 2 days then at 37 °C for 7 days. The DSC

parameters of the retrograded starch were determined as described above.

2.9. Digestibility of raw starch by porcine pancreatic α -amylase

Enzymatic hydrolysis was performed as described by Spence and Jane (1999). Hydrolysis degree was defined as the amount of soluble saccharides (mg) per 100 mg of dry starch.

2.10. Statistical analysis

Determinations of apparent amylose content and thermal properties were done in triplicate; other tests were carried out in duplicate. The correlation coefficients among starch properties were evaluated using SPSS 11.0 software (SPSS, Inc., Chicago, IL, USA).

3. Results and discussion

3.1. Morphology, X-ray diffraction and apparent amylose content

The granule size and shape of the starches were diverse and species specific (Fig. 1, Table 1). A large average

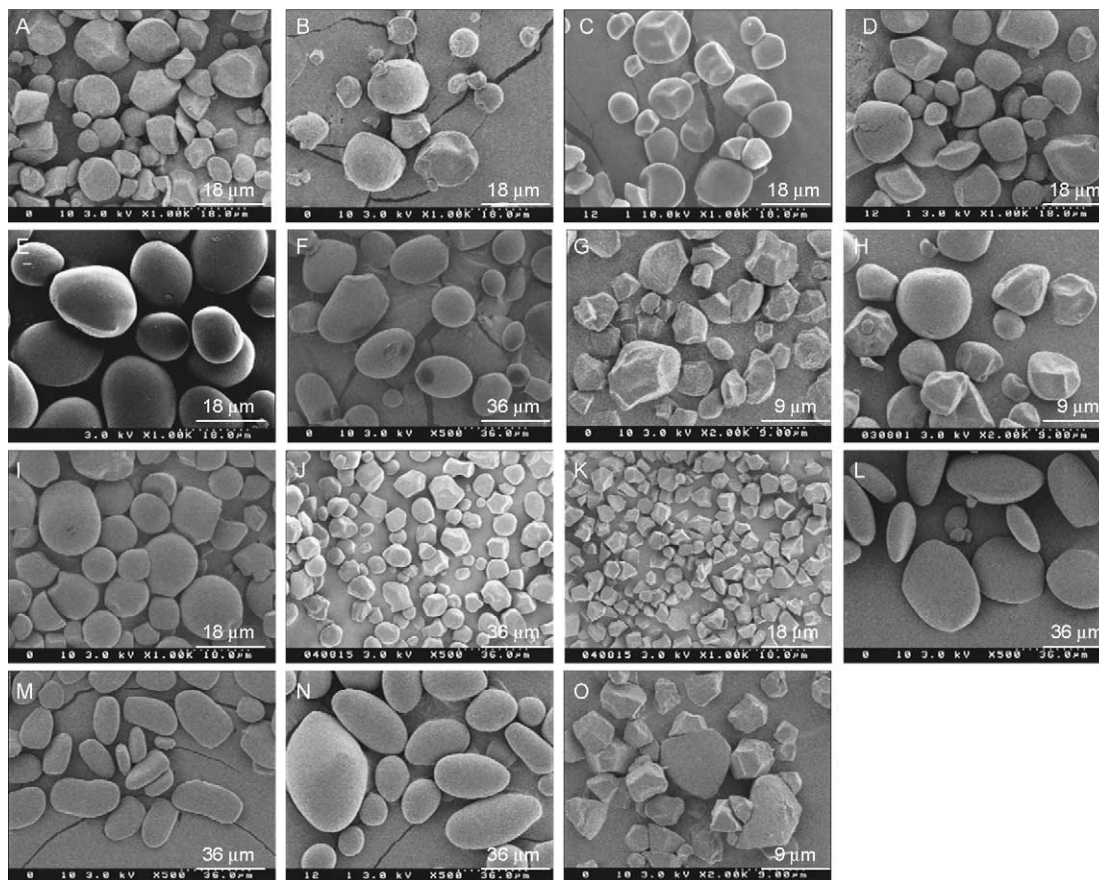


Fig. 1. Scanning electron micrographs of starches: (A) elephant yam, (B) new cocoyam, (C) sweet potato, (D) kudzu, (E) arrowroot, (F) sago, (G) taro, (H) yam bean, (I) cassava, (J) corn, (K) rice, (L) edible canna, (M) water yam, (N) potato and (O) lesser yam.

Table 1
Morphology and X-ray diffraction patterns

Starch source	Average size (μm)	Shape	X-ray type	Relative crystallinity (%)
Elephant yam	17.6 ± 6.8	Polygonal	A	34.2
New cocoyam	20.7 ± 8.1	Spherical, polygonal	A	33.2
Sweet potato	22.7 ± 11.4	Round, polygonal	A	34.4
Kudzu	19.9 ± 7.8	Round, polygonal	A	34.4
Arrowroot	35.1 ± 16.0	Oval, spherical	A	34.6
Sago	34.3 ± 22.5	Oval, spherical	A	32.9
Taro	5.3 ± 1.5	Polygonal	A	35.3
Yam bean	7.7 ± 4.1	Spherical, polygonal	A	36.0
Cassava	23.2 ± 21.4	Round	A	35.8
Corn	21.4 ± 6.2	Round, polygonal	A	31.0
Rice	4.7 ± 1.4	Polygonal	A	37.1
Edible canna	38.7 ± 30.2	Oval, elliptical	B	27.2
Water yam	33.8 ± 14.8	Rod like-round	B	29.5
Potato	42.3 ± 38.1	Oval, Spherical	B	29.8
Lesser yam	4.9 ± 1.3	Polygonal	C	27.8

granule size was shown in arrowroot, sago, edible canna, water yam and potato starches ($33.8\text{--}42.3\ \mu\text{m}$), and very small average size was found in taro, yam bean, rice and lesser yam starches ($4.7\text{--}7.7\ \mu\text{m}$). At high magnification using SEM, pinholes were observed on the surfaces of some

granules prepared from cereal crops (corn and rice), whereas the granules of the other plant species were smooth (data not shown). It has been postulated that pinholes are the result of enzyme degradation during seed germination (Jane et al., 2003).

The starches of elephant yam, new cocoyam, arrowroot, taro, yam bean, cassava, corn and rice showed a typical A-type X-ray diffraction pattern (Table 1). Sweet potato, kudzu and sago starches were classified into A-type starches, even though their diffraction patterns could be considered Ca-type (type C with characteristics of type A) (data not shown). Edible canna, water yam and potato starches gave the B-type diffraction pattern and lesser yam starch was classified into C-type. It was found that relative crystallinity for the A-type starches ($31.0\text{--}37.1\%$) was higher than those for B- ($27.2\text{--}29.8\%$) and C-type (27.8%) starches. A-type starch is thought to be more densely packed in helical structures (Wang et al., 1998). In addition, the amylopectin of A-type starch is thought to contain a higher proportion of shorter branched chains (Hizukuri, Kaneko, & Takeda, 1983) and a higher number of chains per cluster (Takeda & Hanashiro, 2003) than B-type starch. The C-type pattern is a mixture of A- and B-crystalline types.

Apparent amylose content varied between different plant species (Table 2). The highest value was observed in edible canna starch (27.9%), whereas the lowest value was observed in rice starch (13.2%). Since a limited amount of starch was available in some species, the absolute amylose content was not determined.

3.2. Branch chain-length distribution of amylopectin

To investigate the unit-chain length distribution of amylopectin, unit-chains of debranched starch were labeled

Table 2
Apparent amylose content and unit-chain length distribution of amylopectin

Starch source	Apparent amylose content (%)	Unit-chain length distribution (%)			
		DP 6–8	DP 9–12	DP 13–24	DP 25–30
<i>A-type</i>					
Elephant yam	25.2	5.6	26.8	60.5	7.1
New cocoyam	22.5	7.4	27.3	58.7	6.6
Sweet potato	19.8	11.0	27.9	54.1	7.0
Kudzu	19.6	9.8	26.4	55.8	8.0
Arrowroot	20.0	4.0	27.7	58.4	9.9
Sago	21.9	9.0	28.1	56.2	6.7
Taro	16.3	7.4	28.9	57.3	6.4
Yam bean	18.4	10.3	30.5	52.1	7.1
Cassava	17.9	9.9	36.3	48.3	5.5
Corn	23.4	5.1	31.4	56.7	6.8
Rice	13.2	8.0	34.5	52.1	5.4
<i>B-type</i>					
Edible canna	27.9	7.2	21.5	63.4	7.9
Water yam	20.8	3.9	18.9	67.5	9.7
Potato	18.0	10.2	23.5	58.9	7.4
<i>C-type</i>					
Lesser yam	14.2	11.6	24.9	56.2	7.3

with APTS and subjected to fluorophore-assisted capillary electrophoresis. The distribution profile and relative molar distribution were specific to the starch botanical origin (Fig. 2, Table 2). The profiles showed a maximum at DP 11–12 for A- and C-type starches and at DP 13 for B-type starches. Note that, a wide range of distribution patterns and relative abundances of very short chains with DP 6–8 was observed among botanical sources, and this was in agreement with the results of previous reports (Hanashiro,

Abe, & Hizukuri, 1996; Jane et al., 1999). Table 2 clearly shows that A-type starches contained higher proportions of chains with DP 9–12 (26.4–36.3%) than B- and C-type starches (18.9–24.9%). The proportions of longer chains with DP 13–24 of elephant yam, new cocoyam and arrowroot starches (58.4–60.5%) were comparable to those of B-type starches (58.9–67.5%). According to Hizukuri's revised cluster model of amylopectin (Hanashiro et al., 1996; Hizukuri, 1986), short chains with DP 6–24

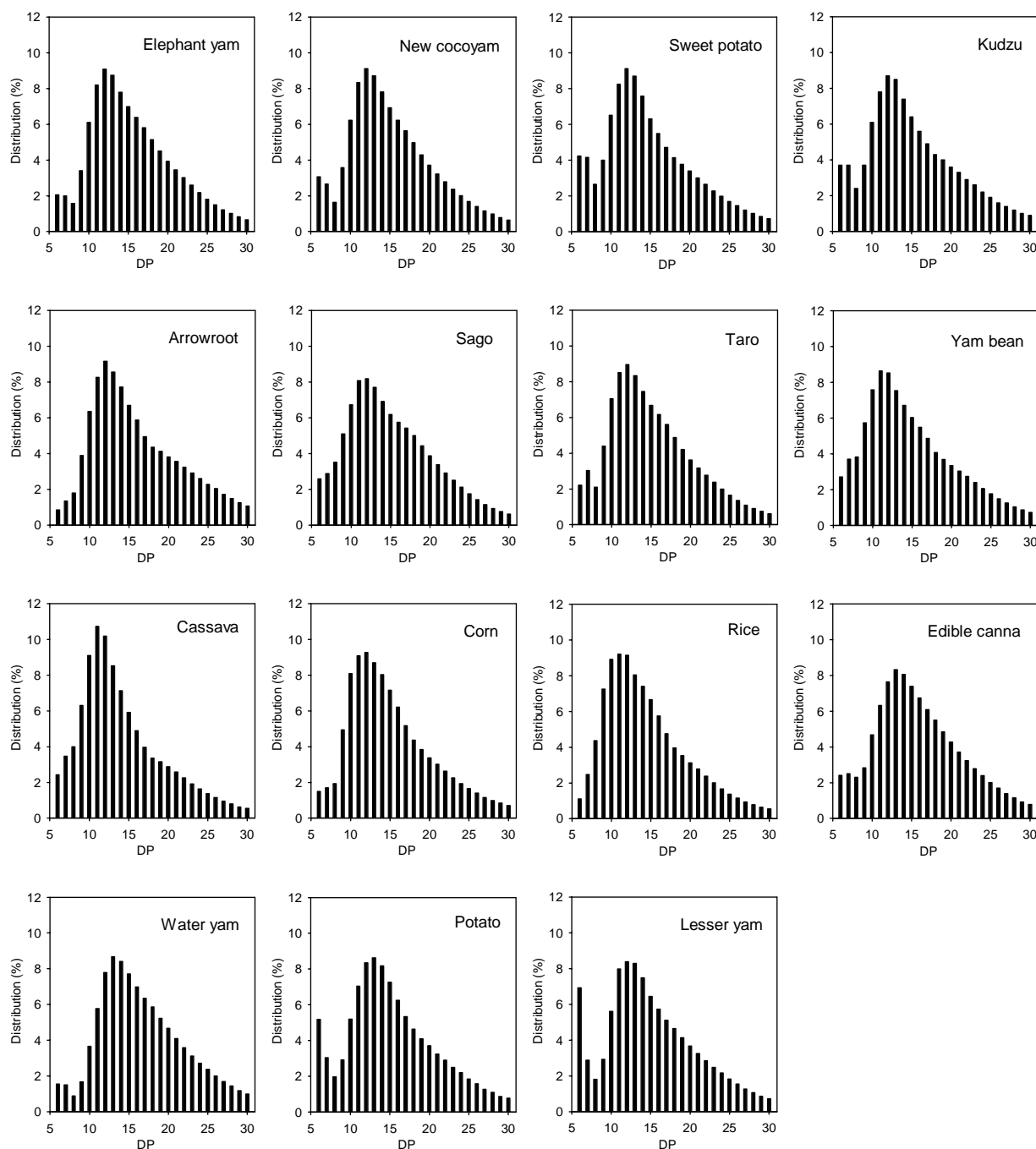


Fig. 2. Unit-chain length distribution of amylopectin analyzed by fluorophore-assisted capillary electrophoresis. Mean areas of peaks between DP 6 and DP 30 were summed and the relative molar distribution (%) of individual peak was expressed as a fraction of this sum.

comprise A and B1 chains. These short chains, which are arranged in double helices, are mostly located in the crystalline region of granules. Accordingly, the difference in distribution of unit-chains between DP 6 and 24 would very likely affect the crystalline structures of starches.

3.3. Thermal properties

Table 3 presents the gelatinization temperatures of native starches, namely, onset temperature (T_{oG}), peak temperature (T_{pG}) and conclusion temperature (T_{cG}) as well as gelatinization enthalpy on a dry starch basis (ΔH_G). Gelatinization temperature is a measurement of perfectness of starch crystallites (Tester & Morrison, 1990). High gelatinization temperatures were noticed in starches of elephant yam, new cocoyam, arrowroot, taro, water yam and lesser yam (T_{oG} , 71.9–78.2 °C; T_{pG} , 74.8–81.0 °C; T_{cG} , 82.4–91.4 °C). Cassava, corn, rice and potato starches were gelatinized by low temperatures (T_{oG} , 59.3–62.6 °C; T_{pG} , 65.5–67.3 °C; T_{cG} , 77.7–81.3 °C). The wide range of ΔH_G values (13.7–19.8 J/g) among starches might be due to differences in the overall degree of granular crystallinity (Tester & Morrison, 1990). The results of DSC study further support the large variation in the crystalline nature of each starch.

The DSC parameters of retrograded starches are presented in Table 3. The gelatinization temperatures of dissociating retrograded starch were lower than those of native starch. This might result from improper alignment of the starch chains during re-association, which causes formation of less ordered and/or less stable crystalline structures than those existing in native starch. Among

the parameters, the range of T_{oR} values (52.5–55.8 °C) was narrower than those of T_{pR} (60.3–66.6 °C) and T_{cR} (65.4–77.9 °C). According to DSC parameters, the re-crystallization degree of water yam was the greatest whereas those of cassava and rice starches were very small. The T_{oR} , T_{pR} and T_{cR} of A-type starches were lower than those of B-type starches. Similar findings were previously reported (Jane et al., 1999; Kalichevsky, Orford, & Ring, 1990). It was found that T_{pR} and T_{cR} were positively correlated with T_{pG} and T_{cG} , respectively ($P < 0.05$) (data not shown), except for those of edible canna and potato starches.

3.4. Digestibility by porcine pancreatic α -amylase

Remarkable differences in the digestibility of granular starches by α -amylase were observed (Fig. 3). As expected, A-type starches were more sensitively digested than B-type starches, and the digestibility of C-type starch (lesser yam) was intermediate between A and B-types. A wide range of digestibility was also observed within starches showing the same crystalline polymorphic forms (e.g. A-type starches). After 3 h, the hydrolysis degree of yam bean (40.0%), cassava (44.7%), corn (29.1%) and rice (61.7%) starches were much higher than those of other starches (less than 20%). At hour 72 of incubation, the greatest hydrolysis degree was shown in rice starch (89.0%) followed by yam bean (88.9%) and cassava (88.4%) starches. Sago starch was hydrolyzed to a lesser degree than other A-type starches (44.6% after 72 h). It was found that the hydrolysis degree of B-type starches did not significantly change with increased incubation time and only 2.5–7.2% of starch was hydrolyzed after 72 h.

Table 3
Thermal properties of starches

Starch source	Gelatinization ^a				Retrogradation ^b			
	T_{oG} (°C)	T_{pG} (°C)	T_{cG} (°C)	ΔH_G (J/g)	T_{oR} (°C)	T_{pR} (°C)	T_{cR} (°C)	ΔH_R (J/g)
<i>A-type starch</i>								
Elephant yam	77.9	80.2	89.9	19.7	53.8	63.2	72.0	9.2
New cocoyam	74.3	77.2	87.3	13.7	53.0	62.1	70.5	9.2
Sweet potato	66.7	74.0	86.6	18.4	53.9	63.3	70.2	7.5
Kudzu	68.4	74.8	88.2	17.4	53.7	63.3	70.8	8.1
Arrowroot	73.5	75.9	86.8	17.5	53.6	63.3	72.8	8.5
Sago	65.4	70.4	81.9	17.0	52.5	61.5	69.5	7.8
Taro	74.2	77.4	86.4	16.2	53.6	62.5	69.5	7.7
Yam bean	66.4	70.9	81.5	16.0	53.2	61.7	69.2	6.8
Cassava	59.3	65.7	79.6	17.6	53.1	61.5	67.1	3.1
Corn	62.6	66.7	81.3	16.9	53.8	61.0	67.8	5.6
Rice	61.6	67.3	80.0	18.7	53.5	60.3	65.4	2.9
<i>B-type starch</i>								
Edible canna	67.4	70.0	78.9	18.7	55.2	65.8	76.2	8.7
Water yam	78.2	81.0	91.4	19.4	55.8	66.6	77.9	11.3
Potato	61.4	65.5	77.7	19.8	54.4	65.1	75.0	9.1
<i>C-type starch</i>								
Lesser yam	71.9	74.8	82.4	14.3	54.0	64.6	73.5	11.1

^a Onset temperature (T_{oG}), peak temperature (T_{pG}), conclusion temperature (T_{cG}) and enthalpy change (ΔH_G) of native starch.

^b Onset temperature (T_{oR}), peak temperature (T_{pR}), conclusion temperature (T_{cR}) and enthalpy change (ΔH_R) of retrograded starch.

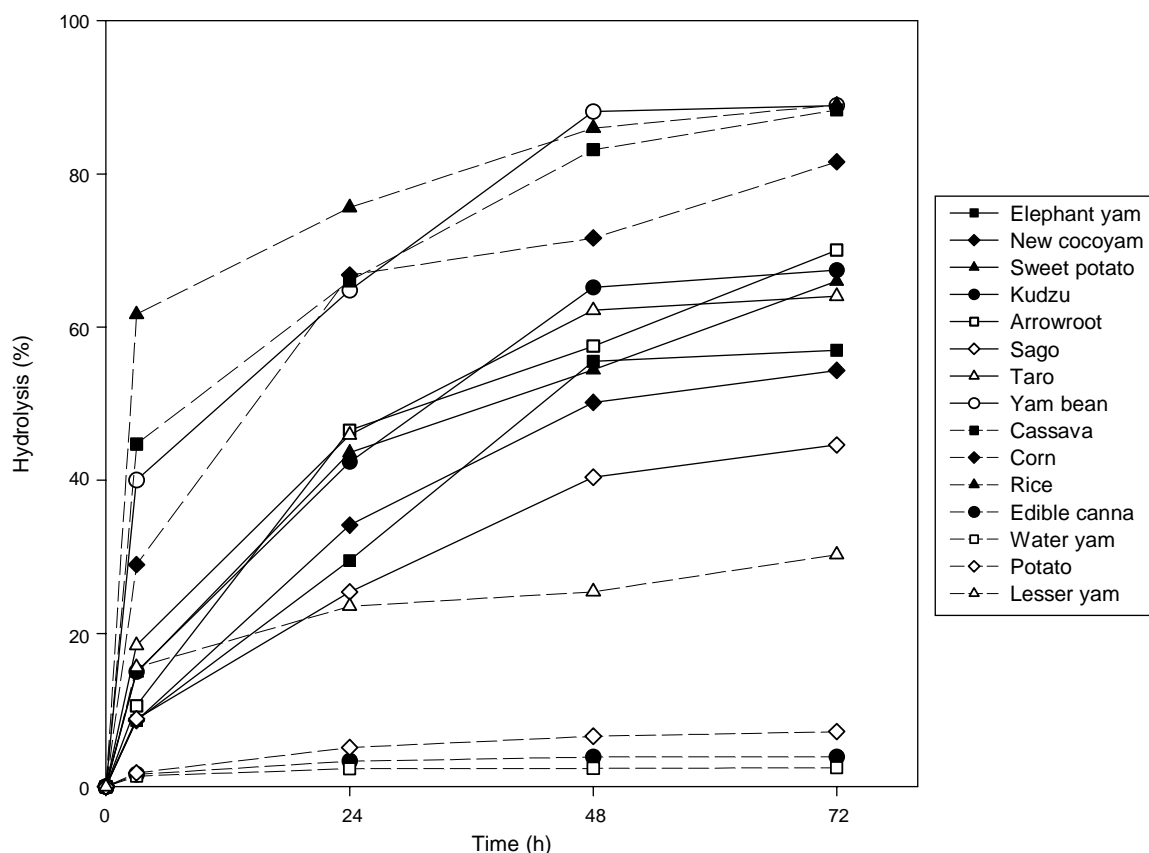


Fig. 3. Hydrolysis of starch granules by porcine pancreatic α -amylase.

3.5. Correlation analysis

No significant correlation was noticed between functional properties and average granule size, granule shape and apparent amylose content. In contrast, it was found that the relative abundances of amylopectin unit-chains were significantly correlated with gelatinization, retrogradation properties and enzyme digestibility (Fig. 4a–c, respectively). The results showed that the amylopectin unit-chains could be sorted into distinct groups by positive or negative correlation to functional properties.

It was previously mentioned that DSC gelatinization parameters are correlated with the amylopectin unit-chain length distribution of starches from the same botanical origins (Matsuki et al., 2003; Nakamura et al., 2002; Noda et al., 1998; Vandeputte et al., 2003a; Wong et al., 2003). This type of relationship is rarely reported when using starches from different botanical origins. Interestingly, regardless of the parameters of edible canna and potato starches, significant relationships between amylopectin unit-chain length distribution and gelatinization temperatures were obtained. The results showed that T_{oG} , T_{pG} and T_{cG} were negatively correlated with the proportion of each chain from DP 8 to 11, whereas positive correlations were found with longer chains from DP 16 to 25 ($n=13$,

$P<0.01$) (Fig. 4a). It is possible that gelatinization of edible canna and potato starches is influenced by their phosphorus content (Srichuwong, Sunarti, Mishima, Isono, & Hisamatsu, submitted). Phosphate monoesters on long B-chains of amylopectin may decrease the interaction between double helices and reduce gelatinization temperatures (Jane et al., 1999; Takeda & Hizukuri, 1982). Blennow, Bay-Smidt, Olsen, & Møller (2000) observed the weak positive correlations between gelatinization temperatures and the phosphate content of starches, the unit-chain length distribution of which was distinct from each other. The authors suggested that gelatinization of highly phosphorylated starches is probably affected by both unit-chain length distribution and phosphorus content. Our results suggest that gelatinization temperatures increase with longer unit-chains; nevertheless, a significant correlation between chain lengths and ΔH_G was not observed in this study. This might be due to differences in the total content of double helices of each species, which might be associated with the complexity of molecular order and amylopectin content (Russell, 1987).

The correlation plot in Fig. 4b shows that the values of T_{oR} , T_{pR} , T_{cR} , and ΔH_R were negatively correlated with the proportions of chains with DP 8–12, and positively with those of chains with DP 16–26 ($n=15$, $P<0.01$).

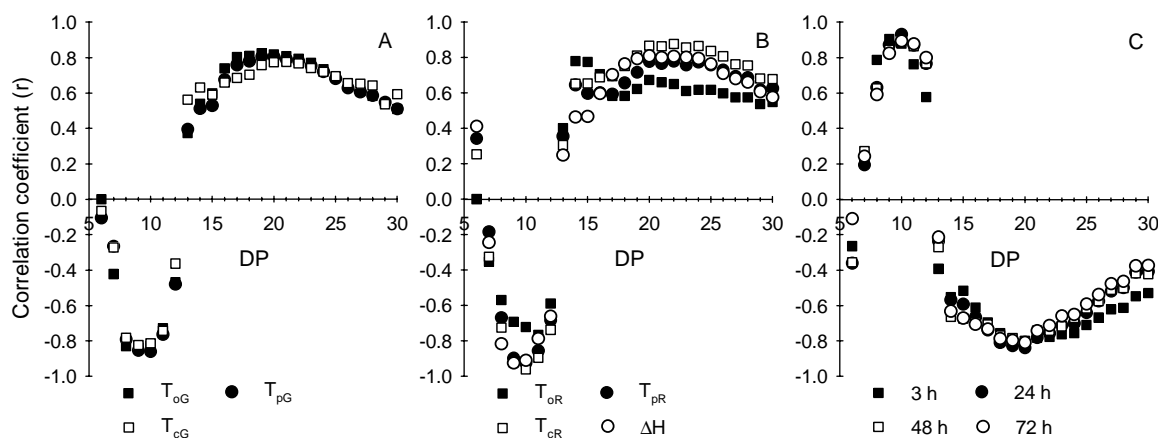


Fig. 4. The correlation coefficient between the proportion of amylopectin unit-chains with DP 6–30 and functional properties: (A) DSC parameters of native starches ($n=13$), (B) DSC parameters of retrograded starches ($n=15$) and (C) enzyme digestibility ($n=15$).

The results agree with previous reports where longer branch-chains increase the extent of retrogradation (Kaličevsky et al., 1990; Shi & Seib, 1992, 1995; Silverio et al., 2000; Vandeputte et al., 2003b). The significant correlation with T_{oR} , T_{pR} , T_{cR} , and ΔH_R implied that both the quality and quantity of ordered structures formed during constant conditions would be primarily affected by amylopectin unit-chain length distribution.

As shown in Fig. 4c, hydrolysis of starch granules by α -amylase was positively and negatively correlated with the proportions of unit-chains with DP 8–12 and DP 16–26, respectively ($n=15$, $P<0.01$). Such significant correlations were also found within A-type starches with chains approximately DP 8–11 and DP 18–23 ($n=10$, $P<0.01$) (data not shown). It is likely that the penetration of α -amylase at surface and internal channels of starch granules is influenced, to some extent, by the unit-chain length of amylopectin. This result also supports the finding that a decreased susceptibility to α -amylase hydrolysis is associated with a high gelatinization temperature (Zhang & Oates, 1999). One of the main factors for the digestibility of starch granules by amylase has been considered to be granule size (Snow & O'Dea, 1981; Valetudie et al., 1993). Weak negative correlations between enzyme digestibility and average granule size were also found in this study ($P>0.05$) (data not shown). Although the correlations were not significant, higher sedimentation rate and lower surface area of larger granules might also reduce the rate of digestibility.

Our statistical analysis revealed that relationships between amylopectin unit-chain length distribution and functional properties of starch can be obtained from starches with different botanical origins. These findings show that the molecular structure of amylopectin is a critical factor determining physicochemical properties. Longer chains would make long helices and strengthen

hydrogen bonds between chains, spanning the entire crystalline region. On the other hand, the existence of shorter chains, forming short or weak double helices, would produce inferior crystalline structures (Jane et al., 1999). Consequently, crystalline regions packed by high proportions of longer chains are more stable, which could retard gelatinization and enzymatic hydrolysis but facilitate re-crystallization, whereas a high proportion of shorter chains inversely affects these properties. As mentioned earlier, the distribution of very short chains ranging from DP 6 to 8 is characteristic for each starch; thus, insignificant correlations with functional properties could possibly be obtained (DP 6 and 7, Fig. 4). This result was similar to that observed in a previous study of different starches (Silverio et al., 2000), but different from studies on starches of the same botanical origins (Noda et al., 1998; Vandeputte et al., 2003a,b). In addition, it was noted that functional properties had a low correlation coefficients with unit-chains with DP 13 (Fig. 4). Possibly, the periodicity of chains with an approximate DP 13 might equally exist in crystallites of most starches and affect the different functional properties to a lesser extent.

4. Conclusion

Botanical source greatly affected the composition and functional properties of starch. Our results reveal the influences of amylopectin unit-chain length distribution on thermal properties and α -amylase digestibility of different starches. Unit-chains with approximately DP 8–12 and DP 16–26 critically affect those properties. In addition, very short branch-chains (DP 6–7) might not exhibit significant correlation with functional properties, if a wide range of botanical sources is considered. Further information on the roles of fine structures on swelling and pasting properties of

starch granules was reported in our accompanying paper (Srichuwong et al., submitted).

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