ELSEVIER

Carbohydrate Polymers 40 (1999) 57–70

Carbohydrate Polymers

Comparison of waxy potato with other root and tuber starches ☆

A.E. McPherson, J. Jane*

Center for Crops Utilization and Research and Department of Food Science and Human Nutrition, Iowa State University, 122 MacKay Hall, Ames, IA 50011-1120, USA

Received 13 July 1998; received in revised form 16 February 1999; accepted 22 February 1999

Abstract

The physicochemical properties of normal potato, waxy potato, yam and sweet potato starches were examined and compared. Normal potato and waxy potato starches displayed the B-type X-ray diffraction pattern, whereas yam and sweet potato displayed the C_A- and C-type, respectively. X-ray patterns of Naegeli dextrins of normal potato and waxy potato remained the B-type, but those of yam and sweet potato changed to the A-type. ^{31}P NMR showed the phosphorus contents of the starches to be primarily phosphate monoesters with no detectable phospholipid in any of the four starches. The chain-length distributions of debranched amylopectins of the starches were analyzed using high performance anion-exchange chromatography equipped with a post-column amyloglucosidase reactor and a pulsed amperometric detector. Normal potato and waxy potato starches displayed lower proportions (13 and 14.8%, respectively) of short branch chains of chain length dp 6–12 than did yam and sweet potato starches (17.1 and 19.0%, respectively). Normal potato displayed a larger proportion of long branch chains than did waxy potato amylopectin. The average amylopectin branch chain lengths of normal potato, waxy potato, yam and sweet potato starches were dp 28.6, 25.8, 25.8 and 26.3, respectively. The Naegeli dextrins of all four starches displayed linear and singly branched chains, but no multiply branched chains. The Naegeli dextrins of normal potato, waxy potato, yam and sweet potato starches displayed ratios of branched to linear branch chains of 0.31, 0.36, 0.42 and 0.51, respectively. The absolute amylose contents of the four starches were normal potato, 18.3%; waxy potato, 0%; yam, 17.7%; and sweet potato, 22.8%.

Keywords: Naegeli dextrins; X-ray diffraction; Pasting; Starch; Amylopectin

1. Introduction

Normal potato starch is widely used in food and industrial applications and is economically important in the United States and Europe (Mitch, 1984). Normal potato starch has been well-studied and is known to give a B-type X-ray diffraction pattern. Waxy potato starch is a recently developed potato mutant that is devoid of amylose content and has not been extensively studied. Sweet potato starch is widely used in Asia in a variety of food and industrial applications (Tian, Rickard, & Blanshard, 1991). Yam starch is used in parts of Africa for food and limited industrial applications (Coursey, 1967; Emiola & DeLarosa, 1981). Sweet potato starch has been reported to be of the A-, C_A- and C-type X-ray diffraction pattern (Watanabe et al., 1982; Takeda, Tokunaga, Takeda, & Hizukuri, 1986; Hanashiro, Abe, & Hizukuri, 1996). The X-ray diffraction pattern for many starches is affected by sample preparation (Nara, Mori, & Komiya, 1978) and by growth conditions and maturity of the parent plant at the time of harvest (Sugimoto, Yamamoto, Abe, & Fuwa, 1987; Noda et al., 1995). These effects may be more profound in C-type starches, because they are reported to be a mixture of A- and B-type crystalline polymorphs (Wu & Sarko, 1978; Watanabe et al., 1982; Zobel, 1988).

Average branch chain lengths of amylopectins are highly correlated to the crystalline polymorphs observed in the native starch (Hizukuri, 1985). A-type starches contain shorter average branch chain lengths of amylopectins, whereas B-type starches contain longer average branch chain lengths (Hizukuri, Kaneko, & Takeda, 1983; Hizukuri, 1985; Hanashiro, Abe, & Hizukuri, 1996). C-type starches contain amylopectins with both long and short branch-chain lengths. Recently, Hanashiro et al. (1996) investigated the branch chain distributions of a number of starches by use of high performance anion exchange chromatography with pulsed amperometric detection. The authors examined starches of the A-, B-, and C-types and divided the proportions of branch chains into dp 6–12, 13–24, 25–36 and ≥ 37.

In this study, we investigated chemical structures, including apparent and absolute amylose contents, amylopectin

☆ Journal paper no. 17964 of the Iowa Agriculture and Home Economics Experiment Station, Ames, IA, project no. 3258.

* Corresponding author. Tel.: + 1-515-294-5980.

0144-8617/99/$ - see front matter
PII: S0144-8617(99)00039-9

branch chain lengths and distributions, phosphate contents, Naegeli dextrin structures and physical properties including X-ray diffraction patterns, gelatinization and retrogradation properties. The results helped us to understand how chemical structures affect the properties of starch.

2. Materials and methods

Normal potato starch was purchased from Sigma Chemical Co. (St. Louis, MO, USA). Waxy potato starch was a gift from Lykkeby Starkelsen Food and Fiber AB, Lykkeby, Sweden. Yams (Dioscorea) and sweet potatoes (Ipomoea) were purchased from local markets, and their starches were isolated following the method of DeWilligen (1964).

2.1. Scanning electron microscopy

Scanning electron microscopy was performed by the method of Jane, Kasemsuwan, Leas, Zobel, and Robyt (1994). Starches were suspended in absolute methanol, and a drop of the suspension was placed on silver tape, sticky side down, attached to a brass disk and sputter coated with gold/palladium (60/40). The mounted specimens were observed using a scanning electron microscope (JEOL model 1850, Tokyo, Japan).

2.2. X-Ray diffraction patterns

The X-ray patterns of the starches and their Naegeli dextrins were obtained with copper, nickel foil filtered, Kα radiation using a diffractometer (D-500 Siemens, Madison, WI, USA) following the method of Jane, Wong, and McPherson (1997). The diffractometer was operated at 27 mA and 50 kV. The scanning region of the diffraction angle (2θ) was from 4 to 40 at 0.05 step size with a count time of 2 s. Starch and Naegeli dextrins were equilibrated at 100% relative humidity for 24 h at 25°C prior to examination.

2.3. Phosphorus content

Total phosphorus contents were determined chemically by the method of Smith and Caruso (1964). Samples were examined in triplicate. Structures and quantities of phosphorus derivatives also were determined with ^{31}P nuclear magnetic resonance (NMR) following the method of Kasemsuwan and Jane (1996).

2.4. Preparation of naegeli dextrins

Naegeli dextrins were prepared following the method of Umeki and Kainuma (1981). The starch (20 g, dry starch basis (dsb)) was suspended in 15.3% (vol/vol) H_2SO_4 and held at 38°C in an incubator. Starch suspensions were shaken daily by hand. Samples were taken on days 3, 6, 9, and 12, and the supernatant was siphoned off. An aliquot of the supernatant was analyzed for the total carbohydrate content to calculate the percentage starch hydrolyzed (Dubois, Gilles, Hamilton, Rebers, & Smith, 1956). The starch residues were washed with water until the washings reached pH 7. The samples were then dehydrated with absolute ethanol and dried at 30°C. Naegeli dextrins of normal potato starch were also prepared at 25°C for 3 months by the method of Kainuma and French (1971).

2.5. Molecular size distribution by gel permeation chromatography

An aliquot (5 ml) containing 15 mg starch with a glucose marker (0.5 mg) was injected into a column (2.6 cm, I.D. × 80 cm) packed with Sepharose CL-2B gel (Pharmacia, Inc., Piscataway, NJ, USA). Distilled and deionized water containing 10 mM NaOH and 50 mM NaCl was used to elute the sample in an ascending direction at 30 ml/h flow rate. Fractions of 4.8 ml were collected and analyzed using an Autoanalyzer II (Technicon Instrument Corp., Elmsford, NY, USA). The total carbohydrate by anthrone–sulfuric acid reaction and amylose–iodine blue value were measured at 630 and 640 nm, respectively (Jane & Chen, 1992). The blue value was used to identify the locations of the amylose and amylopectin in the chromatograms.

2.6. Amylose contents

Apparent amylose contents were determined by measuring iodine affinities of defatted starches by use of a potentiometric autotitrator with Metrodata recording software (702 SM Titrino, Brinkman Instrument, Westbury, NY, USA). The analysis was based on the Schoch (1964) method. Iodine affinities were measured in triplicate. Amylose was separated from amylopectin by the methods of Schoch (1942) and Jane and Chen (1992). The amylopectin fraction was purified five times by recrystallization. The iodine affinities of purified amylopectins were also determined and then were used to correct the overestimation of amylose content (Takeda, Takeda, & Hizukuri, 1983; Kasemsuwan, Jane, Schnable, Stinard, & Robertson, 1995). Absolute amylose contents were assessed by subtracting the iodine affinity of amylopectin from that of the defatted starch (Kasemsuwan et al., 1995).

2.7. Chain-length analysis by anion-exchange chromatography

Isolated amylopectins and Naegeli dextrins were subjected to enzymatic debranching by isoamylase following the method of Jane and Chen (1992). Chain-length distributions of the debranched amylopectins, the Naegeli dextrins and debranched Naegeli dextrins were quantitatively analyzed using a high-performance anion-exchange chromatograph equipped with a post column amyloglucosidase reactor and a pulsed amperometric detector (HPAEC-ENZ-PAD) (Wong & Jane, 1997). A mixture of homologous maltodextrins (dp 1–7) that contained equivalent

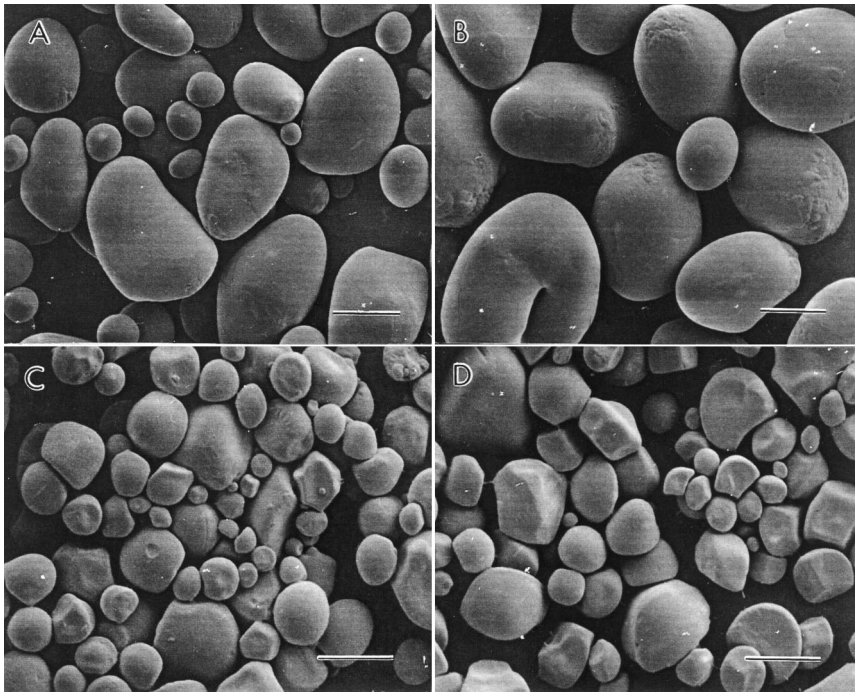

Fig. 1. Scanning electron micrographs of normal potato (A), waxy potato (B), sweet potato (C) and yam (D) starch granules. (Bars are 20 and 10 μm for A and B, and C and D, respectively.)

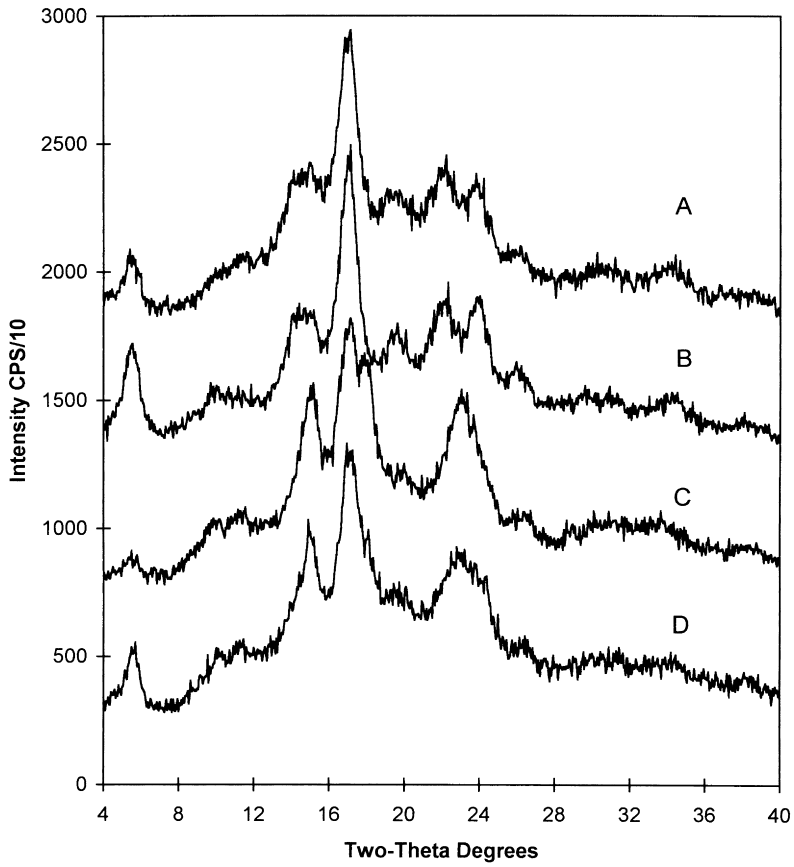

Fig. 2. X-ray diffraction patterns of normal potato (A), waxy potato (B), yam (C) and sweet potato (D) starches.

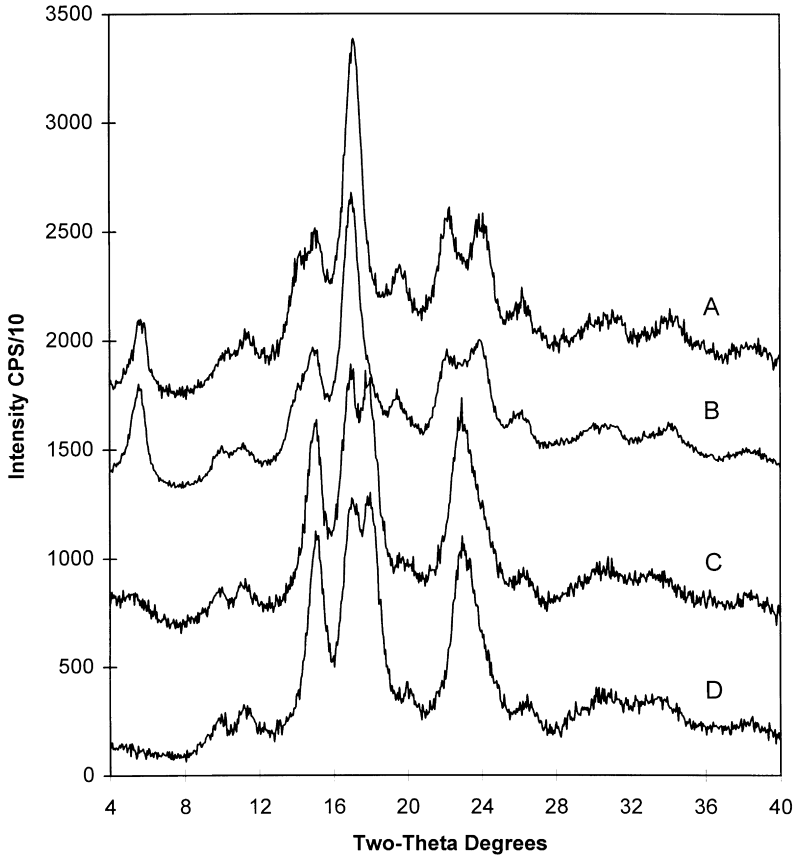

Fig. 3. X-ray diffraction patterns of 12-day Naegeli dextrins of normal potato (A), waxy potato (B), yam (C), and sweet potato (D).

concentrations (0.1 mg/ml) of each sugar was used to monitor the activity of the enzyme reactor and to calibrate the eluting volumes of the maltodextrins. The separation of a sample (25 μl, 1 mg/ml) with the system employed a PA-100 anion-exchange analytical column and a PA-100 guard column (Dionex, Sunnyvale, CA, USA) with a gradient composed of eluent A (100 mM NaOH) and eluent B (100 mM NaOH, 300 mM $NaNO_3$) at a flow rate of 0.5 ml/min. The separation gradient was: 0–5 min, 99% A and 1% B; 5–30 min, linear gradient to 8% B; 30–150 min, linear gradient to 30% B; 150–200 min, linear gradient to 45% B.

2.8. Thermal properties of starches determined by differential scanning calorimetry

Thermal properties of the starches were analyzed using a differential scanning calorimeter (DSC) (Perkin Elmer DSC-7) equipped with an Intracooler II System and Pyris thermal analysis software (Perkin–Elmer Corp., Norwalk, CT, USA). Starch and water suspensions (1:3) were sealed in aluminum pans and equilibrated at room temperature for 2 h before analysis. An empty aluminum pan was used as the reference. The samples were heated at 10°C/min over a temperature range of 25–100°C. Indium and naphthyl ethyl ether were used as reference standards. The gelatinization temperature and enthalpy change were determined following the procedure of Jane and Chen (1992). Enthalpy change (ΔH), onset temperature, (T_o), peak temperature (T_p) and conclusion temperature (T_c) were recorded. The analysis of the retrograded starches was done using the same method with the gelatinized samples having been stored at 4°C for 7 days. The data were calculated from at least three replications.

2.9. Pasting properties

Pasting properties of starches (8% dsb; 30 g total weight) were determined by using a rapid ViscoAnalyzer RVA-4 (Newport Scientific Pty. Ltd., Warriewood, NSW, Australia). A heating profile was programmed as follows: 1 min at 50°C, heat to 95°C at 6°C/min, hold for 5 min and cool to 50°C at 6°C/min. The rotating speed of the paddle was kept at 160 rpm throughout the measurement.

3. Results and discussion

Scanning electron micrographs of the four starches are shown in Fig. 1. Normal potato and waxy potato starches both showed large, rounded or oval granular shapes with axial diameters of 12–70 and 12–37 μm for normal potato and 12–72 and 14–44 μm for waxy potato starch. Yam and

Table 1
Phosphorus contents of starches and potato Naegeli dextrins

	Chemical method[a]	^{31}P NMR method[b]			
	Total phosphorus (%)	Total phosphorus(%)	Monoester phosphate	Inorganic phosphate	Phospholipid
Normal potato	0.075 ± 0.001	0.075 ± 0.006	0.073 ± 0.005	0.001 ± 0.001	ND[c]
Waxy potato	0.066 ± 0.001	0.069 ± 0.003	0.069 ± 0.003	0.001 ± 0.000	ND
Yam	0.012 ± 0.000	0.012 ± 0.005	0.011 ± 0.005	0.001 ± 0.000	ND
Sweet potato	0.020 ± 0.000	0.021 ± 0.007	0.020 ± 0.007	0.000 ± 0.000	ND

[a] Determined by the method of Smith and Caruso (1964).
[b] Determined by the method of Kasemsuwan and Jane (1994).
[c] ND: not detected.

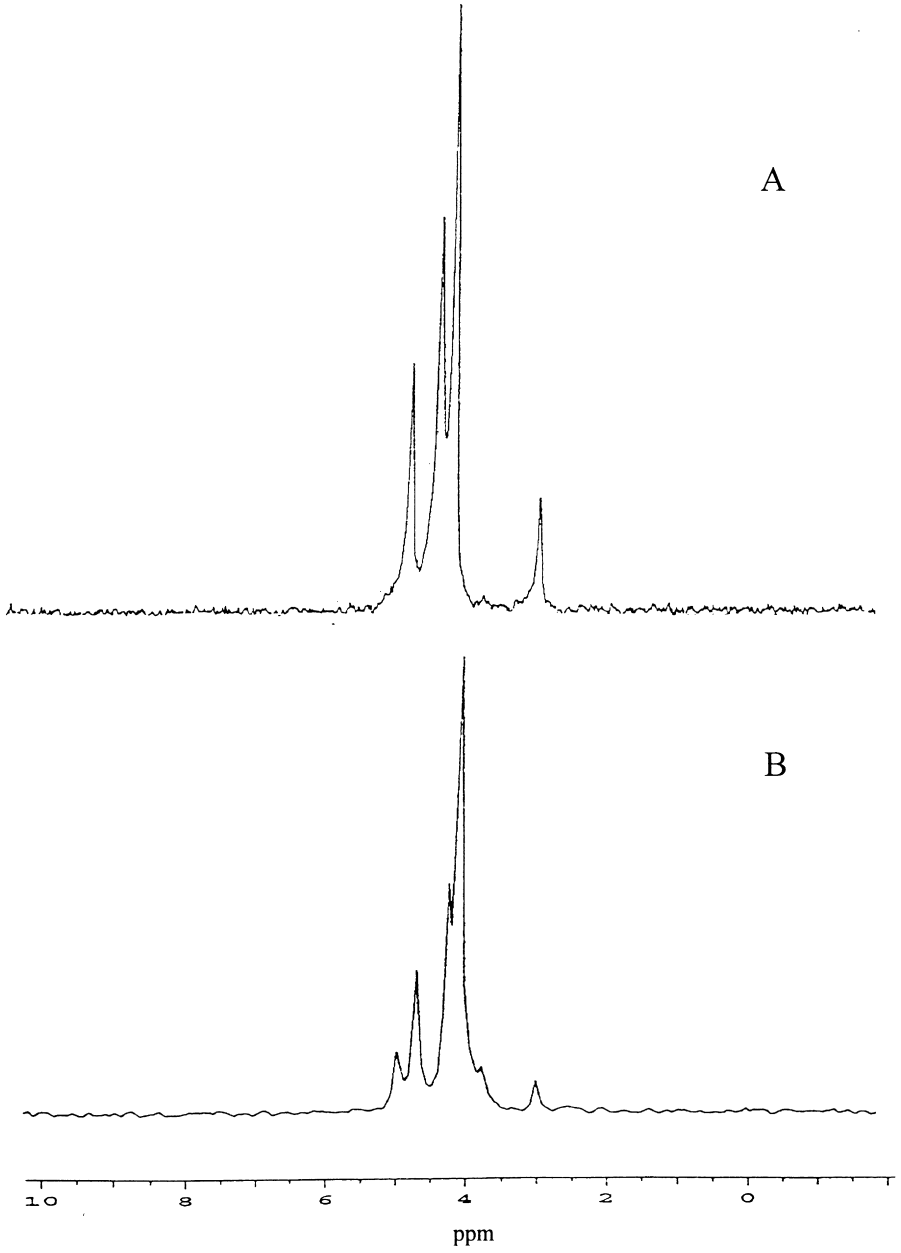

Fig. 4. The ^{31}P NMR spectra of (A) normal potato starch and (B) the Naegeli dextrin of potato starch.

Table 2
Percentage of amylose contents and iodine affinity in starches. (Amylose contents were determined by iodine potentiometric titration. The amylose contents were calculated by dividing iodine affinity by a factor of 0.20)

Starch	Iodine affinity of starch[a]	Iodine affinity of amylopectin and intermediate component[a]	Apparent amylose content (%)	Absolute amylose content (%)[b]
Normal potato	7.2 ± 0.3	4.6 ± 0.1	37.8 ± 1.4	18.3
Waxy potato	3.6 ± 0.4	3.6 ± 0.3	19.2 ± 2.0	0
Yam	5.4 ± 0.2	2.7 ± 0.3	29.2 ± 0.9	17.7
Sweet potato	6.3 ± 0.4	2.5 ± 0.4	33.1 ± 1.8	22.8

[a] Iodine affinities were calculated from at least three replications of each sample.
[b] Absolute amylose contents were calculated from the following equation: $C = (IA_S - IA_{AP+IC})/[0.19 - (IA_{AP+IC}/100)]$; C is the percentage of the real amylose content; IA_S is the iodine affinity of the whole defatted starch; IA_{AP+IC} is the iodine affinity of the amylopectin and intermediate component.

sweet potato starches had angular granules with diameters of 4–20 and 4–15 μm, respectively. The results were consistent with those reported by Jane et al. (1994). The presence of angular granule features may indicate the presence of the compound starch granules as reported by Shannon and Garwood (1984) for sweet potato.

X-ray diffraction patterns of the four starches are shown in Fig. 2. Normal potato and waxy potato starches both gave B-type X-ray diffraction patterns, whereas yam starch gave a C_A-type and sweet potato starch gave a C-type pattern. The X-ray diffraction patterns of the Naegeli dextrins of the starches after 12 days of acid hydrolysis are shown in Fig. 3. Naegeli dextrins of normal potato and waxy potato retained the same type X-ray diffraction pattern as their respective native parent starches with increased peak intensity, as previously reported by Kainuma and French (1971) and Jane et al., (1997). Whereas, the X-ray diffraction patterns of the 12-day Naegeli dextrins of yam and sweet potato displayed pronounced A-type characteristics (Fig. 3). As the C-polymorph is a combination of the A- and B-polymorphs, the results suggest that the B-polymorph of the starches is preferentially hydrolyzed. Bogracheva, Morris, Ring, and Hedley (1998) have reported that C-type pea starch has both the A- and B-polymorphs present in a single granule and the B-polymorph being at the hilum and the A-polymorph at the periphery. We also observed that more birefringence was retained at the periphery of acid-treated starch granules. More studies are needed to reveal if the B-polymorph is located at the hilum of the sweet potato and yam starches and is hydrolyzed during the acid treatment.

Phosphorus contents of the starches are shown in Table 1. Both normal potato and waxy potato starches contained more phosphorus than yam and sweet potato starches. ^{31}P NMR spectra showed the majority of the phosphorus in the starches was phosphate monoester with minor amounts as inorganic phosphate (Table 1), which was in agreement with those reported in the literature (Muhrbeck & Eliasson, 1991; Muhrbeck & Tellier, 1991; Lim & Seib, 1993; Bay-Smidt, Wischman, Olson, & Nielsen, 1994; Lim, Kasemsuwan, & Jane, 1994; Kasemsuwan, & Jane, 1996). None of these tuber and root starches contained phospholipids. The Naegeli dextrin of potato starch prepared by acid hydrolysis at 25°C for 3 months retained 65.1% of the total phosphorus and 45.2% of the original carbohydrate of the native starch. ^{31}P NMR spectra of potato starch and potato Naegeli dextrin, in aqueous solutions, showed that the structures of phosphate monoesters were preserved (δ 4.08 and δ 4.25 ppm for C-6 phosphate and δ 4.70 ppm for C-3 phosphate) as shown in Fig. 4. A small peak of free glucose 6-phosphate (δ 4.97 ppm), generated during acid hydrolysis, appeared in the spectra of the Naegeli dextrin. These results were consistent with the phosphate monoesters being present on amylopectin long B-chains at least nine glucose residues away from α-1, 6 branch points (Takeda & Hizukuri, 1982) and located within the crystalline region (Muhrbeck & Eliasson, 1991; Muhrbeck, Svensson & Eliasson, 1991). Thus, the phosphate monoesters were protected from acid hydrolysis.

Iodine titration of the defatted starch showed that normal potato starch contained more apparent amylose (37.8%) than sweet potato starch (33.1%), yam starch (29.2%) and waxy potato starch (19.4%) (Table 2). The apparent amylose content of sweet potato starch has been reported to range from 28 to 38% (Martin & Deshpande, 1985) and that of yam starch from 21.6 to 25.4% (Emiola & Delarosa, 1981) and 22% (Suzuki, Kanayama, Takeda, & Hizukuri, 1986). After subtraction of the iodine affinities of the amylopectins from those of the whole starches the absolute amylose contents were normal potato, 18.3%; waxy potato, 0%; sweet potato, 22.8%; and yam, 17.7% (Table 2). Molecular size distributions of the starches determined by gel permeation chromatography confirmed that waxy potato starch contained no amylose (Fig. 5). The proportions of amylose to amylopectin, calculated by the total carbohydrate in each peak, arbitrarily cut at the minimum points of both blue value and total carbohydrate, showed the amylose fraction of normal potato starch, 27.3%; yam starch, 25.0%; and sweet potato starch, 21.1%. The differences between these and the absolute amylose contents obtained by iodine titration may be attributed to amylopectin of smaller molecular weight present in the second peak. The molecular weight distributions also showed normal potato starch to have amylose of larger molecular weight

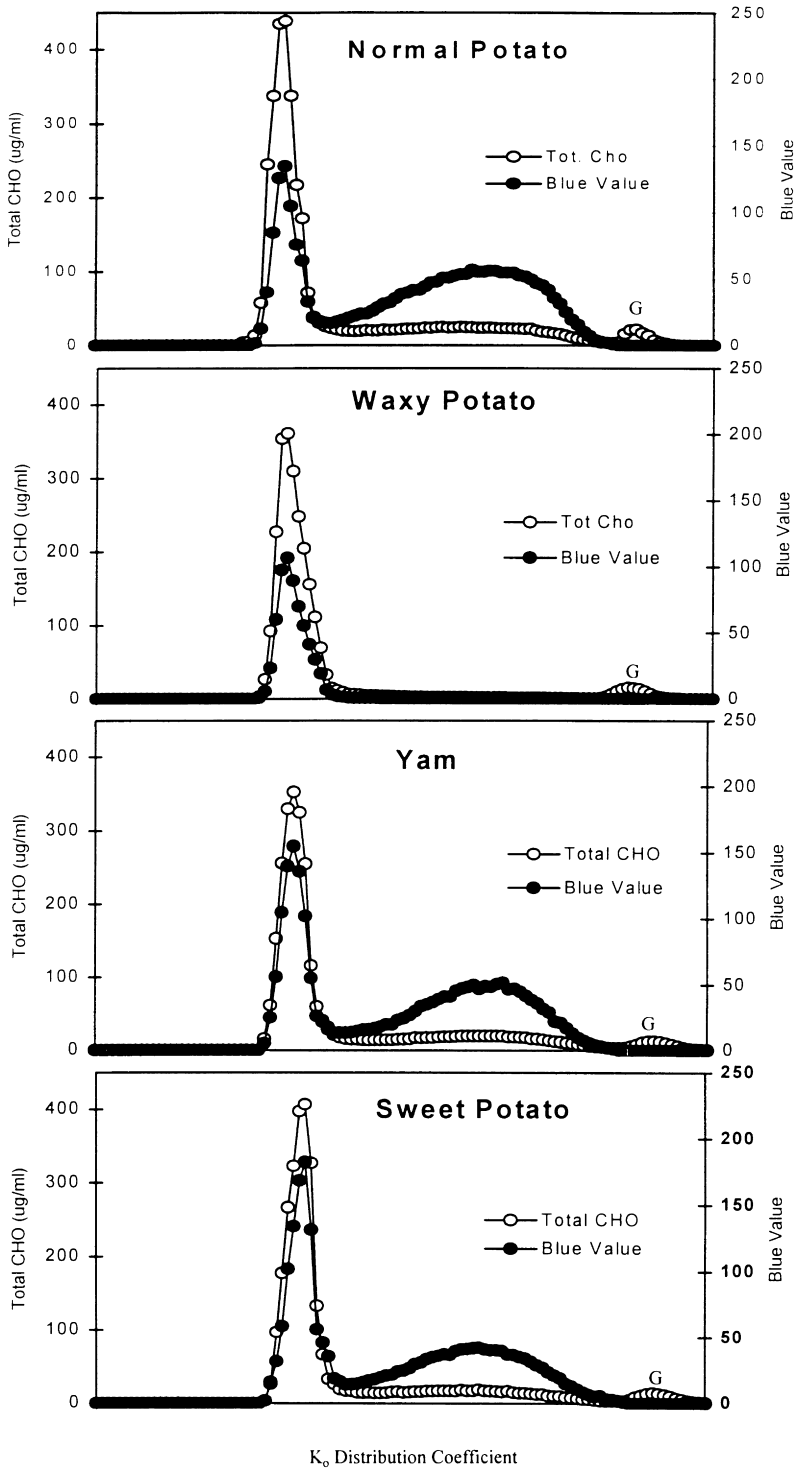

Fig. 5. Sepharose CL-2B column profiles of normal potato, waxy potato, yam and sweet potato starches.

than that of yam and sweet potato starches. The ratios of blue value to total carbohydrate peak intensities showed the amylopectins of normal potato and waxy potato starches developed less blue color than yam and sweet potato amylopectins, which may be attributed to the interference of phosphate monoesters.

The normalized branch chain length distributions of debranched amylopectins of the starches are shown in Fig. 6. The first peak in the bimodal peak distribution had a peak chain length of dp 14 for normal potato and waxy potato starches and dp 13 for the yam and sweet potato starches, while the second peak varied from chain length of dp 48–52 for all four starches (Table 3). Among the four starches, normal potato had the largest average chain length of dp

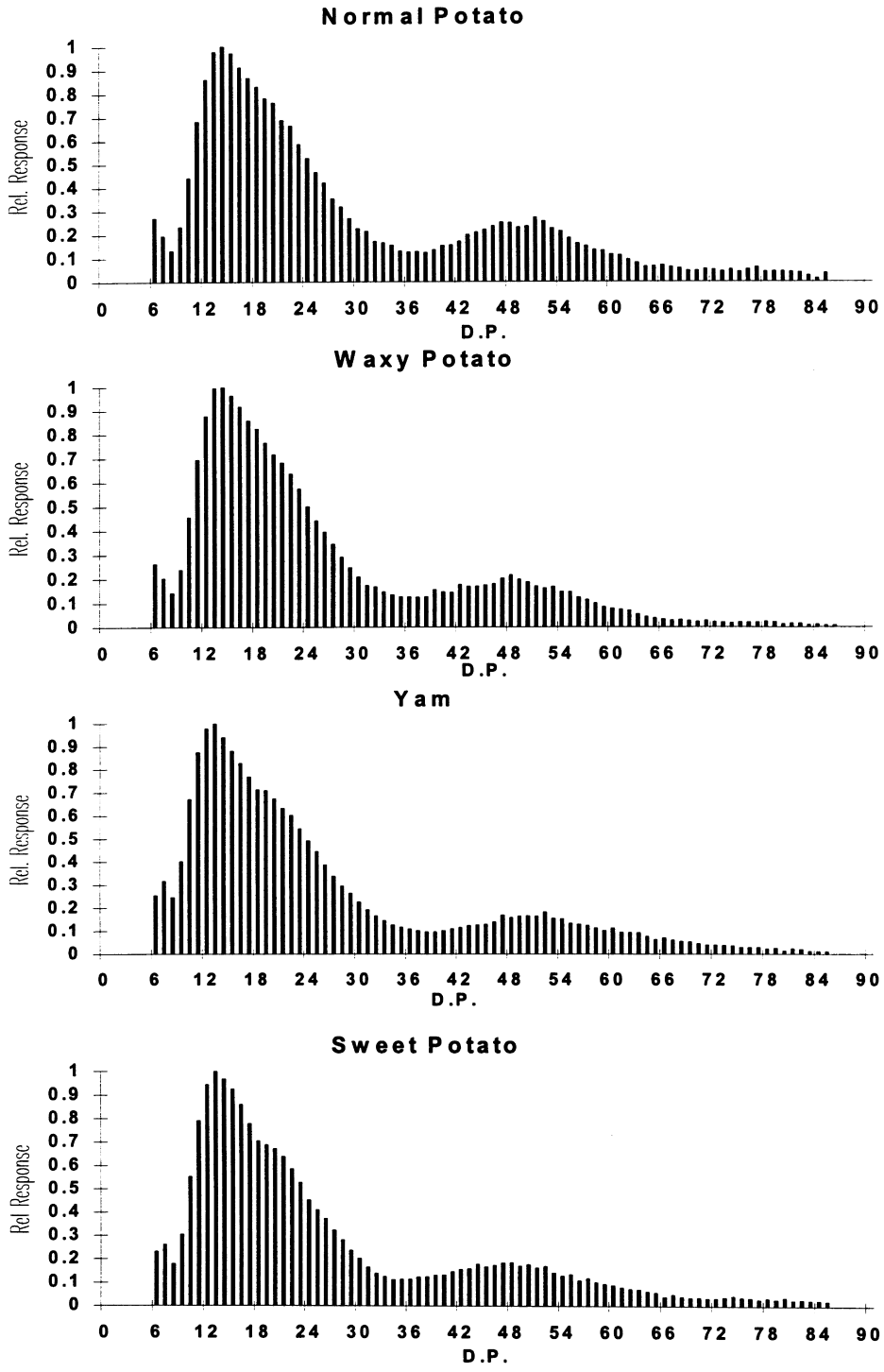

Fig. 6. Normalized peak area chromatograms of isoamylase debranched amylopectins of normal potato, waxy potato, yam and sweet potato starches produced by using high performance anion exchange chromatography equipped with an on-line amyloglucosidase reactor and a pulsed amperometric detector.

28.6. Sweet potato had an average chain length of dp 26.3, and yam and waxy potato both had an average chain length of dp 25.8. The yam and sweet potato amylopectins had larger proportions (19.09 and 17.05%, respectively) of short branch chains (dp 6–12), in comparison to normal and waxy potato amylopectins (13.07 and 14.75%, respectively) (Table 3). This result was consistent with that reported by Takeda et al. (1986). Normal potato amylopectin had a larger proportion (28.5%) of long branches (dp $\geq$ 37) than did waxy potato (22.43%), yam (21.80%) and sweet potato (23.44%) (Table 3). All the four starches had maximum detectable chain lengths at dp 85. These results are in agreement with previous work that B-type starches have

Table 3
Branch chain length (CL) distributions (results are the means of three replicates from the high performance anion-exchange chromatograph with pulsed amperometric detection (Fig. 6). The total relative peak area was used to calculate percent distribution

	First peak	Second peak	Percent distribution				Average CL	Maximum detectable DP
			DP 6–12	DP 13–24	DP 25–36	DP ≥ 37		
Normal potato	14	51	13.07 ± 0.02	44.39 ± 0.05	14.00 ± 0.02	28.54 ± 0.13	28.6	85
Waxy potato	14	49	14.75 ± 0.02	48.43 ± 0.04	14.38 ± 0.10	22.43 ± 0.03	25.8	85
Yam	13	52	19.09 ± 0.01	44.81 ± 0.09	14.32 ± 0.03	21.80 ± 0.05	25.8	85
Sweet potato	13	48	17.05 ± 0.02	48.10 ± 0.02	13.56 ± 0.02	23.40 ± 0.02	26.3	85

longer branch chains than do A- and C-type starches (Hizukuri, 1985).

Acid hydrolysis rates of the starches differed (Fig. 7). After 6 days, waxy potato starch had a higher extent of hydrolysis than did normal potato, yam and sweet potato starches (Fig. 7). HPAEC-ENZ-PAD chromatograms of the Naegeli dextrins after 12 days hydrolysis showed a peak chain length at dp 15 (65.0 min retention time) for the normal and waxy potato starches and dp 16 (66.4 min retention time) for the yam and sweet potato starches. A second peak was observed in each chromatogram, which corresponded to singly branched molecules, and occurred at dp 25–26 (~ 100 min retention time) (Fig. 8). After isoamylase debranching, the singly branched molecules were hydrolyzed to two linear molecules and the second peak disappeared (Fig. 9). The ratios of the peak heights of the branched molecules to those of the linear molecules were 0.31, 0.36, 0.42 and 0.52 for normal potato, waxy potato, yam and sweet potato Naegeli dextrins, respectively, and indicated that more branch chains were present in the

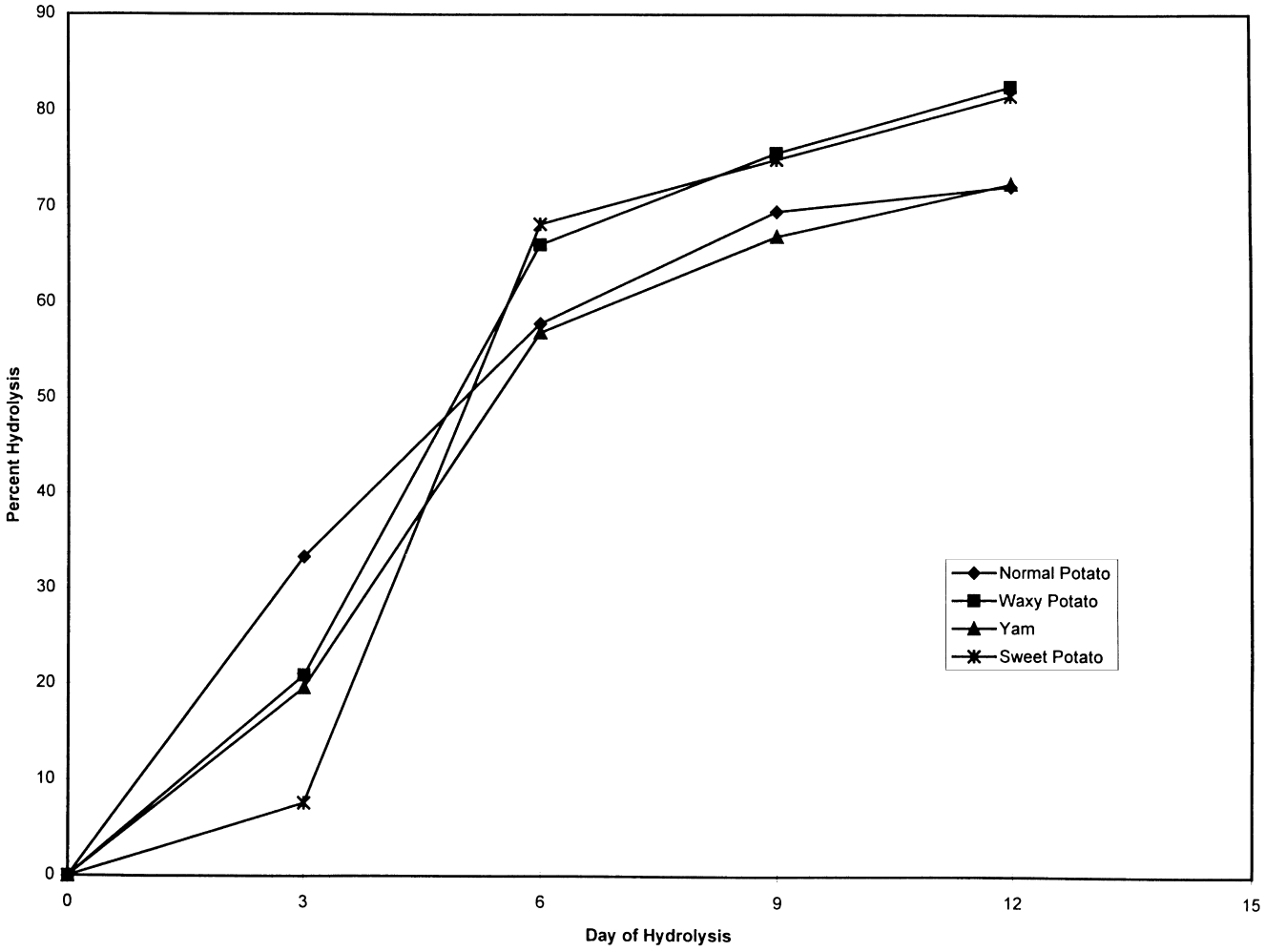

Fig. 7. Acid hydrolysis rates (15.3% H_2SO_4 v/v) of normal potato, waxy potato, yam and sweet potato starches.

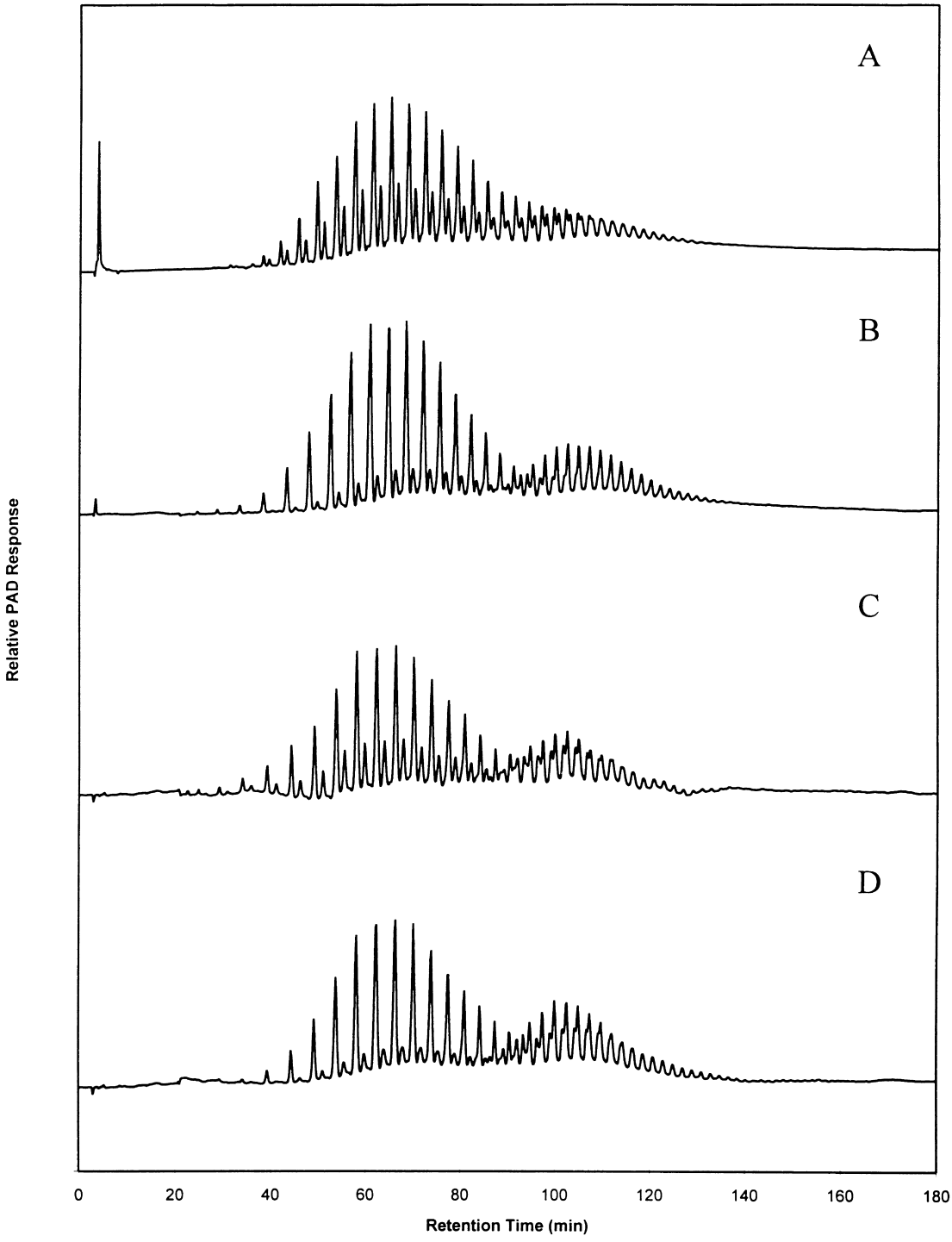

Fig. 8. Chromatograms of normal potato (A), waxy potato (B), yam (C) and sweet potato (D) 12-day Naegeli dextrins analyzed by use of high performance anion exchange chromatography equipped with an on-line amyloglucosidase reactor and a pulsed amperometric detector. Dextrin of dp 15 is eluted at 65 min.

Naegeli dextrins of yam and sweet potato starch. These results agreed with the models proposed by Jane et al. (1997), in which branch points in A-type starches are scattered throughout the amorphous and crystalline regions. Those α1-6 linkages present in the crystalline region were preserved in Naegeli dextrins of A-type starches. The majority of branch linkages of B-type starches are clustered in the amorphous regions, which were susceptible to acid hydrolysis. Thus, fewer branches were found in the Naegeli dextrins of B-type starches.

Thermal analysis by DSC (Table 4) showed gelatinization onset temperatures to be 60.8, 62.5, 64.6 and 57.9°C for

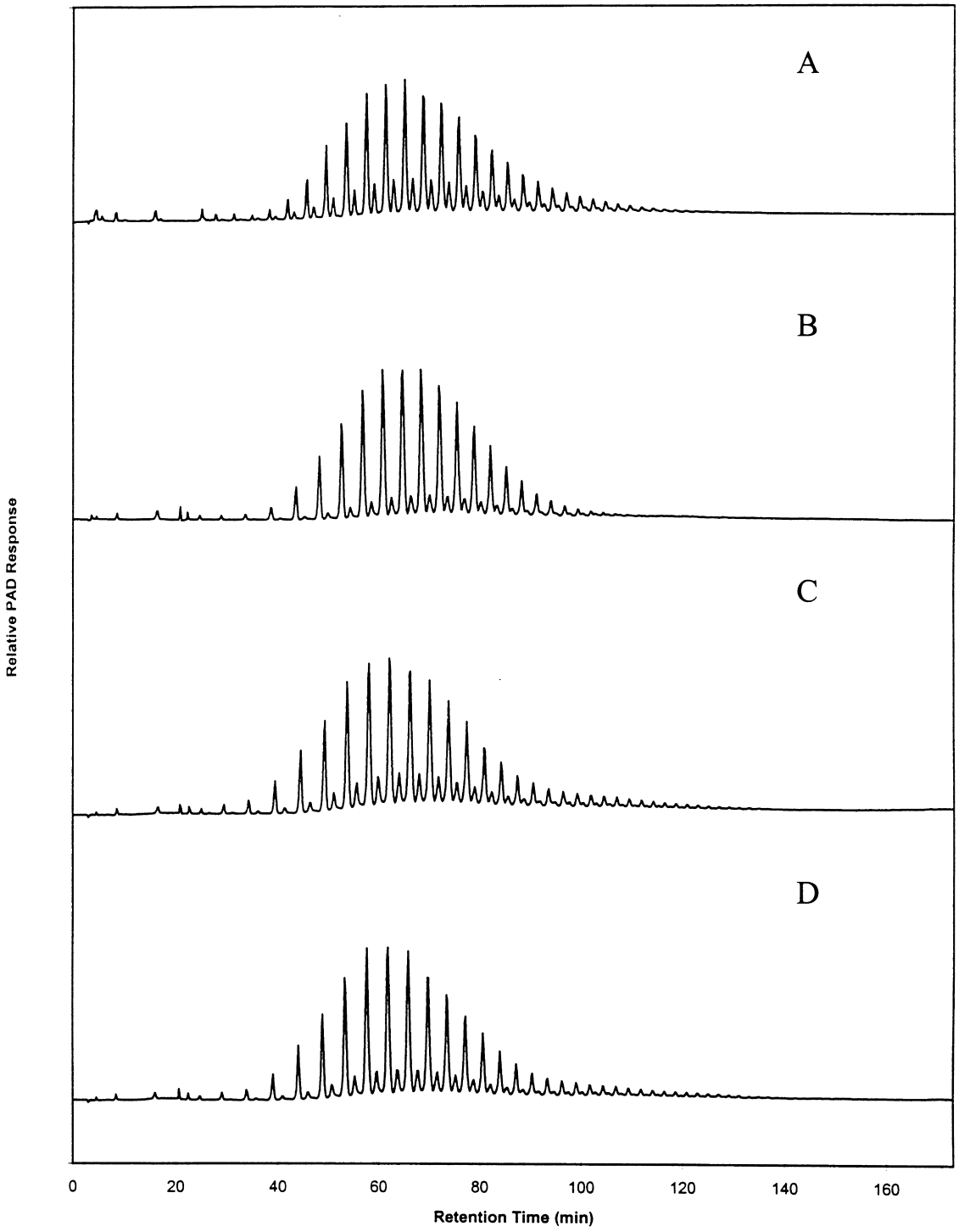

Fig. 9. Chromatograms of isoamylase debranched normal potato (A), waxy potato (B), yam (C) and sweet potato (D) 12-d Naegeli dextrins analyzed by use of high performance anion exchange chromatography equipped with an on-line amyloglucosidase reactor and a pulsed amperometric detector. Dextrin of dp 15 is eluted at 65 min.

normal potato, waxy potato, yam and sweet potato starches, respectively. Phosphate monoesters on amylopectin are known to decrease the gelatinization temperatures. Therefore, normal potato and waxy potato starches, despite their long amylopectin average branch chain lengths, had low onset gelatinization temperatures because of their large phosphate monoester contents. Yam starch, having a low concentration of phosphate monoester on its amylopectin, longer long B chains (peak dp 52) and more characteristics of the A-type polymorph, displayed a higher onset

Table 4
Thermal properties of starch gelatinization for native and retrograded starch as determined by differential scanning calorimetry (the values are the averages of at least three replications (mean ± standard deviation))

	Native starch				Retrograded starch				
	T_o[a] (°C)	T_p[b] (°C)	T_c[c] (°C)	ΔH[d] (J/g)	T_o[a] (°C)	T_p[b] (°C)	T_c[c] (°C)	ΔH[d] (J/g)	% Retrogradation[e]
Normal potato	60.8 ± 0.1	65.2 ± 0.0	70.6 ± 0.4	17.3 ± 0.3	41.1 ± 0.3	56.1 ± 0.1	66.4 ± 0.1	6.9 ± 0.5	40.1
Waxy potato	62.5 ± 0.2	66.6 ± 0.2	70.2 ± 0.4	18.2 ± 0.5	38.6 ± 0.3	56.0 ± 0.2	65.2 ± 0.2	7.8 ± 0.3	42.0
Yam	64.6 ± 0.2	70.9 ± 0.3	77.8 ± 0.4	13.3 ± 0.3	39.2 ± 0.1	51.9 ± 0.5	61.5 ± 0.2	5.0 ± 0.1	37.5
Sweet potato	57.9 ± 0.2	63.1 ± 0.1	71.9 ± 0.3	13.5 ± 0.6	39.9 ± 0.3	52.7 ± 0.4	63.2 ± 0.4	6.1 ± 0.3	44.8

[a] Onset temperature.
[b] Peak temperature.
[c] Conclusion temperature.
[d] Gelatinization enthalpy of starch.
[e] Percent retrogradation (retrograded starch enthalpy/native starch enthalpy).

gelatinization temperature. Sweet potato starch had relatively short B2 chains (peak chain length of dp 48), substantial phosphate derivatives (0.020%), more α1–6 branch linkages in its amylopectin crystalline region and a more pronounced shoulder at dp 18–20 indicating a defective crystalline structure, which may account for its lower onset gelatinization temperature. Normal potato and waxy potato starches had narrower ranges of gelatinization temperatures (8–10°C) than did yam and sweet potato starches (13–14°C). Enthalpy changes for the normal potato, waxy potato, yam and sweet potato starches were 17.3, 18.2, 13.5 and 13.3 J/g, respectively. Increasing amylose content decreases the enthalpy change (Inouchi, Glover, Sugimoto, & Fuwa, 1984). The large enthalpy changes in normal potato and waxy potato starches result from long amylopectin branch chains packing into large crystallites and waxy potato being composed of only amylopectin. The percentages of retrogradation of the four starches were similar.

Pasting properties of the starches determined by Rapid ViscoAnalyzer (RVA) are shown in Fig. 10. In contrast to most normal and waxy cereal starches, normal potato starch displayed a larger peak viscosity than waxy potato starch. This difference between normal potato and waxy potato starch was attributed to amylose, which by physically

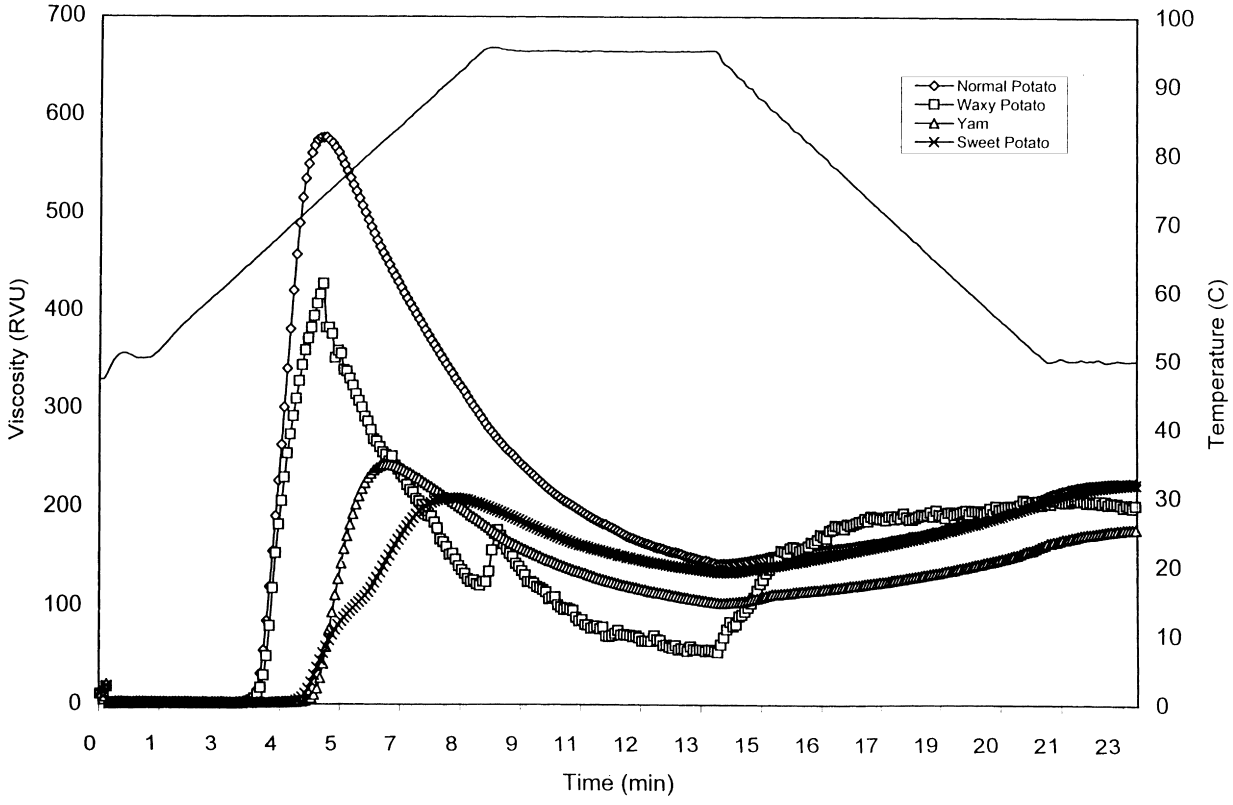

Fig. 10. Rapid ViscoAnalyzer pasting profiles of normal potato, waxy potato, yam and sweet potato starches (8% dsb).

interacting with amylopectin, maintained the integrity of normal potato starch granules and allowed it to swell to a greater degree and to achieve a higher pasting peak viscosity than waxy potato starch. Without amylose, waxy potato starch granules were rapidly dispersed as the granules imbibed water and swelled, which resulted in a substantially lower pasting peak viscosity, more rapid shear thinning and less set-back viscosity. The fewer long branch chains and less phosphate monoesters also contributed to the lower pasting peak viscosity of waxy potato starch. The difference in pasting behavior between normal cereal and potato starches can be attributed to starch lipids and phospholipids in normal cereal starches, which complex with amylose and long branch-chains of amylopectin, and severely retard swelling and inhibit amylose leaching (Larson, 1980). By comparison, waxy cereal starches, which have negligible lipid contents, swell rapidly and achieve a higher pasting peak viscosity. Sweet potato and yam starches were similar in pasting profiles except that sweet potato had a stepwise increase in viscosity. Reasons for this phenomenon are not known and are of interest. Pasting temperatures were 64.3, 64.4, 72.0 and 70.3°C for normal potato, waxy potato, yam and sweet potato starches, respectively. The large phosphate monoester contents of normal potato and waxy potato starches resulted in the lower pasting temperatures. The high amylose content of sweet potato starch might contribute to its lower peak viscosity and resistance to shear thinning in comparison to yam. Sweet potato starch showed a final viscosity similar to that of normal potato starch, whereas yam and waxy potato were somewhat lower. Waxy potato starch gave a jagged pasting profile which was also observed for waxy maize starch at a lesser extent. This could be the results of highly stringy (long) pastes of the starches.

References

Bay-Smidt, A. M., Wischman, B., Olson, C. E., & Nielsen, T. H. (1994). Starch bound phosphate in potato as studied by a simple method for determination of organic phosphate and ^{31}P NMR. *Starch/Staerke*, *46*, 167–172.

Bogracheva, T., Morris, V. J., Ring, S. G., & Hedley, C. L. (1998). The granular structure of C-type pea starch and its role in gelatinization. *Biopolymers*, *45*, 323–332.

Coursey, D. G. (1967). Yams. London: Longman.

DeWilligen, A. H. A. (1964). Potato starch isolation. In R. L. W. Starch & R. J. Smith & J. N. BeMiller & M. L. Wolfram (Eds.), *Methods in carbohydrate chemistry*, 4. London, UK: Academic Press.

Dubois, M., Gilles, K. A., Hamilton, P. A., Rebers, P. A., & Smith, F. (1956). Colorimetric method for determination of sugars and related substances. *Anal. Chem.*, *28*, 350–356.

Emiola, L. O., & Delarosa, L. C. (1981). Physicochemical properties of yam starches, . *J. Food Biochem.*, *5*, 115–130.

Hanashiro, I., Abe, J., & Hizukuri, S. (1996). A periodic distribution of the chain length of amylopectin as revealed by high performance anion-exchange chromatography. *Carbohydr. Res.*, *283*, 151–159.

Hizukuri, S. (1985). Relationship between the distribution of the chain length of amylopectin and the crystalline structure of starch granules. *Carbohydr. Res.*, *141*, 295–306.

Hizukuri, S., Kaneko, T., & Takeda, Y. (1983). Measurement of the chain length of amylopectin and its relevance to the origin of crystalline polymorphism of starch granules. *Biochim. Biophys. Acta*, *760*, 188–191.

Inouchi, N., Glover, D. V., Sugimoto, Y., & Fuwa, H. (1984). Developmental changes in starch properties of several endosperm mutants of maize. *Starch/Staerke*, *36*, 8–12.

Jane, J., & Chen, J. F. (1992). Effect of amylose molecular size and amylopectin branch chain length on paste properties of starch. *Cereal Chem.*, *69*, 60–65.

Jane, J., Kasemsuwan, T., Leas, S., Zobel, H., & Robyt, J. F. (1994). Anthology of starch granule morphology by scanning electron microscopy. *Starch/Staerke*, *46*, 121–129.

Jane, J., Wong, K., & McPherson, A. (1997). Branch-structure difference in starches of A- and B-type X-ray patterns revealed by their Naegeli dextrins. *Carbohydr. Res.*, *300*, 219–227.

Kainuma, K., & French, D. (1971). Naegeli amylodextrin and its relationship to starch granule structure. I. Preparation and properties of amylodextrins from various starch types. *Biopolymers*, *10*, 1673–1680.

Kasemsuwan, T., & Jane, J. (1994). Location of amylose in normal starch granules. II locations of phosphodiester cross-linking revealed by phosphorus-31 nuclear magnetic resonance. *Cereal Chem.*, *71*, 282–287.

Kasemsuwan, T., & Jane, J. (1996). Quantitative method for the survey of starch phosphate derivatives and starch phospholipids by ^{31}P nuclear magnetic resonance spectroscopy. *Cereal Chem.*, *73*, 702–707.

Kasemsuwan, K., Jane, J., Schnable, P., Stinard, P., & Robertson, D. (1995). Characterization of the dominant mutant amylose-extender (Ae1-5180) maize starch. *Cereal Chem.*, *72*, 457–464.

Larson, K. (1980). Inhibition of starch gelatinization by amylose-lipid complex formation. *Starch/Staerke*, *32*, 125–129.

Lim, S. T., Kasemsuwan, T., & Jane, J. (1994). Characterization of phosphorus in starch by ^{31}P nuclear magnetic resonance spectroscopy. *Cereal Chem*, *71*, 488–493.

Lim, S., & Seib, P. A. (1993). Location of phosphate esters in a wheat starch phosphate by ^{31}P-nuclear magnetic resonance spectroscopy. *Cereal Chem.*, *70*, 145–152.

Martin, F. W., & Deshpande, S. N. (1985). Sugars and starches of non sweet potato compared to those of conventional cultivars. *J. Agric. Univ. P. R.*, *69*, 169–176.

Mitch, E. L. (1984). Potato starch: production and utilization. In R. L. Whistler & J. N. BeMiller & E. F. Paschall (Eds.), *Starch chemistry and technology*, 2. (pp. 479). London, UK: Academic Press.

Muhrbeck, P., & Eliasson, A. C. (1991). Influence of the naturally occurring phosphate esters on the crystallinity of potato starch. *J. Sci. Food Agric.*, *55*, 13–18.

Muhrbeck, P., Svensson, E., & Eliasson, A. C. (1991). Effect of the degree of phosphorylation of the crystallinity of native potato starch. *Starch/Staerke*, *43*, 466–468.

Muhrbeck, P., & Tellier, C. (1991). Determination of the phosphorylation of starch from native potato varieties by ^{31}P-NMR. *Starch/Staerke*, *46*, 25–27.

Nara, S., Mori, A., & Komiya, T. (1978). Study on relative crystallinity of moist potato starch. *Starch/Staerke*, *30*, 111–114.

Noda, T., Takahata, Y., & Sato, T. (1995). Distributions of the amylopectin chain length of sweet potatoes differing in stages of development, tissue zone and variety. *Nippon Shokuhin Kagaku Kogaku Kaishi*, *42*, 200–206.

Schoch, T. J. (1942). Fractionation of starch by selective precipitation with butanol. *J. Am. Chem. Soc.*, *64*, 2957–2961.

Schoch, T. J. (1964). Iodometric determination of amylose. Potentiometric titration: standard method. In R. L. Whistler & R. J. Smith & J. N. BeMiller & M. L. Wolfram (Eds.), (pp. 157). *Methods in carbohydrate chemistry (Starch)*, 4. London, UK: Academic Press.

Shannon, J. C., & Garwood, D. L. (1984). Genetics and physiology of starch development. In R. L. Whistler & J. N. BeMiller & E. F. Paschall (Eds.), *Starch chemistry and technology*, 2. (pp. 25). London, UK: Academic Press.

Smith, R. J., & Caruso, J. L. (1964). Determination of phosphorus. In R. L. Whistler & R. J. Smith & J. N. BeMiller & M. L. Wolfram (Eds.), (pp. 42). *Methods in carbohydrate chemistry (Starch)*, 4. London, UK: Academic Press.

Sugimoto, Y., Yamamoto, M., Abe, K., & Fuwa, H. (1987). Developmental changes in starch properties of the Chinese yam. *J. Jpn. Soc. Starch Sci.*, *34*, 11–20.

Suzuki, A., Kanayama, M., Takeda, Y., & Hizukuri, S. (1986). Physicochemical properties of Nagiamo (yam) starch. *J. Jpn. Soc. Starch Sci.*, *33*, 191–198.

Takeda, Y., & Hizukuri, S. (1982). Location of phosphate groups in potato amylopectin. *Carbohydr. Res.*, *102*, 321–327.

Takeda, C., Takeda, Y., & Hizukuri, S. (1983). Physicochemical properties of lily starch. *Cereal Chem.*, *60*, 212–216.

Takeda, Y., Tokunaga, N., Takeda, C., & Hizukuri, S. (1986). Physicochemical properties of sweet potato starches. *Starch/Staerke*, *38*, 345–350.

Tian, S. J., Rickard, J. E., & Blanshard, J. M. V. (1991). Physicochemical properties of sweet potato starch. *J. Sci. Food Agric.*, *57*, 459–491.

Umeki, K., & Kainuma, K. (1981). Fine structure of Naegeli amylodextrin obtained by acid treatment of defatted waxy-maize starch-structural evidence to support the double helix hypothesis. *Carbohydr. Res.*, *96*, 143–159.

Watanabe, T., Akiyama, Y., Takahashi, H., Adachi, T., Matsumoto, A., & Matsuda, K. (1982). Structural features and properties of Naegeli amylodextrin from waxy maize, sweet potato, and potato starches. *Carbohydr. Res.*, *109*, 221–232.

Wong, K. S., & Jane, J. (1997). Quantitative analysis of debranched amylopectin by HPAEC-PAD with a postcolumn enzyme reactor. *J. Liq. Chrom. Rel. Technol.*, *20*, 297–310.

Wu, H. C. H., & Sarko, A. (1978). The crystal structures of A- B- and C-type polymorphs of amylose and starch. *Starch/Staerke*, *30*, 73–78.

Zobel, H. F. (1988). Starch crystal transformations and their industrial importance. *Starch/Staerke*, *40*, 1–7.