

Physicochemical Properties of Small- and Large-Granule Starches of Waxy, Regular, and High-Amylose Barleys

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ABSTRACT

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Small- and large-granule starches were isolated from pin-milled and air-classified fractions of waxy (SB 89528), regular (Condor), and high-amylase (Glacier) barleys, and their physicochemical properties were investigated. The isolations contained 95–97% starch, 0.1–0.3% protein, and 0.1–0.2% ash. Scanning electron microscopy showed that the starch granules were oval to round in shape with diameter ranges of 2–10 μm for small and 12–26 μm for large granules. The starches had A-type X-ray diffraction patterns, typical of cereal starches. The differences in the

physicochemical properties such as X-ray diffraction relative intensities, swelling factor, amylose leaching, Brabender pasting, differential scanning calorimetry thermal characteristics, and resistance to acid and α -amylase hydrolysis were greater among the three genotypes than between the small- and large-granule starches from the same genotype. The large-granule barley starches may be substituted for corn starches because their physicochemical properties are generally similar.

Starch is the major component of barley grain; barley can contain up to 64%, the balance of which is largely protein, β -glucan, fiber, and lipids. Canada produces, on this basis, an average of about 7 million tonnes of barley starch annually; none of which is used in the food or non-malting industries. Canadian industries import native and modified corn and potato starches despite the abundant availability of barley as a starch source. There is thus need to promote the use of barley starch in Canada.

Barley starches have bimodal granule size distribution. The large granules (A type) in barley constitute a small proportion (~10–20%) of the total number of starch granules but a high proportion (85–95%) of the total weight of starch (Morrison et al 1986). High-amylase barley starch contains more small starch granules by weight than do waxy or regular barley starches (Morrison et al 1986). Vasanthan and Bhatti (1995) reported that pin milling and air-classification of barley separates small- and large-granule starches into different fractions; one such fraction (fine 3) was purified to yield an almost pure large-granule (>10 μm) starch. Several studies on granule size, molecular characteristics, and enzymatic hydrolysis of barley starches have been reported (Banks et al 1971, Bathgate and Palmer 1972, DeHaas and Goering 1972, Goering et al 1973, Goering and Eslick 1976, Ellis 1976, Kano et al 1981, Greenwood 1989, Morrison and Scott 1986, Morrison et al 1986). However, other properties such as crystallinity, gelatinization, Brabender pasting, solubility, swelling power, and resistance to acid hydrolysis of barley starches have not been investigated to as great an extent. The present study complements published investigations on barley starch. The objective was to compare the physicochemical properties of small- and large-granule waxy, regular, and high-amylase barley starches purified from pin-milled and air-classified barley fractions and to report that barley starches have potential for replacing corn starch in non-malting food and industrial applications.

MATERIALS AND METHODS

Condor (regular), SB 89528 (waxy), and Glacier (high-amylase) barleys; their sources; pin-milling and air-classification; and isolation of large- and small-granule starches from the barleys have been described earlier (Vasanthan and Bhatti 1995). The crystalline porcine pancreatic α -amylase (one unit will liberate 1 mg of maltose from starch in 3 min at pH 6.9 at 20°C) was obtained from Sigma Chemical Co., St. Louis, MO.

Analyses

AACC methods (AACC 1983) were used to determine moisture (44-19), nitrogen (46-13), and starch damage (76-30A). Starch was determined by the method of Holm et al (1986) on samples boiled with 80% ethanol for 5 min. Apparent amylose content of the starches was determined by the method of Chrastil (1987) and true amylose in the same manner after defatting starches with *n*-propanol-water mixture (3:1, v/v) for 7 hr at 95°C.

Physicochemical Properties

Scanning electron microscopy. Small- and large-granule barley starches were examined by scanning electron microscopy before and after (12 hr of hydrolysis) treatment with α -amylase. The starch was sprinkled on double-sided adhesive tapes mounted on aluminum stubs, coated with gold, and examined in a Phillips 505 SEM at an accelerating potential of 20 kV.

X-ray diffractometry. X-ray diffractograms were obtained with a Phillips (model 42273) X-ray diffractometer. Reagent grade alumina powder (Anachemia, 200 mesh Al_2O_3) was used as an internal standard (reference peak at 38.50°, 2 θ). Traces were obtained using Cu-K α radiation ($\tau = 1.5478$) at 1.6 kVA. The starch powder (0.45 g) was thoroughly mixed with alumina (0.04 g) and packed into an aluminum sample holder. The samples were scanned through the 2 θ (diffraction angle) range of 3–40° at an equivalent angular velocity of approximately 0.6° 2 θ per min. A step interval of 0.01° 2 θ and a count time of 1 sec were used. Relative intensities of the major diffraction peaks of starch were obtained from the ratio between the absolute intensity of the starch peak and the reference (Al_2O_3) peak. The *d*-spacings were calculated from diffraction angles (2 θ) according to Bragg's equation ($n\lambda = 2d \sin\theta$; where *d* = intercrystalline spacing, *n* = 1, and $\lambda = 1.5487 \text{ \AA}$).

Swelling factor. The swelling factor (SF) of starches, heated between 50 and 95°C in excess water, was measured according to the method of Tester and Morrison (1990).

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Amylose leaching. Starch added to distilled water (~1 mg/ml) was heated from 50 to 95°C in sealed tubes for 30 min, cooled to ambient temperature, and centrifuged at 1,500 × g for 10 min. Aliquots of the supernatant were assayed for leached amylose (Chrastil 1987). Amylose leaching was expressed as milligrams of amylose leached per 100 mg of dry starch.

Brabender viscoamylography. Pasting characteristics of starch slurries at a concentration of 8% (w/v) and pH 5.5 were determined using a viscoamylograph (C. W. Brabender Instruments, Inc., South Hackensack, NJ), equipped with a 700-cm/g cartridge, operating at a bowl speed of 75 rpm. The starch slurry was heated from 30 to 96°C at the rate of 1.5°C/min, maintained at 96°C for 30 min, and then cooled to 51°C at the same rate. The pasting temperature was taken when viscosity reached 10 BU during the heating period. The thermal stability was evaluated from the viscosity breakdown during the heating and holding (96°C for 30 min) periods.

Acid hydrolysis. The starches were hydrolyzed with 2.2N HCl at 35°C (1.0 g starch/40 ml acid) for 17 days in a shaking water bath at 35°C. Aliquots (1.0 ml) of the reaction mixtures were withdrawn at various times, neutralized, and centrifuged (1,500 × g for 10 min), and the supernatant liquid was assayed for carbohydrates (Bruner 1964). Appropriate controls (without acid) were prepared under the above experimental conditions. The degree of hydrolysis was expressed as milligrams of starch solubilized per 100 mg of dry starch.

α-Amylase Hydrolysis. The procedure was essentially that of Knutson et al (1982). However, a higher starch-α-amylase ratio (1 mg/12 units) was used. Starch (200 mg) was suspended in 50 ml of distilled water and 10-ml aliquots were placed in a water bath at 37°C. Then 8.0 ml of 0.1M phosphate buffer (pH 6.9) containing 0.006M NaCl and 480 units of the enzyme were added. The reaction mixture was shaken continuously. A 0.5- to 1.0-ml ali-

quot was removed at appropriate time intervals, pipetted into 0.2 ml of 95% ethanol, and centrifuged at 1,500 × g for 10 min. The supernatant was analyzed for soluble carbohydrate (Bruner 1964). Percent hydrolysis was expressed as milligrams of maltose released per 100 mg of dry starch. Appropriate controls without the enzyme were prepared.

Differential scanning calorimetry. Starch gelatinization was studied on a Mettler (TA 4000) differential scanning calorimeter. Water (21 μl) was added with a microsyringe to starch (5.5 mg, db) in aluminum DSC pans, which were then hermetically sealed and allowed to stand overnight at room temperature. The scanning temperature range and the heating rate were 20–120°C and 10°C/min, respectively. The thermograms were recorded with water as reference. Indium was used for calibration.

RESULTS

Scanning Electron Microscopy

The small- and large-granule starches from the three barleys were observed under a scanning electron microscope. Due to their general similarities, micrographs of only Condor barley are shown in Figure 1. The small- and large-granule starches were oval to round in shape with diameter ranges of 2–10 and 12–26 μm, respectively. The surface of the small- and large-granule starches at 2,000× magnification (not shown) appeared to be smooth and showed no evidence of cracks or abrasions due to pin milling; this suggested low starch damage in agreement with data given in Table I.

Chemical Composition

The isolated starches were almost pure and contained 95–97% starch, 0.1–0.3% protein (N × 6.25), and 0.1–0.2% ash (Table I). The internal lipid contents of the small- and large-granule starches

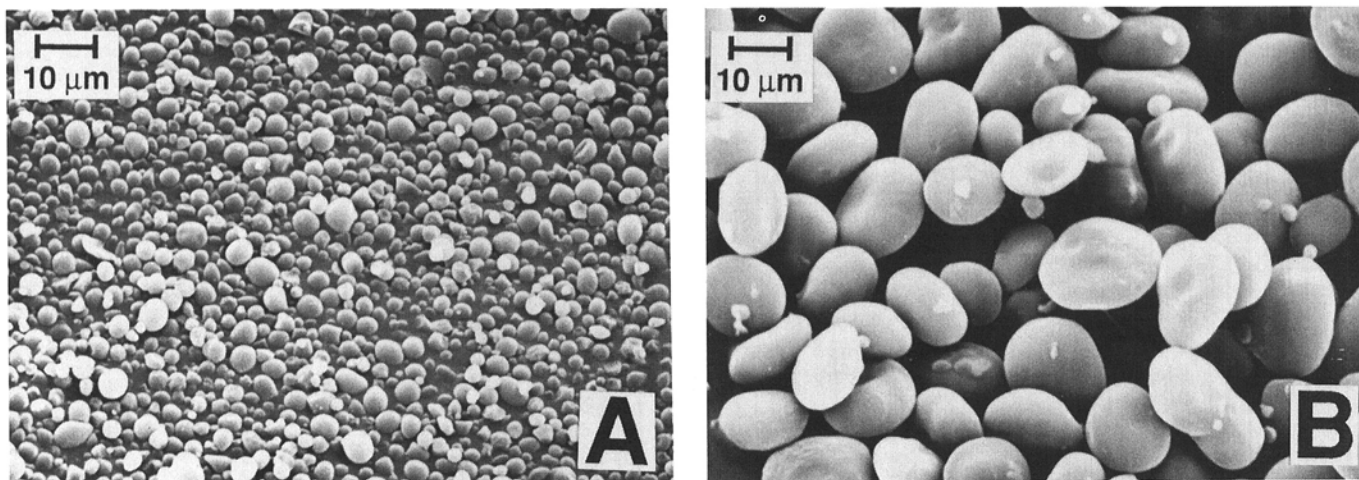


Fig. 1. Scanning electron micrographs of the small- (A) and large- (B) granule starches from Condor barley.

TABLE I
Chemical Composition (% dry basis) of Barley Starches^a

Genotype	Granule Size	Starch	Protein (N × 6.25)	Ash	Lipid ^b	Amylose Content		Starch Damage
						True	Apparent	
SB 89528	Small	96.8	0.1	0.1	0.4	3.2	2.6	5.7
(waxy)	Large	97.2	0.3	0.2	0.3	2.8	2.2	5.8
Condor	Small	96.8	0.1	0.1	0.8	31.3	23.4	4.3
(regular amylose)	Large	95.0	0.2	0.2	0.6	28.8	25.6	3.8
Glacier	Small	95.2	0.2	0.2	1.0	45.7	33.6	5.5
(high amylose)	Large	94.8	0.1	0.2	0.7	40.2	36.1	4.9
LSD (<i>P</i> < 0.05)		1.3	0.1	0.1	0.1	1.5	1.8	0.9

^a Values are averages of three determinations.

^b Starch internal lipid content.

were: Glacier, 1.04 and 0.69%; Condor, 0.83 and 0.55%; and SB 89528, 0.39 and 0.28%, respectively. The true and apparent amylose contents of barley starches were considerably different among the three genotypes. In Glacier and Condor barleys, small-granule starches had higher ($P < 0.05$) true amylose (TA) but lower apparent amylose (AA) than did the large-granule starches. This is a positive indication for higher internal lipids and of amylose-lipid complex of small-granule starches. The amounts of amylose complexed with lipids (TA - AA) in the small- and large-granule barley starches were: Glacier, 12.1 and 4.1%, and Condor, 7.1 and 3.2%; respectively.

Starch damage, which may occur during pin milling of cereals, results in altered physicochemical properties of starches, such as increased susceptibility to α -amylolysis. Starch damage was only 4.0–6.0% (Table I). Such a low level of starch damage was unlikely to have any influence on the physicochemical properties of the barley starches investigated.

X-ray Diffractometry

The X-ray diffraction patterns and the percent relative intensities (PRI) of the d -spacings of the major diffraction peaks are given in Figure 2 and Table II, respectively. In all of the starches, major peaks were observed around d -spacings 5.8, 5.2, 4.8, 4.4, and 3.8 Å. Zobel (1988) reported that the X-ray d -spacings 5.8, 5.2, and 3.8 are characteristic of an A-type starch crystal that is common to most cereal starches; the d -spacing at 4.4 Å ($2\theta = 20.2^\circ$) is characteristic of amylose-lipid complex. Small- and large-granule starches from SB 89528 showed very low intensity peak at 4.4 Å d -spacing. However, the 4.4 Å peak was clearly visible in Condor and Glacier starches, whereas the peak intensity was higher in Glacier than in Condor starch, which is in agreement with the internal lipid contents of barley starches given in Table I.

The PRI of the d -spacings of the major diffraction peaks were different among the barley starches (Table II). The PRI of small-granule starches were the highest for Glacier but generally similar for the SB 89528 and Condor barley starches. The PRI of large-granule starches was: Glacier > SB 89528 > Condor. The large-granule starches had higher PRI than did the small-granule starches. Higher PRI of starch indicates their higher degree of crystallinity.

Swelling Factor

The SF of all starches increased with rise in temperature but the extent of swelling was significantly different ($P < 0.05$) among the genotypes: SB 89528 > Condor > Glacier (Fig. 3). In SB 89528 and Condor barleys, small-granule starches had higher ($P < 0.05$) SF than did the large-granule starches. However, in Glacier barley, small-granule starch had lower ($P < 0.05$) SF than the large granule starch. The differences in the SF, among the genotypes and between the small- and large-granule starches from the same genotype, were greater above 80°C.

Amylose Leaching

Amylose leaching (AML) occurs from swelling starch granules in water, at temperatures generally above 55°C. The small- and large-granule waxy starches, as expected, showed little AML (<2.5%) at 95°C (Fig. 4). However, during AML measurement at 95°C, a dark purple color developed on addition of iodine reagent, indicating that considerable amounts of branched components were leached from the starch granules. The AML of Condor and Glacier barley starches increased with rise in temperature (Fig. 4). Among the small-granule starches, Glacier had higher ($P < 0.05$) AML than did Condor barley starch, whereas among the large-granule starches, Condor had higher ($P < 0.05$) AML than did Glacier barley starch.

Viscoamylography

The pasting curves of the barley starches are given in Figure 5. Among the genotypes, the pasting temperature (PT) was highest in Glacier. The small- and large-granule starches had generally

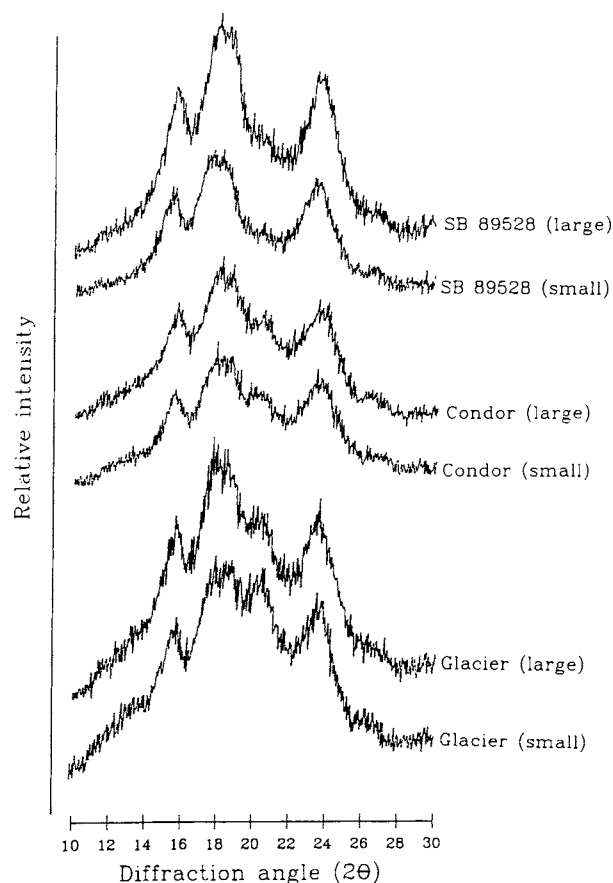


Fig. 2. X-ray diffraction patterns of small- and large-granule starches from SB 89528, Condor, and Glacier barleys.

TABLE II
Percent Relative Intensities (PRI)^a of Major Peaks in the X-ray Diffraction Patterns of Barley Starches

Genotype	Granule Size	X-ray Diffraction Angle (2θ)				
		15.2 (5.8) ^b	17.2 (5.2)	18.4 (4.8)	20.2 (4.4)	23.1 (3.8)
SB 89528 (waxy)	Small	23.5	29.2	25.4	—	26.3
	Large	38.1	46.6	43.4	—	39.8
Condor (regular amylose)	Small	23.2	29.1	27.1	23.8	25.9
	Large	25.5	32.8	30.4	25.9	27.9
Glacier (high amylose)	Small	32.6	42.3	43.9	42.3	38.4
	Large	38.7	49.0	48.4	41.9	42.5

^a Starch peak intensity/alumina peak intensity] × 100.

^b Numbers in parentheses are starch crystal d -spacings (Å) of the major diffraction peaks calculated according to Bragg's equation ($n\lambda = 2d\sin\theta$; where, $n = 1$, $\lambda = 1.5487\text{Å}$, and $\theta =$ diffraction angle).

similar PT in all three barley genotypes. The maximum viscosity (MV) of the barley starch pastes was: SB 89528 > Condor > Glacier. In SB 89528 barley, small-granule starch had higher paste MV than did large-granule starch, but the small- and large-granule starches from Condor or Glacier had generally similar MV. During heating and holding periods, viscosity of the Glacier starches progressively increased, without any breakdown (highest shear stability). However, in SB 89528 and Condor barley starches, the viscosities increased to MV and then broke down; the loss of viscosity was higher in SB 89528 barley starch.

Acid Hydrolysis

The hydrated protons (H_3O^+) from aqueous HCl randomly hydrolyze glycosidic bonds of starch chains and thereby solubilize starch granules. All of the barley starches showed a two-stage hydrolysis pattern; a relatively faster rate of hydrolysis during the first six days followed by a slower rate from 6 to 17 days (Fig. 6). Starches from Glacier barley were hydrolyzed slower than were

those of SB 89528 or Condor barleys. The SB 89528 and Condor starches had generally similar ($P < 0.05$) hydrolysis up to three days, but after that, differences in hydrolysis became significantly larger ($P < 0.05$); SB 89528 > Condor barley. The small-granule starches from all three barley genotypes were hydrolyzed to a greater extent ($P < 0.05$) than were the large-granule starches.

Enzyme Hydrolysis

The hydrolysis of the three barley starches by α -amylase is given in Figure 7. A relatively faster rate of hydrolysis at initial stages (from 0 to 22 hr in Glacier and Condor starches and 0 to 16 hr in SB 89528), followed by a slower rate to 72 hr, was observed. The degree of hydrolysis (DH) in the initial stages was considerably different ($P < 0.05$) among the barley starches; SB 89528 > Condor > Glacier. At later stages, the DH was: Condor > SB 89528 > Glacier. During the entire time of hydrolysis, the small-granule starches had higher ($P < 0.05$) DH than did large-granule starches.

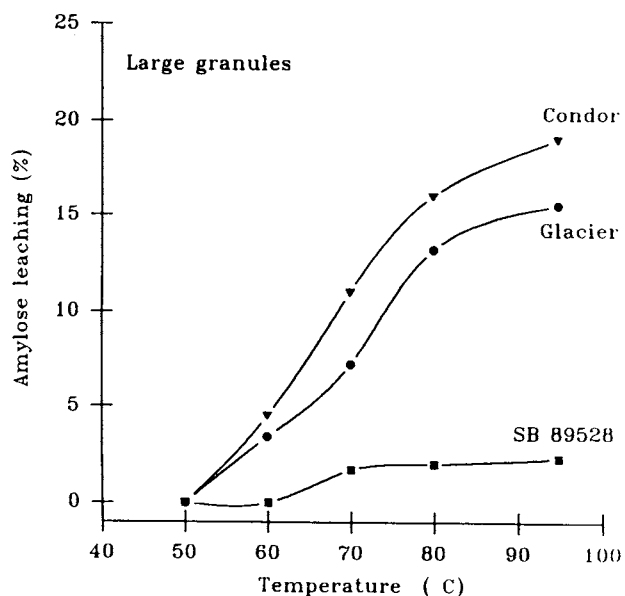
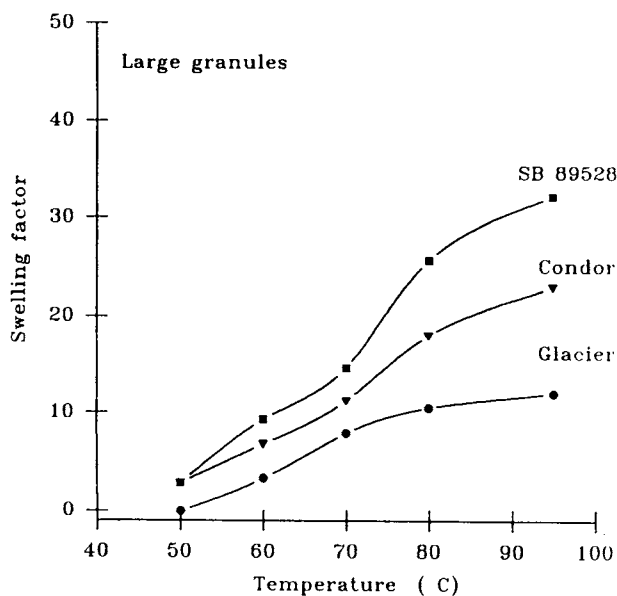
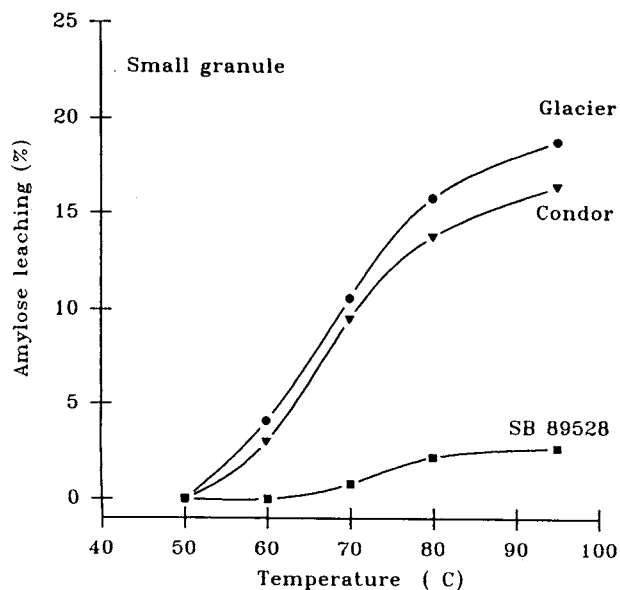
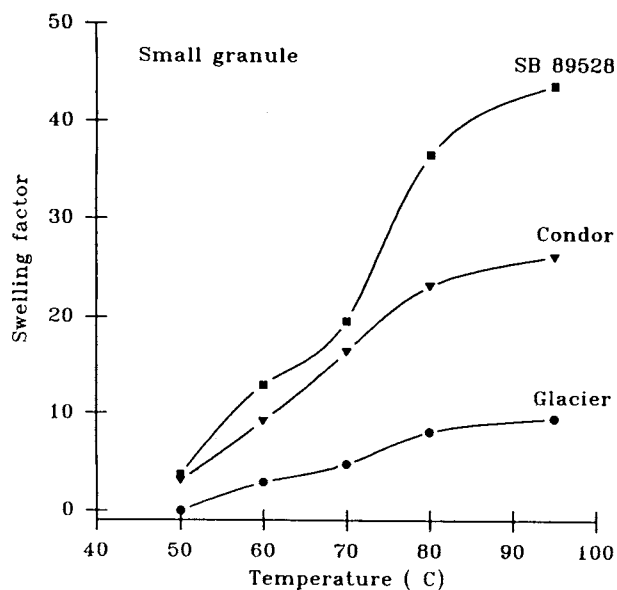


Fig. 3. Swelling factor of small- (top) and large- (bottom) granule starches from SB 89528, Condor and Glacier barleys. LSD ($P < 0.05$) at 50, 60, 70, 80, and 95°C for small-granule is 1.0, 1.9, 2.3, 3.8, and 3.4; for large granule is 2.5, 3.0, 2.3, 2.8, and 2.6, respectively.

Fig. 4. Amylose leaching of small- (top) and large- (bottom) granule starches from SB 89528, Condor, and Glacier barleys. LSD ($P < 0.05$) at 60, 70, 80, and 95°C for small-granule starch is 1.5, 2.1, 1.9, and 1.7%; for large-granule starch is 1.2, 1.8, 2.0, and 1.5%, respectively.

Figure 8 shows the scanning electron micrographs of the small- and large-granule starches after 12 hr of α -amylolysis. The difference in the susceptibility to enzyme attack was clearly visible between the small- and large-granule starches from SB 89528 (Fig. 8A and B); small-granule starch from SB 89528 was more easily degraded than was the large-granule starch and lost its granular identity. However, similar enzyme susceptibility was observed between the small- and large-granule starches of Condor (Fig. 8C and D) and Glacier (Fig. 8E and F) barleys. The pattern of enzyme attack was different among the cultivars; small-granule starches from SB 89528 had erosions on the exterior granule surface (Fig. 8A) and large-granules had surface erosions and pinholes (Fig. 8B); Condor starches had pinholes (Fig. 8C and D) and appeared to be hydrolyzed from inside out; Glacier starches showed surface erosions (Fig. 8E and F).

Differential Scanning Calorimetry

Starch granules heated in the presence of sufficient water exhibit an order-disorder phase transition (gelatinization). The transition temperatures (onset, T_o ; peak, T_p ; and conclusion, T_c),

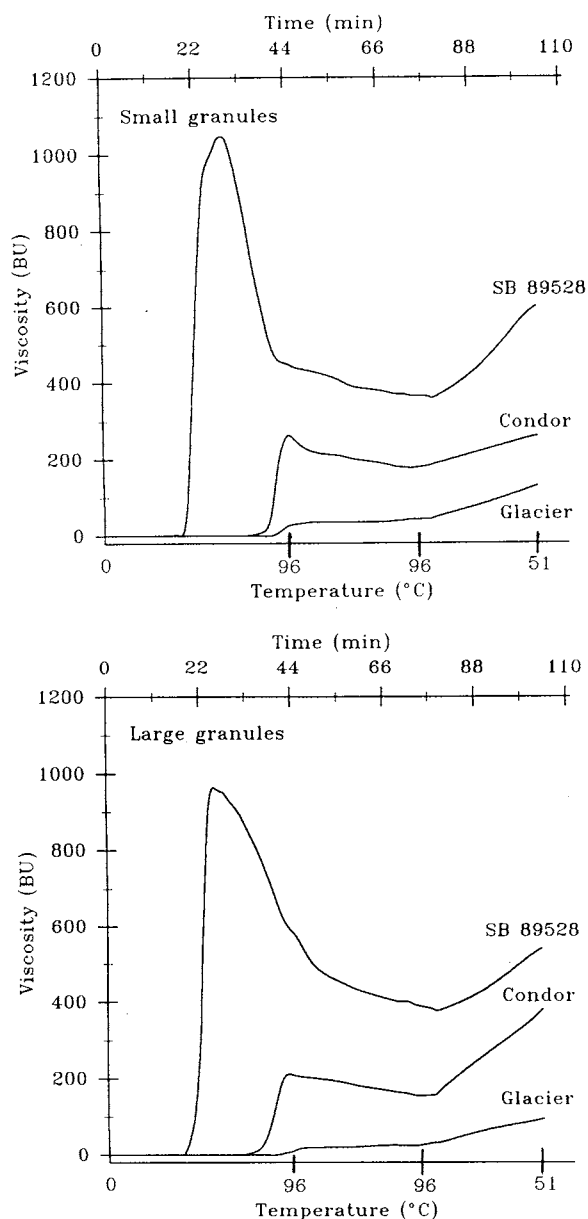


Fig. 5. Viscoamylographs of small- (top) and large- (bottom) granule starches from SB 89528, Condor, and Glacier barleys.

ranges (T_c-T_o), and enthalpies of gelatinization are given in Table III. The T_o of small- or large-granule barley starches from SB 89528 and Glacier were generally similar but higher ($P < 0.05$) than that of Condor starches. The T_p and T_c were highest in Glacier followed by SB 89528 and Condor. In all three barley starches, little differences in T_o were observed between the small- and large-granule starches, but small-granule starches had higher T_p and T_c than did the large-granule starches ($P < 0.05$). The enthalpies of gelatinization of barley starches were highest in SB 89528 but were generally similar for Condor and Glacier barleys. Furthermore, within each barley small-granule starch had ~15–20% lower enthalpy than the large-granule starch. The T_c-T_o showed: Glacier > Condor ~ SB 89528. In each barley, small-granule starches had higher T_c-T_o than did the large-granule starches.

DISCUSSION

Barley starch differs in shape and granule size range from corn starch. The amylose and internal lipid contents of SB 89528, Condor, and Glacier barley starches are comparable to that of waxy, regular, and high-amylose corn starches.

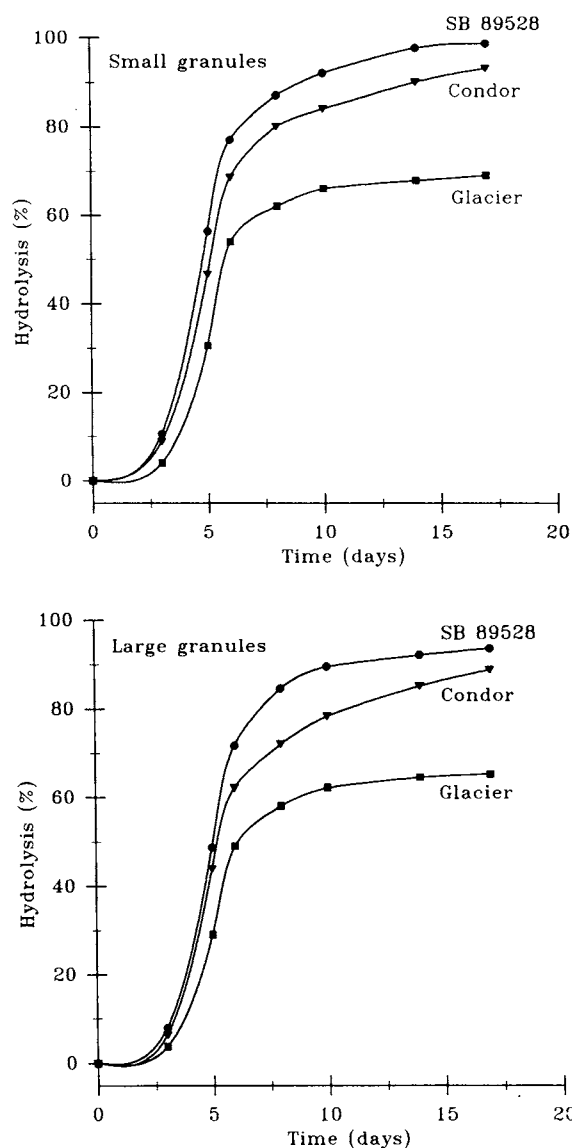


Fig. 6. Acid hydrolysis of small- and large-granule starches from SB 89528, Condor, and Glacier barleys. LSD ($P < 0.05$) at 3, 5, 6, 8, 10, 14, and 17 days for small-granule starch is 1.7, 1.2, 1.1, 1.9, 1.0, 1.2, and 1.5%; for large granule is 1.6, 1.3, 2.0, 2.4, 1.9, 2.2, and 1.6, respectively.

Hydrocarbon chains of internal lipids suppress hydration of starch granule amorphous regions and thereby influence swelling, amylose leaching, pasting, and gelatinization of starches (Medcalf et al 1968, Goering et al 1975, Melvin 1979, Lorenz 1976, Maningat and Juliano 1980, Goshima et al 1985, Tester and Morrison 1990, Vasanthan and Hoover 1992). In small- and large-granule barley starches, the differences in SF (Fig. 3) among the barley genotypes may be attributed to starch internal lipid contents (Table I). However, small-granule starches from SB 89528 or Condor barleys, despite their higher lipid contents (Table I), had SF (Fig. 3) significantly higher than the large-granule starches. Starch granule size may influence granule hydration and swelling. The small-granule starches have higher ratio of surface area to unit weight of starch and thus, hydrate and swell more efficiently than the large-granule starches. Therefore, it seems that an interplay of internal lipid content and granule size is responsible for the net swelling of barley starch.

Higher amylose content and swelling enhances AML; but the high degree of amylose associations with other starch components decreases AML. In the present study, among the small-granule barley starches, the higher AML in Glacier compared

with that in Condor barley (Fig. 4) may be attributed to its higher apparent amylose content (Table I). However, among the large-granule starches, Glacier had significantly lower AML than that of Condor, despite having higher apparent amylose content. This suggests a greater degree of inter-chain associations (amylose-amylose and/or amylose-amylopectin) within these starch granules, in addition to amylose-lipid complex, restricts AML. Furthermore, these inter-chain associations could improve starch granular integrity by cross-linking molecules and thereby reduce their potential for swelling; lower swelling would also restrict AML.

The viscoamylograph properties (PT, MV, and shear stabilities) of the barley starches may be attributed to the differences in their SF (Fig. 3), which is in turn dictated by starch granule internal lipid content, size, and integrity (due to inter-chain associations). High swelling starch granules occupy a larger volume fraction in a paste and pack very close to each other (Evans and Haisman 1979, Doublier 1987). They would thus impart higher intergranular friction (low PT and high MV) during movement. Furthermore, the susceptibility of starch granules to shear deformation has been shown to increase with increase in the degree of swelling due to granule softening (Christianson and Bagley 1983, Doublier 1987, Steeneken 1989, Hoover and Vasanthan 1994). The amylograph properties of large-granule barley starches were generally similar to those of corn starches varying in amylose and amylopectin contents reported by Greenwood (1976).

Acid and α -amylase preferentially attack the more amorphous regions of the starch granules (faster rate of hydrolysis at initial stages); the crystalline regions are less accessible and are hydrolyzed at a slower rate. The differences in the rate of acid (Fig. 6) and enzyme (Fig. 7) hydrolysis (at initial stages) among the barley starches may be due to variations in the starch granule amorphous region composition (amylose, lipid, and amylose-lipid complex contents) and structure (starch chain organization and the degree of inter-chain associations) among the genotypes. Vasanthan and Hoover (1992) reported that amylose complexed with lipids does not resist degradation by acid hydrolysis. Therefore, at initial stages the lower susceptibility of the Glacier starches to acid hydrolysis suggested that the starch chains in the amorphous regions are more compactly organized, due to higher extent of inter-chain associations, than are those of Condor or SB 89528 starches; highly compact amorphous regions would resist the penetration of acid (H_3O^+) and α -amylase and their binding to the substrate, thereby suppressing hydrolysis. The data on acid hydrolysis study also supports that the high degree of inter-chain associations in the amorphous regions is responsible for lower SF (Fig. 3) and AML (Fig. 4) of Glacier starches.

Amylose complexed with lipids shows reduced susceptibility to α -amylase hydrolysis (Larsson and Meizis 1979, Holm et al 1983, Seneviratne and Biliaderis 1991, Vasanthan and Hoover 1992). This was attributed to a conformational change (random coil to helix) in amylose chains that interferes with the mechanism of enzyme-starch binding. Therefore, in the present study, it is plausible that, despite the variation in the amorphous region compactness among barley starches, as indicated by the acid hydrolysis study (Fig. 6), the lipid contents (Table I) may also have imparted some degree of resistance to barley starches against α -amylolysis at initial stages. Furthermore, within each barley genotype, small-granule starches having higher DH than large granules may be due to their higher surface area per unit weight of starch. At the later stages of hydrolysis, the acid and enzyme attack is mainly confined to starch granule crystalline regions; the rate of hydrolysis was thus dependent on starch crystallinity (Table II).

The melting of ordered crystals is an important event during starch gelatinization. The crystallites of starch are due to sequential packing of double helices (Wu and Sarco 1978a,b) that are formed between the flexible A-chains of amylopectins (French

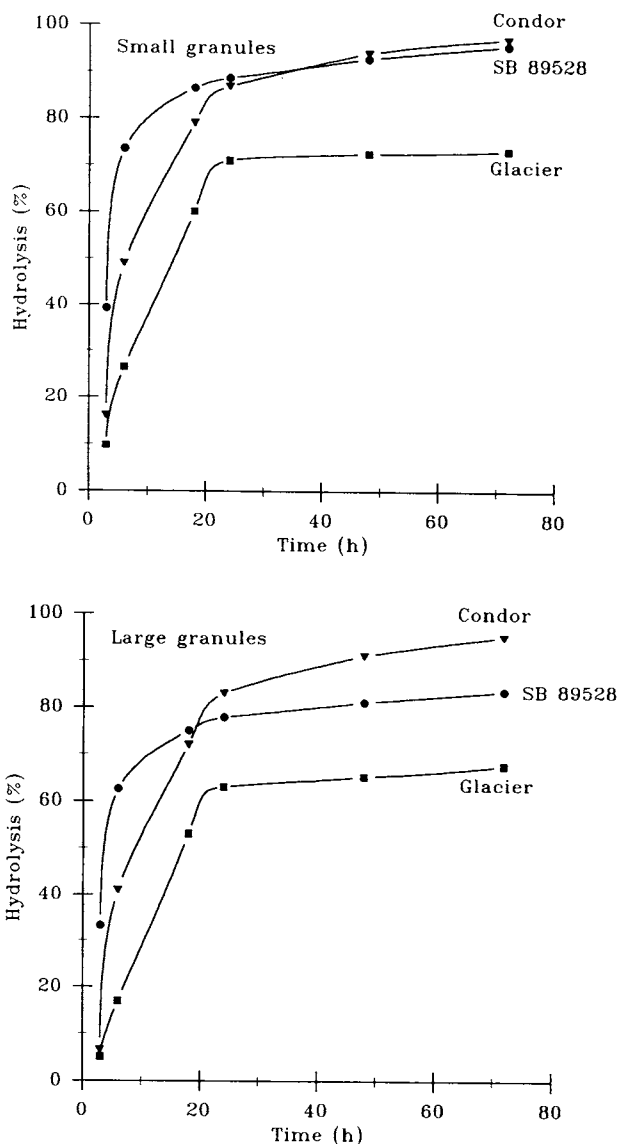


Fig. 7. Enzyme hydrolysis of small- and large-granule starches from SB 89528, Condor, and Glacier barleys. LSD ($P < 0.05$) at 3, 6, 18, 24, 48, and 72 hr for small-granule starch is 1.9, 2.0, 1.4, 1.9, 1.7, and 2.2%; and for large granule is 1.5, 2.2, 1.8, 2.3, 1.6, and 2.2, respectively.

1972). Cook and Gidley (1992) showed by X-ray and ^{13}C solid state NMR spectroscopy that gelatinization enthalpy values reflect mainly the loss of double helical rather than crystalline order; they postulated that the forces holding the starch granule were largely at the double helical level. Therefore, higher starch gelatinization enthalpies should lead to higher granule stability and gelatinization temperatures. However, it is difficult to explain the following data in Table III: 1) starches from SB 89528 (small and large) had higher enthalpies but gelatinized at lower temperatures (T_p and T_c) than Glacier starches; 2) small- or large-granule starches from Condor and Glacier barleys had generally similar enthalpies, but Glacier starches gelatinized at considerably higher

temperatures (T_p and T_c) than did Condor starches; and 3) in all three cultivars, large-granule barley starches gelatinized at temperatures (T_p and T_c) lower than those of small-granule starches, despite their higher enthalpies. Variation in lipid contents and amorphous region compactness among barley starches would be responsible.

Donovan (1979) reported that the crystalline and double helical melting during starch gelatinization are assisted by hydration and swelling of starch granule amorphous regions. The swelling of amorphous regions impart a stress on the crystalline regions and thereby strips polymer chains from the surface of starch crystallites (crystal melting). Therefore, any starch attributes that sup-

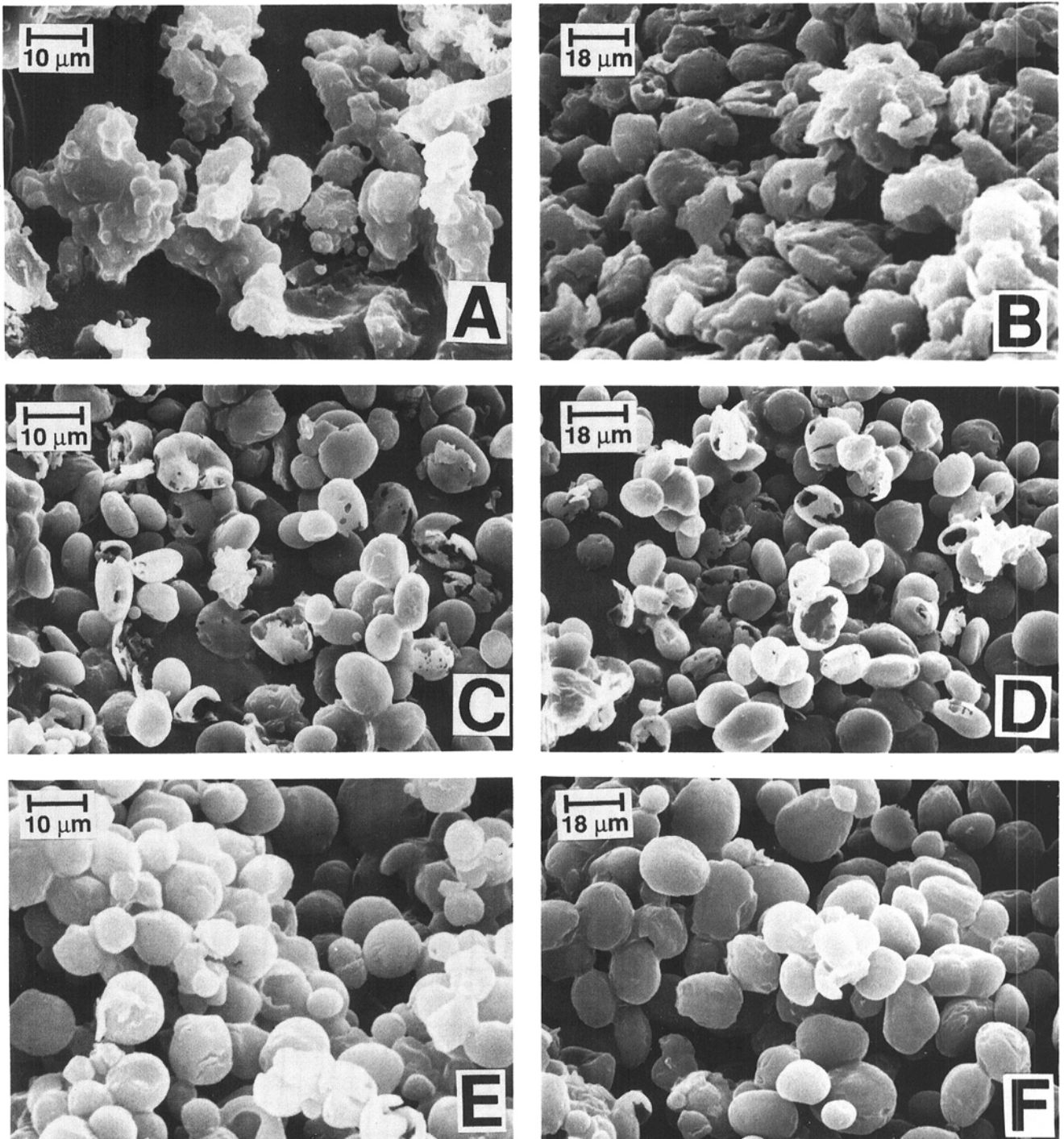


Fig. 8. Scanning electron micrographs of enzyme hydrolyzed (12 hr hydrolysis) small- and large-granule starches from SB 89528 (A and B, respectively), Condor (C and D, respectively), and Glacier (E and F, respectively) barleys.

TABLE III
Thermal Characteristics of Small- and Large-Granule Barley Starches

Genotype	Granule Size	Transition Temperature ^a , °C			Range ^b (°C)	Enthalpy ^a (J/g)
		Onset (T_o)	Peak (T_p)	Conclusion (T_c)		
SB 89528	Small	60.0	64.0	76.0	16.0	9.9
(waxy)	Large	59.0	62.6	72.0	13.0	11.4
Condor	Small	54.0	61.0	70.0	16.0	6.8
(regular amylose)	Large	54.0	58.0	67.5	13.5	7.9
Glacier	Small	58.0	68.4	79.5	21.5	6.5
(high amylose)	Large	59.3	65.7	77.3	18.0	7.8
LSD ($P < 0.05$)		0.9	1.0	0.7	0.9	0.4

^a Values are means of three determinations \pm SD.

^b Range = $T_c - T_o$.

press swelling would delay gelatinization and thus lead to a higher T_o , T_p , and T_c . Tester and Morrison (1990) have shown that the hydration and swelling of starch granules were suppressed by the presence of amylose-lipid complexes. Leach et al (1959) reported that a starch granule with an extensive and strongly associated micellar network would be resistant to swelling. Furthermore, it is likely that the double helices when existing individually (amorphous) would hydrate more efficiently than when they are present as part of a starch crystal. Therefore, information regarding the distribution of double helices within a starch granule among amorphous and crystalline regions would be useful to better understand the hydration, swelling, and gelatinization properties of starch granules.

The differences in the range ($T_c - T_o$) among the barley starches may be due to crystalline regions within a starch granule that are composed of small crystallites, each having a slightly different crystal strength; gelatinization represents the sum of individual crystal meltings (Banks and Greenwood 1975). Higher gelatinization temperature range of small granule barley starch may be due to its higher number of granules per unit weight of starch when compared to large-granule starch; the more granules, the wider the gelatinization range is likely to be. The gelatinization temperatures, ranges and enthalpies of barley starches (Table III) are lower than the values reported for corn starches (Krueger et al 1987, Vasanthan et al 1995).

CONCLUSIONS

The differences in physicochemical properties of barley starches were greater among the genotypes than between small- and large-granule starches from the same genotype. The properties of barley starch will not be substantially affected by the small granules because small granules comprise a minor proportion of total starch mass and their physicochemical properties does not differ drastically from large granules. Barley starch closely resembled corn starch in SF, AML, viscoamylographic properties and resistance to acid and α -amylase hydrolysis; thus, it may be substituted for corn starch in food and industrial applications.

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