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Characterization of beach pea (*Lathyrus maritimus* L.) starch

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Abstract

Starch from beach pea (*Lathyrus maritimus* L.) was isolated and its physicochemical properties were compared with those of grass pea and green pea starches. The yield of beach pea starch was 12.3% on a whole seed basis. The shape of the granules was round to elliptical, with granules 6–17 μm in diameter. Scanning electron micrographs revealed the presence of smooth surfaces with many granules occurring in clusters. The total amylose content was 29%, of which 5.9% was complexed by native lipids. The X-ray diffraction pattern was of the C type and the X-ray intensities were much weaker than in other legume starches. The starch exhibited a restricted two-stage swelling pattern and moderate amylose leaching. Native granules of beach pea were hydrolyzed readily by 2.2 N HCl (49% in 20 days) and porcine pancreatic α-amylase (35% in 24 h). The gelatinization temperature range was 60–64.5–74.2°C and the enthalpy of gelatinization was 1.6 cal g^{-1}. The results showed that starch chain associations within the amorphous and crystalline domains of beach pea starch are much weaker than in grass pea and green pea starches.

Keywords: Beach pea; *Lathyrus maritimus*; Grass pea; Green pea; Starch

1. Introduction

The grain legumes collectively (including soybean and groundnut) are ranked fifth in terms of annual world grain production (171 million metric tons), after wheat, rice, corn and barley (Deshpande & Damodaran, 1990). Leguminosae (16,000–19,000 species in ~750 genera) is the third largest family of flowering plants. However, only about 12 species are used widely in the food industry in the form of unripe pods, immature seeds or mature dry seeds. These include the common beans, field peas, chickpeas, cowpeas, green gram, black gram, lentils, pigeonpeas, and the two oil seeds soybeans and groundnuts (Deshpande & Damodaran, 1990). The production of legumes in Canada amounted to 1.3 million metric tons in 1993. The major legumes produced in Canada are lentils, peas and faba beans. The food legumes are a rich source of protein (20–25%), starch (22–45%), dietary fibre, minerals, and water-soluble vitamins. Because of their importance in the human diet, the evaluation of the biological quality and availability of legume proteins have received considerable attention. However, detailed information on the structure, gelatinization and retrogradation properties of legume starches is lacking. The structure and phase transition of legume starches are important aspects of functionality of this biopolymer since they have a profound influence on texture, appearance, water-holding capacity and enzyme digestibility of processed starch foodstuffs (Biliaderis, 1991). Thus, a key approach to understanding and predicting legume starch functionality would be to establish structure–property relationships for legume starches from the same and different biotypes.

Beach pea (*Lathyrus maritimus* L.) grows along the shorelines of Arctic and Subarctic regions from Greenland to Siberia and Japan (Fernald, 1950; Talbot & Talbot, 1994). In Canada, it is mostly found in Newfoundland, Nova Scotia and Quebec (Hitchcock, 1952; Lamourex & Grandtner, 1977). Beach pea is a relatively unknown food legume which may serve as a potential source of several important nutrients for humans. In previous papers, we have reported the compositional characteristics, nutritional value and physicochemical properties of beach pea seeds and plant parts (Chavan, Shahidi, Bal, & McKenzie, 1998a, b; Shahidi, Chavan, Bal, & McKenzie, 1998). However, the physicochemical properties of the starch of beach pea have not previously been studied. Thus, as part of our studies on

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beach pea and legume starches, it was considered worthwhile to isolate the starch fraction from beach pea and to determine its microscopic, thermal and digestibility characteristics in comparison to green pea (*Pisum sativum*) and grass pea (*Lathyrus sativus*) starches. An understanding of the physico-chemical characteristics of beach pea starch would form the basis for further investigations on physical (annealing) and chemical (cross-linking) modification to improve the use of beach pea starch in food formulations.

2. Materials and methods

2.1. Materials

The pods of beach pea (*L. maritimus*) were collected from Bellevue Beach, Newfoundland in October, 1996. The grains and pod shells were separated manually. Seeds of green pea (*P. sativum*) and grass pea (*L. sativus*) (harvested in 1994–1995 growing season) were obtained from the Department of Crop Science and Plant Ecology, University of Saskatchewan and Agriculture and Agri-Food Canada Manitoba, respectively. Crystalline porcine pancreatic α-amylase (EC 3211) type 1A was obtained from Sigma Chemical Co (St Louis, MO). Other chemicals and solvents were analytical grade. Solvents were distilled from glass before use.

2.2. Starch isolation

Beach pea, green pea and grass pea seeds were divided into two lots representing whole samples. Each lot was further subdivided into two parts and starch was extracted from them using the procedure of Hoover and Sosulski (1985).

2.3. Chemical composition of starch

Quantitative estimations of moisture, ash, nitrogen and starch damage were performed by the standard American Association of Cereal Chemists (AACC, 1984) procedures. Starch lipids were determined by procedures outlined in an earlier publication (Vasanthan & Hoover, 1992). Apparent and total amylose content were determined by the method of Chrastil (1987).

2.4. Swelling factor

The swelling factor (SF) of starches when heated from 50–95°C in excess water was measured according to the method of Tester and Morrison (1990). This method measures only intragranular water and, hence, the true swelling factor at a given temperature. The swelling factor is reported as a ratio of the volume of swollen starch granules to the volume of the dry starch. Results used for calculation were means of triplicate measurements.

2.5. Extent of amylose leaching

Starches (20 mg) in distilled water (10 ml) were heated in volume-calibrated sealed tubes (50–95°C) for 30 min. The tubes were then cooled to ambient temperature and centrifuged at 4000 ***g*** for 20 min. The supernatant liquid (1 ml) was withdrawn and its amylose content determined by the method of Chrastil (1987). Results used for calculation are means of triplicate measurements.

2.6. X-ray diffraction

X-ray diffractograms were obtained with a Rigaku RU 200 R X-ray diffractometer with a chart speed of 20 mm min^{-1}. The operating conditions were as described elsewhere (Hoover & Vasanthan, 1992).

2.7. Differential scanning calorimetry

Gelatinization temperature was measured and recorded on a Perkin–Elmer DSC-2 (Norwalk, CT) differential scanning calorimeter (DSC) equipped with a thermal analysis data station as reported previously (Vasanthan & Hoover, 1992). All DSC experiments were replicated at least three times.

2.8. Enzymatic hydrolysis

Enzymatic digestion studies on starches were carried out using crystalline porcine pancreatic α-amylase in 2.9 M NaCl containing 3 mM $CaCl_2$ (Sigma Chemical Co., St. Louis, MO), in which the concentration of α-amylase was 30 mg ml^{-1}, and the specific activity was 790 units per milligram of protein. The details of the procedure have been outlined in an earlier publication (Hoover & Vasanthan, 1994).

2.9. Scanning electron microscopy (SEM)

Granule morphology was examined using SEM. Starch samples were mounted on circular aluminium stubs with double sticky tape, and then coated with 20 nm of gold and examined and photographed in a Hitachi (S 570) scanning electron microscope at an accelerating potential of 20 kV.

2.10. Acid hydrolysis

Starches were hydrolyzed with 2.2 N HCl at 35°C (1.0 g starch 40 ml $acid^{-1}$) for periods ranging from 1 to 20 days. The extent of hydrolysis was estimated by the procedure described elsewhere (Hoover & Vasanthan,

1994). Results used for calculation were means of triplicate measurements.

2.11. Statistical analysis

All determinations were replicated three times or more and mean values and standard deviations reported. Analyses of variance (ANOVA) were performed and differences in mean values were performed using Tukey's studentized test at $p < 0.05$ and employing ANOVA and Tuckey's procedures of statistical analytical systems (SAS, 1990).

3. Results and discussion

3.1. Morphological granular characteristics of the starches

Microscopic examination showed that beach pea, green pea and grass pea starch granules had irregular shapes which varied from round (6–33 μm) to elliptical (shorter diameter, 11–22 μm; longer diameter, 17–35 μm) (Fig. 1). The size of beach pea starch granules was also smaller than those reported for other legume starches (Hoover & Sosulski, 1991). The surfaces of the above starches appeared to be smooth and showed no evidence of fissures when viewed under the SEM (Fig. 1). Granule clustering was more evident in beach pea (Fig. 1A) than in green pea (Fig. 1C) and grass pea (Fig. 1E) starches.

3.2. Chemical composition of the starches

The data on composition and yield are presented in Table 1. The purity of the starches was judged on the basis of composition and microscopic examination. The yields of starch from beach pea, green pea and grass pea starches were 12, 30 and 26%, respectively. The value for beach pea starch was much lower than the range (18–45%) reported (Hoover & Sosulski, 1991) for most legume starches. Isolation of starches from legumes is generally difficult owing to the presence of a highly hydrated fine fibre fraction (Vose, 1977) which is derived from the cell wall enclosing the starch granules (Schoch & Maywald, 1968). The ash content (beach pea $>>$ green pea $\sim$ grass pea) (Table 1) which reflects contamination by fine fibre, suggests that the low yield of starch from beach pea seeds is due to its higher fine fibre content. The nitrogen contents were 0.08, 0.09 and 0.07% in beach pea, green pea and grass pea starches, respectively. These low values indicated the absence of non-starch lipids (lipids associated with endosperm proteins). Therefore, total lipids (obtained by acid hydrolysis) in beach pea (0.16%), green pea (0.19%) and grass pea (0.12%) starches (Table 1) mainly represent the free and bound starch lipids. The total lipid content (Table 1) of beach pea starch was within the range reported for most legume starches (Hoover & Sosulski, 1991). The amount of bound lipids (extracted with propanol–water) (Table 1) was higher (0.10%) than that of grass pea (0.07%) but lower than that of green pea (0.12%) starch. These values were within the range reported for other legume starches (Hoover & Manuel, 1996). A comparison of the apparent and total amylose content (Table 1) showed that 5.9, 11.0 and 5.1% of the total amylose was complexed by native starch lipids in beach pea, green pea and grass pea starches, respectively. The value for beach pea (5.9%) was comparable to that of CC gold lentil starch (5.6%) (Hoover & Manuel, 1995), but was lower than those reported for mung bean (12.1%) (Hoover, Li, Hynes, & Senanayake, 1997) and laird lentil (12.4%) starches (Hoover & Manuel, 1995). The extent of starch damage during wet milling was more pronounced in beach pea (4.9%) than in grass pea (1.7%) and green pea (1.9%) (Table 1). This was not surprising, since the seed coat of beach pea did not soften (steeping in water at 50°C for 24 h) to the same extent as the seed coats of the other two legume seeds.

3.3. X-ray diffraction

Beach pea and grass pea starches showed the characteristic 'C' pattern of legume starches. (Colonna, Buleon, & Mercier, 1981; Gernat, Radosta, Damaschun, & Schierbaum, 1990; Hoover & Sosulski, 1985; Hoover & Manuel, 1996; Hoover et al., 1997). In beach pea starch the X-ray pattern was characterized by a strong intensity peak at 5.12 Å, a medium intensity peak at 3.86 Å and a weak intensity peak at 5.80 Å (Fig. 2, Table 2). In grass pea starch, the strong intensity peak occurred at 5.19 Å and the medium and weak intensity peaks occurred at 3.89 Å and 5.86 Å, respectively (Fig. 2, Table 2). Green pea starch showed a strong intensity peak at 5.15 Å, two medium intensity peaks at 5.85 and 3.82 Å and a weak intensity peak at 15.7 Å (the peak at 15.7 Å is characteristic of tuber starches). Gernat et al. (1990) have shown that the legume starch 'C' crystalline polymorph is a mixture of 'A' and 'B' unit cells, and that these starches contain pure 'A' and 'B' polymorphs in varying proportions. The results suggest that beach pea and grass pea starches have a higher proportion of 'A' unit cells than green pea starch. Starch crystallites are due to sequential packing of double helices (Wu & Sarko, 1978a, b) that are found between the flexible 'A' chains of amylopectin (French, 1972). The difference in X-ray intensities among the starches cannot be attributed to differences in crystallite size (since all these starches exhibit sharp X-ray patterns (Fig. 2)) or to amylopectin content (since beach pea starch with a higher amylopectin content (Table 2) exhibits the weakest X-ray pattern (Fig. 2)). Therefore,

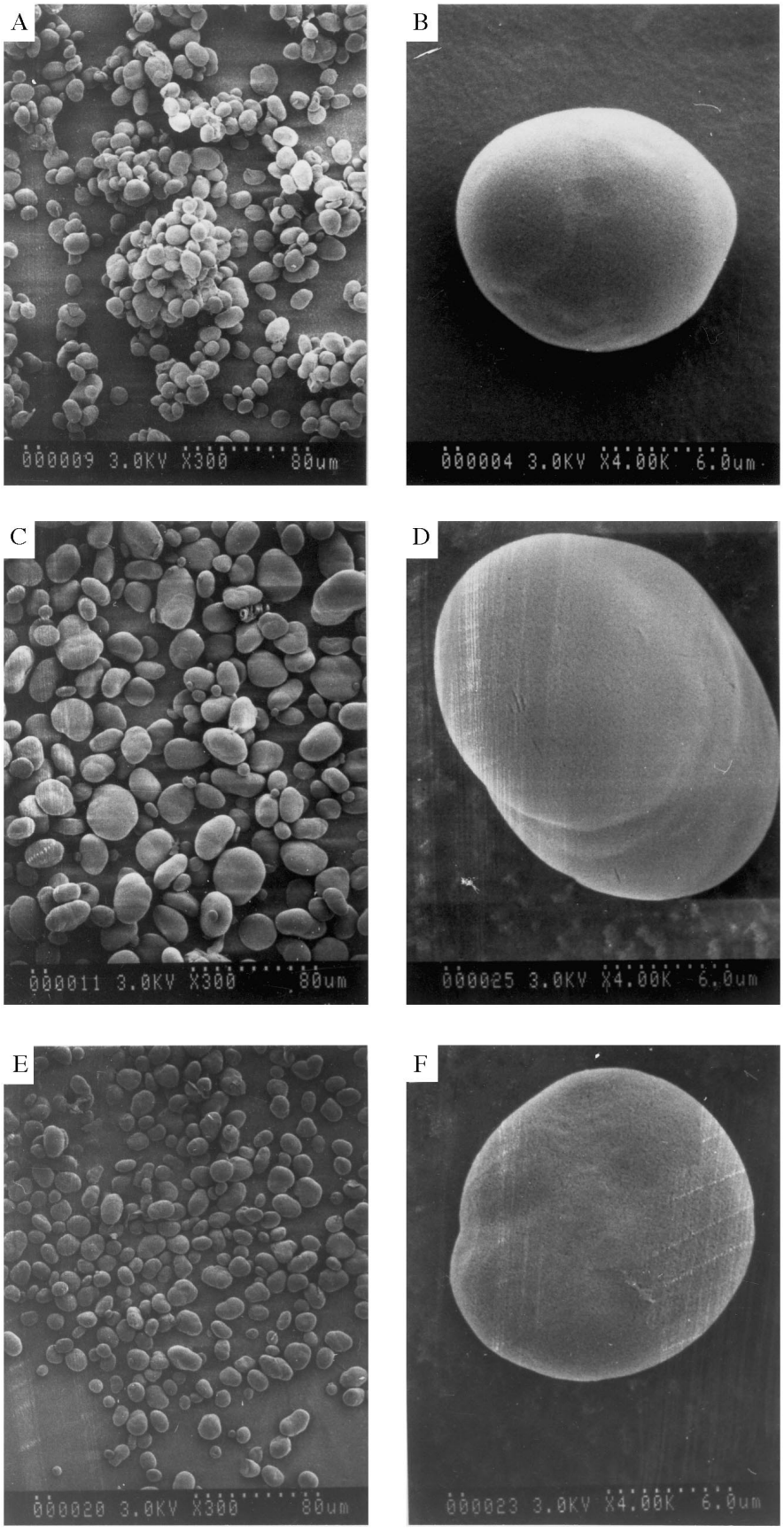

Fig. 1. Scanning electron micrographs of legume starches: (A) and (B), beach pea; (C) and (D), green pea; and (E) and (F), grass pea.

Table 1
Chemical composition (%) of beach pea, green pea and grass pea starches [1]

Characteristics	Starch source		
	Composition %		
	Beach pea	Green pea	Grass pea
Yield (% initial material)	12.3 ± 2.2[c]	30.0 ± 1.9[a]	26.0 ± 1.1[b]
Moisture	10.57 ± 0.07[a]	10.60 ± 0.42[a]	10.87 ± 0.03[a]
Ash	0.22 ± 0.03[a]	0.07 ± 0.01[bc]	0.05 ± 0.01[c]
Nitrogen	0.08 ± 0.01[a]	0.09 ± 0.02[a]	0.07 ± 0.01[a]
Lipid			
Acid hydrolyzed[2]	0.16 ± 0.02[ab]	0.19 ± 0.02[a]	0.12 ± 0.01[b]
Solvent extracted:			
Chloroform:methanol (2:1)[3]	0.06 ± 0.02[a]	0.07 ± 0.02[a]	0.05 ± 0.01[a]
1-Propanol:water (3:1)[4]	0.10 ± 0.00[b]	0.12 ± 0.01[a]	0.07 ± 0.01[c]
Amylose content (% of total starch)			
Apparent[5]	27.30 ± 0.43[c]	32.67 ± 0.17[b]	34.52 ± 0.35[a]
Total[6]	29.02 ± 0.20[b]	36.70 ± 0.26[a]	36.37 ± 0.31[a]
Amylose complexed by native lipid[7]	5.9	11.0	5.1
Starch damage	4.9 ± 0.1[a]	1.9 ± 0.1[b]	1.7 ± 0.1[b]
Granule shape	round to elliptical	round to elliptical	round to elliptical
Granule size (μm)			
Round	6 to 17	14 to 33	13 to 17
Ellipitical			
Short diameter	11	22	13
Long diameter	17	35	21

[1] All data reported on dry basis and represent the mean of three determinations ± SD. Means in each row with different superscripts are significantly different ($p < 0.05$).
[2] Lipids obtained by acid hydrolysis (24% HCl) of the native starch (total lipids).
[3] Lipids extracted from native starch by chloroform:methanol 2:1 (v/v) at 25°C (mainly unbound lipids).
[4] Lipids extracted by hot 1-propanol:water 3:1 (v/v) from the residue left after chloroform:methanol extraction (mainly bound lipids).
[5] Apparent amylose was determined by iodine binding without removal of free and bound lipids.
[6] Total amylose was determined by iodine binding after removal of free and bound lipids.
[7] $\frac{\text{Total amylose} - \text{apparent amylose} \times 100}{\text{Total amylose}}$.

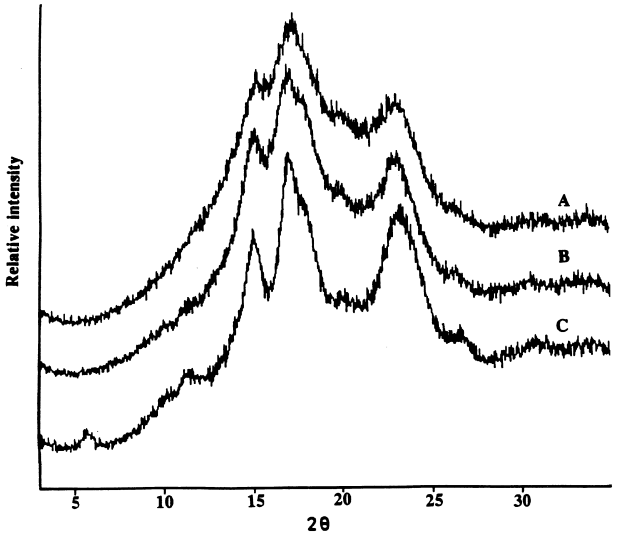

Fig. 2. X-ray diffraction patterns of: (A) beach pea starch; (B) grass pea starch; and (C) green pea starch.

differences in X-ray intensities (Table 2) are probably due to the manner in which the double helices are arranged within the crystalline domains of the granule. The results indicate that the double helices of beach pea starch are less compactly packed and/or less well arranged to diffract X-rays than those of grass pea and green pea starches.

Table 2
X-ray diffraction intensities of the major peaks of beach pea, green pea, and grass pea starches

Starch source	Interplanar spacings (d) in Å with intensities (CPS)[a]
Beach pea[b]	5.80 (490), 5.12 (1149), 3.86 (843)
Grass pea[c]	5.86 (901), 5.19 (1478), 3.89 (1022)
Green pea[d]	15.73 (192), 5.85 (967), 5.15 (1750), 3.82 (1331)

[a] Counts per second.
[b] Moisture content 10.57%.
[c] Moisture content 10.60%.
[d] Moisture content 10.87%.

3.4. Swelling factor (SF) and amylose leaching (AML)

The SF and AML were investigated over the temperature range 50–95°C. The results are presented in

Table 3
Swelling factor of beach pea, green pea and grass pea starches at different temperatures [1,2]

Temperature (°C)	Beach pea	Green pea	Grass pea
50	7.33 ± 0.17^{a}	7.52 ± 1.02^{a}	1.42 ± 0.14^{b}
60	8.55 ± 0.05^{a}	8.94 ± 1.08^{a}	1.56 ± 0.20^{b}
70	16.73 ± 0.18^{a}	17.70 ± 1.06^{a}	10.02 ± 0.08^{b}
80	18.43 ± 0.10^{b}	21.11 ± 1.07^{a}	13.03 ± 0.07^{c}
85	19.61 ± 0.13^{b}	22.41 ± 1.03^{a}	14.91 ± 0.07^{c}
90	24.92 ± 0.21^{b}	28.01 ± 0.37^{a}	19.58 ± 0.13^{c}
95	30.72 ± 0.82^{b}	34.13 ± 0.24^{a}	26.01 ± 0.07^{c}

[1] The data represent the mean of four determinations ± SD. Means in each row with different superscripts are significantly different ($p < 0.05$).
[2] Swelling factor is ratio of volumes of wet to dry granules.

Table 4
Leached amylose (% dry weight) of beach pea, green pea and grass pea starches at different temperatures [1]

Temperature (°C)	Beach pea	Green pea	Grass pea
50	—	—	—
60	—	—	—
70	3.43 ± 0.03^{b}	6.16 ± 1.09^{a}	6.25 ± 0.09^{a}
80	7.54 ± 0.08^{b}	14.33 ± 1.03^{a}	15.07 ± 0.54^{a}
85	9.84 ± 0.29^{b}	15.08 ± 1.10^{a}	15.66 ± 0.53^{a}
90	11.55 ± 0.52^{b}	16.69 ± 1.02^{a}	17.68 ± 0.10^{a}
95	12.94 ± 0.18^{b}	17.08 ± 1.57^{a}	19.07 ± 0.13^{a}

[1] The data represent the mean of four determinations ± SD. Means in each row with different superscripts are significantly different ($p < 0.05$).
— Amylose leaching was not observed at these temperatures.

Tables 3 and 4, respectively. The SF followed the order: green pea > beach pea > grass pea (Table 3), whereas, the corresponding order for AML was: grass pea ~ green pea > beach pea (Table 4). The SF and AML were within the range reported for other legume starches (Hoover & Manuel, 1996). Starch granule swelling is known to begin in the bulk relatively mobile amorphous fraction and in the more restrained amorphous regions immediately adjacent to the crystalline region (Donovan, 1979). Furthermore, amylose–lipid complexes have been shown to inhibit granule swelling (Hoover & Manuel, 1996; Maningat & Juliano, 1980; Tester & Morrison, 1990). The observed order in SF (Table 4) suggests that bound lipid content (Table 1) is not a factor influencing granule swelling. It is likely that interactions between amylose chains within the amorphous domains of the granule (these interactions would reduce hydration of amylose chains) negate the influence of bound-lipids on granular swelling. The results indicate that the magnitude of this interaction follows the order: grass pea > beach pea > green pea. The results on AML (Table 4) suggest that the extent of AML in these starches is influenced by the interplay between differences in amylose content (green pea ~ grass pea > beach pea), bound lipid content (green pea > beach pea > grass pea) and by the magnitude of interaction between amylose chains within the native granule (grass pea > beach pea > green pea).

3.5. Acid hydrolysis

The hydrolysis of the legume starches by 2.2 N HCl is presented in Fig. 3. All three starches exhibited a two-stage solubilization pattern. A relatively higher rate was observed during the first 10 days, followed by a slower rate between 10 and 20 days. At the end of the 10th day of hydrolysis (corresponding to the degradation of the amorphous region of the granule (Cairns, Leloup, Miles, Ring, & Morris, 1990; Kainuma & French, 1971)), beach pea, grass pea and green pea starches were hydrolyzed to the extents of 27, 23 and 21%, respectively. These values were comparable to that of other legume starches (Hoover & Manuel, 1995, 1996; Hoover, Swamidas, & Vasanthan, 1993). The rate of increase in hydrolysis beyond day 10 (corresponding to degradation of the crystallite region (Cairns et al., 1990; Kainuma & French, 1971)) followed the order: beach pea > grass pea > green pea. After 20 days, beach pea, grass pea and green pea starches were hydrolyzed to the extents of 49, 41 and 37%, respectively. Morrison, Tester, Gidley, and Karkalas (1993) have shown by studies on lintnerized barley starches (covering a wide range of amylose and lipid contents) that lipid-complexed amylose chains are resistant to acid hydrolysis. Furthermore, several researchers (BeMiller, 1967; Hoover & Manuel, 1996; Kainuma & French, 1971) have shown that a change in conformation of D-glucopyranose units

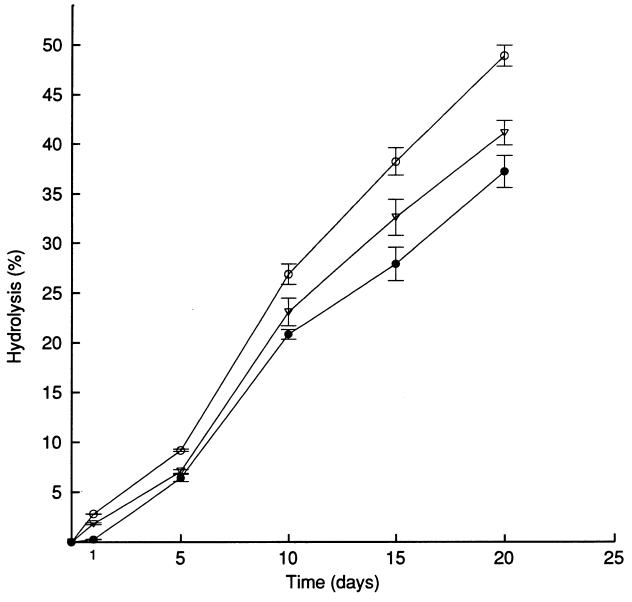

Fig. 3. Time course of acid hydrolysis (2.2 N HCl) of beach pea (○—○) green pea (●—●), and grass pea (▽—▽) starches. The data represent the mean of three determinations.

(chair → half chair) is a pre-requisite for hydrolysis of glucosidic bonds by H_3O^+. These transformations would be more difficult in lipid-complexed amylose chains (due to a decrease in chain flexibility). Thus, the higher resistance of green pea starch towards acid hydrolysis can be attributed to its higher content of amylose–lipid complexes (Table 1). On this basis, grass pea starch should have been hydrolyzed to a greater extent than beach pea starch due to its lower bound lipid content (Table 1). However, the observed extent of hydrolysis (beach pea > grass pea) suggests that this difference in hydrolysis is mainly influenced by the magnitude of interaction between amylose chains (grass pea > beach pea) within the amorphous domains of the starch granules. Strong associations between amylose chains will decrease the accessibility of the glucosidic linkages towards H_3O^+. The above results have shown that susceptibility towards acid hydrolysis during the first 10 days is influenced by the interplay of bound-lipid content and amylose chain associations within the amorphous domains of the starch granule.

The crystalline regions (consisting basically of double helices of external A and B chains of amylopectin) are generally less accessible than the amorphous regions to attack by hydrated protons (Cairns et al., 1990; Kainuma & French, 1971; Robin, Mercier, Charbonniere, & Guilbot, 1974;), due to dense packing of starch chains within the starch crystallites and to the high energy of activation (Wu & Sarko, 1978a, b) required to cause the conformational change of the glucose units (within the starch crystallites) from chair to half chair (a pre-requisite for acid hydrolysis). The extent of increase in hydrolysis (beach pea > grass pea > green pea) beyond the 10th day (Fig. 3) suggests that crystallites in beach pea starch are less compactly packed and/or are fewer in number than in grass pea and green pea starches. This seems possible, since the X-ray diffraction pattern (Fig. 2) of beach pea starch was much weaker than those of grass pea and green pea starches (Fig. 2).

3.6. Enzyme hydrolysis

The extent of hydrolysis by porcine pancreatic α-amylase is presented in Figs. 4 and 5. From the results it is apparent that beach pea is a better substrate than the other two legume starches, undergoing 35% hydrolysis in 24 h. The corresponding values for grass pea and green pea starches were 22 and 16%, respectively. Furthermore, the rate of increase in hydrolysis during the 24 h period, was more pronounced in beach pea than in the other two starches (grass pea > green pea). The mode of attack by α-amylase on native granules (after 24 h) was investigated by SEM (Fig. 5A–F). Granules of beach pea starch was more extensively degraded (Fig. 5A and B) than those of green pea (Fig. 5C and D) and grass pea (Fig. 5E and F) starches (grass pea > green pea). α-Amylase attack on green pea starch granules manifested itself in only mild superficial surface erosion (Fig. 5C and D). In contrast, the surface of beach pea starch granules was extensively eroded with numerous fissures on the entire granule surface (Fig. 5B). Furthermore, many granules of beach pea starch were split open (Fig. 5B). The surface of grass pea starch granules was also covered with fissures. However, the extent of erosion was less pronounced than in beach pea starch (Fig. 5F). Granule splitting due to α-amylase action was not evident in grass pea starch.

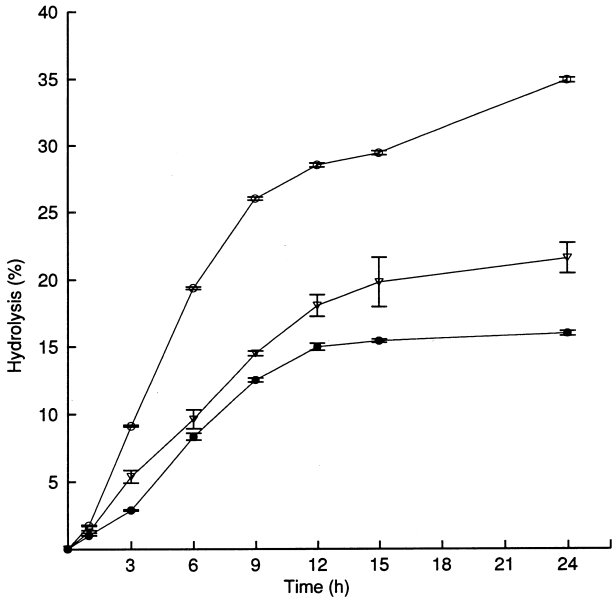

Fig. 4. Time course of hydrolysis of beach pea (○—○), green pea (●—●), and grass pea (▽—▽) starches by porcine pancreatic α-amylase. The data represent the mean of four determinations.

Thoma (1968) postulated that the enzyme-catalyzed hydrolysis of the α-D-(1→4) glycosidic bonds of the starch molecule involves enzyme-induced ring distortion of one of the D-glucosyl residues from the $^4C_1$ chair conformation to a half chair conformation. This ring distortion decreases the enthalpy of activation and increases the susceptibility of the glucosyl residues to nucleophilic attack by functional groups on the enzyme and water. László, Hólló, Hoschke, and Sárasi (1978) have shown that ring distortion or a half chair conformation is involved in the transition state of α-amylase. It is therefore possible that conformational changes (chair → half chair) during α-amylase hydrolysis may be difficult for those amylose chains that are complexed by native lipids (due to decreased chain flexibility). This would then explain the differences in the degree of susceptibility between green pea (11.0% of amylose complexed by lipid) and the other two starches (5.1–5.9% amylose complexed by lipid). On this basis, grass pea starch (5.1% amylose complexed by lipid) should have been hydrolyzed to a greater extent than beach pea starch (5.9% amylose complexed by lipid).

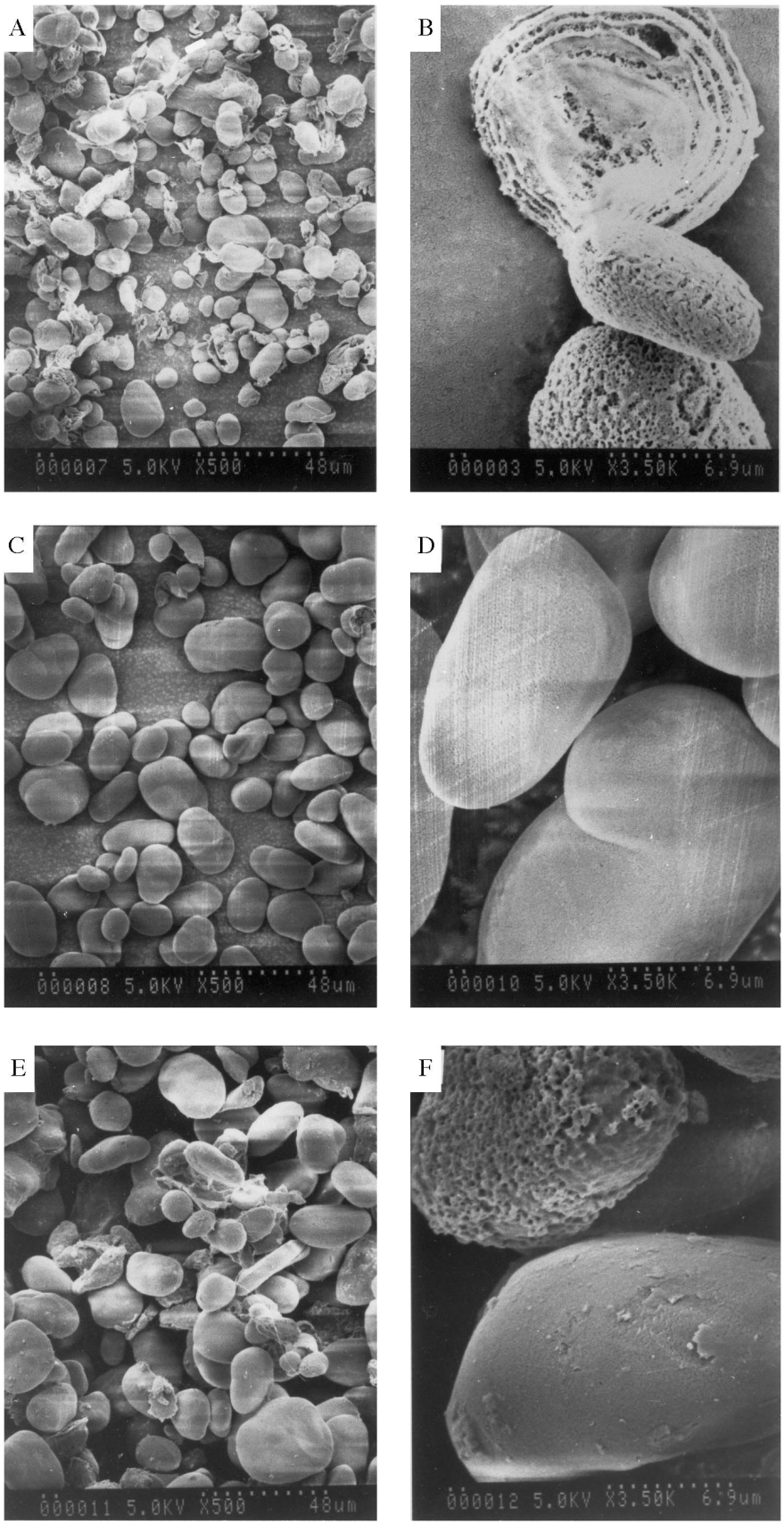

Fig. 5. Scanning electron micrographs of native starches after attack (24 h) by porcine pancreatic α-amylase: (A) and (B), beach pea; (C) and (D), green pea; and (E) and (F), grass pea.

Table 5
Differential scanning calorimetry parameters for beach pea, green pea, and grass pea starches [1]

Starch source	Transition temperatures (°C)[2]				ΔH (cal g^{-1})[4]
	T_o[3]	T_p[3]	T_c[3]	$\Delta T(T_c-T_o)$	
Beach pea	60.0 ± 0.6^c	64.5 ± 1.0^b	74.2 ± 1.2^a	14.2	1.6 ± 0.04^a
Green pea	69.4 ± 1.6^a	72.0 ± 0.8^a	76.3 ± 0.7^a	6.6	1.2 ± 0.13^c
Grass pea	65.7 ± 1.5^b	71.0 ± 0.8^a	74.2 ± 1.0^a	8.5	1.4 ± 0.03^b

[1] The data represent the mean of three determinations ± SD. Means in each column with different superscripts are significantly different ($p < 0.05$).
[2] Starch:water (1:3).
[3] T_o, T_p and T_c indicate the temperature of the onset, mid-point and conclusion of gelatinization.
[4] Enthalpy of gelatinization.

The difference in hydrolysis between beach pea and green pea starches is, thus, probably due to amylose chains being more loosely organized (this increases the rate of diffusion of α-amylase into the granule interior) within the amorphous regions of beach pea starch. This seems plausible since, in spite of its lower amylose content (27.3%) (Table 1), the rate and extent of hydrolysis of beach pea starch was higher than that of grass pea starch (Fig. 4). The results suggest that the interplay of bound lipid content and amylose chain associations within the amorphous regions influence granule susceptibility to α-amylase hydrolysis.

3.7. Differential scanning calorimetry

The gelatinization transition temperatures (at a volume fraction of water (v_1) = 0.85) and the enthalpy of gelatinization (ΔH) of beach pea, green pea and grass pea starches are presented in Table 5. The onset (T_0), mid-point (T_p) and conclusion (T_c) temperatures of the gelatinization endotherm of the starches followed the order: green pea > grass pea > beach pea, whereas, ΔH followed the order: beach pea > grass pea > green pea.

Gelatinization involves the uncoiling and melting of the external chains of amylopectin that are packed together as double helices in clusters. Cooke and Gidley (1992) have shown, through studies of starches isolated at various steps of the gelatinization process, that the relative decreases in double helix content parallel the relative decrease in both crystallinity and residual gelatinization enthalpy, but occur at higher temperatures than the relative decrease in granular birefrigence. The above authors have shown by studies on granular starch and model crystallites, that ΔH is due mainly to the disruption of the double helices rather than the long range disruption of crystallinity.

The lower T_0, T_p, T_c and the higher ΔH of beach pea starch suggest that disruption of double helices (in the amorphous and crystalline regions) during gelatinization is more pronounced in beach pea than in grass pea and green pea starches (grass pea > green pea). This indicates that the degrees of association between double helical chain clusters in these starches follow the order: green pea > grass pea > beach pea. Furthermore, differences ΔT (T_c–T_o) among the starches (beach pea >> grass pea > green pea) suggest that crystallites within the crystalline domains of beach pea starch granules have varying stability.

4. Conclusion

The results showed that beach pea starch differs significantly from other legume starches with respect to starch yield (low), amylose content (low), X-ray diffraction intensities (low) and the extent of interaction (weak) between starch chains within the amorphous and crystalline domains of the native granule. Work is now in progress to study the rheological and retrogradation properties of beach pea starch in order to assess the suitability of this starch for food and non-food related applications. However, this will necessitate the development of a wet- or dry-milling commercial process for isolation (with increased yield and minimum starch damage) of beach pea starch to make it competitive with starch from other legume seeds.

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