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Physicochemical properties of Canadian oat starches

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Abstract

Starch from six cultivars of oat grains (grown under the same environmental conditions) was isolated and some of the characteristics determined. The yield of starch ranged from 30.9 to 32.3% on a whole grain basis. The shape of the granule ranged from irregular to polygonal in shape with an average granule diameter of 7.0–7.8 μm within a range of 3.8–10.5 μm. Lipids were extracted by acid hydrolysis and by selective solvent extraction with chloroform–methanol 2:1 v/v (CM) at ambient temperature followed by *n*-propanol–water 3:1 v/v (PW) at 90–100 °C. The acid hydrolyzed extracts, which represented the total starch lipids ranged from 0.85 to 1.31%. The free lipids in the CM extract ranged from 0.05 to 0.09%, whereas the free and bound lipids in the PW extracts ranged from 0.75 to 1.18%. The total amylose content ranged from 10.60 to 24.50%, of which 9.02–18.91% was complexed by native starch lipids. The X-ray diffraction pattern was of the 'A' type. The relative crystallinity (RC) ranged from 28.0 to 36.5%. The starches differed widely in the degree of granular swelling, extent of amylose leaching, paste viscosity, gelatinization transition temperatures, gelatinization enthalpy, susceptibility towards acid hydrolysis, and retrogradation characteristics. The results showed that the above differences were influenced by variations in bound lipid content, RC and amylopectin branch chain length.
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Keywords: Oat starches; Physicochemical properties

1. Introduction

The production of cereal grains in Canada is regionalized with the prairie provinces of Alberta, Saskatchewan and Manitoba producing most of Canada's red spring wheat, durum wheat, barley, oats and rye. Corn is grown mainly in Ontario and Quebec (Agriculture and Agri-Food Canada, 1999). In 1998, oat production totaled about 4 Mt and accounted for approximately 7% of the total grain production. Canada is the largest exporter of oats in the world comprising 80% of the world market (Agriculture and Agri-Food Canada, 2000). Although predominantly oats have been in Canada as feed for animals, a small proportion of the oat crop is milled to provide products for the human diet. These include: oat meal for porridge, oat flour for baby foods and for the manufacture of ready to eat breakfast cereals. Starch constitutes nearly 60% of the dry matter of the oat grain. It mainly occurs in the endosperm. In the studies conducted so far, considerable differences have been observed between the physicochemical properties of oat starch and other cereal starches. These differences have been attributed to the higher bound lipid content, co-leaching of amylose and amylopectin (during heating of oat starch dispersions), higher relative crystallinity (RC), smaller amylose chain length and the smaller granule size of oat starches (Gudmundsson & Eliasson, 1989; Hoover & Vasanthan, 1992; Mua & Jackson, 1995; Paton, 1986; Shamekh, Forssell, & Poutanen, 1994; Sowa & White, 1992; Tester & Karkalas, 1996; Wang & White, 1994; Zhou, Robards, Holmes, & Helliwell, 1998). Furthermore, starches from different oat cultivars have been shown to differ in their physicochemical properties (Gudmundsson & Eliasson, 1989; Wang & White, 1994; Zhou et al., 1998). The above studies have been conducted mainly on Swedish, American and Australian oat cultivars. Zhou et al. (1998) have shown that the properties of oat starch from Australian oat cultivars differ significantly from those from the Northern Hemisphere. They have attributed these differences to moisture availability, growth temperature and day length. A survey of the literature revealed that there has been very little investigation on oat starches from Canadian cultivars. Therefore, it was considered worthwhile to determine the composition and physicochemical properties of starches from some newly introduced Canadian oat cultivars grown under identical environmental conditions.

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The properties of these starches were compared with those of wheat and maize starches.

2. Materials and methods

2.1. Materials

Oat grain cultivars (alymer, antoine, baton, ernie, francis, gosline) were grown on experimental plots (under identical environment and soil conditions) at the Central Experimental Farm in Ottawa, Ontario. All chemicals and solvents were of ACS certified grade. Solvents were distilled from glass before use. Crystalline porcine pancreatic α-amylase (EC 3.2.1.1, type 1A) was purchased from Sigma Chemical Co. (St Louis, MO).

2.2. Starch isolation

Three lots of oat grains were taken representing whole samples from the experimental plot of each cultivar. Starch was extracted from each lot using the procedure of Hoover and Vasanthan (1992).

2.3. Granule morphology

The size and shape of native starches were examined by a Carl Zeiss microscope. The range of granule size was determined by measuring the length and width of 100 granules from a 1.0% starch suspension at 50 × measured with an eye-piece micrometer. Granule surface was studied by scanning electron microscopy. Starch samples were mounted on circular aluminum 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 (Nissei Sang Yo Inc., Rexdale, ON, Canada) at an accelerating potential of 20 kV.

2.4. Chemical composition of starch

Quantitative estimation of moisture, ash, nitrogen, and starch damage were performed by the standard AACC (1984) methods. Starch lipids were determined by procedures outlined in an earlier publication (Vasanthan & Hoover, 1992).

2.5. Amylose content

Apparent and total amylose content was determined by a modification (Hoover & Ratnayake, 2001) of the method of McGrance, Cornell, and Rix (1998).

2.6. Apparent amylose content

Starch (20 mg, db) was dissolved in 90% dimethylsulfoxide (8 ml) in 10 ml screw-cap reaction vials. The contents of the vials were vigorously mixed for 20 min and then heated in a water bath (with intermittent shaking) at 85 °C for 15 min. The vials were then cooled to ambient temperature, and the contents diluted with water to 25 ml in a volumetric flask. 1.0 ml of the diluted solution was mixed with water (40 ml) and 5 ml I_2/KI solution (0.0025 M I_2 and 0.0065 M KI) and then adjusted to a final volume of 50 ml. The contents were allowed to stand for 15 min at ambient temperature, before absorbance measurements at 600 nm.

2.7. Total amylose content

The total amylose content of starch samples was determined by the above procedure, but with prior defatting with hot *n*-propanol–water (PW) (3:1 v/v) for 7 h. In order to correct for over estimation of apparent and total amylose content (due to complex formation between I_2 and the outer branches of amylopectin), amylose content was calculated from a standard curve prepared using mixtures of pure potato amylose and amylopectin (over the range 0–100% amylose).

2.8. X-ray pattern and relative crystallinity

X-ray diffractograms were obtained with a Rigaku RU 200R X-ray diffractometer (Rigaku-Denki Co., Tokyo, Japan) with operating conditions as: target voltage—40 kV, target current—100 mA, aging time—5 min, scanning range—3–35°, scan speed—2.000°/min, step time—4.5 s, divergence slit width—1.00, scatter slit width—1.00 and receiving slit width—0.60. RC of the starches was calculated using the method of Nara, Mori, and Komiya (1978) using a peak-fitting software (Origin-Version 6.0, Microcal Inc., Northampton, MA). Amorphous starch was prepared by heating a 10% starch solution at 95 °C for 30 min with continuous agitation and then drying it at 100 °C for 24 h. The dried sample was ground into a free flowing powder using a RP 202 Pulaerit comminutator (Geoscience Instruments Corp., New York, NY) with denatured alcohol as the solvent. The ground sample was air dried for 24 h and passed through a 250 μm sieve. The moisture content of all starches used in X-ray analysis was ~16%. Powdered quartz was used as the 100% crystalline reference.

2.9. Swelling factor

The swelling factor (SF) of the starches when heated at 60 °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 SF at a given temperature. The SF is reported as a ratio of the volume of swollen starch granules to the volume of the dry starch.

2.10. Amylose leaching

Starches (20 mg, db) in water (10 ml) were heated at 60 °C in volume calibrated sealed tubes for 30 min. The tubes were then cooled at ambient temperature (25–27 °C) and centrifuged at 2000*g* for 10 min. The supernatant liquid (1 ml) was withdrawn and its amylose content was determined as described by Hoover and Ratnayake (2001). Percentage amylose leaching was expressed as mg of amylose leached per 100 g of dry starch.

2.11. Differential scanning calorimetry

Gelatinization parameters of native starches were measured using a Seiko differential scanning calorimetry (DSC) 210 (Seiko Instruments Inc., Chiba, Japan) differential scanning calorimeter equipped with a thermal analysis data station and data recording software. Water (11 μl) was added with a microsyringe to starch (3.0 mg) in the DSC pans, which were then sealed, reweighed and allowed to stand for 2 h at room temperature before DSC analysis to attain an even distribution of water. The scanning temperature range and the heating rates were 20–120 °C and 10 °C/min, respectively. In all measurements, the thermogram was recorded with an empty aluminum pan as the reference. The transition temperatures reported are the onset (T_o), peak (T_p) and conclusion (T_c). The enthalpy of gelatinization (ΔH) was estimated by integrating the area between the thermogram and a base line under the peak and was expressed in terms of Joules per gram of dry starch.

Melting of retrograded amylopectin was also determined by DSC. The samples were prepared with a starch to water ratio of 2:1. After the initial DSC run samples pans containing the gelatinized starch was stored at 4 °C for periods ranging from 7 to 28 days. Stored samples were equilibrated at 25 °C for 1 h before rescanning. The scanning temperature range and heating rate were identical to that used for the study of gelatinization parameters.

2.12. Pasting properties

A Brabender viscoamylograph (Model VA-V) equipped with a 700 cm cartridge (C.W. Brabender Instruments Inc., South Hackensack, NJ) was used to study pasting properties at a concentration of 6% (w/v) and pH 5.5.

2.13. Acid hydrolysis

Starches were hydrolyzed in triplicate with 2.2 M HCl at 35 °C (1.0 g starch/40 ml acid) for periods ranging from 1 to 15 days. The starch slurries were shaken daily by hand to resuspend the deposited granules. Aliquots taken at specific time intervals were neutralized and centrifuged (10 min at 2000*g*) and the supernatant liquid was assayed for carbohydrates (Dubois, Gilles, Hamilton, Rebers, & Smith, 1956). The extent of hydrolysis was determined by expressing the solubilized carbohydrates (Jane & Robyt, 1984) as a percentage of the initial starch.

2.14. Statistical analysis

All determinations were replicated three times and mean values and standard deviations reported. Analysis of variance (ANOVA) were performed and the mean separations were performed by Tukey's HSD test ($P < 0.05$) using the SigmaStat version 2.0 (Jandel Scientific/SPSS Science, Chicago, IL).

3. Results and discussion

3.1. Chemical composition

The data on yield and composition are presented in Table 1. The nitrogen content of isolated starches represents the contributions of endosperm storage proteins, lysophospholipids and proteins located inside starch granules (Morrison, 1981). The nitrogen content of the purified starches were in the range 0.02–0.09% (dry basis), indicating the absence of endosperm proteins and by implication most of the non-starch lipids. The total starch lipids obtained by acid hydrolysis was in the range 0.85–1.29% (Table 1). The corresponding range for wheat (Tester & Morrison, 1990) and maize (Morrison, Milligan, & Azudin, 1984) are 0.80–0.85 and 0.61–0.82%, respectively. The amylose content of oat starches has generally been reported to be in the range 25.2–29.4 (Gudmundsson & Eliasson, 1989; MacArthur & D'Appolonia, 1979; Tester & Karkalas, 1996; Zhou et al., 1998). However, the corresponding value for the oat starches examined in this study was in the range 19.60–24.50 (Table 1). Hoover and Senanayake (1996) and Hoover and Vasanthan (1992) have also reported lower values (19.4–22.7%) for the amylose content of some other Canadian oat cultivars (AC hull, AC stewart, Avena nuda). The corresponding values for the amylose content of wheat (Morrison & Laignelet, 1983) and maize (Hoover & Manuel, 1996) starches are 28.0 and 29.9%, respectively. The amount of lipid complexed amylose chains ranged from 9.02% (ernie) to 18.9% (gosline) (Table 1). This range was much lower than that reported for wheat (18.7–22.2%) (Morrison & Laignelet, 1983) and maize (18.7–21.0%) (Hoover & Manuel, 1996; Morrison & Laignelet, 1983). The solvent extracted starch lipids (Table 1) which refers to the lipids obtained by the combined action of chloroform–methanol (CM) and propanol–water was in the range 0.93–1.23%. The difference between the amount of lipids extractable by acid hydrolysis and solvent extraction (Table 1) was more pronounced in baton (0.06%) and gosline (0.08%) than in the other cultivars (0–0.02%). This implies, that lipid–amylose interactions are of a higher order of magnitude in baton and gosline starches. Granule damage during starch

Table 1
Chemical composition (%) of oat starches

Characteristics	Oat cultivars					
	Alymer	Antoine	Baton	Francis	Ernie	Gosline
Yield (% initial material)	32.2 ± 0.3[p]	31.6 ± 0.5[p]	32.3 ± 0.2[p]	31.5 ± 0.6[p]	30.9 ± 0.2[p]	32 ± 1.0[p]
Ash	0.20 ± 0.02[q]	0.15 ± 0.01[q]	0.15 ± 0.02[q]	0.15 ± 0.01[q]	0.13 ± 0.01[q]	0.14 ± 0.01[q]
Nitrogen	0.02 ± 0.01[p]	0.03 ± 0.02[q]	0.09 ± 0.01[p]	0.04 ± 0.02[p]	0.05 ± 0.03[p]	0.02 ± 0.02[p]
Lipid						
Acid hydrolyzed[a]	0.95 ± 0.01[p]	1.08 ± 0.01[q]	1.29 ± 0.02[r]	1.10 ± 0.01[s]	0.85 ± 0.01[t]	1.31 ± 0.01[r]
Solvent extracted						
Chloroform–methanol[b]	0.08 ± 0.01[q]	0.05 ± 0.02[q]	0.09 ± 0.03[q]	0.06 ± 0.04[q]	0.09 ± 0.02[q]	0.05 ± 0.03[q]
n-propanol–water[c]	0.85 ± 0.03[p]	1.01 ± 0.02[q]	1.14 ± 0.05[t]	0.94 ± 0.02[s]	0.75 ± 0.01[t]	1.18 ± 0.01[t]
Starch damage	2.3 ± 0.1[p]	2.5 ± 0.2[p]	2.8 ± 0.4[p]	2.5 ± 0.4[p]	2.7 ± 0.2[p]	2.0 ± 1.0[p]
Amylose content (% of total starch)[d]						
Apparent	16.86 ± 0.04[p]	16.95 ± 0.02[q]	20.06 ± 0.04[t]	18.37 ± 0.01[s]	18.65 ± 0.02[t]	19.50 ± 0.04[u]
Total	19.60 ± 0.02[p]	19.85 ± 0.01[q]	24.50 ± 0.02[r]	22.02 ± 0.03[s]	20.50 ± 0.02[t]	24.05 ± 0.02[u]
Amylose complexed by native lipids[e]	13.70 ± 0.02[p]	14.60 ± 0.01[q]	18.12 ± 0.02[r]	16.57 ± 0.02[s]	9.02 ± 0.02[t]	18.91 ± 0.03[u]
Granule size distribution[f]						
Diameter (range μm)	4.2–10.2	4.4–10.5	3.8–9.6	4.0–9.5	4.5–10.5	4.0–9.2
Diameter (average mm)	7.0 ± 1.2[p]	7.2 ± 1.2[p]	7.5 ± 0.9[p]	7.0 ± 0.6[p]	7.8 ± 1.5[p]	7.2 ± 0.5[p]

All data reported on dry basis and represent the mean of three replicates. Values followed by the same superscript in each row are not significantly different ($P < 0.05$) by Tukey's HSD test.

[a] Lipids obtained by acid hydrolysis (24% HCl) of the native starch (total lipids).

[b] Lipids extracted by 2:1 chloroform–methanol at 25 °C (mainly unbound lipids).

[c] Lipids extracted by 1:1 1-propanol–water from the residue left after chloroform–methanol extraction (mainly bound lipids).

[d] Apparent and total amylose determined by I_2 binding before and after removal of bound lipids by hot 1-propanol–water extraction.

[e] $\frac{\text{Total amylose} - \text{apparent amylose}}{\text{Total amylose}} \times 100$.

[f] Values are the average ± standard deviation of 45 starch granules, 15 each from three micrographs for each cultivar.

isolation was very low in all starches and ranged from 2.0 to 2.8% (Table 1).

3.2. Granule morphology

Oat starch granules tend to exist in clusters of individual granules. The granules of all starches ranged from irregular to polygonal in shape with average granule diameters of 7.0–7.8 μm within a range of 3.8–10.5 μm (Table 1). The surfaces appeared to be smooth with no evidence of fissures. The granule morphology of these oat starches was similar to those of other oat cultivars (Hoover & Senanayake, 1996; Hoover & Vasanthan, 1992).

3.3. X-ray diffraction pattern and relative crystallinity

The X-ray pattern of all starches was of the A-type representative of cereal starches, with spacing at 3.8, 4.8, 5.2, and 5.8 Å. At approximately the same moisture content (~16%), the RC followed the order: baton ~ gosline > francis > alymer ~ antoine > ernie. The reported values for the RC of maize and wheat starches have been determined at different moisture contents; therefore a direct comparison is not possible. None of the oat starches exhibited an intensity peak at 2θ of 20°. This peak has been attributed to the presence of highly ordered crystalline structures of amylose–lipid complexes in the granule. The presence of a peak at 2θ of 20° has been observed in high amylose maize (V and VII) starches and low amylopectin maize starch (Shi, Capitani, Trzasko, & Jeffcoat, 1998). Hoover and Manuel (1996) have shown that 20% of the amylose chains are complexed by native starch lipids in amylomaize V starches, this suggests, that either the percentage of lipid complexed amylose chains (13.70–18.91%) in the oat starches are too low, or the amylose–lipid crystallites are not properly ordered to diffract X-rays, or both. Generally, differences in RC between starches could be attributed to the following: (1) crystal size, (2) amount of crystalline regions (influenced by amylopectin content and amylopectin chain length, (3) orientation of the double helices within the crystalline domains and (4) extent of interaction between double helices. The difference in RC among the starches cannot be attributed to difference in crystallite size (since the sharpness in X-ray pattern was identical in all starches) or to amylopectin content (since baton and gosline with the lowest amylopectin content exhibited RC that were higher than that of the other cultivars). Therefore, the higher RC of baton and gosline could be due to an interplay of the following factors: (1) higher extent of interaction between double helices, (2) better orientation of the crystallites, and (3) longer amylopectin chain length.

3.4. Swelling factor and amylose leaching

The SF expressed on a starch basis and in terms of amylopectin content and the extent of amylose leaching (AML) at 70 °C are presented in Table 3. There was a significant difference ($P < 0.05$) in SF (based on amylopectin content) among the starches (ernie > alymer > antoine ~ francis > baton > gosline). Starch granule swelling is known to begin in the bulk, relatively mobile amorphous fraction and in the more restrained amorphous region immediately adjacent to the crystalline regions. The SF has been shown to be inhibited by amylose–lipid complexes (Hoover & Manuel, 1996; Maningat & Juliano, 1980; Tester & Morrison, 1990; Tester, Morrison, & Schuiman, 1993) and by long amylopectin chains (Hoover & Ratnayake, 2001; Sasaki & Matsuki, 1998; Tester et al., 1993). In this study, the SF correlated positively ($r = 0.871$) with the amount of lipid complexed amylose chains. Gosline having the highest amount of lipid-complexed amylose chains (18.9%) had the lowest SF (Table 3). In addition, ernie with the lowest amount of lipid complexed chains (9.0%) had the highest SF (Table 3). Sasaki and Matsuki (1998) have shown by studies on starches from different wheat cultivars, that starches with higher swelling power tend to contain higher proportion of long chains in amylopectin, and the difference in amylopectin structure is related to variations in starch swelling properties. Association between long amylopectin chains could result in the formation of a large number of crystallites, which could increase granular stability thereby reducing the extent of granular swelling. The lower SF of gosline (7.4) and baton (7.9) (Table 3) indicate that their amylopectin chains are probably longer than those of the other cultivars. Thus, the SF of the oat starches is most likely influenced by the amount of lipid complexed amylose chains and/or by amylopectin chain length. The SF of baton (7.9) and gosline (7.4) were lower than those reported by Hoover and Manuel (1996) and Hoover and Vasanthan (1992) for wheat (11.0) and maize (12.1) starches, respectively.

The extent of AML at 70 °C followed the order: ernie > alymer > antoine > francis > baton ~ gosline (Table 3). There was a strong positive correlation ($r = 0.855$) between the amount of lipid complexed amylose chains (Table 1) and the extent of AML. The very low extent of AML in gosline (1.2%) and baton (1.1%) is indicative of strong interactions between amylose–amylose, and/or between amylose and the long outer branches of amylopectin within the native granule. At the same temperature, AML in wheat (Hoover & Vasanthan, 1992) and maize (Hoover & Manuel, 1996) are 4.8 and 5.2%, respectively. Hoover and Senanayake (1996) have shown that the wavelength of maximum absorption (λ_{max}) of the solubles leached at 70 °C for native oat (Avena nuda) and wheat starches occur at 600 and 630 nm, respectively. (The λ_{max} of pure amylose and pure amylopectin being 640 and 500 nm, respectively). On this basis, they concluded that amylose and a molecule less branched than amylopectin are co-leached from the granules of oat, but preferential leaching of amylose occurs in wheat. Tester and Karkalas (1996) have postulated that gelatinized oat starch granules disintegrate more readily than granules of other sources, resulting in the presence of soluble amylopectin fragments in the leachate together with leached amylose. Among cereal starches, only granules of oat starch exist in tightly packed clusters (Hoover & Senanayake, 1996). Thus, during heating, friction between swollen granules could result in their disintegration. This would then explain the release of both starch components in the leachate at 70 °C.

3.5. Gelatinization characteristics

The gelatinization transition temperatures, [T_o (onset), T_p (mid point), T_c (conclusion)], and the enthalpy of gelatinization (ΔH) are presented in Table 4. The gelatinization temperatures of the oat starches ranged from 56.0 to 74.0 °C. There were significant differences in T_o, T_p and T_c between the oat cultivars (Table 4). The T_o of baton and gosline were higher than that of the other oat starches. The ΔH calculated on the basis of amylopectin content ranged from 12.4 J/g (gosline) to 14.6 J/g (ernie). The gelatinization parameters were within the range reported for other oat cultivars (Gudmundsson & Eliasson, 1989; Hoover & Vasanthan, 1992; Tester & Karkalas, 1996; Wang & White, 1994). For maize (Hoover & Manuel, 1996) and wheat (Hoover & Vasanthan, 1992) the T_o and ΔH are 66 °C and 14.3 J/g and 62 °C and 11.5 J/g, respectively. The transition temperature (T_{cx}) and enthalpy of melting of the amylose–lipid complex (ΔH_{cx}) ranged from 96 °C (ernie) to 104 °C (gosline) and 2.6 J/g (ernie) to 4.2 J/g (gosline). The corresponding values for maize (Gudmundsson & Eliasson, 1989) and wheat (Hoover & Vasanthan, 1992) are 98.6 °C and 1.25 J/g and 105 °C and 1.39 J/g, respectively.

Noda et al. (1998) have postulated that the gelatinization temperature is influenced by the molecular architecture of the crystalline region, which corresponds to the distribution of amylopectin short chains (dP6-11) and not by the proportion of crystalline region, which corresponds to the amylose/amylopectin ratio. The above authors showed that a low T_o, T_p and T_c reflect the presence of abundant short amylopectin chains. Patindol and Wang (2002) have shown by studies on rice cultivars that ΔH increases with increase in amylopectin branch length. Similar observations have been made on cultivars of maize and potato starches having long amylopectin branches (Jane et al., 1999). Our data on X-ray (Table 2) and SF (Table 3) suggested the presence of longer amylopectin branch chains in baton and gosline. Therefore, both these starches should have exhibited a higher ΔH than the other cultivars. The lower ΔH values for baton and gosline reflect the influence of the amylose–lipid complex melting transition on the gelatinization endotherm. Biliaderis, Page, Maurice, and Juliano (1986) have shown that there are two processes occurring

Table 2
Relative crystallinity of oat starches

Oat cultivar	Relative crystallinity[a]
Aylmer	32.0 ± 0.5[a]
Antoine	32.5 ± 0.2[a]
Baton	36.5 ± 0.2[b]
Francis	33.6 ± 0.2[c]
Ernie	28.0 ± 0.2[d]
Gosline	35.0 ± 0.1[b]

The moisture content of the starches was 16% (w/w). Values followed by the same letter, in the same column are not significantly different ($P < 0.05$) by Tukey's HSD test.

[a] %crystallinity $= \sum|I_s - I_a|/|I_c - I_a| \times 100$, where $I_s - I_a$ = difference between the sample and amorphous intensities and $I_c - I_a$ = difference between the 100% crystalline (quartz) and amorphous intensities.

during gelatinization first, the melting of crystallites (endothermic process) and second, formation of the amylose–lipid complex (exothermic process). A net endothermic process is detected by DSC, and the net energy required to form the endothermic peak is less when amylose–lipid complexes are present in the starch-water than when they are not. Kugimiya, Donovan, and Wang (1980) showed that lipid complexed potato starch exhibited a lower ΔH value than did native potato starch. This suggests that the low ΔH values for baton and gosline is due to their higher content of amylose–lipid complexes (Table 1). Jenkins (1994) has postulated that, in excess water, gelatinization is a primarily swelling driven process. Water uptake by the bulk amorphous and the intercrystalline amorphous areas is accompanied by swelling within these regions. The swelling acts to destabilize the amylopectin crystallites within the crystalline lamella, which are ripped apart. The presence of amylose–lipid complexes in the starch granule could decrease the extent of hydration of amylose chains (present in the bulk amorphous regions),

Table 3
Swelling factor and amylose leaching of oat starches at 70 °C

Cultivar	Swelling factor	Swelling factor[a] (based on amylopectin content)	Amylose leaching (%)
Aylmer	20.1 ± 0.5[a]	19.3 ± 0.1[a]	2.3 ± 0.1[a]
Antoine	15.0 ± 0.5[a]	18.7 ± 0.6[b]	1.9 ± 0.1[b]
Baton	6.0 ± 0.2[b]	7.9 ± 0.2[c]	1.2 ± 0.1[c]
Francis	14.2 ± 0.1[c]	18.2 ± 0.1[b]	1.6 ± 0.2[b]
Ernie	18.2 ± 0.2[d]	22.9 ± 0.2[d]	3.7 ± 0.2[d]
Gosline	5.6 ± 0.2[e]	7.4 ± 0.2[e]	1.1 ± 0.1[c]

The values of SF and AML followed by the same superscript in the same column are not significantly different ($P < 0.05$) by Tukey's HSD test. The data represent the mean of three determinations.

[a] Tester et al. (1993) have attributed variations in SF to differences in amylopectin structure. Morrison et al. (1993a,b) have shown that swelling is primarily a property of the amylopectin fraction. Thus, expressing SF on the basis of amylopectin content would be more meaningful than if it were expressed on a starch basis.

Table 4
Gelatinization characteristics of oat starches

Oat cultivar	Transition temperatures (°C)			
	T_o[a]	T_p[a]	T_c[a]	ΔH/(AP) J/g[b]
Aylmer	57.0 ± 0.3[a]	61.5 ± 0.2[a]	69.0 ± 0.5[a]	13.7 ± 0.1[a]
Antoine	58.5 ± 0.1[b]	63.5 ± 0.1[b]	70.5 ± 0.2[b]	13.2 ± 0.1[b]
Baton	63.0 ± 0.1[c]	64.5 ± 0.1[c]	72.0 ± 0.1[c]	12.9 ± 0.1[c]
Francis	60.0 ± 0.1[b]	63.5 ± 0.0[b]	70.5 ± 0.1[b]	13.5 ± 0.2[b]
Ernie	56.0 ± 0.1[d]	59.5 ± 0.1[d]	65.5 ± 0.2[d]	14.6 ± 0.3[d]
Gosline	63.5 ± 0.1[c]	66.0 ± 0.1[e]	74.0 ± 0.1[e]	12.4 ± 0.1[e]

Starch/water ratio = 1:3 (w/w dry basis). Values followed by the same letter, in the same column are not significantly different ($P < 0.05$) by Tukey's HSD test. The data represent the mean of three determinations.

[a] T_o, T_p and T_c indicate the temperature of the onest, midpoint and end of gelatinization, respectively.

[b] Enthalpy of gelatinization (ΔH) expressed on the basis of amylopectin content (AP).

thereby decreasing granular swelling. Consequently, the unraveling and melting of the double helices forming the crystallites would require a higher input of thermal energy. Thus, the higher T_o values (Table 4) for baton and gosline stands explained.

3.6. Acid hydrolysis

Hydrolysis of oat starches by 2.2 M HCl during a 15 day period is presented in Table 5. A relatively high rate was observed during the first 9 days (corresponding mainly to the degradation of the amorphous region of the granule), followed by a slower rate thereafter. At the end of the ninth day of hydrolysis, alymer, antoine, baton, francis, ernie and gosline were hydrolyzed to the extent of 65.3, 60.5, 55.5, 59.0, 68.5 and 52.5%, respectively (Table 5). During the same time interval, maize and wheat starches are hydrolyzed to the extent of 64.1 and 60.0%, respectively (Jayakody & Hoover, 2002; Hoover & Vasanthan, 1992). Between the 9th and 15th day (corresponding mainly to the degradation of starch crystallites), the increase in the extent of hydrolysis followed the order: antoine > ernie > francis > alymer > baton ~ gosline (Table 5). At the end of the 15th day, alymer, antoine, baton, francis, ernie and gosline were hydrolyzed to the extent of 78.0, 77.6, 66.0, 72.4, 82.5 and 62.5%, respectively. The corresponding value for maize (Jayakody & Hoover, 2002) and wheat (Hoover & Vasanthan, 1992) starches being 73.4 and 69.5%, respectively. Differences in the extent and rate of hydrolysis among the starches during the initial stages (1–9 days) of hydrolysis has been attributed to differences in: (1) granule size (Vasanthan & Bhatty, 1996), (2) amount of lipid complexed amylose chains (Inouchi, Glover, & Fuwa, 1987; Morrison, Low, & Snape, 1993a; Morrison, Tester, Snap, Law, & Gidley, 1993b), (3) extent of interaction between starch chains within the amorphous domains of the granule (Hoover & Manuel, 1996) and (4) amount of pores

Table 5
Acid hydrolysis of oat starches

Oat cultivar	Number of days				
	1	3	9	11	15
Alymer	17.5 ± 0.1[a]	36.7 ± 0.0[a]	63.3 ± 0.3[a]	73.6 ± 0.5[a]	76.0 ± 0.3[a]
Antoine	15.6 ± 0.2[b]	31.5 ± 0.2[b]	63.5 ± 0.5	70.0 ± 0.2[b]	76.6 ± 0.5[a]
Baton	13.2 ± 0.1[c]	27.7 ± 0.4[c]	55.5 ± 0.5[b]	63.0 ± 0.5[c]	65.0 ± 0.5[b]
Francis	15.0 ± 0.1[d]	29.5 ± 0.1[d]	59.0 ± 0.2[c]	68.0 ± 0.5[d]	72.4 ± 0.5[c]
Ernie	20.5 ± 0.2[e]	40.5 ± 0.5[e]	66.5 ± 0.5[d]	77.5 ± 0.5[e]	84.5 ± 1.5[d]
Gosline	12.6 ± 0.2[f]	24.5 ± 0.2[f]	52.5 ± 0.1[e]	60.6 ± 0.5[f]	62.5 ± 0.5[e]

All data represent the mean of three replicates and the values followed by the same superscript in each column are not significantly different ($P < 0.05$) by Tukey's HSD test.

on the granule surface (Jayakody & Hoover, 2002). In this study, the observed extent of hydrolysis during the initial stages (1–9 days) of hydrolysis is probably influenced mainly by factors 2 and 3, since the surfaces of all granules were devoid of pores, and differences in granule size among the starches was not significant (Table 1). This seems plausible, since baton and gosline containing the highest amount of lipid complexed amylose chains (Table 1) were hydrolyzed to a lesser extent than the other cultivars (Table 5). Whereas, ernie containing the least amount of lipid complexed amylose chains was hydrolyzed to the greatest extent (Table 5). Lipids within the amylose helix decrease the extent and rate of acid hydrolysis by hindering the conformational transformation (chair → half chair) required for protonation of the glycosidic oxygens (Hoover, 2000). Differences in hydrolysis among the starches beyond the ninth day can be attributed to the degree of packing of the double helices that form the crystalline lamellae. Closely packed double helices could slow the rate of acid hydrolysis by: (1) decreasing the extent of penetration of H_3O^+ into the crystalline lamellae and (2) sterically hindering the change in conformation (chair → half chair) of the D-glycopyranosyl unit. The results suggest that double helices that form the crystalline lamella are more closely associated in baton.

3.7. Pasting characteristics

The pasting properties of the starches are presented in Table 6. Baton and gosline differed significantly from the other starches in exhibiting a higher pasting temperature, lower viscosity at 95 °C and higher thermal stability during the holding period at 95 °C. It has been postulated (Doublier, Paton, & Llamas, 1987; Hoover & Vasanthan, 1992; Wang & White, 1994) that pasting properties are influenced by the amount of leached starch components, starch lipid content, and by the magnitude of interactions between starch chains within the granule interior. The higher crystallinity (Table 2) and the lower extent of amylose leaching (due to higher content of amylose–lipid complexes) (Table 3) are probably the caustive factors responsible for the higher pasting temperature, lower 95 °C viscosity and higher thermal stability shown by baton and gosline starches (Table 6). Under identical experimental conditions, the pasting temperature, viscosity at 95 °C viscosity after 30 min at 95 °C and the viscosity at 50 °C for maize starch (Hoover & Manuel, 1996) is 86.0 °C, 160, 140 and 360 BU, respectively. The corresponding values for wheat starch (Hoover & Vasanthan 1992) being, 80.5 °C, 52, 60 and 120 BU, respectively.

3.8. Retrogradation

The retrogradation endotherm appeared after 14 days of storage (at 25 °C) in alymer, antoine and francis. However, the endotherm occurred earlier (10 days) in ernie and after 18 days in baton and gosline (Table 7). At the end of the storage period (28 days), the retrogradation enthalpy (ΔH_R) of baton (2.1 J/g) and gosline (1.9 J/g) was smaller than

Table 6
Pasting characteristics of oat starches

Cultivar	Pasting temperature (°C)	Viscosity at 95 °C (BU)[a]	Viscosity after 30 min at 95 °C (BU)[a]	Viscosity at 50° (BU)[a]
Alymer	83.6 ± 1.0[a]	275 ± 5[a]	270 ± 5[a]	570 ± 5[a]
Antoine	87.0 ± 0.0[b]	275 ± 0[a]	195 ± 0[b]	570 ± 5[a]
Baton	93.5 ± 0.0[c]	40 ± 5[b]	280 ± 5[a]	580 ± 1[a]
Francis	88.0 ± 1.0[b]	285 ± 5[a]	250 ± 0[c]	585 ± 0[a]
Ernie	80.0 ± 1.0[d]	320 ± 5[c]	280 ± 5[a]	595 ± 5[a]
Gosline	94.0 ± 1.0[c]	45 ± 5[b]	260 ± 0[d]	570 ± 5[a]

Strach concentration 6% (w/w) and pH 5.5. All data represent the mean of two determinations. Mean values ($n = 2$) in each column sharing the same superscript are not significantly different ($P < 0.05$) by Tukey's HSD test.

[a] Brabender units.

Table 7
Enthalpy of retrogradation of oat starches as a function of storage time

Cultivar	Enthalpy (ΔH_R, J/g) storage time (days)					
	7	10	14	18	21	28
Alymer	–	–	1.8 ± 0.1^a	2.1 ± 0.1^a	2.4 ± 0.0^a	2.6 ± 0.1^a
Antoine	–	–	1.8 ± 0.1^a	2.2 ± 0.1^a	2.4 ± 0.1^a	2.5 ± 0.1^a
Baton	–	–	–	1.4 ± 0.0^b	1.8 ± 0.1^b	2.1 ± 0.1^b
Francis	–	–	1.5 ± 0.1^c	1.7 ± 0.0^c	2.0 ± 0.1^b	2.3 ± 0.1^b
Ernie	–	1.8 ± 0.2	2.2 ± 0.1^d	2.6 ± 0.2^d	2.6 ± 0.0^c	2.8 ± 0.1^c
Gosline	–	–	–	1.2 ± 0.1^e	1.4 ± 0.0^d	1.9 ± 0.1^b

Starch/water ratio 1:2. All data represent the means of three determinations. Mean values in each column sharing the same superscript are not significantly different ($P < 0.05$) by Tukey's HSD test.

the values observed for the other four cultivars (2.3–2.8 J/g) (Table 7). No direct comparison with other cereal starches is possible, due to different techniques and moisture content that have been used to assess the extent of retrogradation. However, the results of all studies (Gudmundsson & Eliasson, 1989; Hoover, Vasanthan, Senanayake, & Martin, 1994; Paton, 1986; Sowa & White, 1992; White, Abbas, & Johnson, 1989) have shown that oat starches retrograde to a lesser extent than maize and wheat starches. It has been postulated (Doublier et al., 1987; Gudmundsson & Eliasson, 1989; Sowa & White, 1992) that the higher lipid content of oat starches may be the causative factor responsible for the slower retrogradation. Yuan, Thomspon, and Boyer (1993) reported that the chain length and chain length distribution of amylopectin could influence the extent of retrogradation by forming a mixture of crystallites of different sizes, with longer chain lengths forming longer double helices. Wang and White (1994) showed that in oat starch cultivars, a close relationship exists between the extent of retrogradation, weight average chain length and the degree of multiple branching. Since ΔH_R values reflect the melting of amylopectin crystallites (formed by association between adjacent double helices) during storage, both baton and gosline should have exhibited higher ΔH_R values (due to their longer amylopectin chain length). Under the specified conditions, the lower ΔH_R values (Table 7) for the above starches, suggests that starch lipids may have complexed with the long outer branches of amylopectin, thereby hindering their association during storage.

4. Conclusions

Oat starches isolated from the six cultivars differed in physicochemical properties. These differences were more marked in baton and gosline starches, due to their higher bound lipid content, higher crystallinity and longer amylopectin branch chain length. In general, oat starches had a higher lipid content, less swelling power and amylose leaching at 70 °C, a lower percentage of lipid complexed amylose chains and a lower extent of retrogradation than maize and wheat starches.

Studies are underway to obtain very pure samples of amylose and amylopectin from the above starches. This will enable us to obtain a more precise insight into how oat starch structure influence functionality.

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