Swelling and Gelatinization of Oat Starches

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ABSTRACT

A comparison was made between the structure and physicochemical properties of starches extracted from five normal and one naked cultivar of oat. There was little difference in the molecular size or polydispersity of the native amylose and amylopectin determined by gel permeation chromatography (GPC), or in the unit chain distribution of isoamylase-debranched amylopectin, where three peaks were resolved at modal degree of polymerization of 15, 23, and 46. Apparent, total, and Δ-amylose (difference between apparent and total amylose due to lipid complexing) contents ranged from 19.7 to 22.0%, 27.5 to 29.8%, and 7.1 to 8.1, respectively, with lipid content, as fatty acid methyl esters, ranging from 0.66 to 0.75% on a dry basis and comprising the following fatty acids: 46.6% C16; 2.1% C18; 15.0% C18:1; 35.3% C18:2, and 0.7% C18:3. The naked oat starch had the lowest lipid content and Δ-amylose. Lintner type solubilization in 2*M* HCl (six days of incubation at 35°C) ranged from 56.6 to 60.0% of the original dry α-glucan. The 80°C swelling factor corresponding to postgelatinization swelling (determined by a blue dextran dye exclusion method) ranged from 8.6 to 10, with the naked oat being at the top of the range. At this temperature, the amount of α-glucan leached from the granules ranged from 4.1 to 6.6% (dry basis), where the highest value corresponded to the naked oat. Amylose (determined colorimetrically) accounted for 42.1–47.6% of the α-glucan in the leachate. No intermediate material could be detected by GPC. Damaged starch levels were very low in the starches analyzed (1.9–2.2% on a dry basis). The high proportion of branched α-glucan in the leachate was confirmed by GPC and was attributed to the fragile nature of the gelatinized oat starch granules. Gelatinization parameters by differential scanning calorimetry were 44.7–47.3, 56.2–59.5, and 68.7–73.7°C for T_o, T_p and T_c respectively, with ΔH ranging from 8.1 to 9.5 J/g. The mean diameter of native granules, determined by Coulter Counter, ranged from 4.96 to 5.63 μm, with the naked oat starch being at the low end.

Although less extensively researched than barley, maize, wheat, and rice starches, oat starches have received considerable attention in recent years because of increased awareness regarding the nutritional value of this cereal (Lockhart and Hurt 1986). Oats are utilized in breakfast cereals, porridge, biscuits, specialty breads, and for animal feed in the United Kingdom. It is difficult to obtain commercially produced oat starch as a food ingredient, since the starch industry utilizes primarily maize, wheat, potato, and to a lesser extent rice as raw material.

The dimensions of oat starch granules have been studied by Makela and Laakso (1984). Other groups have investigated physicochemical properties, including microscopy, pasting, swelling, gelatinization, and X-ray diffraction (Paton 1977, 1979, 1986, 1987; MacArthur and D'Appolonia 1979; Doublier et al 1987; Gudmundsson and Eliasson 1989; Hoover and Vasanthan 1992, 1994a,b; Virtanen et al 1993; Shamekh et al 1994; Mua and Jackson 1995). Compositional analyses with particular reference to amylose and lipids have been published by Paton (1986), Morrison et al (1984), Hoover and Vasanthan (1992), and Liukkonen and Laakso (1992).

Because of the technological importance of starch, either in the granular form or as solubilized glucan (i.e., leachate) released on gelatinization in food systems, research has been directed toward understanding the composition of the leachate and its properties in foods. Considerable differences have been reported in the literature concerning the nature and quantity of α-glucan leached from oat starches in comparison with that from other cereal starches. Doublier et al (1987) have compared the swelling power of granules and leaching of amylose in maize, oat, and wheat starches and showed that granule swelling and leaching of solubilized glucan, under the conditions that they employed, was greater in oats than in the other cereal starches and that amylose was leached together with amylopectin. Gudmundsson and Eliasson (1989) reported that less carbohydrate was leached from oat starches than from other cereal starches, although the former exhibited greater gel volumes. In a comparison between oat and wheat starches Hoover and Vasanthan (1992) found that oat starch had a greater swelling factor and a decreased solubility of amylose, and that amylose and a branched component were released during pasting. Compared with wheat starch, oat starch was more susceptible to acid hydrolysis but more resistant to hydrolysis with α-amylase. Co-leaching of amylose and amylopectin during swelling has also been discussed by Mua and Jackson (1995), but little has been reported in relation to granule disintegration at high swelling temperatures. It has been suggested that soluble material probably does not contribute to the swelling power of starches (Morrison et al 1993).

Very little work has been done on the structural analysis of amylose and amylopectin of oat starch. Early work by Paton (1979) focused on the gel permeation chromatography (GPC) profile of α-glucan and the β-amylolysis limit of some Canadian oat starches. Recent work by Wang and White (1994a–c) has made some progress in correlating the compositional and architectural characteristics of oat starch with its physico-chemical properties, but the α-glucan distribution profiles published by these authors are of lower resolution than one achieved by other methods (Karkalas and Tester 1992). In addition, these authors advocated the presence of intermediate material, which we could not detect in the course of this work.

It is evident from the articles discussed above that much of the published research on the properties of oat starch is contradictory and gives an incomplete picture concerning structure-functionality relationships. This work was initiated to study some aspects of the functionality of oat starches and its dependence on molecular structure, and to elucidate the reasons for some unusual properties, in particular the presence of intermediate material and the composition of the leachate from swollen granules.

MATERIALS AND METHODS

Oats

Six cultivars of oat were used for this work, five of which (Borrus, Erbgraf, Erich, Pitol, and Selma), originally of German

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origin, were obtained from W. R. Morrison of the University of Strathclyde (Glasgow); the naked oat (Pendragon) was obtained from Semundo Ltd., Cambridge.

Starches

Pure starches were prepared using previously described methodology for other cereals (Tester and Morrison 1990a,b).

Physical Measurements

The dimensions of granules were measured with a Coulter Multisizer counting in 256 channels (Tester et al 1991) according to the general method of Morrison and Scott (1986). Granule swelling factors at 80°C were determined on 50-mg samples of starch by blue dextran dye exclusion (Tester and Morrison 1990a). Gelatinization parameters (onset, peak, and conclusion temperatures, T_o, T_p and T_c, respectively) and enthalpy (ΔH) were determined by differential scanning calorimetry (DSC) on 3-4 mg of starch heated in 15 µl of water (Tester and Morrison 1990a).

Chemical Analysis

Moisture content was determined as loss of weight after heating at 130°C for 1 hr. Starch lipids were extracted in 1-propanol:water (3:1) at 100°C (Morrison and Coventry 1985) and quantified as fatty acid methyl esters (FAME) by gas-liquid chromatography according to Morrison et al (1975, 1980).

Total starch (α-glucan) was determined by the method of Karkalas (1985). The same general method (omitting the α-amylase stage) was used to quantify the amount of solubilized α-glucan after hydrolyzing (lintnerizing) 100 mg of starch in 5 ml of 2*M* HCl for six days at 35°C. Damaged starch was determined by the enzymatic method of Karkalas et al (1992). Amylose was determined colorimetrically (Morrison and Laignelet 1983). The α-glucan distribution profiles of native starches, and those debranched with isoamylase, were determined by GPC on Sepharose CL-2B and CL-6B columns (Karkalas and Tester 1992). Packed columns (100 × 1.6 cm internal diameter) were eluted with degassed 0.05*M* KOH (to prevent oxidation and polysaccharide crystallization, respectively) containing 0.005*M* thiomersal (to prevent microbial growth). The flow rate was typically either 0.25 or 0.50 ml min^{-1}, and the carbohydrate quantitation employed utilized enzymatic postcolumn derivitization as described by Karkalas and Tester (1992). Sample preparation involved solubilization in hot urea dimethyl sulfoxide (UDMSO) followed by precipitation in ethanol to remove lipid. The ethanol was decanted from the centrifuged samples, which were dissolved in 0.05*M* KOH to give a sample concentration of about 0.5 mg ml^{-1}, and 1 ml was loaded onto the columns. Debranching was done in acetate buffer (200 m*M*, pH 3.8) at 35°C using isoamylase (10 µl or about 590 units per 5 mg of starch) from *Pseudomonas amyloderamosa* (Hayashibara Biochemical Laboratories, Okayama, Japan), to give an α-glucan concentration of about 0.5 mg ml^{-1}. A sample (1 ml) of this debranched material (after boiling and centrifugation to remove protein) was loaded. In addition, debranched starches were analyzed by high-performance size exclusion chromatography (HPSEC) (Hizukuri 1985, Tester and Morrison 1990b, Tester et al 1991) using this same debranching procedure, although a more concentrated sample (20 µl via an injection loop of a 5 mg ml^{-1} digest) was applied to chromatographic columns (TSK-PWH guard, two TSK-GEL G300PW and one G2000PW columns in series and in that order) maintained at 37°C in an oven. These columns were eluted with 100 m*M* sodium phosphate buffer (pH 6.2 containing 0.02% sodium azide) at a flow rate of 0.7 ml min^{-1} and detected using a refractive index detector. Soluble leachate was similarly treated and chromatographed after ultracentrifugation or filtration through glass microfiber filters to remove granular fragments.

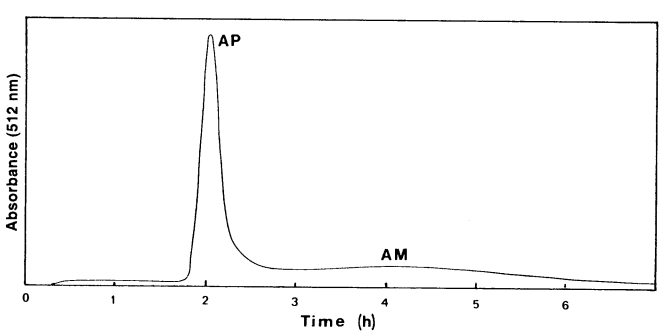

Fig. 1. Gel permeation chromatogram on Sepharose CL-2B column of native oat starch. AP = amylopectin, AM = amylose. For conditions, see Materials and Methods.

Experimental Error

The coefficient of variation of replicate determinations was ≤1% with the exception of the enthalpy by DSC, for which the coefficient of variation was ≤5%.

RESULTS AND DISCUSSION

Gel Permeation Chromatography—Occurrence of Intermediate Material

The distribution profile of the components of a native oat starch is shown in Fig. 1. There were no observable differences in the overall α-glucan distribution profile or ratio of amylopectin:amylose peaks within the group of oat starches studied. Indeed, the elution profile for the oat starches was very similar to that obtained for other normal cereal starches using the same method (Karkalas and Tester 1992).

Although different groups of researchers (Banks and Greenwood 1967, Paton 1979, Wang and White 1994a) have reported that oat starch is composed of three components described as amylose, amylopectin, and intermediate material, the present study shows that intermediate material is not a distinct component of the starch, if it exists at all. There is simply a molecular size distribution (polydispersity) for amylose and amylopectin, with overlapping of the two peaks. Since the elution/quantification method employed here is continuous and not dependent on collecting isolated fractions for analysis, a more accurate α-glucan distribution profile is normally obtained. By cutting and weighing the chromatograms, values of about 28% amylose were obtained, in good agreement with those determined colorimetrically (discussed below).

In a study of the gelatinization and solubility properties of oat starch, Mua and Jackson (1995) observed by HPSEC the presence of intermediate molecular weight material of oat starch solubilized by autoclaving in water or dimethyl sulfoxide (DMSO) followed by sonication for 30 sec. The same authors stated that "these findings suggest that this intermediate fraction may not be inherent to the native granule, but is rather created by depolymerization" and that the intermediate material reported by Wang and White (1994a) may well be the result of the "harsh treatments" (refluxing for 24 hr in 85% methanol at 45°C, dispersing in 90% DMSO, stirring in a boiling water bath for 1 hr followed by further stirring at room temperature for 24 hr) used by these authors to effect dissolution and fractionation of oat starch. In our view, this is probably correct. Indeed, close inspection of Wang and White's HPSEC data for the isoamylase-debranched intermediate-material fractions of three varieties of oat starch does not provide convincing evidence for the occurrence of a native intermediate molecular weight component. Apart from amylopectin hydrolysis, which gives the impression that starch contains intermediate material, an intermediate molecular weight fraction has also been incorrectly identified in "amylose" preparations from

solvent precipitates of solubilized starch, due to amylopectin co-precipitation with amylose.

Takeda et al (1986b) precipitated intermediate material from sweet potato starches with 1-butanol and 3-methyl-1-butanol and reported that "chain length, blue value, β-amylolysis limit and organic phosphorus, were very similar to those of the amylopectins except for iodine affinities which were twice those of the amylopectins." Colonna and Mercier (1984) isolated intermediate material from wrinkled- and smooth-pea starches with the use of thymol and butanol. The GPC elution profiles presented by these authors do not differ significantly from those obtained in our work, and the degree of polymerization (DP) of the isoamylase-debranched intermediate material was 45 and 15 respectively, i.e., identical to the chain distribution of amylopectin.

Several authors have reported the presence of intermediate material in starches from various species. The concept originated from the work of Lansky et al (1949), who precipitated amylose with pentanol and detected a branched component in the precipitated linear fraction, which they attributed to glucan of molecular weight intermediate between those of the strictly linear and branched fractions; this material was not precipitated with butanol. The same authors used 1-octanol for the subfractionation of the linear component and considered the iodine binding capacity of the fractions as an indicator of their purity. Banks and Greenwood (1975), who also used thymol for the precipitation of amylose in some of their work with a variety of starches, devoted a lengthy discussion to the nature of intermediate material. They stated that "it is not clear why particular fractions of amylopectin co-precipitate with the thymol complex; in fact, once the thymol-amylopectin has been isolated, it cannot subsequently be complexed with thymol." We consider that the criterion for an intermediate fraction of a definite molecular weight would be a distinct peak on a continuous GPC chromatogram rather than the merging of two polydisperse components whose profiles inevitably overlap on their sequential elution. In the course of studies of precipitation of amylose complexed with palmitic acid or dodecyl glucoside in the presence of varying amounts of amylopectin, we have found that amylopectin is always coprecipitated in considerable quantities as a result of entrapment with the insoluble amylose-lipid helical structures (Karkalas and Tester, *unpublished*), from very dilute solutions and on the addition of only 10% of ligand with respect to amylose. In our view, the intermediate material reported by most authors is in effect a mixture of amylopectin coprecipitated by complexed amylose; in many cases this might contain hydrolyzed amylopectin as a consequence of the treatments used to extract and solubilize the starch. Further support to this view is provided by the quantitative interaction of amylose with fatty acids: as the molecular weight of the fatty acid increases, a lower molar ratio of fatty acid to amylose is required for the complete precipitation of amylose (Karkalas and Raphaelides 1986). This is in accord with the observations of Lansky et al (1949), who found that intermediate material is precipitated by pentanol but not by butanol. Whistler and Doane (1961) also deduced that 2-nitropropane is a broad-spectrum complexing agent capable of complexing not only the linear amylose molecules but also some slightly branched molecules.

In the present work, the isoamylase-debranched starches had unit chain distributions and sizes very similar to those of barley starches (MacGregor and Morgan 1984, Tester et al 1991) with modal peaks at DP 46, 23, and 15 (Figs. 2 and 3). Variation was not detected within the oat starches studied, in common with studies on a range of barley (Tester and Morrison 1992) and rice (Tester and Morrison 1990b) cultivars. Other investigators (Hizukuri 1985, 1986, 1988, 1993; Takeda et al 1986a, 1989) have studied the structure of α-glucans from a range of starches, but, with the exception of recent work by Wang and White (1994a), little has been done on the architecture of oat amylopectin. These authors proposed that isoamylase-debranched amylopectins contained three fractions having chain lengths of 81.7–204.2, 30.7–31.8, and 16.6–20.1, but the distribution profiles were not typical of high-resolution chromatograms as published by other authors (Hizukuri 1985, Tester et al 1991, Karkalas and Tester 1992).

It is probable that the low molecular weight unit chains, DP 15, are primarily A and B_1, with DP 23 representing B_2 and DP 46 representing longer chains as described by Hizukuri (1986). The A-chains represent the exterior amylopectin chains that are α-(1-6) bonded to B-chains; described as B_1 if they traverse one amylopectin cluster radiating from the hilum to the periphery of the granule, B_2 if they traverse two, and so on. The small exterior chains of amylopectin (DP 15) would be the primary components of starch crystallites, with the longer chains linking the crystallites together in concentric shells.

Chemical Analysis

Starches were purified by sedimentation through CsCl solution to remove surface proteins (Sulaiman and Morrison 1990). Apparent amylose (containing some lipid-complexed amylose) and total amylose (lipid-free) contents ranged from 19.7 to 22.0

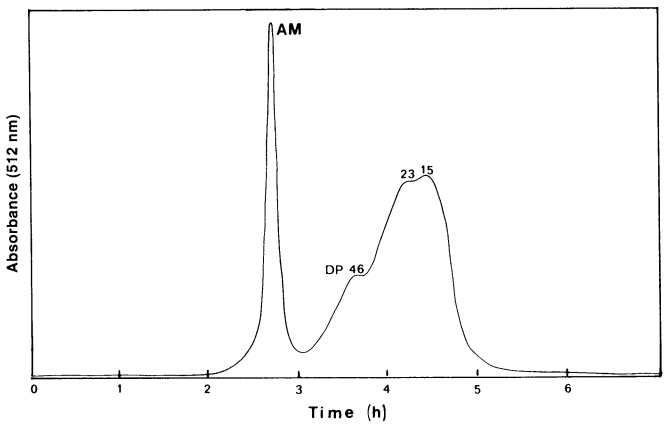

Fig. 2. Gel permeation chromatogram on Sepharose CL-6B column of oat starch amylopectin debranched with isoamylase. AM = amylose, DP = degree of polymerization.

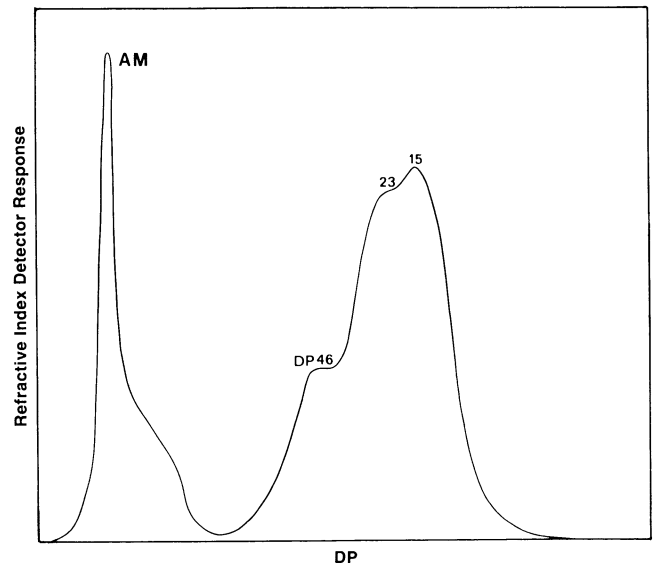

Fig. 3. High-performance size exclusion chromatogram on 2×G300PW TSK columns and 1×G2000 TSK column in series (each 60 cm × 7.5 mm, 13 μm particle size) of oat starch amylopectin debranched with isoamylase. AM = amylose, DP = degree of polymerization. For conditions, see Materials and Methods.

and 27.5 to 29.8%, respectively, with the difference (Δ–amylose) of 7.1–8.1, reflecting differences in lipid content (Table I). The naked oat starch contained less lipid (0.66 mg/100 mg of starch, as FAME) than the normal cultivars, which were clustered around 0.75–0.78 mg/100 mg. Other investigators reported amylose figures ranging from 16.8 to 27.9% (MacArthur and D'Appolonia 1979, Paton 1979) for oat starches, although allowance was not made for lipid complexing and hence apparent and total amylose. Morrison et al (1984) reported the amylose content of six oat starches to range from 17.3 to 20.7 (apparent) and 25.2 to 29.4 (total) with Δ-amylose (total minus apparent) in the range of 7.9–8.8. The amylose content of oat starches, after extraction of lipid, was found by Gudmundson and Eliasson (1989) to range from 27.3 to 29.4%. Other authors (Hoover and Vasanthan 1992) have extracted lipid from a naked oat (AC Hill) and found an apparent amylose content of 16.7% with a total amylose content of 19.4%, well below the figures reported in this work. Paton (1986) used the same German oats as in this study and reported amylose contents ranging from 17.5 to 19.5%, but no distinction was made between apparent and total amylose.

The lipid content (as FAME) determined in the present work ranged from 0.66 to 0.75 mg/100 mg of starch, which is about 10–25% lower than the figures of 0..90–1.09 mg/100 mg of starch (corresponding to 1.35–1.52 mg/100 mg of total lipid) reported by Morrison et al (1984) for Canadian-grown oats. This may be due to specific differences between cultivars, or possibly due to environmental factors, which can have a dramatic effect on the lipid content of cereal starches (Tester et al 1991). MacArthur and D'Appolonia (1979) reported lipid contents of 0.67–1.11%, Hoover and Vasanthan (1992) 1.13%, and Wang and White (1994b) 1.08–1.18% in various oat starches. Although the extraction methods were not strictly comparable, these results demonstrate that large differences in lipid content can exist in oat starches. The Δ-amylose figures reported by Morrison et al (1984) of 7.9–8.8% were correlated with the lipid as FAME (0.90–1.09 mg/100 mg). Figures for Δ-amylose reported here (7.09–8.09%) are lower and correspond to lower lipid levels.

Morrison et al (1993) introduced the concepts of lipid-complexed amylose (LAM) and lipid-free amylose (FAM), where Δ-amylose is comparable to LAM. These authors found that barley starch lipids (which are almost exclusively lysophospholipids, LPL) occur in a ratio of LPL to LAM of 1:7 and that amylose-lipid complexes affect the swelling and gelatinization properties of starches (discussed below). Morrison et al (1984) found that there was a positive amylose-phospholipid correlation (r = +0.8255, P = <0.05) in six oat starches. They pointed out that their results might have been fortuitous (although not subject to environmental variation) because of clustering of the data, as is the case with the present study. Since waxy and high-amylose mutants of oat do not exist, it is not possible to study the broad range of amylose-lipid variation as described by other workers (Morrison et al 1984, South et al 1991, Tester and Morrison 1992) for barley, maize, and rice. Hence it is difficult to define exactly this relationship and its influence on the FAM:LAM ratio. However, there is no reason to expect that oat should be unique in this respect.

The fatty acid distribution profile for the oat starch lipids is presented in Table II. These figures are similar to those reported by Morrison et al (1984), who additionally quantified the respective LPL and free fatty acid contents and found that the relative proportions (by weight) of these lipid classes were about 2.5:1, similar in this respect to rice starches. A comparison between the fatty acid distribution profiles of different cereal starches has been made by Morrison (1988). He reported that palmitic (16:0) and linoleic (18:2) acids are the major components of cereal starch lipids, although the relative proportions can vary between species; in this respect oat starch is similar to sorghum starch.

Swelling, Leaching, and Gelatinization

Starch swelling factors at 80°C ranged from 8.6 to 10.0, corresponding to 12.1–13.8 when expressed on an amylopectin basis, assuming that amylose is an inert diluent (Table III). The correlation coefficients (r) between swelling power and total amylose, Δ-amylose, and lipid contents are -0.5537, -0.8438, and -0.6786, respectively. These coefficients reflect the fact that there is little variation in the amylose and lipid content of these normal starches. The naked oat has the highest swelling factor, which is more evident when expressed on the basis of amylopectin. This can be explained, in part, by the relatively low amylose content, the increased proportion of amylopectin, and the low lipid content (Table I). The low levels of lipid reduce the ratio of LAM to

TABLE I
Amylose and Lipid Content of Six Oat Starches

Cultivar	Amylose, %		Δ-Amylose	Lipid (as FAME) (% db[a])
	Apparent	Total		
Borrus	20.6	28.5	7.9	0.72
Erbgraf	21.0	28.7	7.7	0.71
Erich	22.0	29.8	7.8	0.71
Pendragon	20.5	27.6	7.1	0.66
Pitol	20.1	28.2	8.1	0.75
Selma	19.7	27.5	7.8	0.74

[a] db = dry starch basis.

TABLE II
Percentage of Individual Fatty Acids in Six Oat Starches

Cultivar	C16:0	C18:0	C18:1	C18:2	C18:3
Borrus	43.5	2.8	17.8	35.3	0.6
Erbgraf	47.2	1.5	13.6	36.9	0.8
Erich	49.2	1.2	14.3	34.7	0.6
Pendragon	49.6	2.2	13.9	33.8	0.5
Pitol	45.4	2.4	17.5	34.2	0.5
Selma	46.6	2.6	13.0	36.8	1.0

TABLE III
Swelling and Solubilization Properties of Six Oat Starches

Cultivar	Swelling Factor (80°C)	Swelling Factor Amylopectin (80°C)	Damaged Starch (% db[a])	Leached α-Glucan (% db)	Amylose in Leachate (%)	Acid Solubles[b] (% db)
Borrus	8.6	12.1	1.9	4.9	47.6	56.6
Erbgraf	8.6	12.1	2.0	4.7	46.2	59.5
Erich	8.9	12.7	2.2	5.0	44.2	57.7
Pendragon	10.0	13.8	2.1	6.6	43.8	57.2
Pitol	8.6	12.0	2.2	4.3	42.1	60.0
Selma	9.3	12.9	1.9	4.1	42.1	59.8

[a] db = dry starch basis.
[b] Solubles = solubilization of starch in 2M HCl at 35°C after six days of storage.

FAM, and this is reflected in the lowest figure for Δ-amylose (Table I).

Previous work by Morrison et al (1993) has shown that LAM reduces swelling power, while FAM facilitates swelling. There is no evidence that differences in the swelling factor of oat starch are due to differences in the structure of the α-glucans between cultivars (Figs. 1–3). This is in agreement with previous comparisons within groups of cultivars from other cereals as described by Tester and Morrison (1990b, 1992) and Tester et al (1991). These authors did, however, recognize that differences in swelling factor between different cereal species are, in part, due to differences in amylopectin structure. The mechanism that controls swelling power when the α-glucan distribution is the same is not understood. The low level of granule damage found in these starches (1.9–2.2%, Table III) is unlikely to contribute to the swelling properties, although it is recognized that high levels of damage have a marked effect on the swelling and gelatinization properties of starches (Karkalas et al 1992; Morrison and Tester 1993, 1994; Tester et al 1994).

The leached carbohydrate at 80°C accounted for 4.1–5.0% of the dry starch weight for the normal oats, with the figure for the naked oat starch being substantially higher at 6.6% (Table III). This was associated with a the higher swelling factor for this starch, as discussed above. There was overall little variation in the proportion of amylose (determined colorimetrically) in the leachate from these starches (42.1–47.6%). From GPC analysis of oat starch (Fig. 1), and of the native and debranched leachate, performed on the same type of gel (Sepharose CL-2B) for direct comparison (Figs. 4a and 4b), it is evident that the leached polymer is composed of material corresponding to the retention time of low molecular weight amylose and not native amylopectin originating from swollen granules. When the leached material was debranched with isoamylase (Fig. 4b), two α-glucan populations were found. The larger molecular weight fraction (accounting for about 45% of the debranched leachate) had a retention time slightly longer than the native leachate, indicating a lower molecular weight. The rest of the debranched material was of a much lower molecular weight and appeared near the end of the resolution of the column.

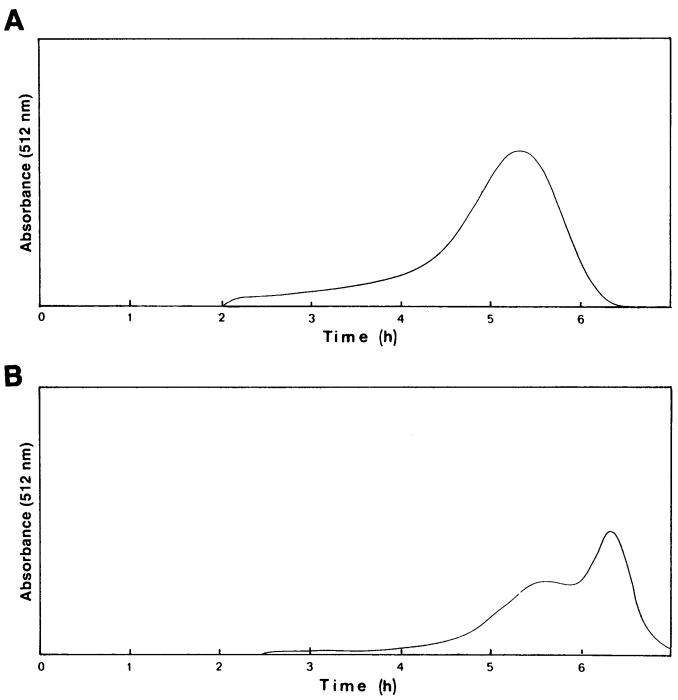

Fig. 4. Gel permeation chromatograms on Sepharose CL-2B of oat starch leachate obtained at 80°C (**A**) and oat starch leachate obtained at 80°C and debranched with isoamylase (**B**).

Doublier et al (1987) studied the leaching profile of oat starch and reported that amylose and amylopectin were co-leached and that this was influenced by the starch lipids. This was also reported by Hoover and Vasanthan (1992) and Shamekh et al (1994). The latter group studied the solubility of oat starch at different temperatures and concluded that most of the leached carbohydrate was amylopectin. They suggested that this was due to different α-glucan distribution profiles in the oat starch, in contrast with other cereal starches, which exude primarily amylose. The reason why native oat starches release branched material to such a large extent compared with other normal undamaged starches, which release essentially amylose (Tester and Morrison 1990a,b) is not certain. It is well established that granule damage due to impact causes amylopectin to fragment and, as a consequence, the soluble fragments are found together with amylose in solution (Morrison and Tester 1993, 1994a,b; Tester and Morrison 1994). The low levels of damage (<2.2%) measured in the present work (Table III) cannot account for all the amylopectin fragments found in the leachate. It is, however, possible that gelatinized oat starch granules disintegrate more readily than granules from other sources, resulting in the presence of soluble amylopectin fragments in the leachate, together with leached amylose.

The solubles generated by acid hydrolysis (lintnerization) are also presented in Table III. There is no obvious relationship between the amount of acid solubles and that of post-gelatinization leachate, as expected, because of their diverse origins (r = 0.6764). However, since the acid solubles are derived primarily from amorphous material, one would have expected a closer relationship if the solubles generated during swelling were also derived from amorphous material.

The onset (T_o), peak (T_p), and conclusion (T_c) gelatinization temperatures by DSC were 44.7–47.3, 56.2–59.5, and 68.7–73.7°C, respectively, with the gelatinization enthalpies for starch and amylopectin (ΔH and ΔH AP) ranging from 8.1 to 9.5 and 11.4 to 13.1 J/g, respectively (Table IV). Similar results have been reported by Gudmundsson and Eliasson (1989), Hoover and Vasanthan (1992), Shamekh et al (1994), and Wang and White (1994c). A strong negative correlation was found between T_p and acid solubles (r = –0.9334), which was expected since material solubilized during lintnerization is inversely correlated with the perfection of amylopectin crystallites (Tester and Morrison 1990b).

There is less information concerning the swelling and gelatinization properties of oat starches in the literature, compared to that for other cereals like wheat and barley. Most of the work has focused on pasting properties of oat starches, which are reported to have some relatively unusual properties compared with those of other cereal starches (Paton 1986) in being particularly susceptible to high temperature (95°C) shear; this is in agreement with the foregoing discussion. The swelling powers (80°C) of oat starches studied here (8.6–10.0) are substantially lower than those of normal barley starches with similar composition, which have swelling factors in the range of 10.2–13.7 (Tester and Morrison

TABLE IV
Oat Starch Gelatinization Parameters[a] by Differential Scanning Calorimetry

Cultivar	T_o (°C)	T_p (°C)	T_c (°C)	ΔH (J/g)	ΔH AP (J/g)
Borrus	46.7	59.5	73.0	9.2	12.9
Erbgraf	46.3	56.8	68.7	8.1	11.4
Erich	45.6	58.5	69.2	8.1	11.5
Pendragon	47.3	58.2	72.3	9.5	13.1
Pitol	44.8	57.1	73.7	9.0	12.5
Selma	44.7	56.2	72.0	9.0	12.4

[a] T_o, T_p, and T_c represent onset, peak, and conclusion temperatures, respectively. ΔH = enthalpy of gelatinization, AP = amylopectin.

TABLE V
Dimensions of Oat Starch Granules Using a Coulter Counter Multisizer

Cultivar	Modal Diameter (μm)	Mean Diameter (μm)	Mean Size, Area (μm^2)	Mean Volume (μm^3)	Specific Size, Area (m^2/g)
Borrus	5.08	5.63	116	146	0.521
Erbgraf	5.03	5.26	101	116	0.576
Erich	5.15	5.14	97	110	0.609
Pendragon	4.97	4.96	89	94	0.656
Pitol	4.91	5.10	95	106	0.591
Selma	4.97	5.43	111	142	0.490

1992). Some workers found that oat starches tend to have lower T_p values than those of wheat or maize starches (Gudmundsson and Eliasson 1989).

The gelatinization temperature (T_p) of starches has been reported as being a measure of the perfection of starch crystallites, while the enthalpy is a measure of the degree of crystallinity (Tester and Morrison 1990b). Other authors (Cooke and Gidley 1992) have claimed that the enthalpy of gelatinization (measured by DSC) "reflects loss of molecular (double helical) order rather than loss of crystalline register" (measured by X-ray crystallography). At the molecular level, gelatinization involves the uncoiling of external chains of amylopectin that are packed together as double helices in clusters (which create crystalline zones in the native starch). Hydrogen bonds stabilizing the structure of the double helices are broken during this uncoiling and are replaced by hydrogen bonds with water.

Swelling is also primarily a property of the amylopectin (Tester and Morrison 1990a), which is regulated by the crystallinity of the starch before full gelatinization. When T_p is high, the onset of swelling is elevated. Swelling factor is negatively correlated with lipid; FAM contributes to swelling, and LAM inhibits it (Morrison et al 1993). Although there is an inherent genetic element to the crystallization of starch, environment is at least as important; particularly temperature (Tester et al 1991). High growth temperatures favor crystallite perfection, which is reflected in elevated gelatinization temperatures (and vice versa). Lipid, through its association with amylose (LAM) also tends to elevate the gelatinization temperature. The extent of variation found within these oat samples may be due to environmental differences encountered by the plants during starch accumulation, although it is probably within the range of variation created genetically when compared with barley (Tester and Morrison 1992) or rice cultivars (Tester and Morrison 1990b) grown under the same conditions.

The mean diameters of the oat starch granules analyzed in this study ranged from 4.96 to 5.63 μm (Table V). The data (obtained with a Coulter Counter Multisizer) are in general agreement with figures obtained by Makela and Laakso (1984) using a Celloscope. However, there is a considerable spread in the dimensions of oat starch granules (3–10 μm) reported in the literature (Lineback 1984). The variations of physicochemical properties of these oat starches were not related to granule size. However, granule dimensions serve as an indicator to the history and stress prevailing during starch synthesis and deposition. In barley samples grown at different temperatures between 10 and 20°C, as the temperature is increased, the size of granules decreases (Tester et al 1991). Similar results have been reported for wheat starch (Tester et al 1995). Variations in the composition and physical properties identified during the present study appear to be under genetic control.

CONCLUSIONS

The data presented in this article indicate that oat starch, in common with other normal cereal starches, consists essentially of amylose and amylopectin. The GPC chromatograms show a polydisperse amylose, with an elution profile that overlaps that of amylopectin. After the starch is debranched with isoamylase, the GPC profile of the unit chains of amylopectin is very similar to that of barley amylopectin. Gelatinization temperatures and enthalpies, swelling factors, and the amount of glucan leached during gelatinization suggest that the oat starches do not differ materially from other normal cereal starches. Oat starch granules appear to be rather fragile when gelatinized and swollen, and, as a consequence, a proportion of the cleaved amylopectin is solubilized together with amylose on heating at 80°C. In other research, authors have claimed on the basis of precipitation studies that intermediate material exists, but we believe that this is contamination of the amylose fraction with native or hydrolyzed amylopectin due to coprecipitation. The presence of a so-called "intermediate material" claimed by various authors is, therefore, very much in doubt.

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