Structure and Physicochemical Properties of Starches from Oats with Different Lipid Contents[1]

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ABSTRACT

Oat (*Avena sativa* L.) starches isolated from three lines of groats containing a range of lipid contents (6.2, 8.0, and 11.2%) were evaluated. The lipid content of the starches varied from 1.08 to 1.18%, which was higher than that of corn (*Zea mays* L.) starches (0.56–0.66%). The amylose content of oat starches (measured by blue value) ranged from 22.1 to 26.6%. In corn starches, it ranged from 24.0 to 24.6 and was positively correlated with the starch-lipid content. The oat starches had a smaller average granule size, lower molecular weight, and lower clarity of starch paste than did corn starches also evaluated in this study, as measured by scanning electron microscopy, limiting viscosity number, and percentage transmittance, respectively. The granule size and clarity of oat starches were negatively correlated to amylose and starch-lipid content. The swelling power and solubility of starches increased with a rise in temperature from 85 to 95°C. The increased values were higher in oat starches than they were in corn starches. Furthermore, as measured by high-performance size-exclusion chromatography, oat starch amyloses had a shorter chain length than did corn starches, and the chain length tended to decrease with increased amylose and starch-lipid content. Differences in chain length and chain-length distribution of amylopectin also were noted among oat starch types, with the short chain length (A and short B chains) of amylopectin increasing with increased amylose and starch-lipid content.

Oat is increasing in popularity as a part of the human diet and is being added, either as whole or fractionated groat, to many food products because of recent health claims describing the nutritional virtues of the oat. The fiber component, β-glucan, and natural antioxidants are two oat components gaining publicity for possible health benefits (Lockhart and Hurt 1986). Starch is the major constituent of oat endosperm, and its importance to the properties of products containing oat is recognized. Starch also is an important industrial raw material. The oat starch, with a small granule size and some unique functional properties (Paton 1986, Sowa and White 1992), may be useful for some industrial purposes, such as paper sizing and pharmaceuticals (Paton 1986, Wilhem et al 1989), and as an ingredient in infant food (Webster 1986).

The starches from various plant species have unique characteristic functional properties that are influenced by the granular and molecular structures. Paton (1979) reported that the oat starch from Canadian oat varieties had a more branched structure and a greater amount of intermediate materials than did corn and wheat starches. Recently, high-performance size-exclusion chromatography (HPSEC) has been used to elucidate the profiles of starch components (Hizukuri 1985, 1986; Kobayashi et al 1986; Kennedy et al 1992). HPSEC is capable of fractionating amylose and amylopectin in starch on the basis of hydrodynamic volume and molecular weight. Most HPSEC work has been done on the structure of amylose (Hizukuri and Takagi 1984; Takeda et al 1986, 1989) and on the chain-length distribution of amylopectin (Hizukuri 1985, 1986). HPSEC offers the advantage of a quick analysis.

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Cereal starches generally contain between 0.5 and 1% lipid, which can affect their physicochemical properties (Swinkels 1985, Schierbaum et al 1991, Radosta et al 1992). Studies in the literature report that oat starch has a greater lipid content than do corn, wheat (*Triticum aestivum* L.), and rice (*Oryza sativa* L.) starches. Most oat starch lipids are lysophospholipids (two-thirds) and free fatty acids (one-third) (Morrison et al 1984, Hoover and Vasanthan 1992, Liukkonen and Laakso 1992). The role of starch lipids in the structure and properties of starch has received considerable attention. Gudmundsson and Eliasson (1989) reported some physicochemical properites of oat starches extracted from varieties with oil contents ranging from 5 to 7.5%. Starch from the groat highest in oil content also gave the stiffest gel and tended to retrograde the least. However, the results were inconclusive. No studies have attempted to relate these physicochemical properties to fine starch structure.

The objectives of the present work were to characterize the structure and physicochemical properties of three oat starch types from groats with widely different lipid contents (6.2–11.2%) and to study the relationship between the fine structure and the physicochemical properties.

MATERIALS AND METHODS

Starch Types

Two oat cultivars (E77 and Dal) and one experimental oat line (L996) with different oil contents in the whole grains (6.2, 8.0, and 11.2%, respectively) and one corn genotype (B73×MO17) were grown in Ames, IA, in 1991. After harvest, the corn kernels and the dehulled oat groats were stored at 4°C and 45% rh until analyzed.

Corn starch (PFP) was obtained from Sigma Chemical Company (St. Louis, MO). The starch had a purity of about 99% calculated on a dry-weight basis. The moisture content of the starch was 11%.

Starch Isolation

The oat starches were isolated as described by Sowa and White (1992), except that a single-speed blender was used instead of a mortar and pestle. The B73×MO17 corn starch was isolated from kernels by using the procedure described for isolating oat starches, except that kernels were soaked in 0.02*M* HCl at 50°C instead of 4°C. The starches were dried overnight at 45°C. Previously, oat starches isolated in our laboratory by this method had residual protein contents ranging from 0.85 to 0.95% (Sowa and White 1992). All starch types were isolated in two replicated extractions. All data on starches are the average of two determinations per replicate unless otherwise stated.

Extraction and Measurement of Starch Lipids

Total lipids in starches was estimated by combining two procedures (Smith 1967, Takahashi and Seib 1988) involving partial hydrolysis of the starch, precipitation of the freed fatty substances, and recovery by solvent extraction. Starch (5.0 g) was suspended in 20 ml of distilled water. Boiling 4*N* hydrochloric acid (60 ml) was added and boiled for about 5 min. The hydrolyzed solution was cooled at 4°C for 30 min to allow complete precipitation of fatty acids. All precipitate was recovered by gravity filtration through Whatman No. 1 filter paper. The residues were washed with distilled water at room temperature until neutral, and evaporated to dryness under vacuum at ~50°C. The residues were extracted (3 times, 20 ml each) with a mixture of chloroform and methanol (2:1, v/v). The combined extracts were filtered and evaporated to dryness. The lipids were dried by three evaporations from absolute ethanol before weighing. Lipid contents were reported on a dry-starch basis.

Iodine Affinity

Iodine affinity (IA) of the defatted starches, accomplished by refluxing in 85% methanol for 24 hr at 85°C in a Soxhlet extractor, was determined by standard potentiometric titration (Schoch 1964) at 30°C. The IA was expressed as milligrams of iodine bound to 100 mg of starch.

Blue Value and Iodine-Absorption Spectrum

The blue value (BV) was determined according to Gilbert and Spragg (1964). The same defatted sample was used to measure the wavelength of maximum absorption (λ_{max}) from 700 to 500 nm. Three separation determinations were done on each defatted starch replicate of each type, and the results were averaged.

Limiting Viscosity Number

The limiting viscosity number ([η]) (ml/g) was determined with an Ostwald viscometer at 22.5°C according to the method of Myers and Smith (1964), except that starch was dissolved in 1*N* KOH.

Percentage Transmittance

The percentage transmittance (%T) of starch solutions was determined by following the method of Craig et al (1989). The starch solutions (1%, w/w in water) were heated in a boiling water bath and stirred for 30 min. After cooling to room temperature, the %T at 650 nm was measured against a water blank with a Hitachi U-2000 Spectrophotometer (Hitachi Instruments, Conroe, TX).

Swelling Power and Solubility

Swelling power and solubility were performed at 85 and 95°C according to Leach et al (1959). Starch (0.5 g) was added to 18 ml of distilled water in an 85°C water bath for 30 min and mixed with a stirring bar at moderate speed. After 30 min of heating, the stirring bar was removed and rinsed with distilled water, and additional water was added to make the total water weight 20.0 g. The starch paste was centrifuged at 2,000 × *g* for 20 min, after which 5 ml of supernatant was pipetted into a weighing dish and dried at 120°C for 2 hr to determine the solubles content. The remaining supernatant was carefully removed by suction and weighed to determine the amount of water absorbed by starch granules. Swelling power (%) was calculated with corrections for solubles.

Scanning Electron Microscopy

For scanning electron microscopy (SEM) preparation, the starch samples previously stirred to obtain a homogeneous mixture were sprinkled onto double-stick tape attached to specimen stubs and coated with gold-palladium. The mounted specimens were examined with a JEOL JSM-35 scanning electron microscope (JEOL Ltd., Tokyo, Japan) at an accelerating voltage of 10 kV. Representative micrographs were taken of each starch type at a magnification of 3,000×. The starch granule diameter was estimated by averaging the largest dimension of 10 random starch granules from three micrographs for each starch type.

High-Performance Size-Exclusion Chromatography

Debranching of starch granules. Defatted starch (50 mg) was suspended in 9 ml of distilled water and heated with stirring in a boiling water bath for 1 hr. After cooling, 1 ml of 0.1*M* acetate buffer (pH 3.5) and 1,180 U (20 μl) of crystalline Pseudomonas isoamylase (Hayashibara Shoji, Olayama, Japan) were added. The sample was incubated at 40°C in a water bath with slight stirring for 48 hr. The digested sample was heated to inactivate the enzyme and evaporated from 10 to 1 ml. The completion of the debranching reaction was confirmed by high-performance size-exclusion chromatography (HPSEC).

Preparation of sample for injection. The debranched samples were prepared for injection as follows: a 0.1-ml aliquot of the digested sample and 0.9 ml of dimethyl sulfoxide (DMSO) were combined to make a 90% DMSO (HPLC grade) solution. The 90% DMSO solution was heated in boiling water with continued stirring for 1 hr and then for another 24 hr at room temperature before filtration through a 0.45-μm nylon filter (Bradbury and Bello 1993). Values for HPSEC are the average of two separate analyses per replicate.

Separation by HPSEC. The HPSEC equipment consisted of a Beckman 110 A pump (Beckman Instruments, Fullerton, CA), 100-μl injector loop, a Beckman 210 sample injector, two Bio-

Sil 125 columns (300 × 7.5 mm), and one guard column (75 × 7.5 mm) (Bio-Rad Laboratories, Richmond, CA), a differential refractometer (Waters, Milford, MA), and a Beckman 10-in. strip-chart recorder (Bradbury and Bello 1993).

A 100-μl sample was injected into the HPSEC system and carried by a flow rate of 0.5 ml/min. The mobile phase (30% DMSO in water) had been filtered through a 0.45-μm nylon filter and then degassed with a vacuum suction device. The columns and the detector were maintained at 30 and 40°C, respectively. The determination of the void volume (V_o) was accomplished with oat AP. Replicate chromatograms of the same type of starch were very similar.

A calibration curve for the chromatograms was constructed by using P-5, 10, 20, 50, 100, and 200 pullulan standards (5,300–186,000 daltons) which were injected separately under the same conditions (Bradbury and Bello 1993, Yuan et al 1993). A plot of the log weight average molecular weight versus retention times produced a standard curve, which was used to estimate the chain length of the debranched fragments within the molecular weight limits of the standards.

Measurement of weight-average chain length (CL_w), weight%, and mole%. The eluted materials were separated into three fractions that were divided at minimum points between the fractions according to the detector response value and labeled as F_1 (apparent amylose), F_2 (long B chains of amylopectin), and F_3 (A and short B chains of amylopectin) (Sargeant and Wycombe 1982; Hizukuri 1985, 1986). Molecules eluting first from the HPSEC columns had the largest hydrodynamic volume and apparent molecular weight. Hydrodynamic volume and apparent molecular weight decreased logarithmically with elution time (Jackson et al 1988). Hence, amylose molecules (F_1) spanned a larger range of apparent molecular weights than did the small linear fractions that came from debranched amylopectin (F_2 and F_3).

The CL_w for each fraction was calculated from the calibration curve generated with pullulan polysaccharide reference standards. The percentages (weight%) of components F_1, F_2, and F_3 were calculated from each fraction area. The mole% of a fraction was obtained from the ratio of the relative mole content (weight% divided by CL_w) of the fraction to the sum of the relative mole contents of all fractions as described by Yuan et al (1993).

Statistical Analyses

Statistical analyses were performed on all replicated data for each experiment (SAS 1990). Individual analyses on each replicate were used to calculate least significant differences, which were computed at a significance level of $P < 0.05$. Correlations were computed with all replicated data (8 degrees of freedom) among physicochemical properties and structural characteristics of the starches.

RESULTS AND DISCUSSION

Physicochemical Properties

Starch lipid levels, iodine affinity, blue value, amylose content (AM%), and iodine-absorption spectrum (λ_{max}). The total lipid contents of oat starches varied from 1.08 to 1.18% (Table I), which was greater than that of corn starches (0.56–0.66%) analyzed by the same procedure. The varieties with the greatest and least lipid content in the groats also had the largest and smallest lipid contents, respectively, in the isolated starches. These results are consistent with data reported by Sowa and White (1992) in their study of oat starches, except that starch lipid contents reported by Sowa and White (1992) were about twice those of the current study, probably because of differences in methodology, which are explained later. The total starch lipid contents in the present study agree with the value reported by Hoover and Vasanthan (1992). Both studies used acid hydrolysis to measure starch lipid. Cereal starches can contain up to 1% lipid, most of which is thought to be present inside the starch granule as an amylose inclusion complex (Acker and Becker 1971). In maize, the starch lipids are mainly free fatty acids, whereas in oat, the lysophospholipids predominate (Morrison 1978).

Percentages of amylose in the various starches are shown in Table I. The amylose content of the starch was calculated from the IA or BV with the following equation (Takeda et al 1983):

$$\frac{\text{IA (or BV) of defatted starch} - \text{IA (or BV) of amylopectin}}{\text{IA (or BV) of amylose} - \text{IA (or BV) of amylopectin}} \times 100$$

For amylose content calculated from IA, values ranged from 20.7 to 25.0% for oat starches and from 24.0 to 24.6% for corn starches. The amylose contents of oat starches calculated from the IA (20.7–25.0%) were slightly less than that calculated from BV (22.1–26.6%). These differences in measurement also were noted for kuzu (*Pueraria hirsuta* Matsum), lily (Maximovicz's lily, *Lilium maximoroiczii* Regel), and lotus (*Nelumbo nucifera* Gaertn.) starches (Suzuki et al 1981, 1992; Takeda et al 1983). Small discrepancies in these calculations are occasionally noted because the chain length dependence of IA and BV are not identical (Suzuki et al 1992). Both values for the amylose content are close to the value of 23–24% generally given as the average percentage amylose in oat starches (Lineback 1984). The values in the present study, however, are lower than percent amylose values previously reported for oat starches (30.3–33.6%) (Sowa and White 1992), probably because of differences in defatting, as just noted. Sowa and White (1992) defatted the starch with 75% *n*-propanol at 100°C, conditions previously reported to yield greater lipid contents and to produce higher IA and BV values than the 85% methanol at 85°C used in the current study (Takahashi and Seib 1988). Also, there may have been differences in the oats themselves

TABLE I
Physicochemical Properties of Starches[a]

Sample	Starch-Lipid %	IA[b] (g/100 g of sample)	Blue Value	AM%[c] IA	AM%[c] BV	λ_{max}[d] (nm)	$[\eta]$[e] (ml/g)	%T[f] (650 nm)	SP[g] 85°C	SP[g] 95°C	SL[h] 85°C	SL[h] 95°C
E77	1.08	4.33	0.366	20.7	22.1	614	254	7.41	9.6	27.8	5.6	33.5
Dal	1.16	4.44	0.404	22.8	25.6	615	263	7.22	8.7	29.0	4.1	37.4
L996	1.18	5.07	0.439	25.0	26.6	620	253	6.27	9.1	34.8	6.0	43.3
B×MO	0.66	4.56	0.394	24.0	...	612	276	9.26	13.9	28.1	10.2	29.6
PFP	0.55	4.67	0.377	24.6	...	614	268	10.29	11.6	24.4	9.2	29.8
LSD[i]	0.03	0.05	0.002	0.7	0.3	2	4	0.08	0.3	0.4	0.5	0.3

[a] Values are the mean of two separate determinations.
[b] Iodine affinity.
[c] For oat starches, amylose percentage (AM%) was calculated from the iodine affinity (IA) of starch, amylose, and amylopectin. For corn starches, amylose percentage was calculated from the iodine affinity of native starch by using an amylose iodine affinity value of 19, or calculated from the blue value (BV) of starch, amylose, and amylopectin.
[d] Maximum absorption.
[e] Limiting viscosity number.
[f] Percentage transmittance.
[g] Swelling power (%).
[h] Solubility (%).
[i] Least significant difference at a significance level of $P < 0.05$.

between the two studies due to environmental effects of the growing year.

The quantity of starch lipid was directly proportional to the AM% of the oat starches ($r = 0.94$, $P = 0.0002$) as shown in Table II. Morrison et al (1984) also found a significant correlation ($r = 0.83$, $P < 0.05$) between total amylose and the content of lysophospholipids of oat starch. It has been suggested that the starch lipid regulates the amylose-to-amylopectin ratio of starch by preventing the branching enzyme from acting on the amylose-lipid complexes during synthesis of the granule, thus decreasing the amount of amylopectin formed (Downton and Hawker 1975). As expected, the percentage of lipids in oat starches also is related to other properties influenced by AM%. For example, the greater the lipid content of the oat starch, the higher are the BV and IA as noted in Table II.

The λ_{max} ranged from 614 to 620 nm for oat starches and from 612 to 614 nm for corn starches (Table I). The L996 starch had a significantly higher λ_{max} (620 nm) than did all other types, which had values ranging from 612 to 615 nm. The λ_{max} of oat starches was positively correlated with IA, BV, and AM% (calculated from BV), but no correlation with starch-lipid content was found (Table II).

Limiting viscosity number. Viscosities of the various starches in 1*N* potassium hydroxide are shown in Table I. Values for oat starches (253–263 ml/g) were significantly less than values (268–276 ml/g) for corn starches, and the Dal starch had a significantly greater [η] than did the E77 and L996 starches. The [η] studies may give evidence of differences in the relative molecular size of the starch molecules (Medcalf and Gilles 1965), suggesting that the oat starches have a smaller molecular size than do corn starches.

Percentage transmittance. The %T values listed in Table I for all starch types were significantly different from each other, with corn starches having higher %T than all oat starches, and all oat starches being significantly different from each other. The %T is used as a measure of clarity. Clarity is affected by whiteness and heterogeneous refraction due to granular remnants. Lipids contribute to paste opacity (Schoch 1942, Swinkels 1985), perhaps by restricting granular swelling (Craig et al 1989). The ionic end-groups of the lysophospholipids previously mentioned as being present in oats (Morrison et al 1984), having both a positive (nitrogen) and a negative (phosphate) charge, could associate with each other (positive attracted to negative), bringing the starch chains close enough to hydrogen bond to each other, thereby increasing whiteness and decreasing %T (Craig et al 1989). The results from this study tend to support this view because the %T values correlated negatively with the lipid content of the starches ($r = -0.72$, $P = 0.03$) (Table II). Moreover, amylose content also may affect the %T. Swinkels (1985) calculated the ratio of amylose molecules to amylopectin molecules for different starches and reported that the starches with a small proportion of amylose were dispersed easily, therefore increasing %T. Results from this study of oat starches confirm this view because the %T was negatively correlated with amylose content ($r = -0.78$, $P = 0.01$).

Swelling power and solubility. The oat starches had less swelling power and solubility at 85°C than did corn starches (Table I). This observation may be related to the higher lipid content of oat starches because the presence of lipids in granules may retard swelling at 85°C and the dispersion of starch molecules. Lipid-amylose complexes in oat starch melt near 100°C, as shown by differential scanning calorimetry (DSC) (Sowa and White 1992). The insoluble amylose-lipid complexes may inhibit swelling by tying up a portion of the starch molecules inside the granule (Melvin 1979, Hoover and Hadziyev 1981). There was a negative correlation ($r = -0.75$, $P = 0.02$) between starch-lipid content and swelling power at 85°C among oat starches (Table II). Correlations between solubility at 85°C and other parameters were all very low, so values were not included in Table II. The swelling power and solubility of starches increased with the rise in temperature from 85 to 95°C, and the increased values were generally higher in oat starches than they were in corn starches (Table I). At 95°C, the swelling power and solubility were significantly higher for oat starches than they were for corn starches, except for E77 starch, which was not significantly different from B73×MO17 starch in swelling power. Correlations between swelling power and solubility at 95°C and starch-lipid content are noted in Table II. Doublier et al (1987) also reported a higher swelling power and solubility for oat starch than for corn starch at 95°C; however, data of Gudmundsson and Eliasson (1989) did not support these findings. Differences in methodology may have accounted for the discrepancies. Like Doublier et al (1987),

TABLE II
Correlations Among Selected Physicochemical Properties of Oat Starches[a]

	Starch-Lipid	IA	BV	AM%	λ_{max}	%T
IA	0.72 (0.03)					
BV	0.89 (0.001)	0.91 (0.0006)				
AM%	0.94 (0.0002)	0.74 (0.02)	0.96 (0.0001)			
λ_{max}	NS[b]	0.89 (0.001)	0.86 (0.003)	0.73 (0.02)		
%T	−0.72 (0.03)	−0.99 (0.0001)	−0.92 (0.0004)	−0.78 (0.01)	−0.92 (0.0004)	
SP[c] at 85°C	−0.75 (0.02)	NS	NS	−0.80 (0.01)	NS	NS
SP at 95°C	0.67 (0.05)	0.97 (0.0001)	0.90 (0.001)	0.76 (0.02)	0.93 (0.0003)	−0.97 (0.0001)
SL[d] at 95°C	0.83 (0.006)	0.95 (0.0001)	0.98 (0.0001)	0.90 (0.001)	0.89 (0.001)	−0.96 (0.0001)
Average granule size	−0.91 (0.0006)	−0.87 (0.002)	−0.99 (0.0001)	−0.97 (0.0001)	−0.82 (0.007)	0.87 (0.002)

[a] IA = iodine affinity; BV = blue value; AM% = amylose percentage calculated from BV; λ_{max}=maximum absorption; %T = percentage transmittance.
[b] Not significant at $P < 0.05$.
[c] Swelling power (%).
[d] Solubility (%).

we measured total solubles leached during centrifugation, which probably included both amylose and amylopection. Gudmundsson and Eliasson (1989) measured only uncomplexed amylose.

Morphology of starch granules. The SEM showed that the oat starch granules were undamaged; the shape of the starch granules was polyhedral and irregular (Fig. 1). The average granule diameter ranged from 4.1 μm for L996 to 5.9 μm for E77 (Table III). Overall, the oat starch granules ranged in diameter from 2.7 to 9.5 μm, which is similar to previous reports by Lineback (1984), Paton (1986), and Sowa and White (1992). Oat starch is similar to rice starch in both size and shape (Paton 1986).

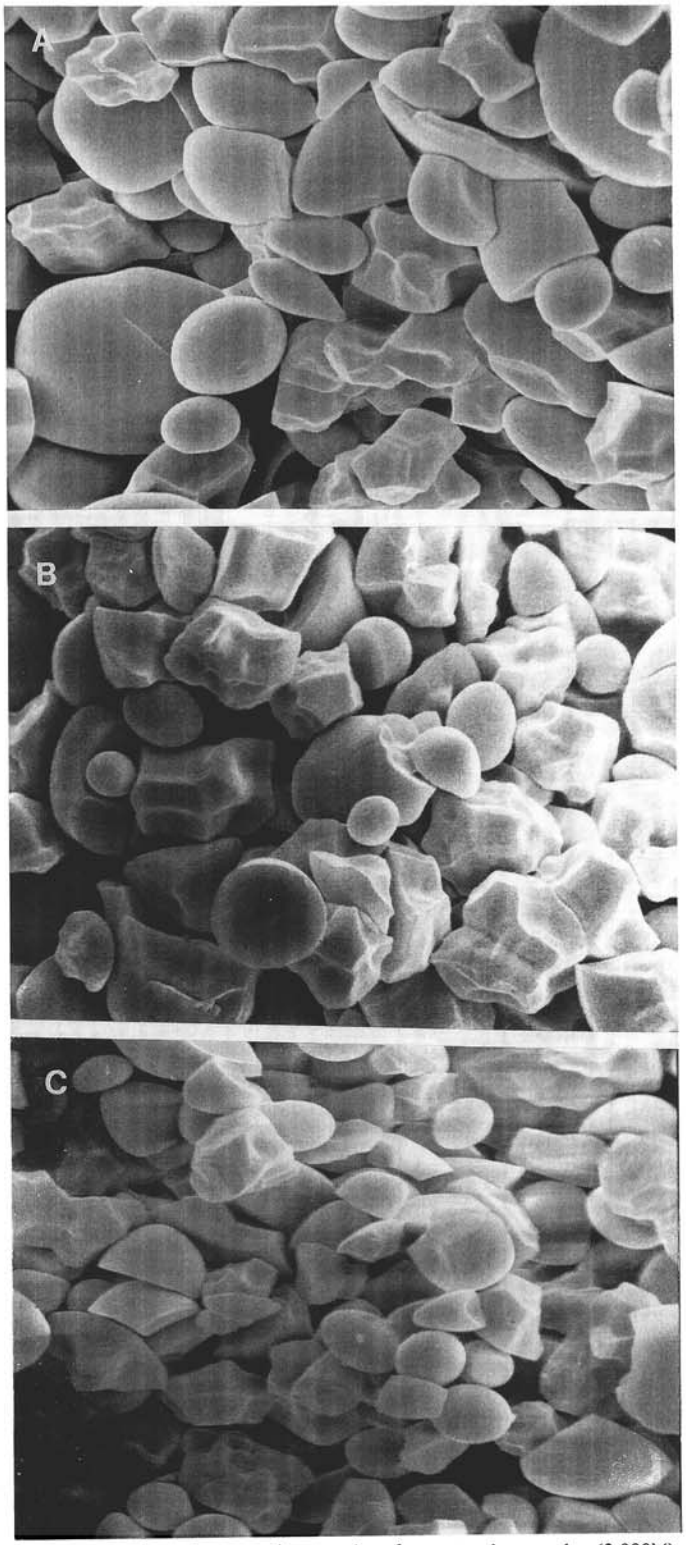

Fig. 1. Scanning electron micrographs of oat starch granules (3,000×). A–C: E77, Dal, and L996, respectively.

The average granule size of oat starch was significantly smaller than the reported value for normal corn starch, which was 15 μm (Lineback 1984). The average granule size of oat starch was positively correlated ($P < 0.01$) with %T and negatively correlated ($P < 0.01$) with lipid content, IA, BV, AM%, and λ_{max} (Table II).

Structure of Starches

Figures 2 and 3 show typical HPSEC profiles of the debranched oat and corn starches, respectively, and indicate that the starches

TABLE III
Size Distribution of Oat Starch Granules

Sample	Range (μm)	Average ± SD[a] (μm)
E77	9.5–3.8	5.9 ± 1.7
Dal	6.6–3.0	4.8 ± 1.2
L996	6.0–2.7	4.1 ± 0.9

[a]Values are the average ± standard deviation of 30 starch granules, 10 each from three micrographs.

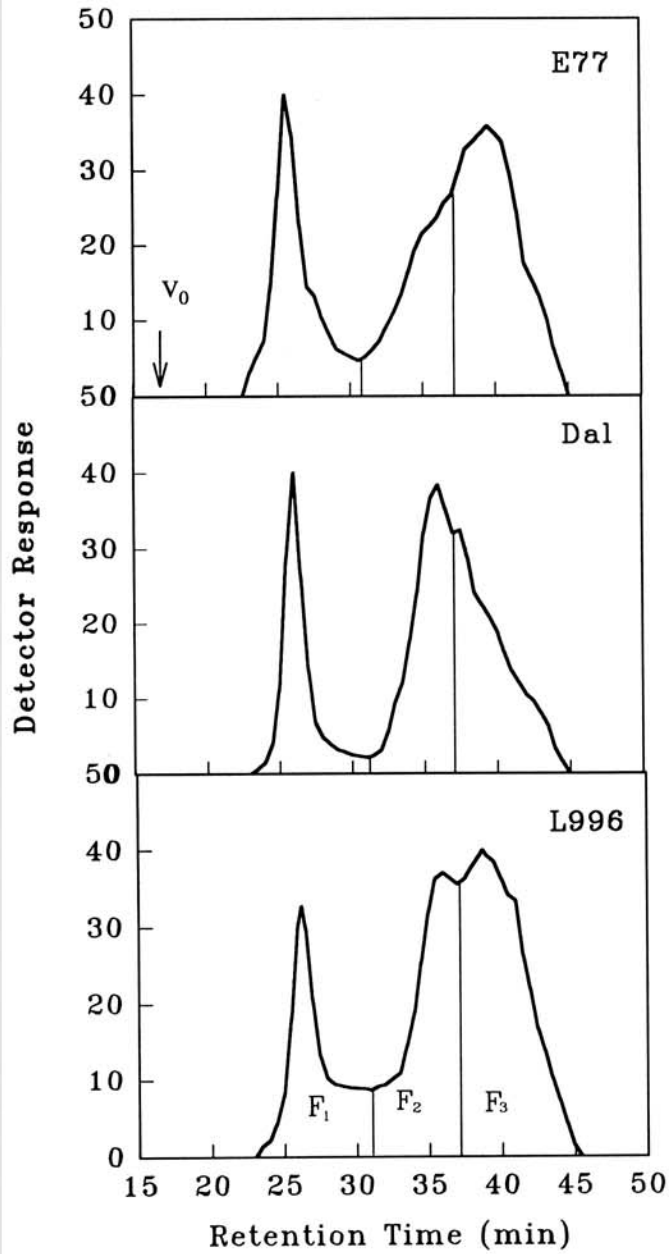

Fig. 2. High-performance size-exclusion chromatography profiles of isoamylase-debranched starches from three oat types. V_o = void volume. Fraction 1 (F_1) was composed of amylose. F_2 included long B chains of amylopectin. F_3 contained A and short B chains of amylopectin.

were debranched, since there was no carbohydrate in the void volume. The shapes of the chromatograms varied among the samples. The profiles were divided into the three fractions (F_1, F_2, and F_3), and the peak CL_w, weight% and mole% of each fraction were measured and calculated as shown in Table IV.

The CL_w of F_1 (amylose) were significantly higher for corn starches than they were for oat starches, but CL_w values differed significantly even among corn and oat starches (Table IV). These data confirm that the molecular weight of oat amyloses is appreciably smaller than that of corn amyloses. Paton (1979), using gel-filtration chromatography, also reported that the molecular weight is lower for oat amylose (Hinoat) than it is for corn and wheat amylose.

The CL_w of F_2 (long B chains of amylopectin) were not significantly different among all oat starches and B73×MO17 corn starch, but CL_w of PFP corn starch (50.8) was significantly higher than all other types. The CL_w of F_3 (A and short B chains of amylopectin) differed significantly among the oat starches, with E77 starch having the shortest short chains (16.7) and L996 having the longest short chains (22.2). The CL_w of F_3 for B73×MO17 and PFP corn starches were similar to those of Dal and L996 oat starches, respectively, but the CL_w of E77 starch was significantly lower than CL_w of all other starch types. Hizukuri (1985) reported a CL_w of 60 and 17 for long and short chains, respectively, of debranched amylopectin from normal corn starch. Data (CL_w) on oat starches from other researchers were not available. Differences between the present study and the Hizukuri study in CL_w of F_2 and F_3 in corn starches may be attributed to differences in the starch sources. In addition, the different chromatographic methods used to separate these fragments could account for variations.

The weight% value of F_1 (apparent amylose) gave values slightly different from AM% values (calculated from IA and BV) reported in Table I. Differences may occur during debranching, when partly branched amylose may be lost, thus decreasing the amount of apparent amylose (Banks and Greenwood 1975). It is also possible that longer fragments (debranched amylopectin) could elute with the amylose, thus increasing the measured amount of amylose. In addition, the presence of intermediate materials in oat starch (Banks and Greenwood 1967, Paton 1979, Sowa and White 1992) may affect the percentage of amylose. Further study of pure amylose and amylopectin fractions was reported earlier (Wang and White 1994).

For both weight% and mole%, the Dal starch generally had the greatest amounts of F_2 (long B chains of amylopectin) and the least amounts of F_3 (A and short B chains of amylopectin) among the three oat starches (Table IV). There were no significant differences in weight% and mole% of F_2 and F_3 between E77 and L996 starches. The weight% and mole% for corn starches of F_2 and F_3 tended to fall between values for Dal starch and the other two oat starches. Thus, excluding Dal starch, the other oat starches had more A and short B chains and fewer long B chains of amylopectin than did corn starches.

The ratios of F_3 to F_2 of weight% and mole% are listed in Table IV. The ratio may be used as a measure of the degree of multiple branching of amylopectin, with the higher the ratio, the higher the degree of branching (Biliaderis et al 1981). Dal had the smallest weight% and mole% ratios (0.8 and 1.7, respectively) among all starches, corn starches were intermediate, and E77 and L996 starches were greatest. These data suggest distinct structural differences in the amylopectin components of the oat starches and of the corn starches.

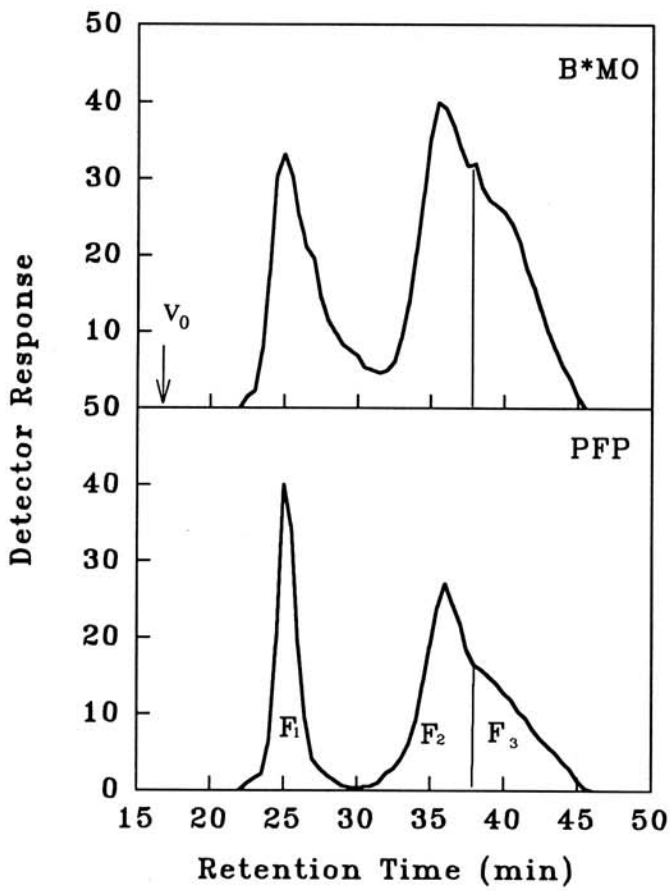

Fig. 3. High-performance size-exclusion chromatography profiles of isoamylase-debranched starches from two corn types. V_0 = void volume. Fraction 1 (F_1) was composed of amylose. F_2 included long B chains of amylopectin. F_3 contained A and short B chains of amylopectin.

Correlations Among Selected Structure and Physicochemical Properties of Oat Starches

Table V lists the correlations among selected structural characteristics and physicochemical properties of oat starches. These statistical analyses are based on only three sample types, so the correlations should be viewed only as possible indications of trends. The CL_w of F_1 (apparent amylose) was negatively cor-

TABLE IV
Characterization of Carbohydrate Compositions and Chain Length Distribution of Isoamylase-Debranched Starches[a]

Sample	Fraction[b] F_1	F_2	F_3	F_3/F_2
Cl_w[c]				
E77	703.0	44.0	16.7	
Dal	627.0	44.1	19.9	
L996	592.5	41.6	22.2	
B×MO	833.5	44.1	19.9	
PFP	907.5	50.8	22.3	
LSD[d]	59.5	4.7	1.8	
Weight%[e]				
E77	21.8	30.8	47.5	1.5
Dal	23.1	43.4	33.6	0.8
L996	23.0	28.0	49.0	1.8
B×MO	23.0	38.9	38.3	1.0
PFP	27.1	31.7	41.2	1.3
LSD	3.0	4.3	4.8	
Mole%[f]				
E77	0.9	19.7	79.6	4.0
Dal	1.4	36.4	62.3	1.7
L996	1.4	23.1	75.6	3.3
B×MO	1.0	31.2	67.9	2.2
PFP	1.3	24.8	73.9	3.0
LSD	0.2	5.0	5.0	

[a] Values are the mean of two separate determinations.
[b] F_1, F_2, and F_3 = amylose, long B chains of amylopectin, and A and short B chains of amylopectin, respectively.
[c] Weight average chain length. Expressed as weight of glucose units.
[d] LSD = least significant difference at a significance level of $P < 0.05$.
[e] Percentages of F_1, F_2, and F_3 within the starch type as measured by peak area.
[f] Percentages of F_1, F_2, and F_3 within the starch type as calculated from weight% and CL_w.

related with starch lipid content, BV, AM% (from BV), solubility at 95°C and was positively correlated with starch granule size. Correlations between CL_w of F_2 and properties were all very low, so they are not reported. The CL_w of F_3 (A and short B chains of amylopectin) was positively correlated with starch lipid content, IA, BV, AM% (from BV), swelling power and solubility at 95°C, and was negatively correlated with %T and starch granule size. Most values correlating negatively with CL_w of F_1 correlated positively with CL_w of F_3 (starch lipid content, BV, AM% from BV, and solubility at 95°C). It follows that as the CL_w of F_3 (A and short B chains of amylopectin) increases, more lipid could bind to the longer branches. Similarly, measurements related to iodine binding would increase. Also, solubility of the starches with longer CL_w of F_3 could increase. Alternatively, longer CL_w of F_1, which are already long, relatively straight chains, could decrease solubility of that fraction, and also provide fewer sites from iodine binding than corresponding shorter chains of amylose. The mole% ratio of F_3/F_2 was correlated only with swelling power at 85°C ($r = 0.93$, $P < 0.08$), so mole% correlations are not shown in Table V.

Banks et al (1974) reported that the degree of polymerization of the amylose of amylomaize starches is lower than that of normal maize. These results correspond to ours, in which the CL_w of starch with a high amylose content (L996) was lower than that of starch with a low amylose content (E77). Granted, the "high" amylose starch in our study was only 25%, whereas the amylomaize starch had 50–75% amylose. Takeda et al (1986) reported that amylopectin with long branch-chains tended to retrograde rapidly, thereby decreasing %T. Our study agrees with this view inasmuch as the %T was negatively correlated with CL_w of F_3 ($r = -0.89$).

CONCLUSIONS

Oat starches isolated from groats with low (6.2%), intermediate (8.0%), and high (11.2%) lipid contents were unique in structure and physicochemical properties. In general, oat starches had greater lipid contents, lower molecular weight, lower %T, smaller granule size, less swelling power and solubility at 85°C, and amylose with shorter chain length (F_1) than did corn starches. There also were differences among the oat starches, possibly related to some structural and physicochemical properties. For example, the oat starch-lipid content was significantly correlated ($P < 0.05$) with CL_w of F_3 ($r = 0.91$), IA ($r = 0.72$), BV ($r = 0.89$), AM% ($r = 0.94$) (from BV), swelling power at 95°C ($r = 0.67$) and solubility ($r = 0.83$) and was negatively correlated with CL_w of F_1 ($r = -0.84$), %T ($r = -0.72$), swelling power at 85°C ($r = -0.75$), and granule size ($r = -0.91$). The AM% also was greatly related to differences in structure and physicochemical properties of the oat starches. The AM% was positively correlated with CL_w of F_3 ($r = 0.94$), IA ($r = 0.74$), BV ($r = 0.96$), λ_{max} ($r = 0.73$), swelling power at 95°C ($r = 0.76$), and solubility at 95°C ($r = 0.90$). The AM% was negatively correlated with CL_w of F_1 ($r = -0.92$), %T ($r = -0.78$), swelling power at 85°C ($r = -0.80$), and granule size ($r = -0.97$). The [η], long B chains of amylopectin (F_2), and degree of multiple branching (F_3/F_2) of oat starches were not significantly correlated with other parameters.

TABLE V
Correlations Among Selected Structural Characteristics and Physicochemical Properties of Oat Starches[a]

	CL_w at F_1 (Amylose)	CL_w at F_3 (A and short B chains)
Starch-lipid%	−0.84 (0.04)	0.91 (0.01)
IA	NS[b]	0.89 (0.02)
BV	−0.91 (0.01)	0.97 (0.001)
AM% (from BV)	−0.92 (0.009)	0.94 (0.005)
%T	NS	−0.89 (0.02)
Swelling power (%) at 85°C	NS	NS
Swelling power (%) at 95°C	NS	0.84 (0.04)
Solubility (%) at 95°C	−0.86 (0.03)	0.95 (0.003)
Average granule size	0.93 (0.006)	−0.97 (0.001)

[a] CL_w = weight average chain length. F_1 = amylose, F_3 = A and short B chains of amylopectin. IA = iodine affinity; BV = blue value; AM% = amylose percentage calculated from BV; %T = percentage transmittance.
[b] Not significant at $P < 0.05$.

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