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STARCH SOURCES

Barley Flour Composition and Use for Starch Production

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Barley is a very inexpensive source of carbohydrate in certain areas in the West and thus a potential source of starch. The alkali process can be used on barley flour to produce a starch of good quality. Barley protein is readily dispersed in alkali and can be recovered in yields of 77 to 86% after removal of the starch by adjustment of the pH. Of the six varieties tested, Compana appears most promising as a starch source. Analysis indicated that the amino acids in two varieties of barley protein were different. The behavior on dispersion in alkali also indicated differences in the nature of the protein. The existence of a new "pectinlike" polysaccharide in barley flour is reported.

BARLEY is rapidly becoming to the Intermountain area what corn is to the Corn Belt—the cheapest source of carbohydrate. This immediately suggests the possibility of using this cereal for starch production.

Very little information has been published on the production of starch from barley. The wet milling technique was found unsatisfactory (*15*). The other logical method is the adaptation of the alkali process developed by Dimler *et al.* (*9*) for use with wheat and tried by him on one variety of barley. This process requires flour as the starting material. The present study was initiated to examine the composition of barley flour and to see if starch could be satisfactorily recovered from it by the alkali process.

Materials and Methods

Six varieties of barley with a known history, which were well adapted to Montana, were used for this study. Flours were prepared in an experimental Buhler flour mill equipped with 10 XX bolting silk. In one case the barley was pearled before milling.

Protein in the various products was determined by a modified Kjeldahl method (*2*), using 6.25 as the conversion factor to convert per cent nitrogen to protein. Starch was determined polarimetrically by the procedure of Clendenning (*6, 7*). However, on the "tailings fraction" it was necessary to use a modified procedure (*10*). Crude fiber and ash were determined by the usual method (*3*). To determine moisture, the samples were dried 16 hours at 110° C. under a vacuum of 28 inches of mercury. Fat in the flour samples was determined by ether extraction (*4*). Fat in the purified starches was determined by acid hydrolysis and extraction from the hydrolyzate, as suggested by Taylor and Nelson (*18*). Magnesium, potassium, and sodium were determined by a modification of the method of Pro and Mathers (*17*). Calcium was determined by the flame photometric procedure suggested by Cooley (*8*), and silica was determined photometrically by the procedure of Kerr and Trubell (*11*). Phosphorus was determined photometrically by the procedure of Allen (*1*). The amino acids were determined by the procedure described by Moore and Stein (*16*). The pentosans were measured by the AOAC procedure (*5*), the distillate being redistilled and the furfural precipitated with thiobarbituric acid. The "pectin" was determined by the evolution of carbon dioxide using the method of McCready, Swenson, and Maclay (*14*) on material isolated with an ammonium oxalate extraction and purified by the procedure described by Kertesz (*12*). The fermentable sugars were determined by suspending 10 grams of flour, which had been autoclaved in a dry state to inactivate the β-amylase, in 100 ml. of water containing 5 ml. of an active distiller's yeast. The loss in weight after 24 hours was used to calculate sugars after making corrections for the fermentable material present in the inoculum.

The alkali process (*9*) developed for the production of starch from wheat was used in this study. This consists of dispersion of the flour protein in a dilute aqueous alkaline solution and removal

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Table I. Analyses of Flour Sample

(All data on moisture-free basis)

Strain of Barley	Lb./Bu.	Milling Yield, %	Starch Content, %	Protein Content, %	Ash, %	Crude Fiber, %	Fat, %	Fermentable Sugar, %	Pectinlike Polymer, %	Pentosan, %
Betzes	50.6	45	73	11.5	1.57	1.25	1.2	3.3	1.41	1.14
Carlsberg	47.3	51	67	11.0	1.98	1.92	0.9	3.8	1.48	1.57
Compana	51.4	58	80	8.4	1.23	1.03	1.2	2.5	1.49	1.06
Pearled Compana[a]	...	57	79	9.9	...	...	...	...	...	...
Hannchen	50.5	66	74	12.3	1.54	1.51	2.2	3.1	2.04	1.16
Vantage	48.8	43	79	12.9	1.27	1.23	1.5	2.8	...	1.11
Ymer	48.6	48	74	11.3	1.43	1.54	1.0	3.2	1.42	1.07

[a] A different sample of Compana. Milling yield was based on whole barley before pearling.

Table II. pH Determination for Maximum Protein Extraction

	Normality													
	0.015		0.020		0.025		0.030		0.035		0.040		0.045	
Strain of Barley	pH	% ext.	pH	% ext.	pH	% ext.	pH	% ext.	pH	% ext.	pH	% ext.	pH	% ext.
Betzes	10.0	93.3	10.5	94.5	10.8	96.6	11.0	99.1	11.1	100.2	11.2	100.0	11.3	100.2
Carlsberg	9.8	83.8	10.4	90.4	10.7	96.0	10.9	95.3	11.1	95.6	11.3	95.6	11.4	95.6
Compana	10.2	92.6	10.6	97.8	10.8	98.3	11.0	100.1	11.1	100.1	11.2	100.3	11.3	100.1
Pearled Compana	10.1	93.2	10.6	100.0	10.9	100.0	11.1	100.0	11.2	100.0	11.3	100.0	11.4	100.0
Hannchen	9.6	76.0	10.3	90.7	10.6	94.6	10.8	94.9	11.1	95.7	11.3	96.9	11.4	97.2
Vantage	10.1	86.6	10.6	91.4	11.0	96.3	11.1	98.9	11.2	99.6	11.3	100.0	11.3	100.0
Ymer	9.8	89.5	10.3	92.4	10.6	96.6	10.8	100.3	11.1	100.0	11.2	99.6	11.3	100.0

of the starch by centrifugation. In our operations a physical separation was made by scraping off the loose top layer of the centrifuge cake. This was referred to as the "tailings" fraction. The alkaline protein solution was then acidified and the precipitated protein was removed by centrifugation. Although many bases and acids can be used, sodium hydroxide and sulfuric acid were used in this study.

Table III. pH Determination for Maximum Protein Precipitation

(Protein calculated as N × 6.25)

	Per Cent Protein Precipitated at pH						
Strain of Barley	4.0	4.5	5.0	5.5	6.0	6.5	7.0
Betzes	77.4	80.0	82.5	80.2	69.6	44.4	38.0
Carlsberg	74.1	80.9	80.3	77.5	53.8	38.9	36.2
Compana	65.5	75.8	80.9	80.2	73.9	35.2	31.4
Pearled Compana	63.3	79.7	83.3	83.4	74.3	47.6	42.4
Hannchen	71.6	76.2	81.6	76.7	43.4	35.0	31.5
Vantage	79.3	84.4	85.7	83.9	72.3	38.3	14.8
Ymer	75.2	81.0	83.3	80.6	71.0	45.1	42.5

Results and Discussion

Effect of Variety on Yield and Composition of Flour. There were considerable differences in the ease with which the various barleys were milled. When Ymer was milled, the flour had a tendency to ball up. Carlsberg, on the other hand, milled readily, but a much greater percentage of hull was retained in the flour. In general, the large heavy kernels milled more readily and gave higher flour yields. Tempered barley had a tendency to ball up. For this reason, barley was milled just as it came from storage with an average moisture content of 6 to 9%. Pearling before milling did not improve flour yields. The flour yields and composition for six varieties are given in Table I.

The galacturonic acid polymer, which for want of a better name was called pectin, was isolated from the flour by first extracting with 0.5% ammonium oxalate at 75°C. This solution was centrifuged to remove starch and protein, cooled, neutralized, and then made up to 0.05*N* with hydrochloric acid. Two volumes of cold 95% ethanol were then added and the "pectin" was removed by filtration. All sugars are eliminated by this treatment, as no trace of free sugar could be detected with paper chromatography. Although this residue gave a sky-blue color with iodine, treatment with crystalline α- and β-amylase produced no detectable amount of maltose.

It gave the characteristic color reactions (*13*) with hydroxylamine and iodine and formed good films. On treatment with pectinase this compound decomposed, yielding galacturonic acid, but the rate of reaction was somewhat slower than that of commercial pectin used as a control. Furthermore, this pectin failed to form good gels with sugar. A chromatograph of the acid hydrolyzate indicated the presence of galacturonic acid, a small amount of glucose, and traces of arabinose but no xylose or galactose. This suggests that it is definitely not a hemicelluose and not a true pectin. The structure of this material is now being determined in this laboratory. From Table I it is observed that from 90 to 99.8% of the total constituents of the flour have been accounted for. Some of these flours gave a positive test for fructosans. Fructosans and glucosans might account for the balance of this material.

Dispersing Action of Alkali on Barley Protein. The solubility of barley proteins in alkali was strikingly different, as shown in Table II.

Only 95.6 and 97.2% of the protein was extracted from Carlsberg and Hannchen, respectively, in a 0.045*N* solution, whereas the protein in the other varieties was completely extracted at this alkalinity. This was not due to the buffering capacity of the flour, as indicated by the pH of these solutions. The fact that the proteins from different varieties of barley show different solubilities at the same pH would indicate distinct differences in their composition.

Effect of pH on Protein Recovery. The dispersed barley proteins were readily recovered on acidification (Table III).

In all cases the optimum pH for protein precipitation was approximately 5. The fact that protein recoveries varied with the variety again suggested that they were somewhat different. This would account for the variations

Table IV. Amino Acid Analysis of Barley Protein

(Values expressed as per cent of total protein)

Amino Acid	Barley Variety	
	Compana	Vantage
Alanine	1.8	3.4
Arginine	3.1	2.6
Aspartic acid	1.4	2.5
Glutamic acid	31.0	31.8
Glycine	1.3	2.0
Histidine	1.8	1.2
Isoleucine	2.9	2.9
Leucine	7.7	5.8
Lysine	3.0	2.2
Methionine	1.0	0.4
Phenylalanine	4.3	4.5
Proline	16.1	7.9
Serine	1.7	3.1
Threonine	1.4	2.1
Tyrosine	2.7	2.5
Valine	5.4	5.4

Cysteine, cystine, hydroxyproline, and tryptophan were not run by this procedure.

Table V. Yield of Starch and Protein from Various Varieties

(All data calculated on flour, moisture-free basis)

Strain of Barley	Crude Starch			Tailings Starch			Precipitated Protein		
	Yield, g./100 g.	Starch content, %	Protein content, %	Yield, g./100 g.	Starch content, %	Protein content, %	Yield, g./100 g.	Protein content, %	Protein recovery, %
Betzes	51	98.5	0.3	24	68	1.1	13.2	72.1	82.8
Carlsberg	47	99.7	0.2	24	80	1.2	11.7	72.7	77.4
Compana	63	99.7	0.1	16	57	1.7	11.6	58.9	81.3
Pearled Compana	60	99.7	0.2	20	69	1.4	11.5	71.9	83.5
Hannchen	56	97.3	0.3	18	77	1.3	14.1	68.9	79.0
Vantage	59	98.5	0.2	16	77	1.3	16.6	67.0	86.2
Ymer	43	99.7	0.2	30	82	1.1	16.6	56.8	83.4

observed in feeding different barleys to livestock. Because the greatest discrepancy in protein recovery, especially at the lower or higher pH values, was between Compana and Vantage, it was considered desirable to run an amino acid assay on these varieties. These data, presented in Table IV, verified the assumption that there were distinct differences in the composition of barley proteins.

Effect of Variety on Yield of Starch and Protein. The yield of starch and protein from six varieties is reported in Table V.

Compana appeared to be the most promising of the varieties tested. Starches of satisfactory purity were obtained by the use of this method. The "tailings fraction" probably could be reduced in amount, if suitable equipment were available. Good yields of high protein residue were obtained by this method.

Noncarbohydrate Constituents of Barley Starch Other Than Proteins. The separated starches were resuspended several times in distilled water, dried, and analyzed for inorganic constituents and "bound" fat. Analyses for P_2O_5, SiO_2, CaO, MgO, K_2O, Na_2O, and fat gave average values of 0.296, 0.013, 0.014, 0.023, 0.059, 0.123, and 0.78%, respectively. Hannchen and Vantage appear to be slightly different from the other varieties, as they contain approximately 25% more phosphorus and 30% more magnesium. In general, the inorganic constituents of barley seem to conform to the data for other common starches.

It would appear that starch of satisfactory quality can be prepared from barleys by the alkali method. Because Compana, the largest seeded variety tested, gave the most satisfactory results, it would appear that kernel size is very important for starch production. With this in mind a program is under way at Montana State College to develop a giant seeded variety of Compana for industrial use.

The physical properties of the barley starch from the various varieties were not determined because of lack of proper equipment. This work will be completed and reported on later.

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