BARLEY STARCH

II. Some Properties of Barley Starch[1]

K. J. GOERING AND D. L. BRELSFORD

ABSTRACT

The price of barley in Montana suggests that it might be competitive with other cereals for starch production, but very little information is available. Starch was prepared from a number of varieties to study the effect of method of preparation as well as variety on starch properties. Solubility and swelling power were measured on five varieties. A detailed study, including Brabender curves, was made on Compana starch, since this variety of barley comprises 75% of Montana production. By selection of variety it appears possible to obtain a wide range in swelling power and solubility. Compana starch prepared by the alkali process shows exceptional resistance to the action of alpha-amylase. This appears to be due to the action of calcium ion on esterified phosphate. This is the first finding of esterified phosphate in a cereal starch.

Barley has become to the Intermountain area what corn is to the Corn Belt — the principal source of feed for livestock and the most

[1]Manuscript received June 8, 1964. Contribution from Montana Agricultural Experiment Station, paper No. 661, Journal Series.

inexpensive source of carbohydrate. The industrial use of starch in the paper industry and the extreme shortage of locally produced protein for the livestock industry suggested the possibility of using barley to fulfill both requirements in this area.

Very little information is available on either the production or properties of barley starch. The wet-milling process was reported to be unsatisfactory by MacMasters and co-workers (1,2). The alkali process developed by Dimler *et al.* (3) was tested on one variety of barley. This process was used for production of limited amounts of barley starch from six varieties of barley by Goering and Imsande (4). Certain problems arising from the use of this process in producing pilot-plant amounts of starch suggested that other procedures should be tried. Only a few reports have been made on the properties of barley starch (5–9), and most of these give a minimum of information.

The present study was initiated to examine the influence of the method of preparation and variety on the properties of barley starch, to evaluate it for possible commercial use.

Materials and Methods

Preparation of Starches. Five varieties of barley, with known history and well adapted to Montana, were used. Because malting barleys usually are somewhat different from feeding varieties, both kinds were included in this study. The flours were prepared in an experimental mill and screened through 10xx bolting silk. The starches were prepared by either the alkali process as described by Goering and Imsande (4) or by a modification of the batter process used by Shewfelt and Adams (10) for the production of wheat starch. When a coherent dough was prepared from barley flour by mixing with an equal weight of water at 52°–55°C., and agitating for 15 min., the dough then being allowed to develop for 20–30 min. before the cutting water was added, the procedure of Shewfelt and Adams worked very effectively. All starch samples were screened through 325-mesh screen and resuspended several times in water, the nearly clear upper layer being decanted before final centrifugation. The starches were carefully dried at a low temperature in a stream of warm, dry air.

Protein, Ash, and Fat. The protein content was determined by a modified Kjeldahl method (11, p. 12) (conversion factor, 6.25). The samples were ashed in a muffled furnace according to the usual procedure (11, p. 284). The total free fat was determined by ether extraction (11, p. 287).

Phosphorus. This was determined colorimetrically after digestion with nitric and perchloric acid, by a slight modification of the method of Allen (12).

Esterified Phosphate. For the determination of esterified phosphate, a 48-hr. extraction with 80% dioxane was used as described by Schoch (13). Phosphorus determinations were made before and after this treatment.

Ionic Character. The ionic character of barley starch was examined by the technique described by Schoch and Maywald (14).

Defatted Starch. The defatted starch was prepared by the procedure described by Schoch (15); i.e., extracting small amounts of starch in a Soxhlet extractor by refluxing for 24 hr. with 85% methanol.

Swelling Power and Solubility. Swelling power and solubility were determined by the procedure described by Leach *et al.* (16).

Brabender Viscosity Curves. Brabender curves were determined and analyzed by the procedure described by Mazurs *et al.* (17), except that maximum temperature was 92.5°C., because the altitude at our laboratory would not permit heating to 95°C. without boiling.

Brabender Pasting Temperatures. The pasting temperature range was determined by amylograms modified by CMC as described by Sandstedt and Abbott (18).

Viscosity Reduction with Alpha-amylase. The effect of alpha-amylase on the various starches was determined by adding 0.006% of Vanzyme, a high-temperature bacterial alpha-amylase, to a 7.6% starch suspension which had previously been adjusted to pH 6.2–6.4 and to a temperature of 25°C. This mixture was introduced into the "viscograph" (Brabender VISCO/amylo/GRAPH) and heated at 1.5° per min. to 92.5°C. and then held for 15 min. at this temperature. These conditions were selected to essentially duplicate paper-mill conditions for the preparation of starch.

Results and Discussion

Starch was prepared from Betzes and Compana barley flours by both the alkali and the batter process. A portion of the Compana starch prepared by the alkali process was defatted so that comparison could be made with the regular starch. In addition, limited amounts of Ymer, Hannchen, and Carlsberg barley starches were prepared by the alkali process. The percentages of protein, fat, and ash in these starch preparations are recorded in Table I.

The swelling power and solubility of the starch from five varieties of barley are given in Table II.

Table II indicates that the method of production did not significantly affect either the swelling power or solubility of Betzes starch. It

TABLE I
ANALYSIS OF BARLEY STARCHES

Variety	Process	Protein	Ash	Fat
		%	%	%
Betzes	Batter	0.42	0.14	0.50
Betzes	Alkali	.52	.21	.45
Compana	Alkali	.36	.23	.43
Compana (defatted)	Alkali	.11	.26	.07
Compana	Batter	.39	.20	.35
Carlsberg	Alkali	.22	.24	.40
Hannchen	Alkali	.33	.36	.44
Ymer	Alkali	0.22	0.23	0.52

also indicates a substantial difference between the different varieties, ranging from a solubility similar to cross-bonded waxy sorghum to a value considerably higher than that of corn starch. The swelling power varied from values somewhat less than those of corn to those in the same range as cross-bonded waxy sorghum (19). The solubility and swelling power of the last three samples were quite unexpected. Repeating the experiment gave the same values. Unfortunately, the production of starch from these varieties ended when no more flour was available. They will be included in a more detailed investigation to be reported at a later date.

TABLE II
SOLUBILITY AND SWELLING POWER OF VARIOUS BARLEY STARCHES[a]

Varieties	Process	Temp.	Swelling Power	Solubles
		°C.		%
Compana (defatted)	Alkali	70	6.6	2.6
		80	7.7	3.0
		85	8.2	3.3
		90	8.7	3.5
Betzes	Alkali	70	5.3	1.7
		80	6.5	3.6
		85	6.9	4.4
		90	7.4	5.3
Betzes	Batter	80	6.6	4.3
		85	6.8	4.7
		90	7.1	5.1
Ymer	Alkali	85	10.8	14.5
Hannchen	Alkali	85	12.5	19.3
Carlsberg	Alkali	85	22.2	22.2

[a] Recent work suggests that high values for the samples in the last group (Ymer, Hannchen, and Carlsberg varieties) may be an artifact or an environmental effect.

Figure 1 shows solubility and swelling power for Compana starch prepared by both the batter and alkali processes.

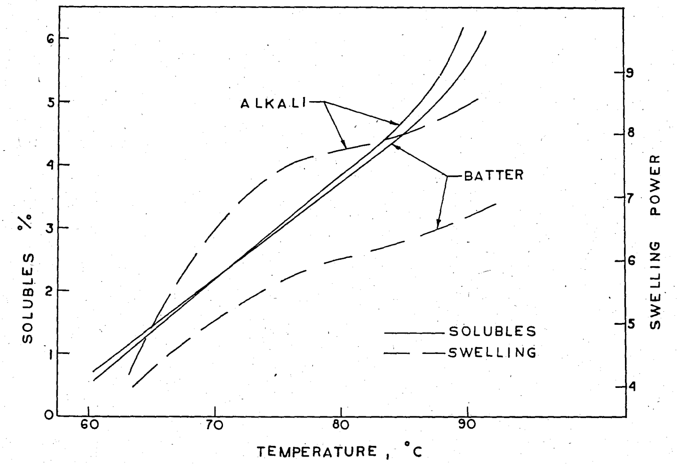

Fig. 1. Swelling power and solubility: comparison of curves obtained from Compana starch prepared by the alkali and batter process.

The determinations were made at 5° intervals over the range of 65° to 90°C. The swelling-power curves have the same general shape as those for corn starch (19), but the total swelling is substantially less. The swelling power for Compana appears to be dependent on method of production, but this was not observed with Betzes. Apparently the method of production did not influence the solubility. Comparison of the data in Table II with those of Fig. 1 indicates that defatting did not appreciably alter swelling power or solubility.

The pasting characteristics of barley starch compared to wheat starch are shown in Fig. 2.

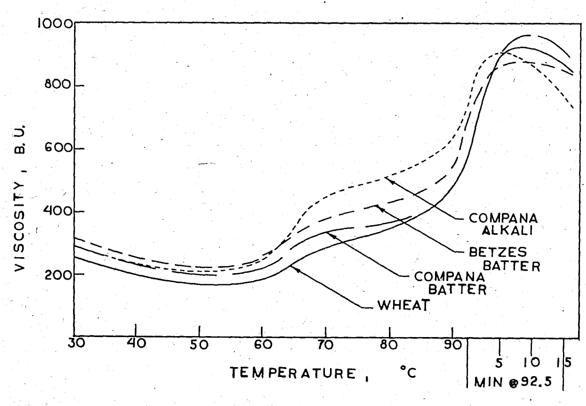

Fig. 2. Barley starch pasting: comparison of curves obtained from Betzes, Compana, and wheat starch; 5.5% starch + 0.8% CMC.

Barley starch shows the same two-stage pasting as does wheat starch. Compana starch prepared by the batter process is almost identical with wheat starch with initial pasting beginning at 60°C. and a second stage at approximately 85°C. Again there appears to be a difference in the behavior of Compana starch, depending on the method of production, and a slight difference between Betzes and Compana starch. The CMC procedure is very effective in showing the initial phase of pasting; examination of the Brabender curves at different starch concentrations failed to give any indication of this initial pasting. Apparently Banasik *et al.* (5) had the same difficulty when using the light-transmission procedure; they reported that "barley starch showed little change until 80° was attained which is quite different from the pasting characteristics of other cereals."

A series of Brabender viscosity curves was run with five different concentrations of Compana starch prepared by two different procedures. In Fig. 3 the viscosities at peak pasting, after 1 hr. at 92.5°C. and after cooling to 50°C. and holding for 1 hr., were plotted against the logarithm of the concentration, according to the procedure recommended by Mazurs *et al.* (17).

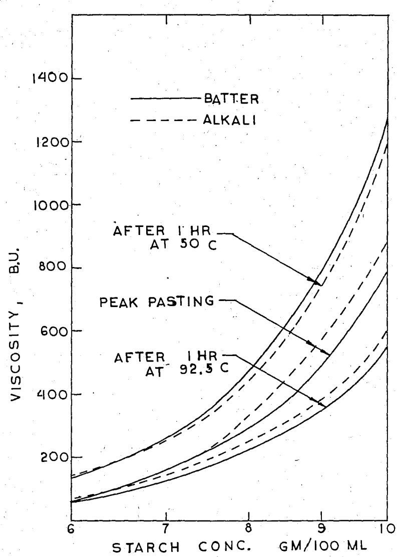

Fig. 3. Graphical analysis of Brabender viscosity curves: comparison of viscosities at peak pasting, cooking, and after holding 1 hr. at 50°C. for Compana starch prepared by the alkali and batter processes.

It is apparent from Fig. 3 that the method of production had very little influence on these values. In general, Compana barley starch seems to have peak pasting and cooking characteristics between the values obtained for corn and wheat (17). It does show a distinct difference after being held for 1 hr. at 50°C., since under these conditions the viscosity does not increase nearly to the extent it does with either wheat or corn starch.

When pilot-plant quantities of barley starch were used on the calender rolls to coat paper, it was observed that it was more resistant to enzymatic liquefaction than was corn starch. Preliminary work with the viscograph indicated distinct differences in final viscosity when barley and corn starch were converted under the same conditions. Betzes starch prepared by the two procedures was compared with Compana starch prepared by the batter process, in one instance in tap water and the other with distilled water (see Fig. 4).

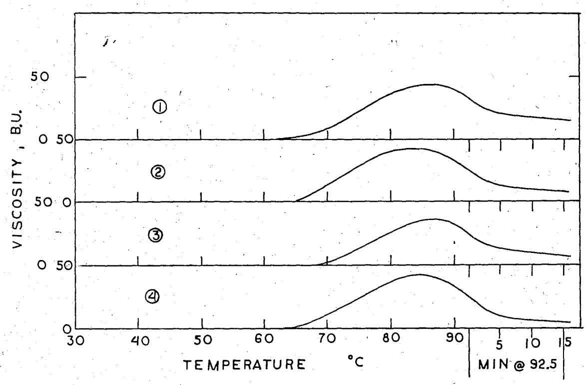

Fig. 4. Starch liquefaction: comparison of variety and method of preparation on viscosity curves obtained after treatment with alpha-amylase. 1, Betzes batter process using tap water; 2, Betzes alkali process, tap water; 3, Compana batter process, tap water; 4, Compana batter process, distilled water. In all, starch concentration was 7.6 and 0.006% Vanzyme.

Examination of these curves indicated no significant differences, although all show a slightly higher final viscosity than does corn starch (see Fig. 5). These results were quite different from the ones obtained earlier with Compana starch made by the alkali process.

Compana barley starch obtained from numerous barley samples always gave the same characteristic curves when the alkali-processed starch was treated with bacterial amylase. This suggested that something in the water, under the alkaline conditions of the starch separation, was reacting with starch to make it more resistant to amylase action. Since this starch was known to contain phosphate (4), the most likely possibility would be a reaction with the calcium in the water, suggesting that at least part of the phosphate present in Compana starch was esterified phosphate. The presence of esterified phosphate has not been previously reported in any cereal starch.[2] This resistance to enzyme action might be due to cross-linking of starch chains, or to the stability of the calcium salt, which might interfere with formation of the enzyme-substrate complex. To test this hypothesis, Compana and Betzes starches were extracted with 80% dioxane, which was reported by Schoch (13) to remove the phospholipids from starch (Table III).

TABLE III
DETERMINATION OF ESTERIFIED PHOSPHATE IN BARLEY STARCH

VARIETY	TREATMENT	INITIAL	AFTER DIOXANE EXTRACT
		% P	% P
Compana	Alkali	0.0565	0.0365
Compana (defatted)	Alkali	.0485	.0340
Betzes	Alkali	.0630	.0370
Wheat[a]		.0540	.0080
Potato[a]		0.0950	0.0870

[a] See reference 13.

Although the results reported in Table III suggested the presence of esterified phosphate, approximately the same amount seemed to be contained in both Betzes and Compana starch, and only Compana starch seemed to be influenced by added calcium. The assumption that these two starches contained esterified phosphate was checked by the methylene blue staining technique; both were dyed a light blue.

To investigate more thoroughly the hypothesis that calcium was involved in the resistance to enzyme action, three Compana starches were prepared by the alkali process. One was prepared with distilled water, one with distilled water with enough calcium chloride added to give 50 p.p.m. of calcium, and one with the local tap water which contains approximately 50 p.p.m. of calcium. These three starches and a corn starch control were treated with bacterial alpha-amylase and examined by means of the viscograph (Fig. 5).

Corn starch was quickly reduced to a viscosity too low to be measured. The Compana starches all required a higher temperature to cause a break in the peak viscosity; this indicated more resistance to the action of alpha-amylase. The Compana starches prepared in the presence of calcium maintain appreciable viscosity even after being held for 15 min. at the cooking temperature, whereas the Compana starch prepared in distilled water shows a viscosity only slightly greater

[2] Schoch, T. J. Private communication, 1963.

than that of corn starch under these conditions. This suggests that calcium is involved in this reaction, although the shape of the tap-water curve appears to indicate that this does not entirely answer the question. It is quite possible that some other ion such as magnesium might be involved.

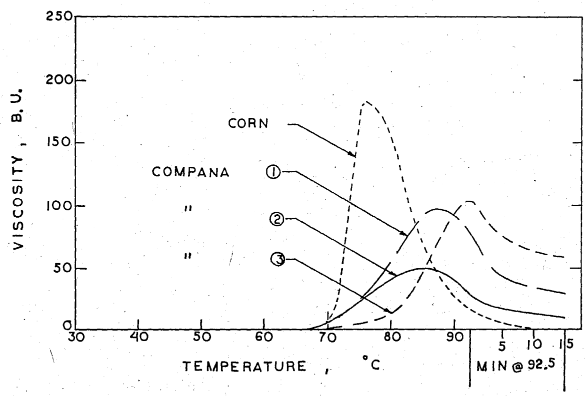

Fig. 5. Starch liquefaction: comparison of effect of calcium concentration during preparation of Compana starch by the alkali process on starch viscosity curves obtained after treatment with alpha-amylase with corn starch control. 1, $CaCl_2$ added to distilled water; 2, distilled water; 3, tap water.

The reason for the failure of Betzes starch to show this calcium effect, even though the dioxane extraction indicates the same amount of esterified phosphate, is not clear at this time. However, it is interesting to observe the differences in these two starches in respect to swelling power. With Betzes, the alkali and batter-process starches were approximately the same. The alkali starch from Compana had a swelling power approximately 25% greater than batter-process starch.

In some of our preliminary screening we have isolated barley starches containing twice as much phosphorus as Compana, to see how they react under these conditions.

Investigations are now in progress in our laboratories to study the nature of the alpha-amylase-resistant fraction.

Conclusions

Barley starches appear to exhibit wide variation in swelling power and solubility. Graphical analyses of the Brabender curves suggest that Compana barley starch has viscosity characteristics between those of wheat and corn, except that it does not become as viscous as starch of either wheat or corn after being held for 1 hr. at 50°C. The barley starches exhibit two-stage gelatinization with approximately the same gelatinization temperatures as wheat starch. Both Betzes and Compana starches appear to be different from any cereal starch reported to date, because they appear to contain esterified phosphate. Compana starch prepared by the alkali process in the presence of calcium produces a starch which shows resistance to the action of bacterial alpha-amylase. The reason for the failure of Betzes starch to show this calcium effect is unknown at this time.

Acknowledgment

The authors wish to express sincere thanks to Mrs. R. Baker for assistance in determining the ash, protein, fat, and phosphorus content of the starch samples.

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