EFFECT OF SOME NONSTARCH COMPONENTS IN CORN AND BARLEY STARCH GRANULES ON THE VISCOSITY OF HEATED STARCH-WATER SUSPENSIONS[1]

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ABSTRACT

Barley and cornstarch granules exhaustively extracted with 85% methanol show negligible pasting peaks, greater cooking stability, and lower setback. Addition of alcohol-free extract to the extracted starches essentially reproduces the curve obtained from the unextracted starch. The addition of pure, unsaturated fatty acids at the concentration found in the original starch essentially reproduces original curve. An examination of the various fatty acids present in the lipid fraction indicated that linolenic acid was most effective in modifying the viscosity curve. It is suggested that the pasting peak is not due to gelatinization and breakdown of granules, but is due to the breakdown of an amylose-fatty acid complex.

Previous work in our laboratory indicated that there was little or no relation between swelling power and the Brabender pasting curves of either barley starch (1) or the small granule starch from *Colocasia esculenta* (2). These observations are contrary to the accepted concept of the causes of pasting viscosity (3). A similar observation was reported on wheat starch by Miller *et al.* (4). It was suggested by these investigators that swelling is related to the exudate obtained from granules in the heating process and that there was a correlation between the amount of exudate and the pasting viscosity.

Our work with barley (1) failed to show a relation between the total amount of solubles and pasting viscosity, which suggests that it is not the total exudate, but some minor constituent in the exudate which is influencing the viscosity.

Fat-free starches are known to give modified Brabender curves. Reports in the literature on the effect of fatty acids on starch pastes are confusing. Mitchell and Zillman (5) and Medcalf *et al.* (6) reported that fatty acids caused increases in viscosities determined by the amylograph; whereas Gray and Schoch (7) indicated all fatty acids reduced the maximum viscosity as determined by this instrument and that they inhibit the breakdown of the resulting pastes.

It has been shown by Saito (8) that when wetting agents are added to polymers there is always an increase in the viscosity of the polymer mixture and the viscosity is related to the concentration of the wetting agent.

These facts suggested that an examination of the lipid fraction of starch granules might produce some interesting results.

MATERIALS AND METHODS

Preparation of Starches

The long awn-covered (LAC) Compana and waxy Compana barley starches

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were prepared as described by Goering *et al.* (1).

The corn starch was unmodified corn starch from CPC International obtained through the courtesy of Dr. Keng. The waxy corn was Amioca Waxy Maize Starch obtained from American Maize Products Co., Roby, Indiana.

Determinations

The Brabender amylographs were run on 8% db starch. When extracts were added back, they were incorporated as part of the water. The unsaturated acids were added directly to the amylograph cup. Palmitic acid was dissolved in dilute sodium hydroxide and partially neutralized before being added. In all cases no detectable change in pH was observed after mixing.

The extracts were obtained by extracting the starch in a Soxhlet with 85% methanol-water for at least 72 hr. The starch was then dried overnight at 60° C. The methanol extract was concentrated in a vacuum rotary evaporator to about 10%, then transferred to a volumetric flask and diluted to the mark with water so that an aliquot equivalent to the starch could be added to the amylogram determination. The precipitate which formed was suspended in the solution by shaking before the aliquot was removed.

For lipid extraction, the 85% methanol-water extract was concentrated 100-fold on a vacuum rotating evaporator at 30° C. The concentrate was partitioned three times each with an equal vol of diethyl ether. The combined ether extracts were washed twice with an equal vol of water. The wash water was added to the concentrate. The concentrate was then subsequently extracted with chloroform-methanol according to the Folch technique (9). The ether extract, containing

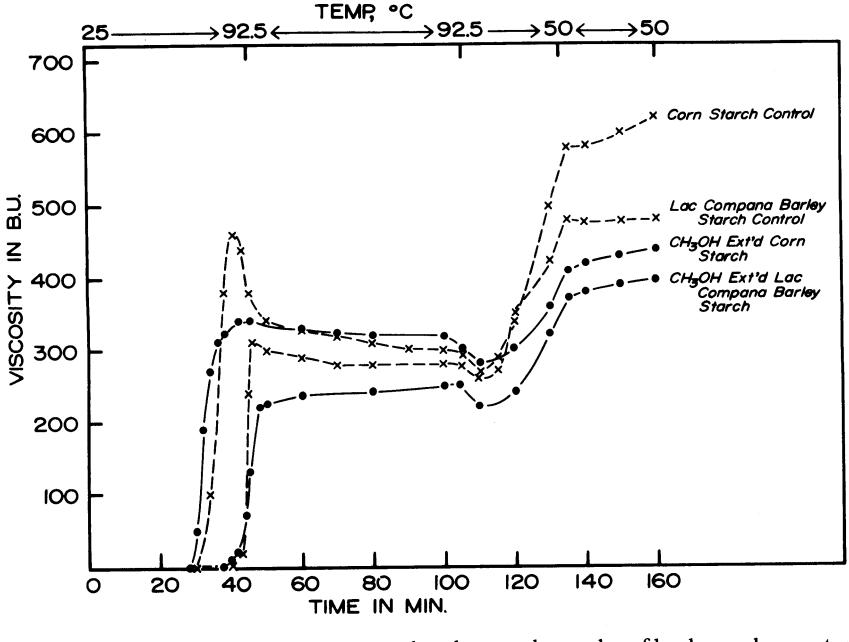

Fig. 1. Brabender amylograms on extracted and control samples of barley and corn starch (8% level).

mostly neutral lipids, and the chloroform-methanol extract, containing mostly polar lipids, were evaporated under a nitrogen sweep and weighed.

Preparative thin-layer chromatography of aliquots of the ether extract and the chloroform-methanol extract on silica gel developed in hexane-diethyl ether-acetic acid (85:15:1), visualized with rhodamine-6G, eluted with toluene, evaporated under nitrogen and weighed, gave an estimation of the polar lipids, diglycerides, and monoglycerides, free fatty acids, triglycerides, fatty acid methyl esters, and sterol esters, wax esters, and hydrocarbons. An aliquot of the free fatty acids was treated with diazomethane (10) to convert them to methyl esters. The monoglycerides and diglycerides were transesterified by the method of Morgan *et al.* (11). Fatty acid compositions were then determined by gas liquid chromatography on a 6 ft × 0.25 in. glass column packed with 15% ethylene glycol succinate on Gas Chrom Z. A flame ionization detector was employed and quantitation was by disc integration.

The upper layer left after Folch extraction of the concentrate was evaporated on the vacuum rotating evaporator to get a weight of the residue. The sample from corn starch came down to dryness nicely and the residue was scraped from the flask and weighed. The sample from the Compana starch concentrated for a while but then started to foam. The foam was trapped in a separate flask on the vacuum evaporator. This process did not, however, allow for a complete separation of "foam" and residue. The residue and "foam" were scraped from their respective flasks into weighing vials to be weighed. During this process, the fine powder became more and more tacky, as though picking up water from the

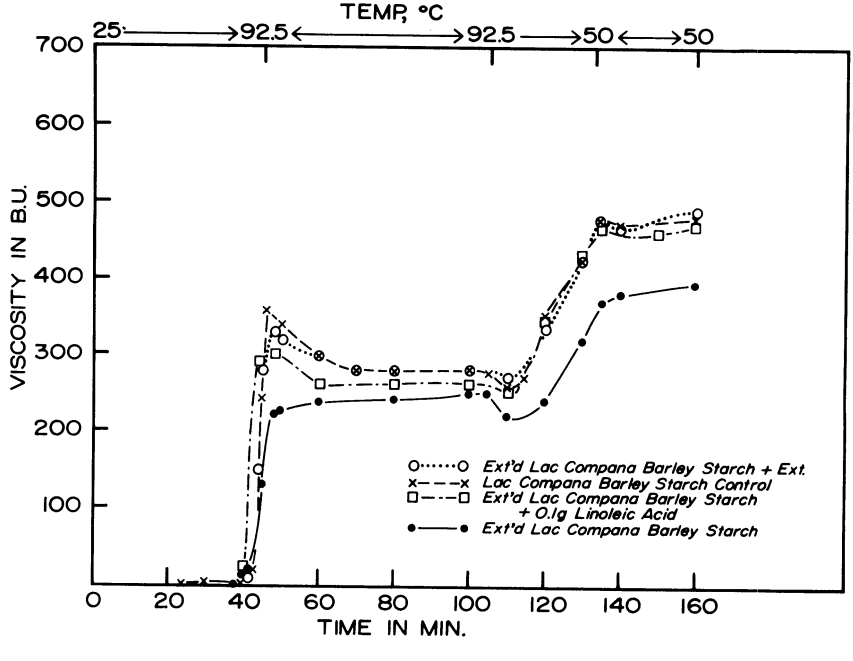

Fig. 2. Brabender amylograms on long awn-covered (LAC) Compana barley starch, extracted starch, extracted starch plus extract, extracted starch plus 0.1 g linoleic acid.

air. Prior to weighing, the residue and "foam" fractions were vacuum desiccated for 3 days over P_2O_5. Then they appeared as a fine powder again.

RESULTS AND DISCUSSION

The Brabender curves for the control samples and the methanol extracted corn and barley starches are shown in Fig. 1.

Both extracted starches show similar characteristics as compared to the untreated samples, namely, a loss of pasting peak, better cooking stability, and a substantial reduction in setback when cooled. Addition of extract in an amount equal to that removed from the original starch gave Brabender curves nearly identical to those of the untreated starch as shown in Figs. 2 and 3.

Preliminary examination of the methanol extract indicated it to be free of starch. It did contain a small amount of carbohydrate and substantial amounts of lipid material. The ratio of free acid to carbohydrate was essentially 10:1. A breakdown of the extract composition is shown in Tables I and II.

The presence of fatty acid methyl esters in the concentrate may be a reflection of their presence in the starch or may be an artifact of the extraction technique. They are not an artifact of the Folch extraction since they were observed in the ether extract prior to extracting the concentrate with chloroform-methanol. Triglycerides were observed only in trace amounts, whereas free fatty acids and mono- and diglycerides are the principal neutral lipid components. The fatty acid

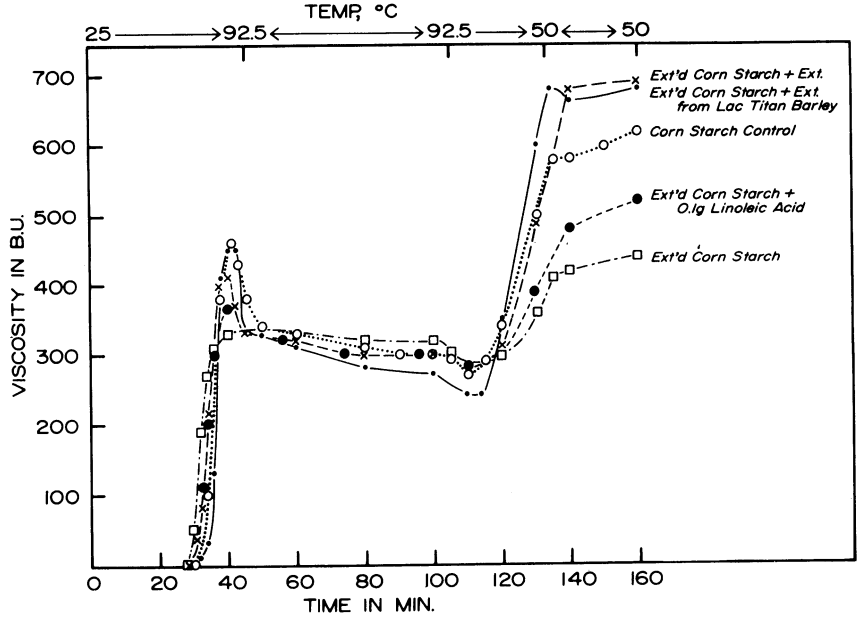

Fig. 3. Brabender amylograms on corn starch, extracted starch, extracted starch + extract, extracted starch + barley extract from long awn-covered (LAC) Titan barley, extracted starch plus 0.1 g linoleic acid.

composition of the fatty acid methyl esters (Table II) does not give a very good indication of the possible origin of the fatty acid methyl esters.

Although there is a difference in solubility in the corn and barley extracts, the most significant difference appears to be in the amount of residue. The tendency of barley extract to foam suggests the possibility of a lipoprotein in this extract. Although the total percentage of free fatty acids and fatty acid methyl esters appears nearly identical in the two extracts, the distribution is different with barley having a higher concentration of the esters. The composition of the free acids, methyl esters, and glycerides indicates no substantial difference in the extract of the two cereals.

Since linoleic acid was present in the highest concentration, 0.1 g was added to fat-free starch from both corn and barley and amylographs were run. This was approximately equal to the amount extracted from barley. These results are recorded in Figs. 2 and 3. In the case of barley, the linoleic acid addition nearly duplicated the original curve suggesting that its removal was the primary cause of the changed amylogram. With corn starch, although it is obvious that linoleic

TABLE I
Composition of the Fractions of the 85% Methanol-Water Extract of Compana and Corn Starch

Fraction	Compana mg/100 g starch		%		Corn mg/100 g starch		%	
Neutral lipids	122		32.7		169		74	
Hydrocarbon sterol and wax esters		17	4.6			30		13.2
Fatty acid methyl esters		28	7.5			22		9.6
Free fatty acids		46	12.3			75		32.9
Diglycerides and monoglycerides		31	8.3			42		18.4
Polar lipids	122		32.7		43		19	
Residue	93[a]		25		16		7	
"Foam"	36		9.6		...			

[a]May contain some "foam" due to incomplete separation.

TABLE II
Fatty Acid Composition of Three Neutral Lipid Fractions of the 85% Methanol-Water Extract of Compana and Corn Starch (per cent)

	Free Fatty Acids		Fatty Acid Methyl Ester		Mono- and Diglycerides	
Fatty Acid	Compana	Corn	Compana	Corn	Compana	Corn
14:0	1.3	2.0	1.0	1.6	tr	tr
16:0	12.7	12.7	25.6	28.8	34	37
16:1	1.1	1.5	1.2	1.5	2	5
18:0	...	...	1.4	1.5	4	5
18:1	8.2	8.7	8.9	9.1	25	32
18:2	73.2	71.4	59.7	55.3	31	21
18:3	3.3	3.6	2.0	2.1	tr	tr

acid helped to establish the original curve, it is still somewhat lower than the control. The higher percentage of free acid in corn starch indicates higher concentration of linoleic acid should have been used.

Although palmitic, oleic, and linolenic acids are present in much lower concentration than is linoleic, amylographs were run with these acids added to compare their effectiveness. These data are shown in Fig. 4.

It appears that linolenic acid has the greatest effect and that there is little difference between oleic and linoleic. Palmitic acid seems to reestablish the pasting peak; however, the final setback is substantially less than the control. The high concentration of linolenic was run to see if concentration would influence viscosity obtained.

Neither waxy corn nor waxy Compana barley starch showed these effects so we must conclude that a fatty acid complex with the amylose released during the cooking cycle is responsible. This is in agreement with the results reported by Mitchell and Zillman (5) on waxy sorghum, although they were using lauric acid at approximately 10 times the concentration used in this study.

It is postulated that the pasting peak observed in nonwaxy shortly before or early in the cooking cycle is not due to gelatinization and rupture of starch granules as commonly believed, but is the result of an unstable complex between the amylose released from the granules and the fatty acids present. It is possible this complex might involve amylose partially extracted from two or more granules which would produce an intergranular adhesion. This complex is

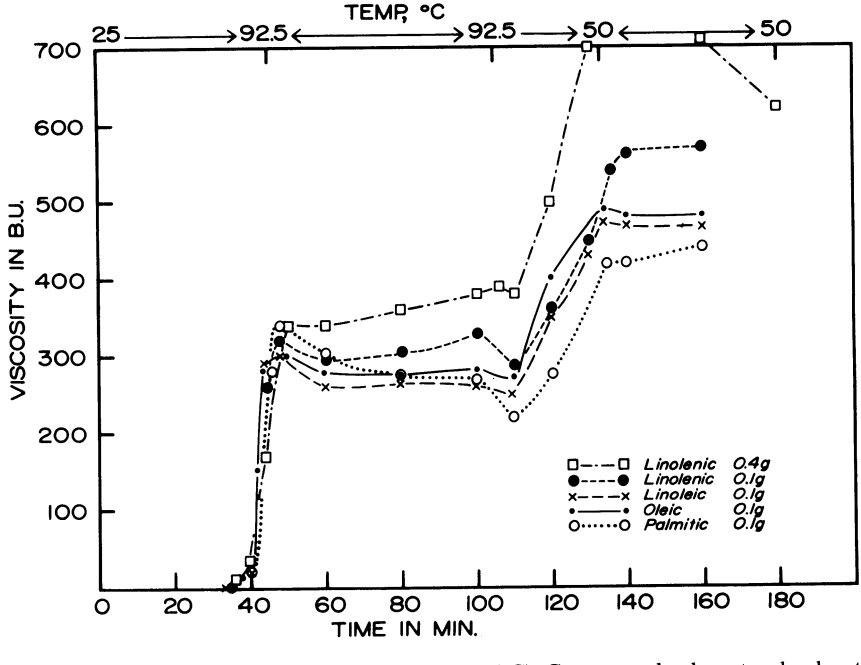

Fig. 4. Brabender amylograms on extracted (LAC) Compana barley starch plus the indicated amounts of several fatty acids.

broken down during the cooking cycle but on cooling it is reestablished. Apparently the highly unsaturated linolenic acid has a structure due to rigid position of double bonds which makes it more able to complex with amylose. It is assumed the increase in viscosity could be the result of more than one amylose molecule being complexed through a single acid molecule which would account for a more viscous paste. It is apparent that minor changes in the lipid composition or content of starch could cause considerable differences in the Brabender curves. However, present data suggest that these differences in composition will be found to be very small.

Numerous investigators (12) have reported that surfactants adsorbed on the surface of granules would reduce the viscosity and swelling power. However, the swelling power in these cases was determined by the amount of sediment produced. Collison *et al.* (12) have shown by microscopic evidence that at least in two cases using ionic surfactants the degree of swelling does not correlate with the amount of sediment produced and suggested that the sediment depends not only on the extent of swelling but also on the degree of flocculation of the granules. Collison (13) suggested that surfactants adsorbed on the surface of granules would reduce the viscosity and that the removal of the natural fat should increase the extent of starch swelling. It appears essential that the swelling must not be confused with Brabender viscosity since our amylograph curves would not support this contention. It must be concluded that the effects thus measured are not limited to adsorption of fatty acids on granules but that they are involved in either intergranular adhesion or the formation of large molecular complexes of amylose.

An examination of Fig. 1 demonstrates a substantial difference in the pasting temperature of Compana barley and corn starch. Since this does not appear to be associated with the lipid extract, it must be due to either granule structure or to the fine structure of barley starch.

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