

Differential Scanning Calorimetry of Heat-Moisture Treated Wheat and Potato Starches¹

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ABSTRACT

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Native potato and wheat starches were heat-treated at 100°C for 16 hr at moisture contents between 18 and 27%. Differential scanning calorimetry of the treated samples showed a broadening of the gelatinization temperature range and a shifting of the endothermal transition toward higher temperatures, compared to the untreated starches. The enthalpy of this transition decreased with increasing moisture content. The change was greater for potato than for wheat starch. The endotherm of the treated samples was biphasic, suggesting that two types of organized structure were present in the granules. For some samples, only one part of the biphasic

endotherm coincided with loss of birefringence. Changes in the endotherm produced by defatting the starches were different when defatting was performed before rather than after heat treatment. When samples were heated in the calorimeter with small amounts of added water, the most extensively modified wheat starch showed three order-disorder transitions in addition to the gelatinization transition. These transitions were those for melting of amylopectin crystallites, of the amylose-lipid complex, and of an unknown structure. The treated potato starch did not show the latter two transitions.

Heating of starches at limited moisture content (heat-moisture treatment) dramatically changes the properties of starches (Sair and Fetzer 1944; Leach et al 1959; Sair 1964, 1967; Kulp and Lorenz 1981; Lorenz and Kulp 1981, 1982a, 1983). Heat-moisture treated wheat and potato starches gelatinize over temperature ranges both broader and higher than those of untreated starches. Water-binding capacities and enzyme susceptibilities of treated starches increase; swelling powers decrease. Viscograph hot paste consistencies decrease, and paste stabilities increase during heating due to treatment.

Heat-moisture treatments of other cereal (barley, triticale, red millet) and tuber starches (arrowroot, cassava) reduced the swelling power of all tested starches. Solubilities of the cereal starches increased while those of the tuber starches were reduced. Enzyme susceptibilities and water-binding capacities were increased by the treatment. X-ray diffraction studies show decreases in degree of crystallinity of cereal starches. The B-pattern of tuber starches changes towards an A-pattern. In general, the physical properties of the tuber starches approach those of the untreated wheat starch. Functional properties of tuber starches improved on treatment, while those of cereal starches deteriorated (Lorenz and Kulp 1982b). These findings suggest that physical changes occur within starch granules due to heat-moisture treatment.

Scanning Calorimetry. In an attempt to understand the changes that occur during heat-moisture treatment, we studied the phase transitions of treated starches by differential scanning calorimetry (DSC). This technique, which detects the heat flow associated with order-disorder transitions, gives a quantitative measure of gelatinization (Stevens and Elton 1971). It can give thermodynamic information about the phase transitions of starches (Lelievre 1973, 1976; Donovan 1979; Kugimiya et al 1980). It is not restricted to transitions that are accompanied by a birefringence change.

The Process of Gelatinization. Native granules contain large amylopectin molecules. Each molecule forms a part of many crystallites in the periodically spaced crystalline shell-like layers of the granule and extends through many layers of crystallites (Yamaguchi et al 1979). The noncrystalline, or amorphous, portions of these molecules thus connect the crystalline layers. The ordered crystalline layers give rise to the birefringence of the granule. When the granules are heated with large amounts of water,

penetration of water into the amorphous regions and swelling of these regions are limited because the carbohydrate chains of the amorphous regions "end" in crystallites. This restricts movement of the chains and thereby restricts penetration of water and swelling. At a sufficiently high temperature (about 60–70°C for many starches), the crystallites, destabilized by thermal motion and by the swelling forces, undergo disruption or melting (Donovan 1979, Evans and Haisman 1982) with simultaneous loss of birefringence. A heat uptake (endothermic transition) is observed by DSC. When only small amounts of water are present, the swelling forces are much less significant, and the crystallites melt at temperatures much higher than the gelatinization temperature (Donovan 1979). At this time, the role of amylose in the gelatinization process is not known. The effect of the heat-moisture treatment on the amylose in the granule is considered below.

MATERIALS AND METHODS

Sample Identification and Preparation

Wheat starch was prepared from a hard red spring wheat (Waldron), through use of the procedure of Adkins and Greenwood (1966). The grain was steeped at 10°C for 24 hr in water buffered at pH 6.5 (0.02 M acetate) and rendered 0.01 M in mercuric chloride. The softened grain was washed and wet-milled in a Waring Blendor. The magma was screened through a bolting cloth. The starch was then recovered from the filtrate by centrifugation, washed repeatedly by being resuspended in distilled water, and air-dried at room temperature.

Potato starch was isolated from white potatoes according to the process of de Willigen (1964), omitting the use of sodium bisulfite. The potato starch was air-dried.

Each starch sample was divided into five subsamples: untreated; defatted (refluxed in 80% methanol for 48 hr); heat-moisture treated; defatted, then heat-moisture treated; and heat-moisture treated, then defatted. Although potato starch contains little or no lipid, for comparison subsamples of potato starch were also refluxed in 80% methanol.

The method of heat-moisture treatment (Lorenz and Kulp 1982b) was essentially that of Sair (1967). Samples of each starch were weighed into glass jars. Starch moisture content was brought to 18, 21, 24, and 27% by spraying the proper amounts of water into the jars. Starch samples were stirred and mixed constantly during moisture adjustment. The glass jars were sealed, kept at room temperature for 6 hr, and then placed in an air oven at 100°C for 16 hr. After they were cooled, the jars were opened, and the starch samples air-dried to a uniform moisture content (about 10%).

Proximate Analysis

Standard AACC methods (1969) were used for moisture, nitrogen, and fat determinations. The analyses are shown in Table I.

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X-Ray Diffraction Measurements

X-ray diffractometer traces were obtained using the following experimental conditions: $\text{CuK}\alpha$ radiation, voltage 35 kV, current 18 mA, scanning speed $1^\circ (2\theta)$ per inch of chart. Values of intensities were read from the curves over the angular range $10\text{--}29^\circ$, which includes most of the crystalline peaks.

Measurement of Birefringence Loss and Swelling

Starch gelatinization was observed microscopically, with a Kofler stage heated at $1^\circ\text{C}/\text{min}$ (Schoch and Maywald 1956). In separate experiments, granule "diameters" were measured as a function of temperature with a linear scale in the eyepiece of the microscope while the birefringence was intermittently checked with the polarizer.

TABLE I
Proximate Composition of Starches

Starch Treatment	Wheat Starch		Potato Starch	
	Nitrogen (%)	Ether-Extractable (%)	Nitrogen (%)	Ether-Extractable (%)
Untreated	0.095	0.23	0.042	0.12
Defatted	0.072	0.11	0.032	0.09
Heat-moisture (18%) treated, then defatted	0.077	0.21	0.036	0.11

Differential Scanning Calorimetry

Differential scanning calorimetric experiments were performed with a Du Pont model 990 instrument, with a model 910 cell base modified as previously described (Donovan 1979). Heating rate was $5^\circ\text{C}/\text{min}$, except for the few runs made at $1^\circ\text{C}/\text{min}$. Samples were placed in Du Pont coated aluminum hermetic pans and sealed in the sample pan press. When small amounts of water were added, the pans were sealed with the lids inverted to reduce interior volume. For samples containing large amounts of water, the reference was a 126- or 151-mg aluminum cylinder the same diameter as the pan platform. For small amounts of water, the reference was an empty pan sealed with one, two, or three lids (weights: 56, 70, 84 mg) to give a suitable heat capacity. Samples containing large amounts of water were usually heated in the standard DSC cell; pan failure was commonly observed near 130°C . Samples heated to higher temperatures (usually those samples containing small amounts of water) were heated in the Du Pont pressure DSC cell with nitrogen gas added to a pressure of 220–250 pounds per square inch gauge. Pan failure seldom occurred below 220°C under these conditions.

Samples were prepared as follows. The pan was weighed before and after addition of starch (1–4 mg). Water was added with a pipette or syringe, and the pan was sealed and reweighed. Samples containing large amounts (12–15 mg) of water were run immediately in the DSC. Samples containing small amounts (0–4 mg) of water were usually kept at $34\text{--}48^\circ\text{C}$ overnight to allow a more uniform distribution of water in the starch granules. These sample pans were generally reweighed before the DSC run to ensure that water had not been lost during overnight heating.

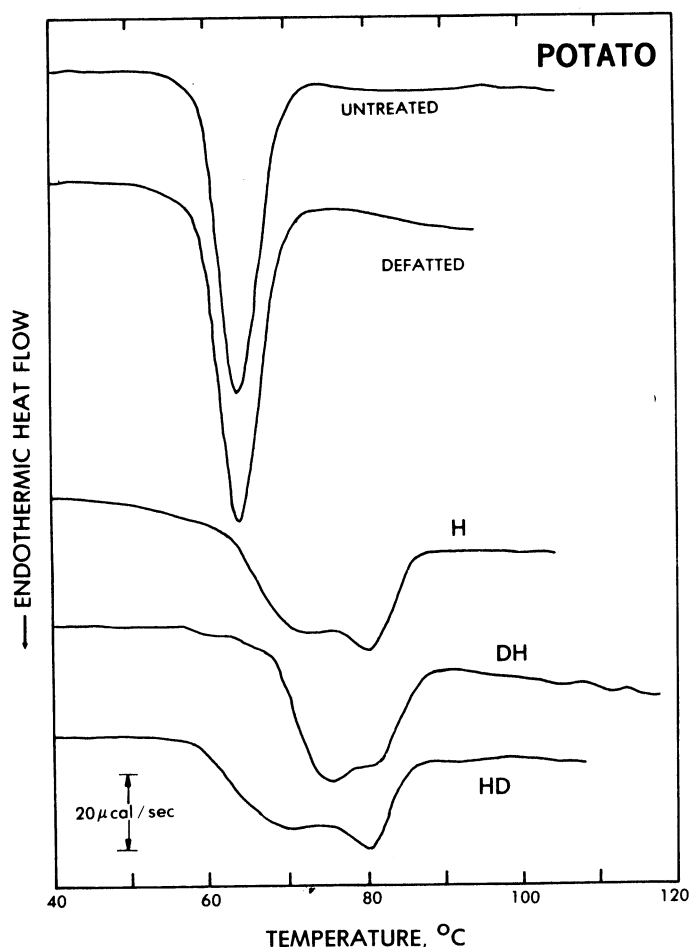


Fig. 1. Differential scanning calorimeter runs for untreated, defatted, and heat-moisture (27%) treated potato starch at $5^\circ\text{C}/\text{min}$. Sample sizes (d.b., top to bottom): 1.92 mg, 1.77 mg, 2.40 mg, 2.22 mg, 1.99 mg, with 12–13 mg of water. H = heat-moisture treated; DH = defatted, then heat-moisture treated; HD = heat-moisture treated, then defatted.

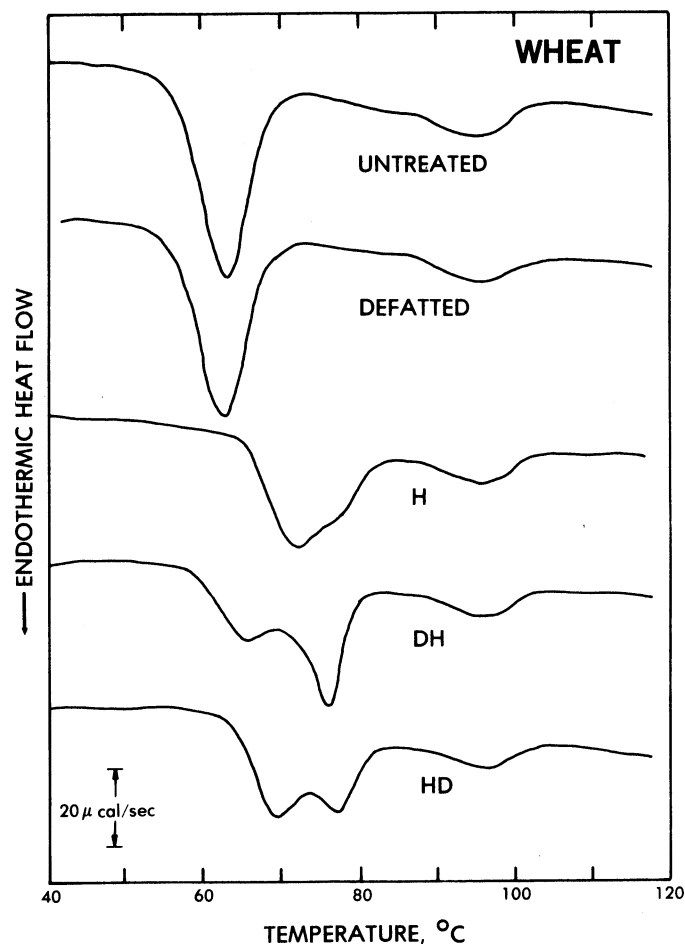


Fig. 2. Differential scanning calorimeter runs for untreated, defatted, and heat-moisture (27%) treated wheat starch at $5^\circ\text{C}/\text{min}$. Sample sizes (d.b., top to bottom): 2.22 mg, 2.09 mg, 1.92 mg, 2.17 mg, 1.89 mg, with 12–13 mg of water. H = heat-moisture treated; DH = defatted, then heat-moisture treated; HD = heat-moisture treated, then defatted.

Thermal grease was used between pan and platform and to reduce the noise in the DSC traces. All calculations were made on the basis of the dry weight of the starch. The density of dry starch was assumed to be 1.60. The moisture content of the starch sample was included in calculating the total water present and the volume fraction of water, v_1 (the total volume of water divided by the total volume of starch plus water).

Enthalpies of gelatinization were determined from the areas of the endotherms with a planimeter. A typical standard deviation (σ_{n-1}) of the mean of three to five DSC runs for the same material was 5% of the mean. Temperature and enthalpy calibration of the DSC has been described (Donovan 1977).

The starch crystallite melting point, T_m° , and the enthalpy of fusion of a repeating unit, ΔH_u , were determined (Lelievre 1973, Donovan 1979) from Flory's (1953) equation:

$$1/T_m - 1/T_m^\circ = (R/\Delta H_u) (V_u/V_1) (v_1 - \chi_1 v_1^2) \quad (1)$$

where R is the gas constant, V_u/V_1 is the ratio of the molar volume of the repeating unit to the molar volume of the diluent, and χ_1 is the Flory-Huggins polymer-diluent interaction parameter. Within the precision of the present data, plots of $1/T_m$ vs v_1 appeared to be linear. Thus, as before, $\chi_1 \approx 0$.

RESULTS AND DISCUSSION

General Effect of Heat-Moisture Treatment

As measured with the calorimeter, the gelatinization

temperature range of wheat and potato starches at high water levels is broadened by heat-moisture treatment (Figs. 1 and 2). The endothermal transition shifts to higher temperatures, compared to the untreated starches. The total enthalpy change for the transition, determined from the area measurement of the endotherm, decreases on heat-moisture treatment (Fig. 3). The decrease is greater for potato starch than for wheat starch. The extent of the change is greater when the moisture content of the heat-treated sample is greater (Figs. 3, 4, and 5).

The gelatinization transition, at least for samples treated at higher moisture contents, appears to become biphasic; two peaks are present in the endotherm. This suggests that two kinds of structures may be present, or one kind of structure in two different environments.

Effect of Defatting

Without the heat treatment, defatting appears to have no effect on the gelatinization temperatures or enthalpies (Figs. 1 and 2). Defatting, either before or after heat treatment, produces changes in the endotherm, but the changes are different when defatting is performed before rather than after treatment. This is true even for potato starch, which is known to contain little or no lipid. Accordingly, much of the effect of defatting must be alteration of the structure of the granule, probably in the amorphous regions. Defatting affects the sharpness of both of the peaks in the biphasic endotherms of the treated starches. It has a considerable effect on the temperature of the lower-temperature peak; it has a lesser effect on the temperature of the higher-temperature peak (Figs. 1 and 2).

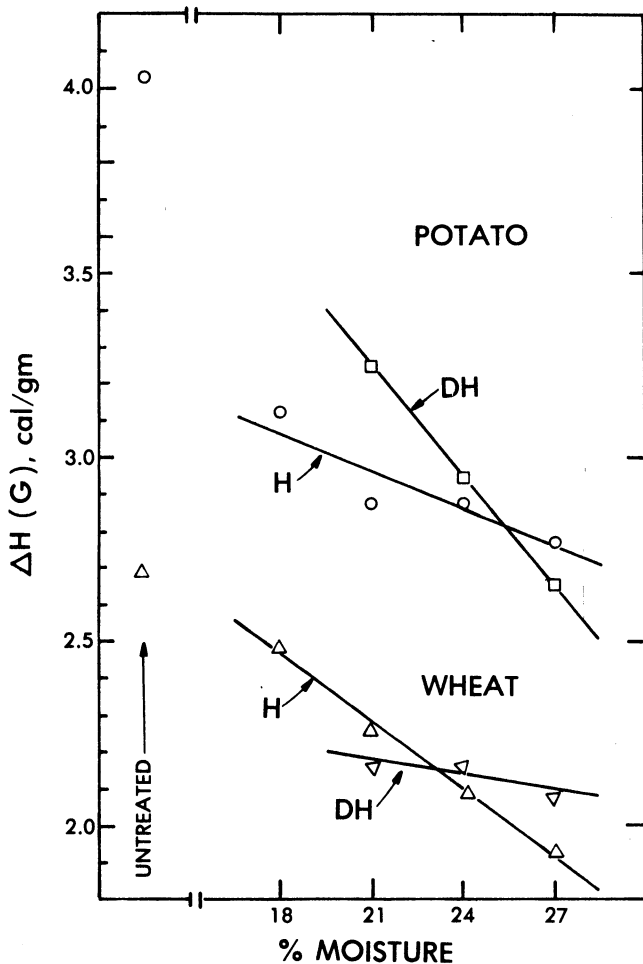


Fig. 3. Enthalpies of gelatinization of heat-moisture treated starches (determined from the total area of the biphasic endotherms, when these are observed by differential scanning calorimetry) measured with a large excess of water present. H = heat-moisture treated; DH = defatted, then heat-moisture treated; HD = heat-moisture treated, then defatted. The enthalpies of gelatinization of the untreated starches are shown at the left of the figure. Quantities plotted are averages of duplicate or triplicate runs.

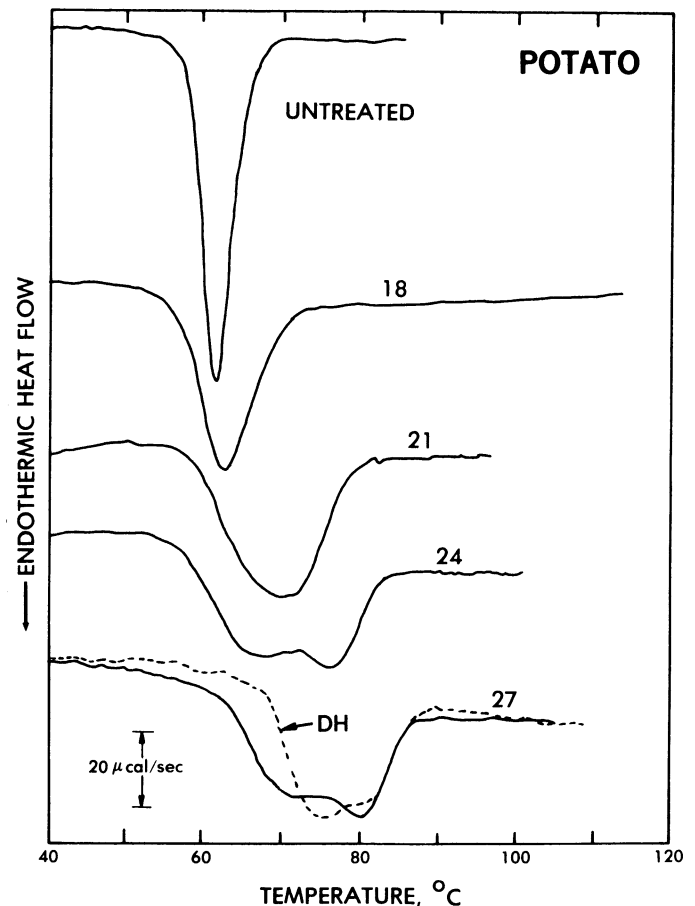


Fig. 4. Differential scanning calorimeter runs for heat-moisture treated potato starch at $5^\circ\text{C}/\text{min}$. Curves are marked with percent moisture to which samples were adjusted before heat treatment (16 hr at 100°C). Sample sizes (d. b., top to bottom): 1.63 mg, 1.66 mg, 2.48 mg, 2.76 mg, 2.73 mg, with 12–13 mg of water. The dashed curve, for comparison, is for a 2.52-mg sample defatted before heat-moisture (27%) treatment. The upper two runs are for a different batch of potato starch than the lower runs, or those runs in Fig. 1.

For wheat starch, defatting either before or after heat treatment produces sharper peaks in the biphasic endotherm (Fig. 2). For both wheat and potato starches, the specific enthalpies of gelatinization of the samples defatted before or after treatment at 27% moisture were approximately the same.

Changes in X-Ray Diffraction Patterns

At 27% moisture, heat treatment appears to have little effect on the X-ray diffraction pattern of wheat starch, an "A" starch (Lorenz and Kulp 1982a). At the same moisture content, large changes are observed in the diffraction pattern of potato starch (Sair 1967, Sair and Fetzer 1944). The diffraction pattern obtained for potato starch at 27% moisture appears to be altered from a "B" pattern, to a combination of "A" and "B" patterns. The X-ray patterns for samples defatted before heating appear slightly sharper than those for nondefatted or defatted after treatment (Lorenz and Kulp 1983).

Effect of Heat Treatment on the Endotherm for the Amylose-Lipid Complex

Heat-moisture treatment of wheat starch appears to have little or no effect on the appearance of the transition of the amylose-lipid complex observed near 100°C (Figs. 2 and 5). Apparently, defatting did not completely remove all the lipid able to form amylose-lipid complexes (Fig. 2). No endotherm for the transition of the amylose-lipid complex is observed for potato starch (Fig. 4).

Comparison of the Gelatinization Endotherm with Loss of Birefringence

When the endotherms obtained by differential scanning calorimetry at a heating rate of 1°C/min are compared with loss of

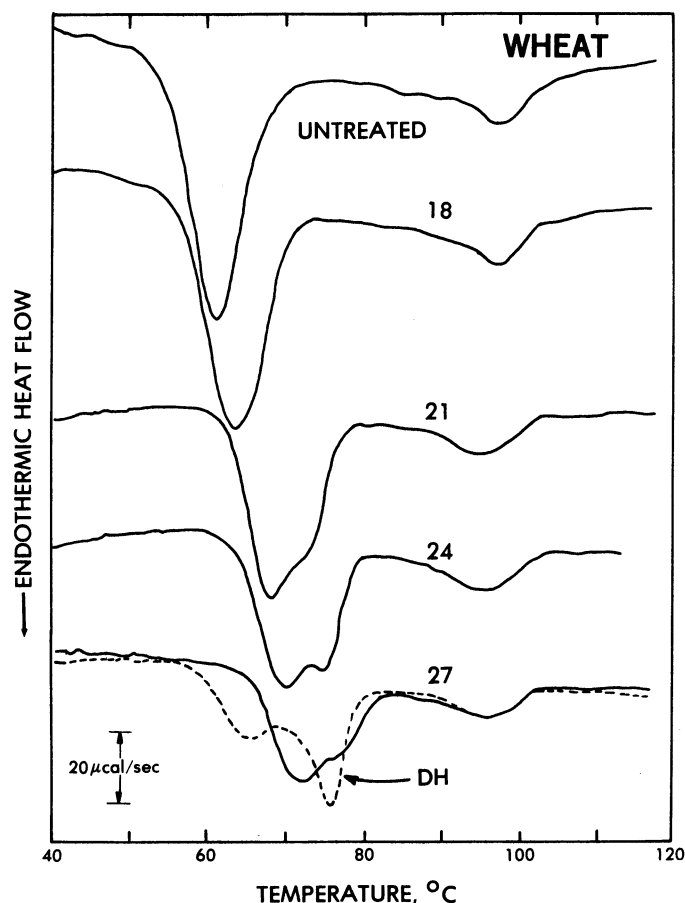


Fig. 5. Differential scanning calorimeter runs for heat-moisture treated wheat starch at 5°C/min. See legend to Fig. 4. Sample sizes: 3.08 mg, 3.08 mg, 2.72 mg, 2.64 mg, 2.18 mg, and (dashed curve) 2.42 mg, with 12–13 mg of water. The two upper runs are for a different sample of wheat starch than the three lower runs. The wheat starch sample for the three lower runs is the same sample as for the runs of Fig. 2.

birefringence of the granules measured at the same heating rate, significant differences are observed for the heat-moisture treated starches (Fig. 6). The endotherms obtained by DSC at 1°C/min heating rate differ from those obtained at 5°C/min heating rate only by being shifted to lower temperature by a few degrees (compare Figs. 1, 2, and 6). Accurate comparisons of the calorimetric experiments with the birefringence experiments can only be done when these experiments are done at the same heating rate.

For the heat-moisture treated potato starch the loss of birefringence on heating appears to occur over the same temperature range as the higher temperature peak observed in the biphasic endotherm. This peak does not correspond to the gelatinization range of the untreated starch granules, as measured both by birefringence loss (Fig. 6) and by DSC (Fig. 1). For the untreated starch, the gelatinization endotherm closely matches the loss in birefringence.

For the heat-moisture treated wheat starch, the loss in birefringence appears to occur over the same temperature range as the lower temperature peak in the biphasic DSC endotherm. This is true for wheat starch defatted, then heat-treated (DH) at 27% moisture (Fig. 6), and for the corresponding HD sample (not shown; refer to Fig. 2). The lower temperature peak of the biphasic endotherm corresponds roughly to the gelatinization range of the untreated starch, as measured both by loss of birefringence and by DSC.

These results suggest that for wheat starch, part of the structure of the granule, or some of the characteristics of the granule, are retained after heat-moisture treatment. For potato starch, alterations induced by the treatment are greater: the structure remaining after heat-moisture treatment which has gelatinization properties similar to the native granule is observed only by DSC, not by birefringence loss.

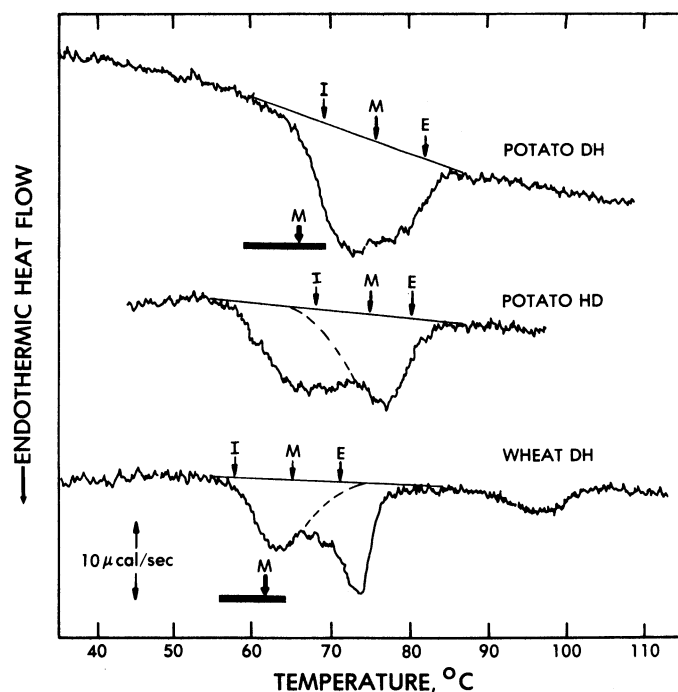


Fig. 6. Comparison of scanning calorimeter measurements with loss of birefringence for samples heat-treated at 27% moisture. Heating rate, 1°C/min for both methods. I, M, and E indicate initiation, midpoint, and end of the birefringence change observed visually. The thick bars show the gelatinization temperature ranges of the untreated starches. Dashed curves are drawn to represent the probable course of birefringence loss (arbitrary vertical scale). Dry weight of DSC samples, from top to bottom: 4.29 mg, 4.33 mg, 4.50 mg, with 15 mg of water. Reference: 151 mg of aluminum. H = heat-moisture treated; DH = defatted, then heat-moisture treated; HD = heat-moisture treated, then defatted. (The marked slope of the upper DSC trace is due to an error in setting the instrument baseline slope adjustment.)

Biphasic Gelatinization of Heat-Moisture Treated Starches

The heat-moisture treated starches show a single-phase loss of birefringence and a biphasic uptake of heat on gelatinization. Clearly, the birefringence loss and one peak in the heat flow must be associated with loss of a significant amount of ordered structure, probably crystallites. The other peak in heat flow must also result from a disordering of the granule. A likely possibility is the disordering of small-scale structures, possibly crystallites, which are not ordered with respect to one another or to the geometry of the granule and thus are without observable birefringence. Such structures, even though comprising a small portion of the granule, still might control access of water to a substantial portion of the granule. (The endothermic heat flow observed by DSC appears to produce simultaneous crystallite melting and hydration of liberated polymer chains.)

Consider the DSC curves for gelatinization of the heat-moisture treated wheat starch (Fig. 6). The first DSC peak and the birefringence loss occur simultaneously. This transition must be the phase transition for the usual crystallites ("A" X-ray type) in the granule. The second DSC peak might arise from a phase transition of crystalline regions that became more perfect on heat-moisture treatment. These crystalline regions must be either "A" type or very similar to "A" type, since no changes in the X-ray diffraction pattern were observed after heat-moisture treatment, and at higher temperatures, the "A" X-ray structural type is the more stable crystalline form (Sarko and Wu 1978). The presence of moisture and the elevated temperature of treatment could allow polymer chain motion and perhaps growth and perfection of some crystalline regions, with interchain hydrogen bonds being replaced temporarily by water molecules in the process. It is not clear why a birefringence change does not also accompany this second DSC peak, since perfected crystallites could be expected to maintain their original orientation. Possibly, at the end of the observed birefringence change (first peak in the biphasic endotherm) remaining crystallites, if present, are not well aligned in the partially swollen granule. As a result, their net birefringence would be negligible.

Observations of Individual Granules

To clarify the nature of the biphasic heat flow observed by DSC, visual observations of individual starch granules were made. The "diameters" of some of the more circular large granules were measured as heating progressed. For wheat starch, the large granules make up three-quarters of the weight of the starch (Meredith 1981), and their specific enthalpy of gelatinization is only slightly less than that of the small granules (Lelievre 1975), so that the major part of the heat flow on gelatinization must arise from the larger granules. As stated by Schoch and Maywald (1956), loss of polarization immediately precedes swelling of the granules. For untreated starches, the polarization of each granule was lost in a narrow temperature range of about 1°C (Gough and Pybus 1971). The spread in gelatinization temperatures for the individual granules corresponded well to the breadth of the endotherms observed by DSC. For the heat-moisture (27%) treated starches (Fig. 6), the loss of the birefringence of some granules extended over as much as a 5°C range. The swelling of one granule of the wheat 27DH sample was observed not to begin until 78°C, at which temperature it lost a very weak birefringence observable only at the circumference of the granule. Similarly, for one granule of the potato 27HD sample, birefringence was still detectable at 82°C, although loss of birefringence and some swelling was first observable at 77°C. These limited observations suggest that some structure is retained in at least some of the granules beyond the temperature range in which the gross birefringence loss occurs, and that the loss of this remaining structure, whether visually observable as a weak birefringence or not, is accompanied by an uptake of heat that gives rise to the second peak in the biphasic DSC endotherm.

The birefringence loss for the heat-moisture treated potato starch, particularly for the HD sample, appears to coincide with the second peak in the biphasic endotherm. The marked change in X-ray pattern of this sample on treatment suggests that

recrystallization has produced A- or C-type crystallites. Sarko and Wu (1978) consider the C structure to be a mixture of A and B unit cells. Sterling (1960) considers some C forms produced by holding and then drying starch gels at 70°C to be separate crystalline structures. These new structures should be of higher stability than the B structures of the untreated potato starch because they contain an extra carbohydrate chain in the place in the B structure that is either empty or contains only water (Sarko and Wu 1978). The new structures might retain the orientation of the original crystallites. These altered crystallites probably have altered gelatinization temperatures. Recrystallization must alter the amorphous regions of the granule; swelling of these regions controls gelatinization (Donovan 1979). DSC experiments performed at low water levels (melting experiments, not gelatinization experiments) suggest that the properties of the crystallites of these two heat-moisture treated starches are quite similar. These experiments are described below.

Defatting potato starch after heat-moisture treatment does not alter the temperature range in which the birefringence loss occurs (Fig. 6). Samples that are not defatted, or defatted after heat-moisture treatment, show a broad DSC peak, the first part of the biphasic endotherm, which precedes the birefringence loss. It seems likely that this broad peak results from gelatinization of regions in which the crystallites are small or linked to amorphous regions that are more easily penetrated by water.

Effect of Heat-Moisture Treatment on Amylose

Heat-moisture treatment, in addition to affecting the state of crystallization of the amylopectin, and with it the arrangement of chains in the amorphous regions of the granule, must also affect the amylose molecules. Leach et al (1959) showed that loss of amylose on gelatinization was drastically reduced by heat-moisture treatment. The amylose, about 25% by weight of potato and wheat starches, is thought not to be highly crystalline, but to be arranged as radial fibrils in the granules (Sterling and Pangborn 1960). For these starches, amylose does not appear to contribute significantly to the X-ray diffraction pattern. It seems possible that heat-moisture treatment allows portions of the amylose molecules to associate or crystallize with portions of amylopectin molecules. If such association occurs, extractability of the amylose and swelling of the granule could be significantly reduced. The experiments described here provide no evidence for or against limited cocrystallization of amylose with amylopectin, either before or after heat-moisture treatment. Recrystallized amylose has a phase transition in the temperature range 110–150°C (Eberstein et al 1980). If amylose cocrystallized with amylopectin, structured regions would necessarily be interrupted because the amylopectin branches are short. Accordingly, the phase transition for a cocrystallite could be expected to be similar to that of amylopectin, both in enthalpy and in transition temperature.

Phase Transitions of Heat-Moisture Treated Starches with Limited Amounts of Water

Wheat Starch. With limited amounts of added water, four endotherms are observed for both untreated wheat starch and the defatted sample heated at 27% moisture content (Fig. 7). The upturn in heat flow above 200°C appears to be exothermic decomposition of the starch. The transition at lowest temperature, which changes only slightly in temperature as the amount of added water is reduced, is considered the gelatinization transition (G). In Fig. 8, plots of reciprocals of the transition temperatures, T_m , as a function of volume fraction of water, v_1 , are shown for the remaining three transitions. By analogy with results obtained with native starches (Donovan 1979, Donovan and Mapes 1980), the transition designated M1 (see sketch in Fig. 8) appears to be melting of ordered regions of amylopectin at reduced water content (under conditions for which swelling is not a significant driving force for crystallite melting or disruption). Since this transition is present when large amounts of water are added to the heat-moisture treated starch (Fig. 2), it seems that these ordered regions are probably not as readily accessible to water as those in the untreated starch. From the "Flory plot" for this transition (Fig. 8), the enthalpy and the extrapolated melting temperature, T_m° , of the

transition are calculated (Eq. 1). The enthalpy and entropy of the M1 transition for the treated and untreated starches are equal, but the extrapolated melting temperature of the treated starch is greater (Table II).

The transition designated M2, which appears at temperatures above 100°C with these amounts of added water, is clearly that of the usual amylose-lipid complex. The "Flory plot" for this transition corresponds closely to that for the amylose-lipid complex in native wheat starch (Kugimiya et al 1980). This transition was not observed after a heated sample was cooled and reheated (Fig. 7, curves C and E). This failure of the complex to reform may be related to the low water content.

The transition designated M3 has a high extrapolated transition temperature, 255°C, but the enthalpy and entropy changes are approximately the same as those for the M1 transition of native starch (Table II). On cooling and immediate reheating (curve E, Fig. 7), the transition is again observed at approximately the same temperature. Since the M3 transition is observed on immediate reheating, this transition may be that of another amylose-lipid

TABLE II
Thermodynamic Functions for Untreated and Heat-Moisture Treated Starches

Starch	Transition	Sample	T_m (°C)	ΔH_u (kcal/mol)	ΔS_u (E.U.) ^a
Wheat	M1	Untreated	216	9.7	20
		27 DH ^b	228	9.7	19
	M2	Untreated	170	21.9	49
		27 DH	173	21.9	49
	M3	Untreated	248	13.2	25
Potato	M1	Untreated	166	13.8	31
		27 DH	242	9.5	19

^a $\Delta S_u = \Delta H_u / T_m$ (°K). E. U. = entropy units.

^bDefatted starch heat-treated for 16 hr at 100°C at 27% moisture.

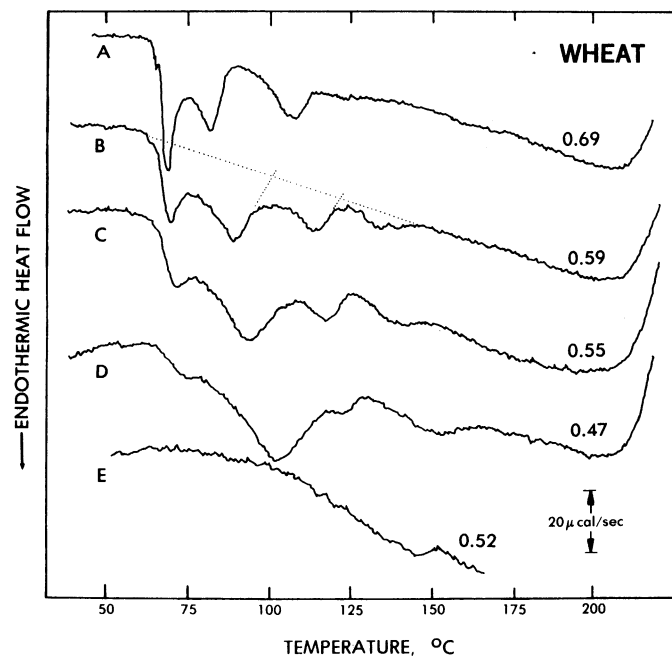


Fig. 7. Calorimeter scans of defatted wheat starch, heat-treated at 27% moisture, at reduced water levels. Heating rate, 5°C/min. Volume fraction of water is shown for each run. Dry weight of starch and total weight of water for these samples, in mg, are: A, 2.58, 3.50; B, 2.73, 2.42; C, 3.18, 2.47; D, 3.08, 1.71; E, 3.05, 2.08. Run E is the reheating of a sample similar to C, which had first been heated only to 160°C. Examples of lines used for extrapolations to determine T_m are shown for run B. The turning up of the curves above 200°C appears to be due to a caramelization reaction (exothermic).

complex. Under certain conditions, biphasic transitions can be observed for these complexes (Kugimiya et al 1980).

Potato Starch. Unlike wheat starch, heat-treated potato starch shows only two endotherms when small amounts of water are added (Fig. 9). When the reciprocal of the melting temperature is plotted as a function of the volume fraction of water (Fig. 8), the "Flory plot" is close to that for the M1 transition for the heat-moisture treated wheat starch. At $\nu_1 = 0.34$ (curve E, Fig. 9), the melting endotherm appears biphasic. This suggests that two different types of crystallites, with different T_m , are present. Since essentially no lipid is present in potato starch, an M2 transition is neither expected nor observed. The high-temperature transition designated M3, which is observed for wheat starch (Fig. 7), is not observed for the treated potato starch. This suggests that the appearance of the M3 transition may require the presence of a lipid. The thermodynamic quantities derived for potato starch from Fig. 8 and equation 1 are listed in Table II.

CONCLUSIONS

Potato and wheat starches subjected to heat-moisture treatment show: biphasic heat uptake on gelatinization for which one phase does not appear to coincide with the observed birefringence loss; reduced enthalpies of gelatinization; and increased temperatures of phase transitions. We interpret these effects of the heat-moisture

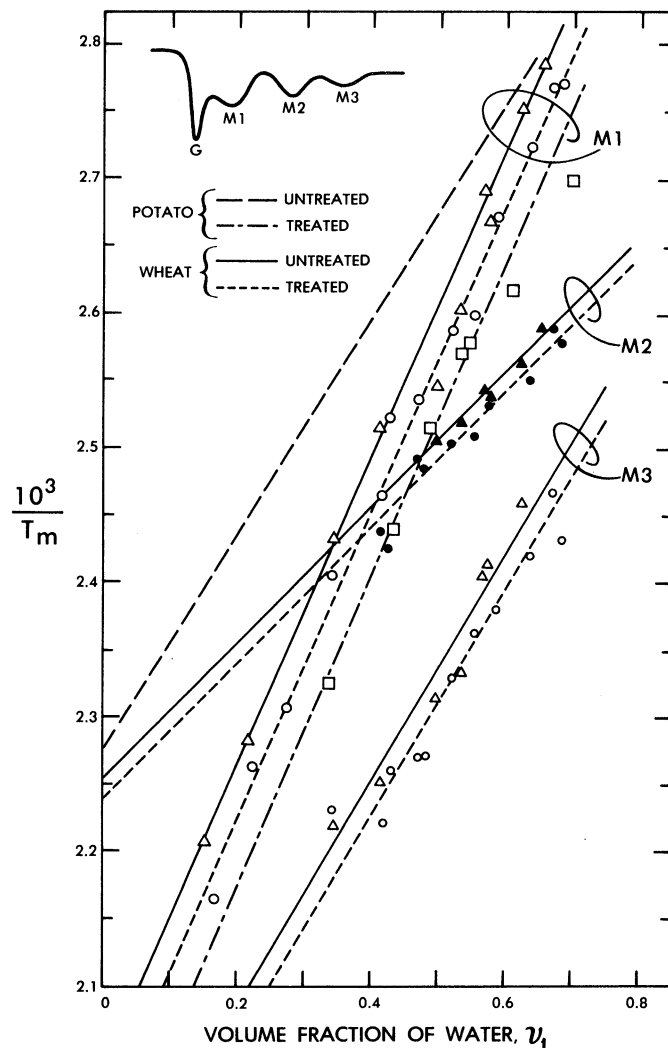


Fig. 8. Plots of reciprocal melting temperatures against volume fraction of water for potato and wheat starches defatted and heat-treated at 27% moisture, compared to those for the untreated starches. The sketch at the top of the figure identifies the transitions. Experimental points are omitted for untreated potato starch.

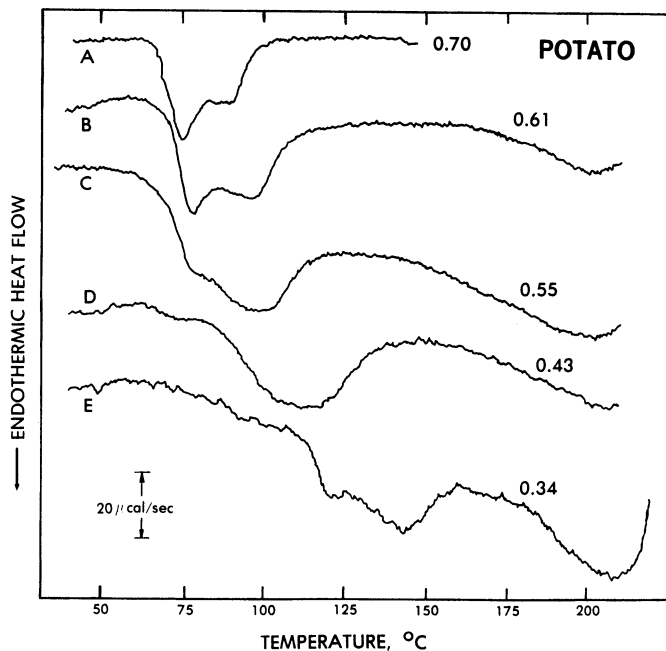


Fig. 9. Calorimeter runs of defatted potato starch, heat-treated at 27% moisture, at reduced water levels. Heating rate, 5°C/min. Volume fraction of water is shown for each run. Dry weight of starch and total weight of water for these samples, in mg, are: **A**, 2.91, 4.26; **B**, 3.70, 3.64; **C**, 4.03, 3.02; **D**, 3.67, 1.76; **E**, 3.03, 0.96.

treatment to be either new crystallization, or recrystallization and perfection of the small crystalline regions of the granule. These starch chain reorientations in crystallites are accompanied by chain reorientation or movement in amorphous regions. Alterations in the amorphous regions have a pronounced effect on the ability of these regions to destabilize crystallites upon imbibition of water by the granule, and thus upon the gelatinization temperature. These calorimetric results indicate that DSC is a valuable technique for studying modified starches.

Only a limited set of variations of moisture content, temperature, and time were explored in these heat-moisture treatments. That the products showed biphasic DSC endotherms for gelatinization suggests that only limited structural alteration of the starches occurred. It is conceivable that a suitable choice of temperature, time, and moisture content would produce structural changes so complete that only a single DSC endotherm would be observed on gelatinization. Such a product would have different functional properties as well as different thermal properties. Investigations into methods that produce more complete conversion into new structures appears to be a desirable extension of these studies.

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LITERATURE CITED

ADKINS, G. K., and GREENWOOD, C. T. 1966. The isolation of cereal starches in the laboratory. *Stärke* 18:213.

- AMERICAN ASSOCIATION OF CEREAL CHEMISTS. 1969. Approved Methods of the AACC. Methods 44-10, 46-12, and 30-20, approved April 1961. The Association, St. Paul, MN.
- De WILLIGEN, A. H. A. 1964. Potato starch. Page 9 in: *Methods of Carbohydrate Chemistry*. Vol. IV. R. L. Whistler, ed. Academic Press, New York.
- DONOVAN, J. W. 1977. A study of the baking process by differential scanning calorimetry. *J. Sci. Food Agric.* 28:571.
- DONOVAN, J. W. 1979. Phase transitions of the starch-water system. *Biopolymers* 18:263.
- DONOVAN, J. W., and MAPES, C. J. 1980. Multiple phase transitions of starches and Naegeli amylopectins. *Stärke* 32:190.
- EBERSTEIN, K., HÖPCKE, R., KONIECZNY-JANDA, G., and STUTE, R. 1980. DSC-Untersuchungen an Stärken. I. Möglichkeiten thermoanalytischer methoden zur Stärkecharakterisierung. *Stärke* 32:397.
- EVANS, I. D., and HAISMAN, D. R. 1982. The effects of solutes on the gelatinization temperature range of potato starch. *Stärke* 34:224.
- FLORY, P. J. 1953. *Principles of Polymer Chemistry*. Cornell Univ. Press, Ithaca, NY.
- GOUGH, B. M., and PYBUS, J. N. 1971. Effect on the gelatinization temperature of wheat starch granules of prolonged treatment with water at 50°C. *Stärke* 23:210.
- KUGIMIYA, M., DONOVAN, J. W., and WONG, R. Y. 1980. Phase transitions of amylose-lipid complexes in starches: A calorimetric study. *Stärke* 32:265.
- KULP, K., and LORENZ, K. 1981. Heat-moisture treatment of starches. I. Physicochemical properties. *Cereal Chem.* 58:46.
- LEACH, H. W., McCOWEN, L. D., and SCHOCH, T. J. 1959. Structure of the starch granule. I. Swelling and solubility patterns of various starches. *Cereal Chem.* 36:534.
- LELIEVRE, J. 1973. Starch gelatinization. *J. Appl. Polym. Sci.* 18:293.
- LELIEVRE, J. 1975. A comparison of the crystallinity of spherical and lenticular starch granules isolated from wheat grains. *Stärke* 27:2.
- LELIEVRE, J. 1976. Theory of gelatinization in a starch-water-solute system. *Polymer* 17:854.
- LORENZ, K., and KULP, K. 1981. Heat-moisture treatment of starches. II. Functional properties and baking potential. *Cereal Chem.* 58:49.
- LORENZ, K., and KULP, K. 1982a. Cereal and root starch modification by heat-moisture treatment. I. Physicochemical properties. *Stärke* 34:50.
- LORENZ, K., and KULP, K. 1982b. Cereal and root starch modification by heat-moisture treatment. II. Functional properties and baking potential. *Stärke* 34:76.
- LORENZ, K., and KULP, K. 1983. Physicochemical properties of defatted heat-moisture treated starches. *Stärke* 35:123.
- MEREDITH, P. 1981. Large and small starch granules in wheat—Are they really different? *Stärke* 33:40.
- SAIR, L. 1964. Heat-moisture treatment of starches. Page 283 in: *Methods of Carbohydrate Chemistry*. Vol IV. R. L. Whistler, ed. Academic Press, New York.
- SAIR, L. 1967. Heat-moisture treatment of starch. *Cereal Chem.* 44:8.
- SAIR, L., and FETZER, W. R. 1944. Water sorption by starches. *Ind. Eng. Chem.* 36:205.
- SARKO, A., and WU, H.-C. H. 1978. The crystal structures of A-, B- and C-polymorphs of amylose and starch. *Stärke* 30:73.
- SCHOCH, T. J., and MAYWALD, E. C. 1956. Microscopic examination of modified starches. *Anal. Chem.* 28:382.
- STERLING, C. 1960. Molecular association of starch at high temperature. *Stärke* 12:78.
- STERLING, C., and PANGBORN, J. 1960. Fine structure of potato starch. *Am. J. Bot.* 47:577.
- STEVENS, D. J., and ELTON, G. A. H. 1971. Thermal properties of the starch/water system. Part I. Measurement of heat of gelatinization by differential scanning calorimetry. *Stärke* 23:8.
- YAMAGUCHI, M., KAINUMA, K., and FRENCH, D. 1979. Electron microscopic observations of waxy maize starch. *J. Ultrastruct. Res.* 69:249.

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