STUDIES ON CEREAL AND TUBER STARCHES

by

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Approved:

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DEDICATION

To my mom and dad.

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LITERATURE REVIEW

INTRODUCTION

Starch, the major source of energy in the diet of man, is found in leaves, stems, seeds, roots and/or fruits of higher plants (Lineback 1984). Depending on botanical origin, the size, shape and chemical composition of each starch can vary considerably. In nature, starch exists as discrete granules. Although no two starch granules from the same source can be considered identical, their chemical compositions are similar.

The granule itself is a highly organized entity composed of two major polymers; amylose and amylopectin. Amylose, the linear polysaccharide occurs as α-(1→4)-linked glucopyranose and constitutes 15% - 30% of the total carbohydrate of the granule. Until recently, amylose was assumed to be completely linear. Evidence now suggests that some molecules are slightly branched (one branch point per 1000 glucose molecules) (Banks and Muir 1980, Ghiasi et al 1982, and Banks et al 1975). Amylopectin, a highly branched polymer, consists of glucose linked α-(1→4) as in amylose along with 4% - 5% of the glucose units combined in α (1→6) linkages (Hodge and Osman 1976). It is the major glucose polymer found in most granules. Stable genetic variants of maize, barley, sorghum and rice exist in which the starch consists entirely of amylopectin. These are referred to as "waxy" starches and their physical properties differ from their 'non-waxy' counterparts. Likewise, corn varieties exist who's starch is enriched (up to 70%) in amylose content (Lineback 1984).

Microscopic examination of starch granules reveals a variety of

different sizes and shapes. Starch granules vary in size from one micron or less (oat) to over 100 μm (potato). Their shapes include nearly perfect spheres, polyhedrals, ovals and irregular shaped granules. These differences allow recognition and differentiation of most food and commercial starches in situ (French 1984, Ghiasi et al 1982a).

STARCH GELATINIZATION

Starch, more specifically, starch gelatinization, plays an important role in the production of baked goods. Beyond this, its properties as a thickener make it important in the production of a variety of other foods (Pomeranz 1971). During the baking of all cereal based foods, starch gelatinization is a critical event. Contradictions concerning the extent or degree of gelatinization in baked foods are found in the literature. This is most probably due to differences in the products, their formulations, the processes used to produce them and the methods used to assess gelatinization (Varriano-Marston et al 1980).

When suspended at ambient temperature (26°C - 27°C) starch granules are freely permeable to water. They are, in fact, able to absorb 30% of their weight with a resultant swelling of 7% - 8% in diameter. This is a reversible process. However, when heat is applied to the starch granule in the presence of water, an irreversible swelling occurs. This has been termed gelatinization (Faubion 1983). In an excess water system, the individual starch granule doubles or triples in diameter, loses its characteristic birefringence (Collison and Chilton 1974) and imbibes several times its weight in water increasing the viscosity of the solution (Wooton and Bamunarachchi 1979 a). This is an irreversible

disruption of the secondary structure of the granule.

Gelatinization results in 1) an increased susceptibility of starch to amylolytic enzyme attack (Varriano-Marston et al 1980), 2) increased dye binding ability (Varriano-Marston et al 1980) and 3) an alteration of the granules' thermal properties as the conformation of the granule is altered (Stevens and Elton 1971). Stevens and Elton (1971) have referred to this as an ordered (native) to disordered (gelatinized) transition. The severity of these order-disorder transitions depends on the degree of gelatinization. By varying the rate of temperature increase and the amount of water available, the degree of gelatinization is controlled (Stevens and Elton 1971, and Wooton and Bamunuarachchi 1979 b).

Since starch is a biological material there is not a single, universal temperature at which gelatinization occurs for all starches regardless of origin. Instead, a range of temperatures exists for a population of granules (Faubion 1983). Wheat starch, for example, has a lower gelatinization temperature than does maize starch. The Tp for potato is intermediate to those two (Table 1) (Stevens and Elton 1971). Therefore, a particular emphasis has been placed on the heating rate and the starch : water ratio of grain based foods to determine the extent of gelatinization (Wooton and Bamunuarachchi 1979 b).

The order-disorder transition that characterizes starch gelatinization is a thermal event. Therefore, the use of Differential Scanning Calorimetry (DSC) for the study of starch gelatinization has increased. DSC possesses several unique advantages over most other analytical methods in that it allows the investigation of starch gelatinization temperature and gelatinization energy over a wide range

TABLE 1. ΔH_G ENDOTHERM CHARACTERISTICS OF VARIOUS STARCHES.

Starch Type	ΔH cal/gm	Endotherm Temperatures (^oC)		
		Onset	Peak	Conclusion
Wheat	2.8	54	69	86
Rice	3.4	66	82	100
Maize	3.7	67	78	95
Tapioka	4.0	66	78	100
Arrowroot	4.6	73	84	106
Potato	5.1	59	71	95

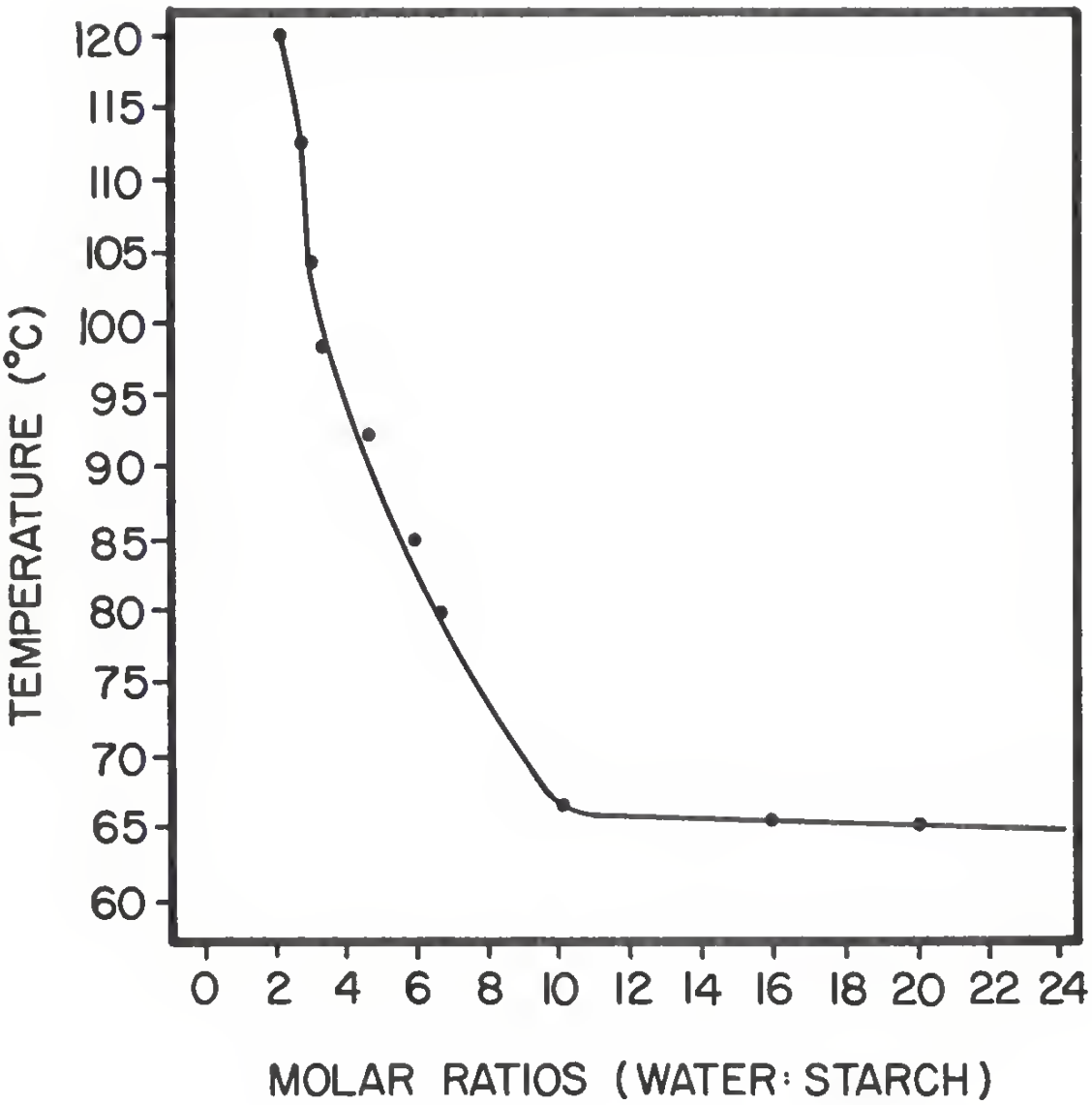
Adopted from Stevens et al 1971.

of water contents (Donovan 1979). Additionally, DSC is amenable to use with very small samples and at temperature ranges above 100°C (Biliaderis et al 1980). The calorimeter uses small samples, minimizing thermal lag within the system, and hermetically sealed pans preventing loss of water (Ghiasi et al 1982 b). The Differential Scanning Calorimeter is also rapid, extremely accurate and sensitive to small thermal effects.

Using this technique workers have investigated the effect of water content on the gelatinization endotherm (Collison 1974, Donovan 1979, Wooton and Bamunuarachchi 1979 b, Eliasson 1980 and Ghiasi et al 1982). The studies indicate that, as water content decreases, the endothermic peak shifts toward higher temperatures (Eliasson 1980). DSC thermograms of potato starch : water mixtures containing decreasing volume fractions of water (Fig. 1) illustrate this phenomenon. As the water level decreases, the endotherm begins to develop a trailing shoulder between 72°C and 130°C (Donovan 1979). At extremely low levels of water (>0.45 H_2O/anhydroglucose), only the shoulder remains (Donovan 1979). As the water available to the starch decreases, the gelatinization energy (measured in cal/g dry starch) decreases as well. Since a linear relationship exists between the water content and the gelatinization energy, a minimum water level required for gelatinization can be calculated (Wootton and Bamunuarachchi 1979 b). This minimum level of water has considerable significance for the formulation and properties of heat processed products which contain starch (Wooton and Bamunuarachchi 1979 b).

Stevens and Elton (1971) accounted for the change in gelatinization energy with water level by proposing that a lower degree of disorder is achieved by the starch during gelatinization in a low

Figure 1. Peak Temperatures of Potato Starch:Water Mixtures Containing Decreasing Molar Ratios (Water:Starch). Adapted from Donovan 1979.


120
115
110
105
100
95
90
85
80
75
70
65
60
TEMPERATURE (°C)
0 2 4 6 8 10 12 14 16 18 20 22 24
MOLAR RATIOS (WATER: STARCH)

level starch:water system. Donovan (1979) suggests, that at lower water levels, the low amount of energy required for gelatinization results from the melting starch crystallites. At higher water levels, granule swelling, extensive hydration of starch molecules and crystallite melting accounts for the higher gelatinization energy.

It is currently unclear whether or not all starches regardless of origin or internal organization, share similar properties in response to gelatinization at varying water levels.

STARCH SOLUBILIZATION

One of the oldest and, at first glance, simplest modifications of the starch granule is prolonged treatment with dilute acid to produce thin boiling starches or amylodextrins (French 1984). During this process, often termed litnerization, it is thought that the amorphous regions of the starch molecules are selectively hydrolyzed and rendered soluble (French 1984). Nageli described the preparation of amylodextrins by heterogeneous aqueous acid hydrolysis of starch granules in 1874 (Kainuma and French 1971). By this method, native starch granules are suspended in 7.5% HCL or 15% H_2SO_4 at room temperature or temperatures up to 35^{o}C. The lengths of such treatment can vary from days to years (French 1984). During this process increasing amounts of the individual starch granules are converted into soluble low molecular weight carbohydrates. The remaining material, apparently acid resistant is termed the amylodextrins. It is interesting to note that during the process the granular nature of the starch is preserved or remains intact (French 1984). Kainuma and French (1971) suggest that the amorphous, non-crystalline areas of the starch granules are preferentially attacked during the litnerization process.

They further suggest that this attack occurs regardless of the location (granule surface vs interior) of the amorphous area and that the "attack" protects the more crystalline portions of the starch granules from acid hydrolysis.

Several variations in the procedure used to create Nageli amylodextrins exist. The modifications encountered in the literature are; differences in sulfuric acid concentrations or lack of H_2SO_4 and/or different treatment temperature. Kainuma and French (1971) treated starch with 16% $H_2 SO_4$ at room temperature (22°C - 25°C). After 3 months of treatment, 24.2% of waxy maize and 12.7% of potato starch were rendered soluble. Umeki and Kainuma (1981) used the same acid concentration but elevated the temperature by 13°C. In spite of the fact that treatment temperature was well below that required for gelatinization, results were quite different from the treatment at room temperature (22°C-25°C), where solubilization was less drastic throughout the entire treatment.

At room temperature, solubilization was slow, with only small increases per month (Kainuma et al 1971). At the elevated temperature (38°C), using waxy maize starch as starting material, 75% of the original carbohydrate was solubilized after only 8 days treatment. In a later report using the same procedure, Matsukura et al (1983) apparently reversed themselves on this figure and reported only 43% and 50% soluble carbohydrate from normal and waxy corn respectively, after 17 days of treatment. This figure is still in higher than that obtained by room temperature treatment. Thus, the question of differences in the rate of carbohydrate hydrolysis from starch granules treated at elevated temperatures is, apparently, unresolved.

RETROGRADED STARCH

When starch gels form, extensive hydrogen bonding among polysaccharide molecules enlarges the micellar regions. This enlargement firms the gel and after a period of time, direct hydrogen bonding between chains replaces water bridges. The gel shrinks, releasing some of the entrapped water. This phenomena in starch gels is referred to as "retrogradation" (Hodge et al 1976). The process, which occurs over extended storage, can be accelerated by repeated cycles of freezing and thawing (Matsukura et al 1983). Retrograded starches have been used extensively for structural studies (Matsukura 1983). These studies have included enzymatic and chromatographic investigations (Matsukura 1983) as well as x-ray crystalographic approaches (Zobel 1959).

The X-ray Diffractometer is used to examine the crystalline structure of biological and non biological. It is capable of detecting crystallinity in native starches as well as changes in crystallinity induced by physical or chemical treatment of the native granular structure. Retrogradation could, in this since be considered a physical change. Depending on its origin and composition, native starch produces one of three different but characteristic x-ray patterns (termed A, B or C).

The A pattern has been known since the early 1950's (Zobel 1964). All cereal starches with one exception (amylomaize) are "A" starches (Zobel 1964). Amylomaize or starches containing more than 40% amylose produce the B pattern, the second characteristic x-ray pattern (Zobel 1964). Starches from legumes and tubers will produce the B pattern (Zobel 1964). The C pattern is considered on intermediate pattern

between the A and B x-ray patterns (Hizukuri 1961). The A and C patterns are similar du to the presence of peaks in the area of 15 - 18 and 23.5, 20 while the B and C patterns are similar due to sharing peaks between 22 - 26, 20 (Zobel 1964). Banks and Muir (1980) contend that when the crystalline form of the starch granules are changing, the C type x-ray pattern predominates.

A fourth pattern designated V (Whistler et al 1984) can also appear in cereal starches once gelatinized. It results from the precipitation of starch from aqueous solutions or amylose complexing with organic molecules (Whistler et al 1984). Granular starches heated in aqueous solutions of polar organic solvents may show a strong V pattern superimposed on their characteristic A or B pattern (Zobel 1964). The "V" x-ray diffraction pattern is apparently the result of the formation of a helical amylose-lipid complex (Kugimiya et al 1980).

A number of factors can affect the x-ray patterns produced by starches. Such changes in diffraction patterns reflect changes in the molecular arrangement of the granule. In 1944, Sair and Fetzer showed that heat-moisture treatment of native potato starch resulted in a change in its x-ray diffraction pattern from the B to A. Later work reported that retrograded starch generally gave a B type pattern regardless of the original pattern (Whistler 1953). Hizukuri (1961) reported that the crystalline pattern type was dependent on the temperature at which retrogradation occurred. At temperatures above 50^{o}C, the A pattern was produced. Below that temperature starch retrograded to produce the B or C type pattern. Retrograded starch diffraction patterns include several peaks at 16 , 19 and 21 (Matsukura et al 1983). Such retrograded starch patterns are distinct from the raw starch patterns indicating a change in the crystalline structure of

highly retrograde starches (Matsukura et al 1983).

STARCH ABSORPTION

Absorption is a wetting process, i.e., the ability to absorb and hold water in the granules' intermolecular spaces. Absorption does not change the properties of either the water or the absorbing substance and the molecules of the substance enter only as supporting structures (Christensen 1982).

Absorption indirectly reflects differences in the internal organization of the starch granule; differences such as the amount or the arrangement of crystalline and amorphous regions present in the granule (French 1984). The assumption here is that crystalline regions absorb relatively little water. Evans and Haisman (1982) estimated solute and water distribution in starch-solvent systems by Blue Dextran exclusion and refractive index changes of solutions before and after coming into equilibrium with starch. They concluded that in the presence of solutes such as sucrose, glycerol, and maltose the amount of water absorbed was reduced in proportion to the amount of solute absorbed. The solute concentration inside the granules was lower than the external concentration, indicating that the water in the starch granule is more tightly bound to the starch than the absorbed solution. These methods, Blue Dextran exclusion and absorbance are capable of providing qualitative information about the distribution of amylose and amylopectin present in the granule (Lindquist 1979).

MATERIAL AND METHODS

STARCHES

Potato, (Solanum tuberosum); triticale, (Triticum secale); oat, (Avena sativa); wheat, (Triticum aestivum); and barley, (Hordeum sativum); were gifts of Dr. R. C. Hoseney, Kansas State University, and were isolated in his laboratory.

Millet, (Pennisetum typhoides); starch was isolated by the procedure outlined in Methods of Carbohydrate Chemistry, 4:6, 1964.

Corn, (Zea mays); starch was commercially isolated and obtained from Best Foods, CPC International Inc., Englewood Cliffs, NJ.

Rye starch, (Secale cereale); was isolated according to the method of Berry et al (1971).

Buffalo gourd (Crucurbita foetadesmida) starch was the kind gift of Dr. James Berry, University of Arizona, Tuscon, AZ.

Wheat Nageli Amylodextrins were a gift of Dr. R. Spies, Kansas State University.

Starch preparations was judged essentially free of contaminating substances by light and scanning electron microscopy (Fig. 2).

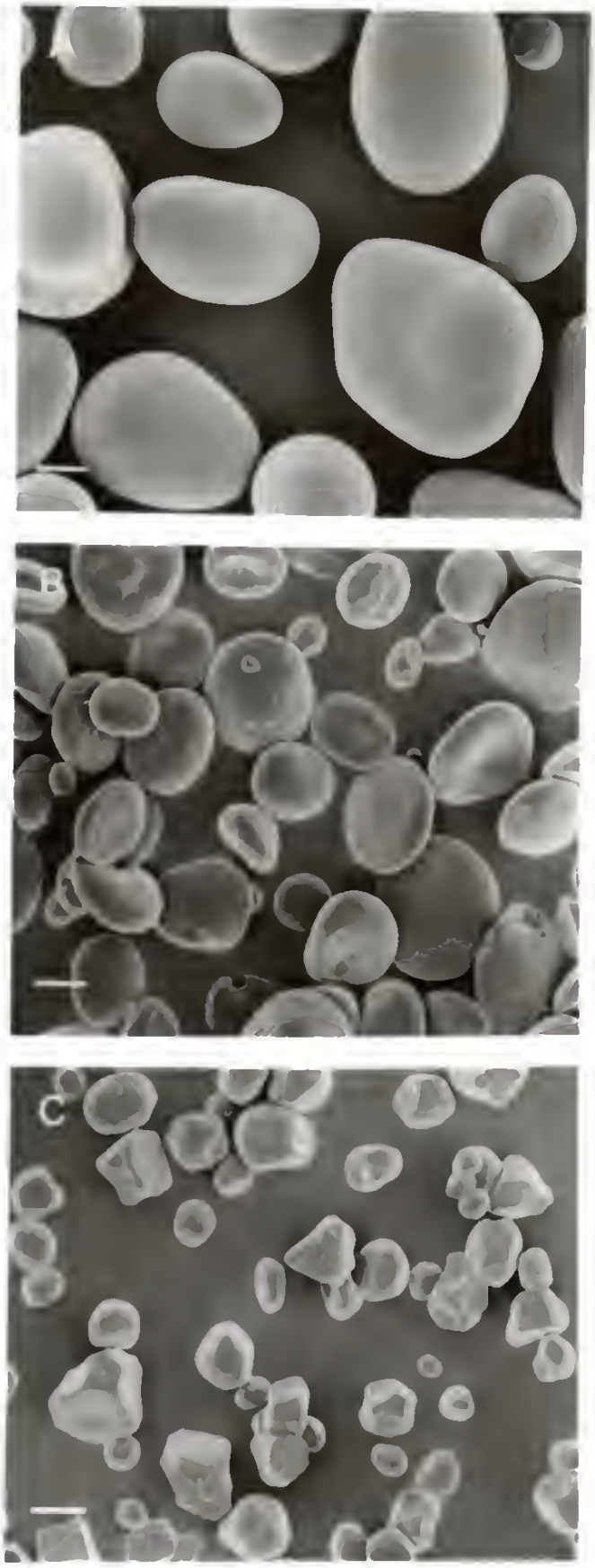
DIFFERENTIAL SCANNING CALORIMETRY (DSC)

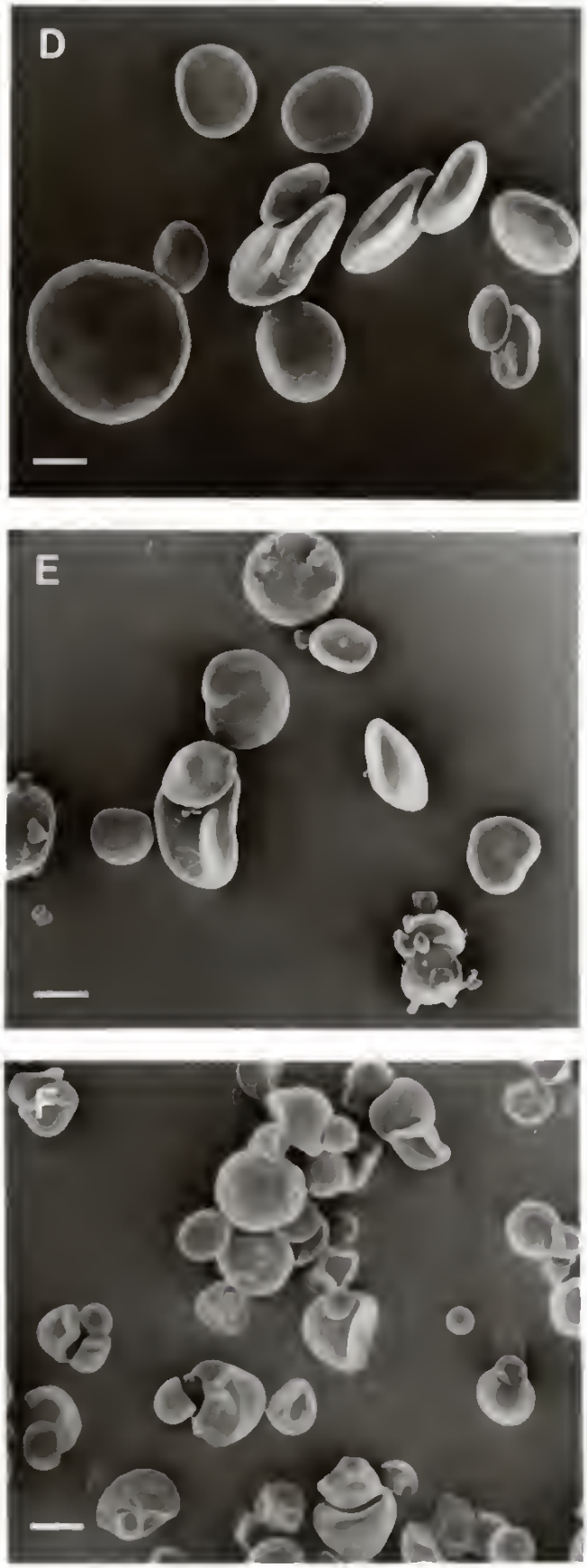
A Perkin-Elmer DSC-2 (Norwalk, Connecticut, USA.) equipped with a Perkin-Elmer 56 recorder and intra cooler was used for all experiments.

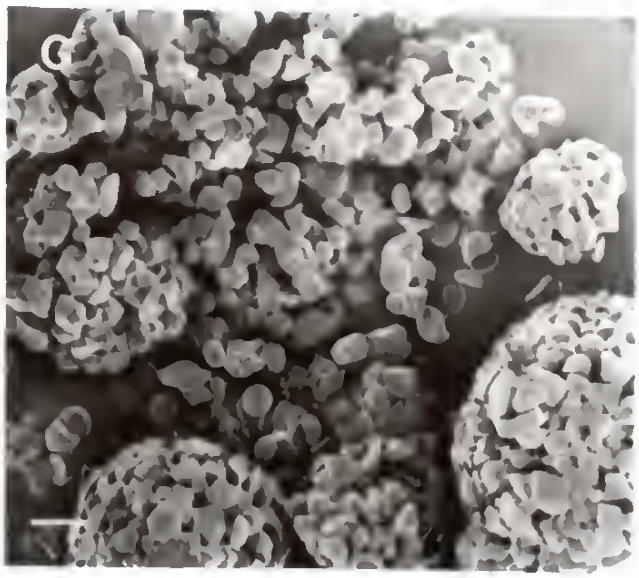
SAMPLE PREPARATION FOR DSC

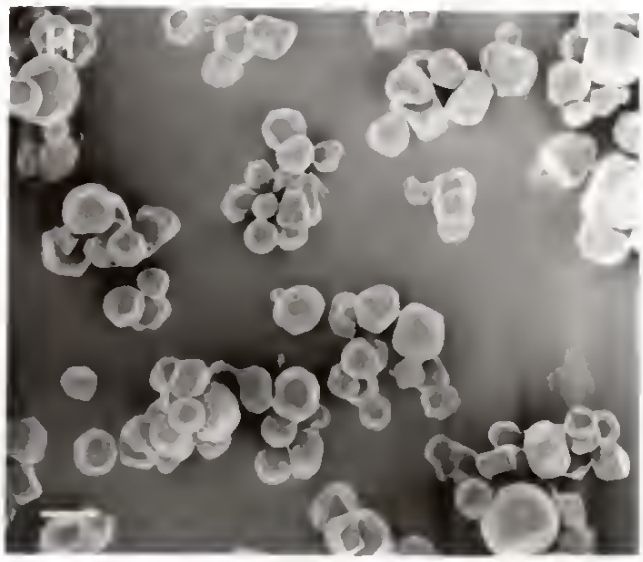
Starch (2 mg $\pm$ 0.05 mg) of known moisture content was placed in Perkin-Elmer aluminum DSC pans (kit #219-0062) and distilled water in excess of the required amount metered in to the pan with a 1 syringe.

Figure 2. Scanning Electron Micrographs of Starches; 2a, Potato; 2b, Wheat; 2c, Corn; 2d, Triticale; 2e, Barley; 2f, Buffalo Gourd; 2g, Oat; 2h, Millet; 2i, Rye.


B
C


D
E
F





The sample pan and its lid were then placed in a tared Cahn 21 automatic electrobalance (Cahn Instruments, Cerritos, CA., USA.) where the water was allowed to slowly evaporate until the required water:starch ratio was reached. The sample pans were immediately sealed and reweighed to determine their exact weight. Water to starch ratios of 2:1, 1:1 and 0.5:1 were used in the subsequent experiments.

THERMOGRAMS

A sample pan containing starch, along with a suitable reference pan (see below) were placed in the DSC head (maintained at 27°C) and the head cooled to a starting temperature of 7°C. Reference pans contained aluminum of mass sufficient to balance the heat capacity of the sample and reference. After the temperature stabilized at 7°C, thermograms were obtained by heating the system to 127°C at a heating rate of 10°C/minute. Instrument sensitivity was maintained at 0.5 mcal/sec. A typical thermogram curve for wheat starch is presented in Fig. 3. After creation of a baseline and extrapolation of the ascending and descending arms of the peak, areas under the endothermic peak were obtained with a polar planimeter.

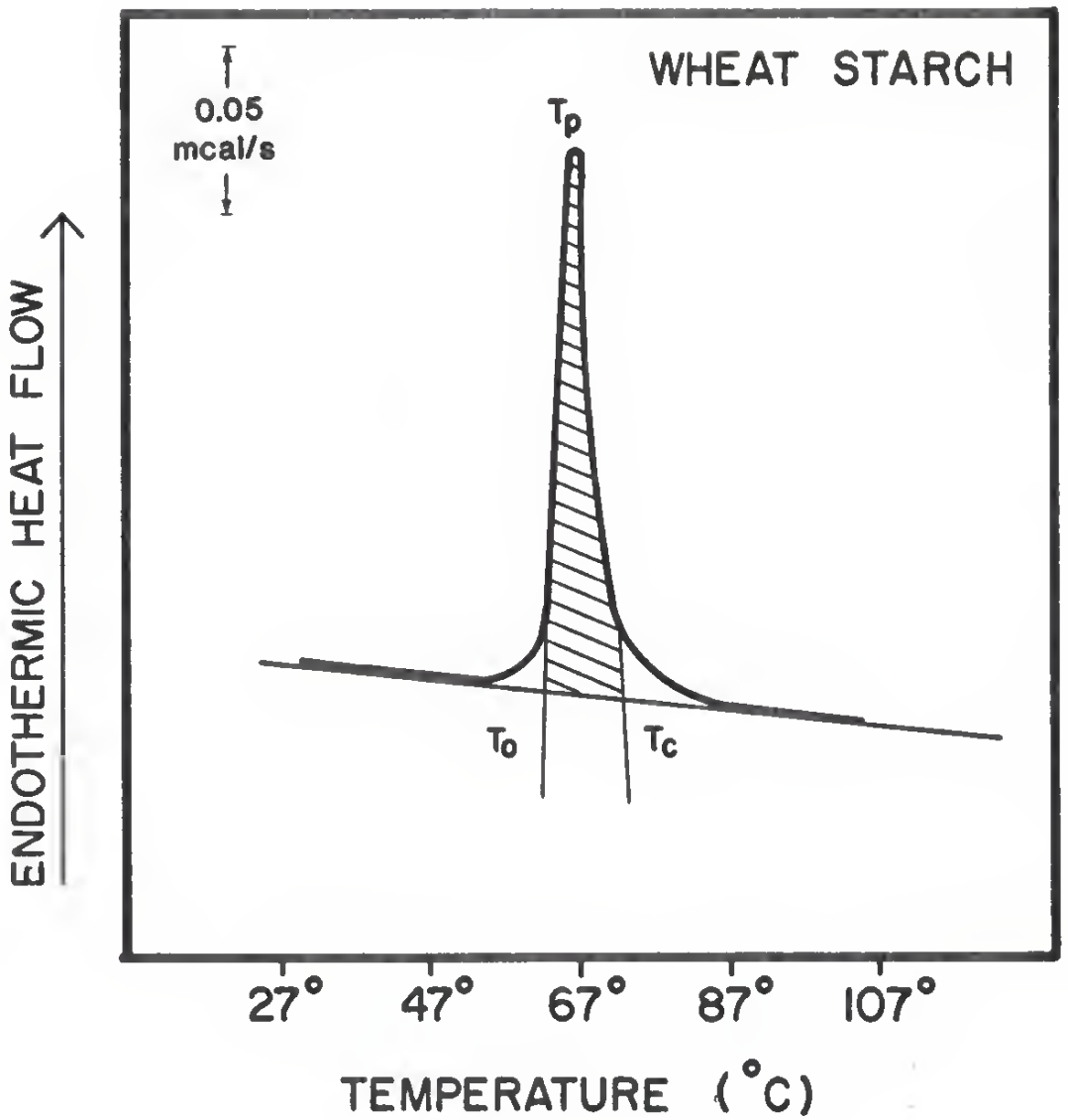
For each thermogram, gelatinization energy or enthalpy ($-\Delta H_G$) was calculated as calories/gm dry sample using the following equation:

$$-\Delta H_G = H_{indium} \times \frac{W_{indium}}{W_{sample}} \times \frac{A_{sample}}{A_{indium}} \times \frac{R_{sample}}{R_{indium}} \times \frac{S_{indium}}{S_{sample}}$$

where:

W sample = dry weight of the sample (mg)
W indium = weight of indium standard (mg)
A = area under the specific curve (planimeter units)
R = range sensitivity
S = recorder chart speed (mm/min.)

Figure 3. DSC Thermogram of Wheat Starch.


WHEAT STARCH
0.05
mcal/s
T_p
T_o
T_c
ENDOTHERMIC HEAT FLOW
27°
47°
67°
87°
107°
TEMPERATURE (°C)

ΔH indium = enthalpy for melting indium (cal/gm)

The data reported are means of triplicate determinations.

PHOTOMICROGRAPHY

Small aliquots of each starch were suspended in either distilled water or nonfluorescent immersion oil and viewed with a Zeiss research microscope using both bright field and polarizing optics. Appropriate photographs of the same field were obtained with a parfocal Olympus OM-2 automatic camera system on Kodak Tri-X film.

ABSORPTION

Water uptake by wheat starch and nageli amylodextrins of wheat starch were estimated from Blue Dextran exclusion and change in refractive index (Spectronic 21, Bausch and Lomb) as described by Evans and Haisman (1982). Data are reported as the means of duplicate determinations of volume absorbed (A 660).

PREPARATIONOF NAGELIAMYLODEXTRINS

Nageli amylodextrins were prepared from raw and retrograded starches (see below) as described by Matsukura et al (1983). Treatment was with excess 16% H_2SO_4 at 38^{o}C. Carbohydrate rendered soluble by this procedure was determined every 48 hrs.

ASSESSMENT OF CARBOHYDRATE SOLUBILIZATION

After neutralizing the suspension with 10N NaOH in an ice bath, samples were centrifuged at 6000 RPMs for 5 minutes and the supernatents discarded. Pellets were rinsed with distilled water and centrifuged being careful to retain all insoluble material. The isolated amylodextrins were weighed and their moisture contents were determined gravimetrically (AACC 44-15)(1975). Soluble carbohydrates

were calculated by:

$$100 - \frac{[\text{Dry weight amylodextrin}]}{[\text{Dry weight native starch}]} \times 100$$

and expressed as % soluble carbohydrate.

In a second set of studies, Nageli amylodextrins were prepared from native potato, wheat and corn starch as described above with the exception that incubation temperature was reduced to 22°C. Percent soluble carbohydrate was determined weekly over 8 weeks.

GELATINIZATION and RETROGRADATION of STARCHES

Starches were defatted by soxhlet extraction for 24 hours with methanol as the extracting solvent. A suspension (50% starch, 50% water) of defatted starch (potato, wheat and corn) was gelatinized as follows. A 64mm X 22mm moisture dish was completely filled with starch:water suspension. A teflon stir bar was placed in pan and the pan sealed. By using a stirring hot plate at 100°C with an attached thermocouple for temperature regulation, the sealed pans were heated at 100°C for 12 minutes, turning top to bottom every 2 minutes. This method provided an uniformly dispersed starch gel with no pockets of dry ungelatinized material (Fig. 4).

X-RAY DIFFRACTION

X-ray diffraction patterns of defatted starches (potato, wheat and corn) were obtained with a General Electric XRD-6 model diffractometer. The instrument was operated using the following conditions: target, Cu and K ; filter, Ni; time constant, 2 sec.; scanning speed, 2°C/minute; angle 6-30 ; 35 kV; 18 mA.

Figure 4. Uniformly Dispersed Wheat Starch Gel.

RESULTS AND DISCUSSION

GELATINIZATION

The DSC was used to determine the gelatinization energy (enthalpy) of a number of cereal, root and tuber starches as a function of water content. Millet, oat, triticale, corn, barley and wheat starch follow the same general trend (Fig. 5). Barley, illustrated in Figure 7 follows the pattern shown by corn starch. At a water:starch ratio of 2:1 the ΔH of these starches ranged between 3.2 and 2.4 cal/gm dry weight and decreased to 2.6 and 1.8 cal/gm at the 0.5:1 ratio. These were small changes. With the exception of triticale, the decreases were less than 0.5 cal/gm over the three water:starch ratios tested.

The endotherms produced by wheat starch are shown in Fig. 6. Its pattern are characteristic of those seen for millet, oat, triticale, corn, and barley. At the 2:1 ratio a single sharp endotherm exists. As the water:starch ratio is reduced to 1:1 the size of the endotherm also decreases and a trailing shoulder develops at a higher temperature. At even lower water availability, 0.5:1, the shoulder shifts progressively to higher temperatures and in fact becomes the predominant peak. These results with wheat starch are similar to those of Donovan (1979) who suggested that, in excess water, the phase transition seen for starch gelatinization was the disordering of the individual starch chains by stripping from the ordered regions of the granules. And at lowest water availability (0.5:1) the gelatinization transition is characterized as a melting of the crystallites in the starch granules. This melting is responsible for the second peak.

Starch from rye showed a different response to reduced water content (Fig. 7). Its ΔH was reduced but the change was larger than

Figure 5. ΔH Required for Gelatinization at 3 Water:Starch Ratios (2:1, 1:1 and 0.5:1) for Millet, Oat, Triticale, Corn, and Wheat Starch.

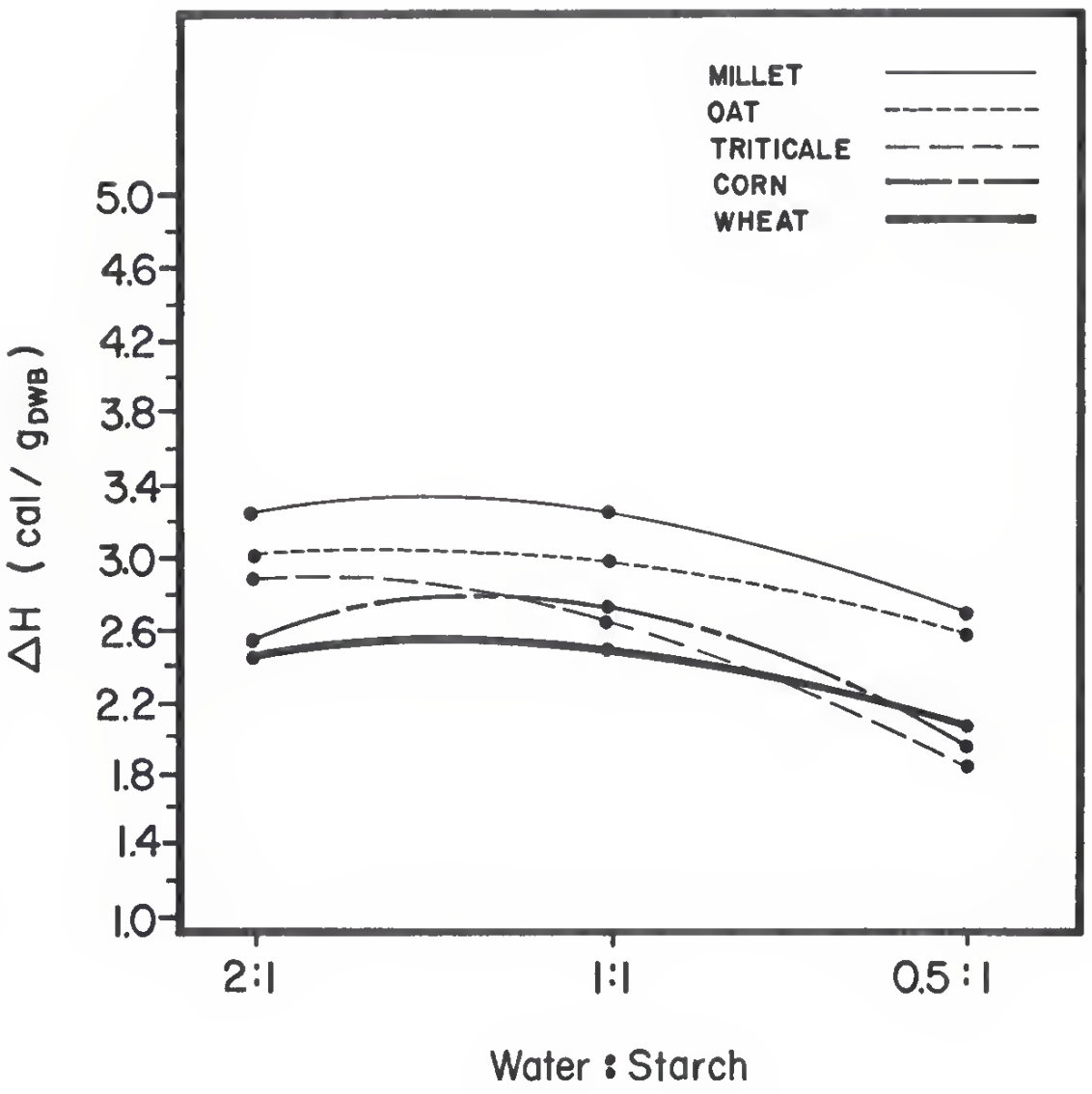

MILLET
OAT
TRITICALE
CORN
WHEAT
5.0
4.6
4.2
3.8
3.4
3.0
2.6
2.2
1.8
1.4
1.0
ΔH (cal / g DWB)
2:1
1:1
0.5 : 1
Water : Starch

Figure 6. DSC Endotherms of Wheat Starch at 3 Water:Starch Ratios (2:1, 1:1 and 0.5:1).

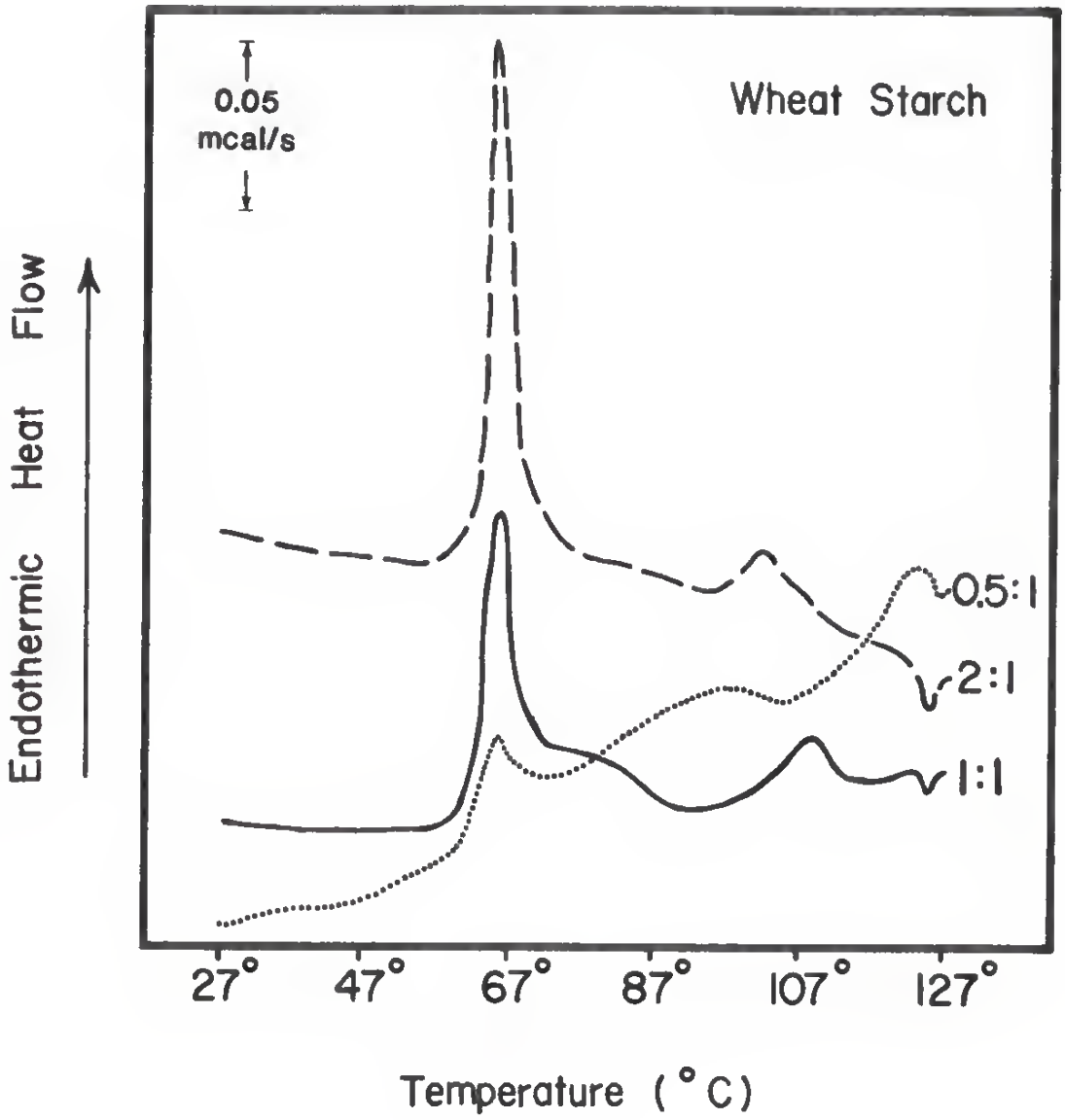
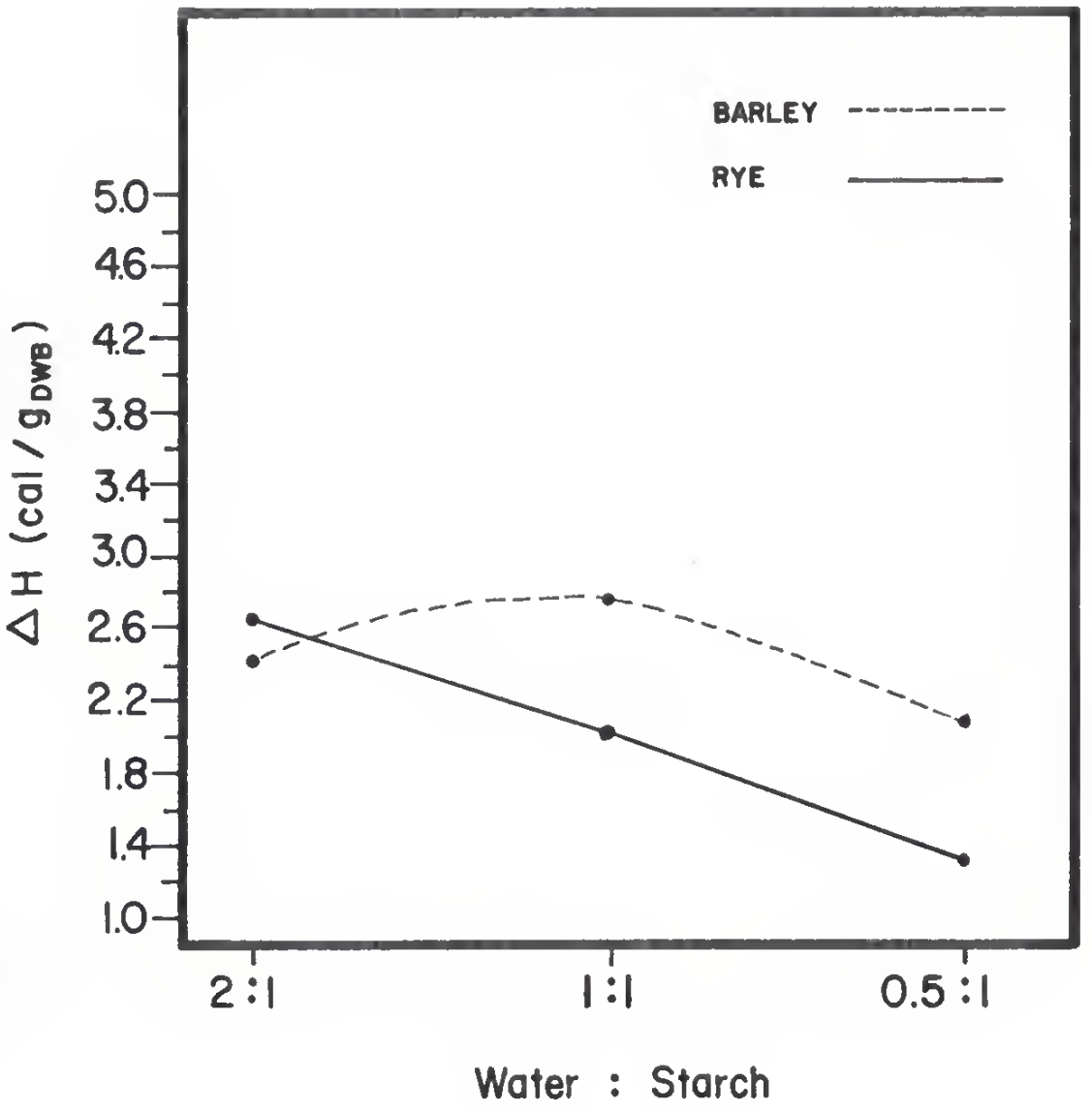

0.05
mcal/s
Wheat Starch
0.5:1
2:1
1:1
Endothermic Heat Flow
27°
47°
67°
87°
107°
127°
Temperature (°C)

Figure 7. ΔH Required for Gelatinization at 3 Water:Starch Ratios (2:1, 1:1 and 0.5:1) for Barley and Rye Starch. Barley is Illustrated on this Graph for Comparison of Rye to the Patterns of the Cereal Starches Previously Mentioned.


BARLEY
RYE
5.0
4.6
4.2
3.8
3.4
3.0
2.6
2.2
1.8
1.4
1.0
ΔH (cal / g DWB)
2 : 1
1 : 1
0.5 : 1
Water : Starch

that previously seen. As previously mentioned, the ΔH of other cereal starches decreased less than 0.5 cal/gm over the water range tested. At 2:1 the energy required for gelatinization of rye starch was 2.66 cal/gm and at 0.5:1 the enthalpy was 1.34 cal/gm. This change of 1.32 cal/gm was almost three times larger than that observed for the other normal starches tested.

Tuber starches (Fig. 8) showed yet another trend in ΔH vs H_2O content. Potato and buffalo gourd starches required higher amounts of energy to gelatinize. In spite of this, their subsequent change was less than 0.4 cal/gm over the 2:1 to 0.5:1 water:starch ratio range. They remaining substantially higher than the cereal starches. The endotherms produced by potato starch (Fig. 9) show a relatively sharp peak at 2:1. The more predominant trailing shoulder appears at lower water levels.

The question of why tuber starches have consistently higher ΔH remains. Other than size and the lack of included lipid, a most prominent difference is the apparent difference in internal molecular organization of the granule. This is reflected by differences in the X-ray diffraction pattern of cereal and tuber starches. The cereal starches give the characteristic A pattern (Zobel 1964) and tuber starches the "B" (Zobel 1964). Sterling (1960) reported that a 22% degree of crystallinity is present in the potato starch compared to 0% - 60% for cereal starches. It is not unreasonable to suspect that differences in crystallinity of crystalline order is the reason for more energy being required for gelatinization of the tuber starches.

The waxy (high amylopectin) varieties of corn, sorghum and barley were tested for their change in ΔH with water content (Fig. 10). The gelatinization energy required for these starches fell between the

Figure 8. ΔH Required for Gelatinization at 3 Water:Starch Ratios (2:1, 1:1 and 0.5:1) for Potato and Buffalo Gourd Starch.

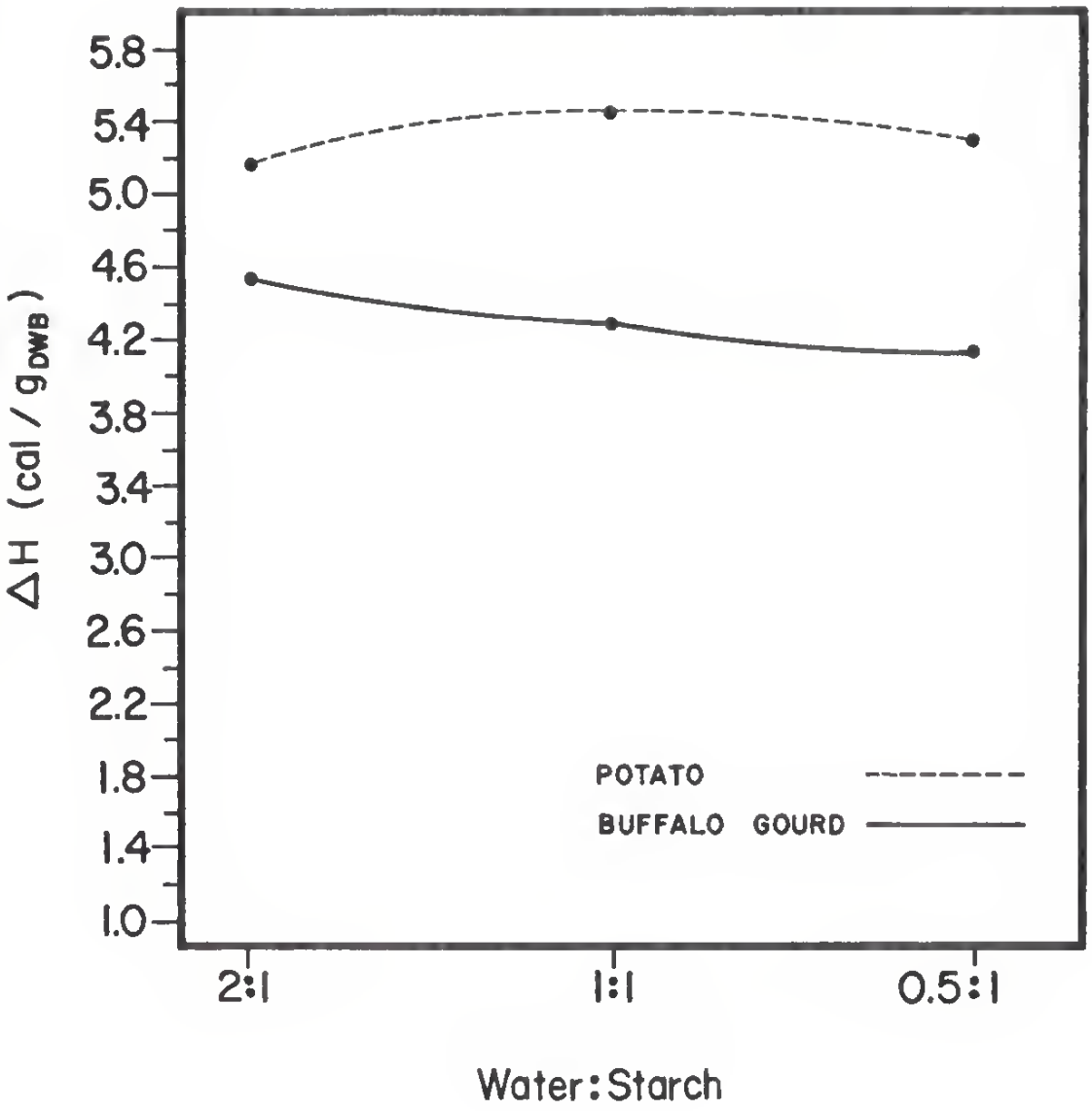
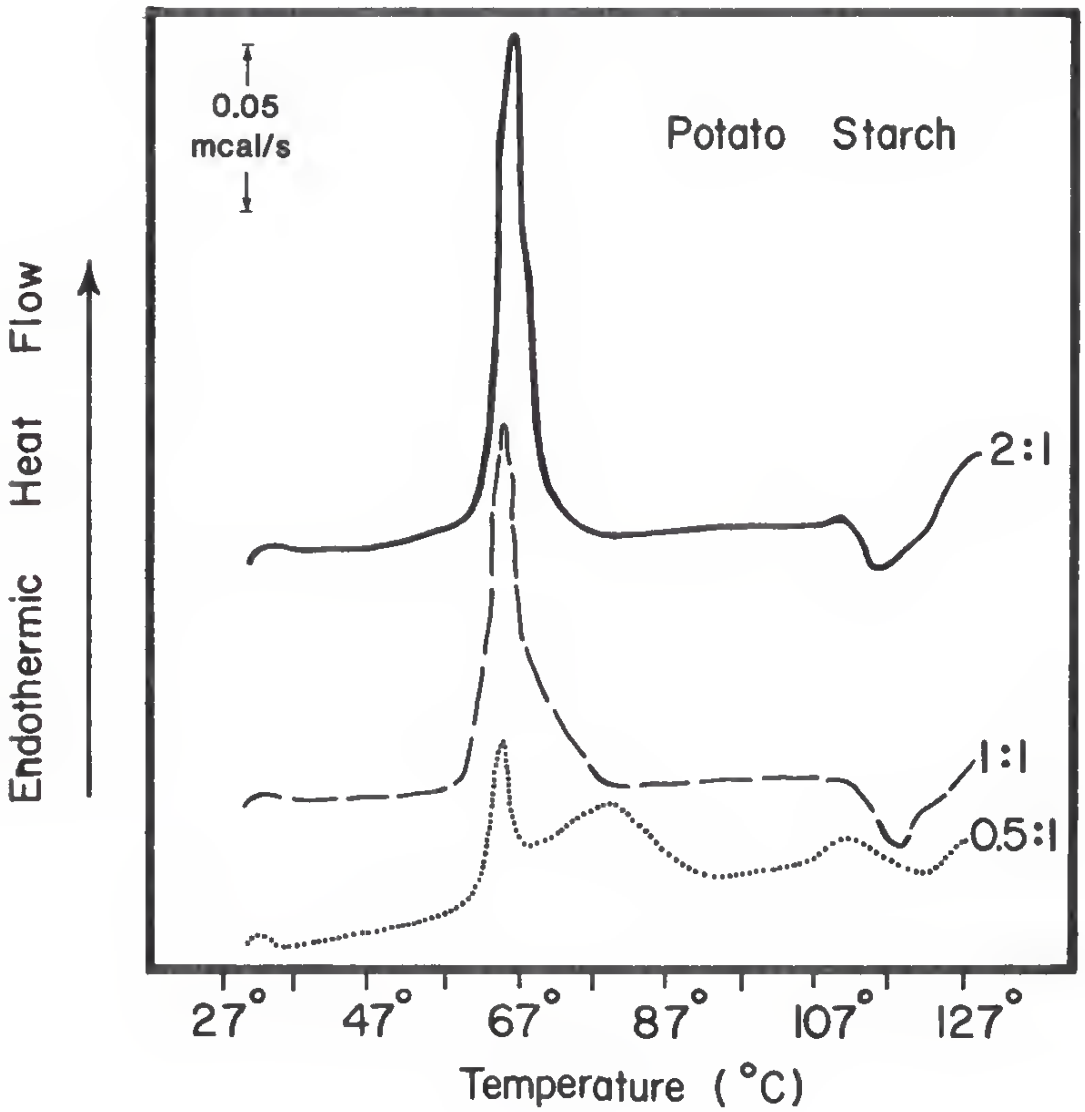

5.8
5.4
5.0
4.6
4.2
3.8
3.4
3.0
2.6
2.2
1.8
1.4
1.0
ΔH (cal / g DWB)
POTATO
BUFFALO GOURD
2:1
1:1
0.5:1
Water:Starch

Figure 9. DSC Endotherms of Potato Starch at 3 Water:Starch Ratios (2:1, 1:1 and 0.5:1).


0.05
mcal/s
Potato Starch
2:1
1:1
0.5:1
Endothermic Heat Flow
27°
47°
67°
87°
107°
127°
Temperature (°C)

values for the cereal starches and the tuber starches. At the highest water:starch ratio, the energy required for gelatinization ranged between 3.8 and 3.2 cal/gm. For these starches, the reduction in ΔH was larger than that for either tuber or normal cereal starches. A drop of almost 1.0 cal/gm (DWB) was noted across the water:starch ratios tested (Fig. 10).

Waxy starches contain primarily amylopectin and the branched amylopectin is the principle crystalline component in the starch granule (Lineback 1984). If this, in fact, results in more crystalline regions or a higher degree of crystallinity, it may account for the higher energy level required for gelatinization. All of the endotherms produced by waxy varieties (Fig. 11) exhibited the shorter and broader peaks noted by other workers (Wootton and Bamunarachchi 1979 a). This may be an indication of a lack of cooperation in the gelatinization transition. The actual cause of the phenomenon is not yet understood. The scanning calorimetric work reported above both agrees with and extends previously reported results suggesting that as water available for the sample decreases, the amounts of energy required for gelatinization decreases. This decrease may be apparent rather than real. Specifically, it may be due to the way in which the instrument acquires its data. Rather that continuously measuring the total amount of energy required for a given transition, the instrument samples. For very rapid transitions such as gelatinization with excess water, this sampling effectively measures all the energy required. For transitions occurring over wide temperature ranges, such as gelatinization in limited water, the accumulated imprecision of each sampling will result in less energy being measured than was actually required. Thus, the ΔH

Figure 10. ΔH Required for Gelatinization at 3 Water:Starch Ratios (2:1, 1:1 and 0.5:1) for Waxy Corn, Waxy Sorghum and Waxy Barley Starch.

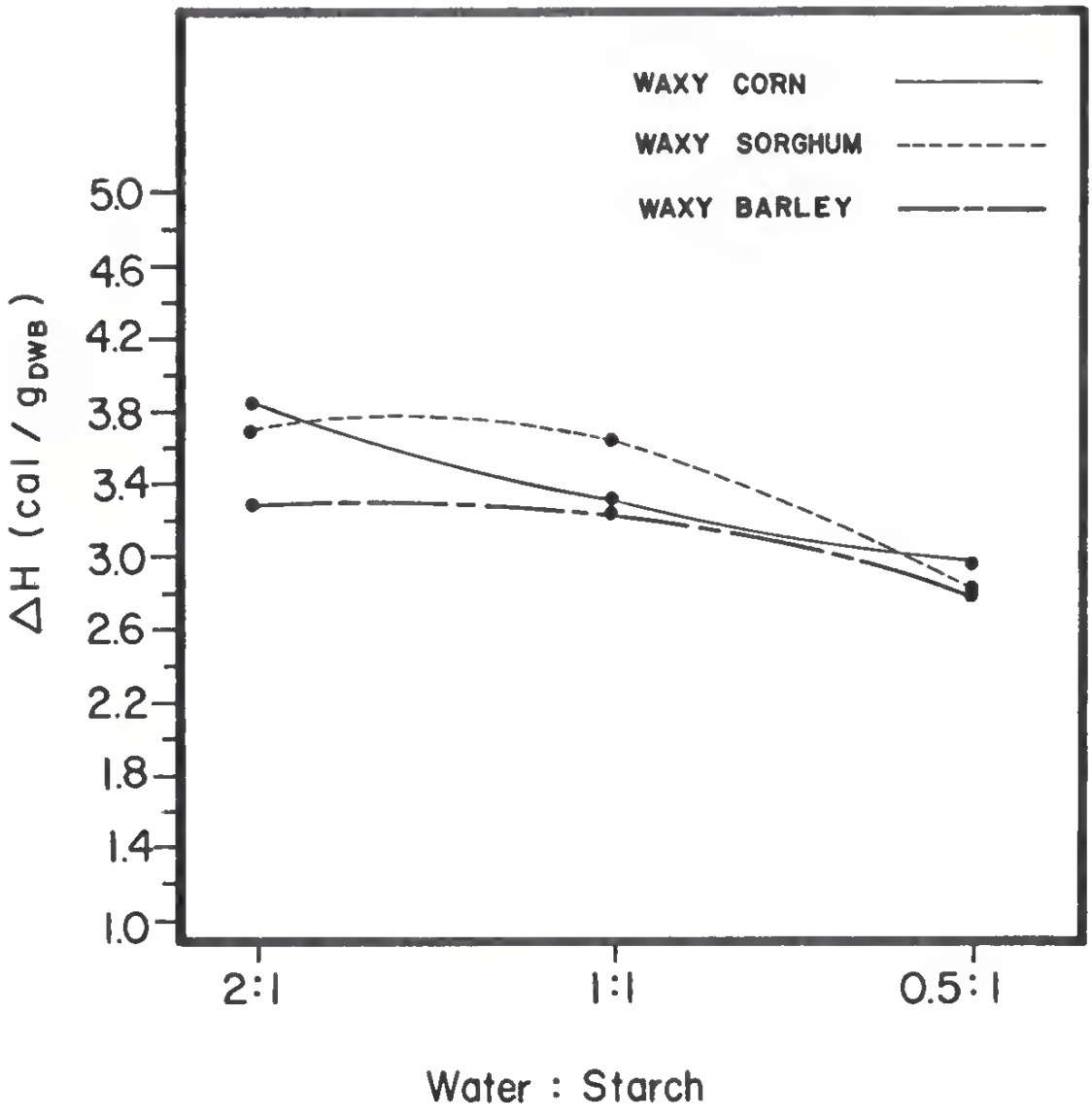
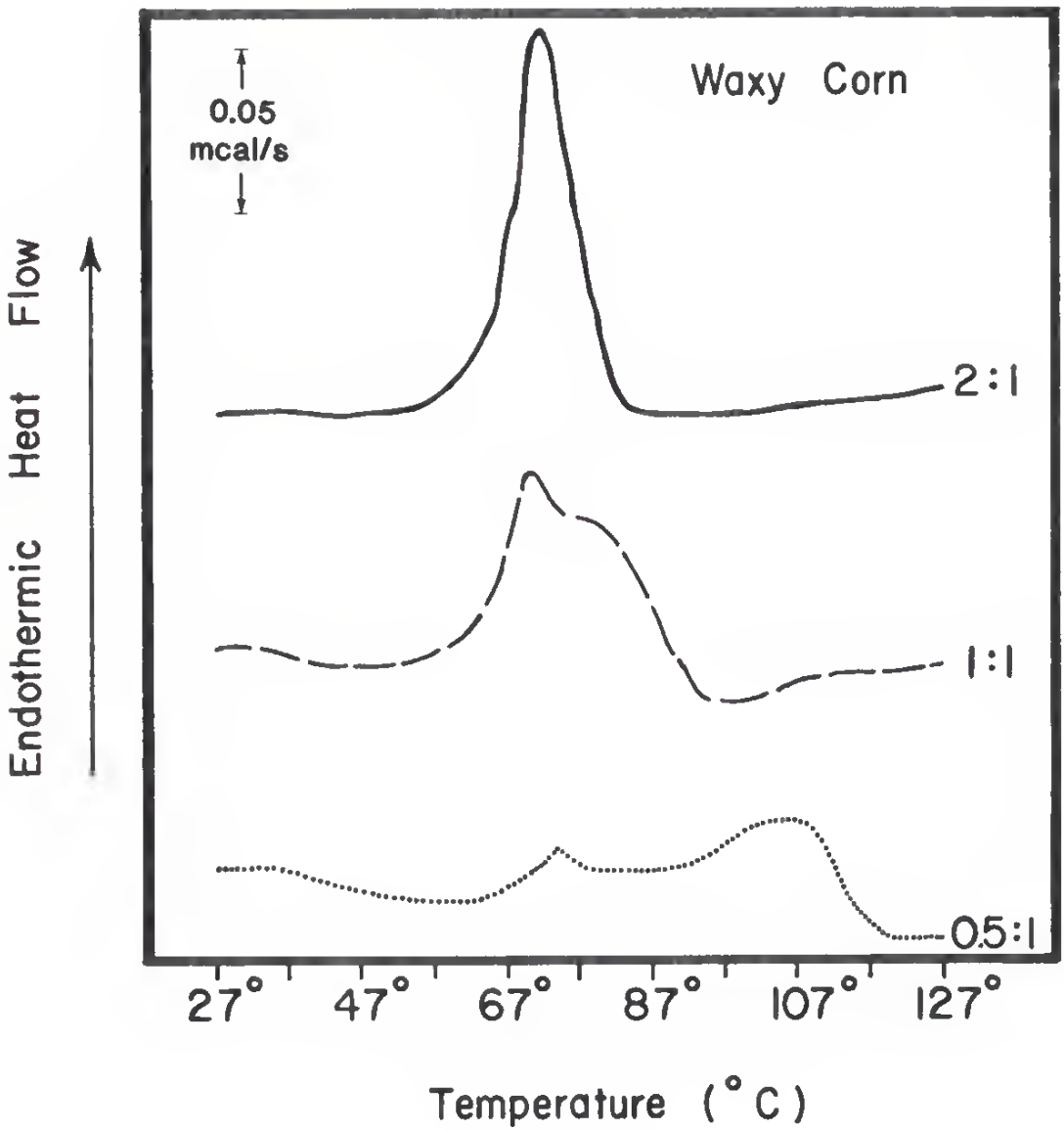

WAXY CORN
WAXY SORGHUM
WAXY BARLEY
5.0
4.6
4.2
3.8
3.4
3.0
2.6
2.2
1.8
1.4
1.0
ΔH (cal / g DWB)
2:1
1:1
0.5:1
Water : Starch

Figure 11. DSC Endotherms of Waxy Corn Starch at 3 Water:Starch Ratios (2:1, 1:1 and 0.5:1).


0.05
mcal/s
Waxy Corn
2:1
1:1
0.5:1
Endothermic Heat Flow
27°
47°
67°
87°
107°
127°
Temperature (°C)

of gelatinization would be artificially low (Wendlandt 1974). This does not explain the differences between starches (e.g., A starches and B starches) in the amount of energy they require to gelatinize even in excess water.

SOLUBILIZATION IN ACID

In preparing the Nageli amylodextrins we were trying to determine the effect of storage temperature (38°C vs 22°C). By elevating the temperature 16 C, the percent of soluble carbohydrate can vary, and the variation may be different for tuber and cereal starches. Being that because the crystalline structure for tuber starches (B pattern) and cereal starches (A pattern) are different, the rate of solubilization may be effected.

After 2 days of treatment at 38°C, over 70% of potato, wheat and corn starch was solubilized (Fig. 12). Microscopic (bright field) observation of these starches (Fig. 13) showed that the granules retained their granular nature in spite of the large loss of soluble material. They seem to be completely intact with cracks along their surfaces. After 2 days of treatment the carbohydrate loss was similar but differences appeared in the retention of birefringence. Under polarization optics, the 3 varieties of starch retained birefringence after the treatment. Potato starch (Fig. 13a), which showed the most extensive granule breakdown under brightfield retained the strongest birefringence (Fig. 13b). After 2 days at either treatment temperature, wheat starch (Fig. 13c and d) lost some of its birefringence over all of the granule. Corn was different from wheat or potato starch in that it retained its birefringence characteristics essentially intact (Fig. 13e and f).

Figure 12. Percent Soluble Carbohydrate for Native Starch (Potato, Wheat and Corn) Treated with 16% H_2SO_4 at 38 ^{o}C.

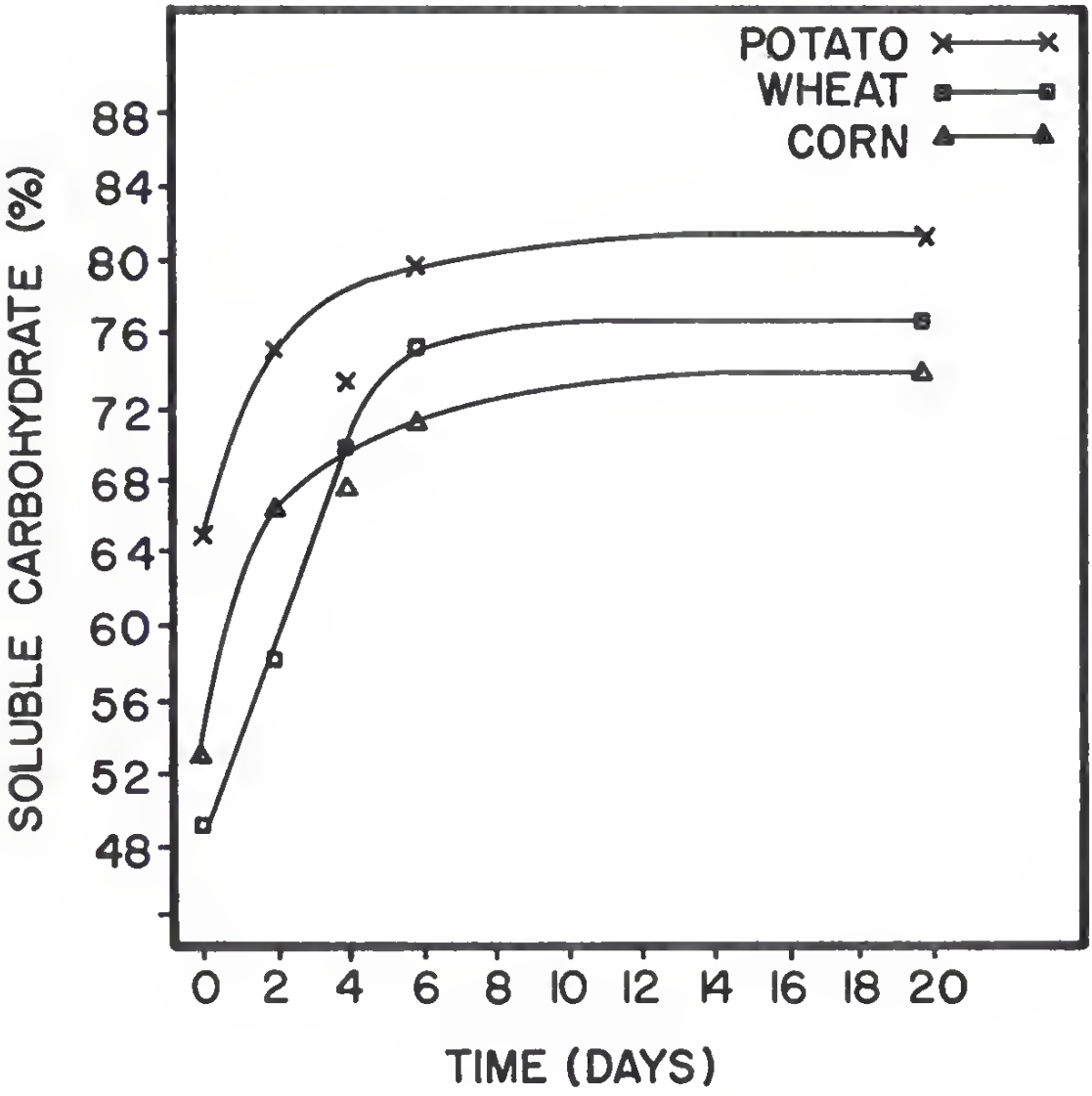
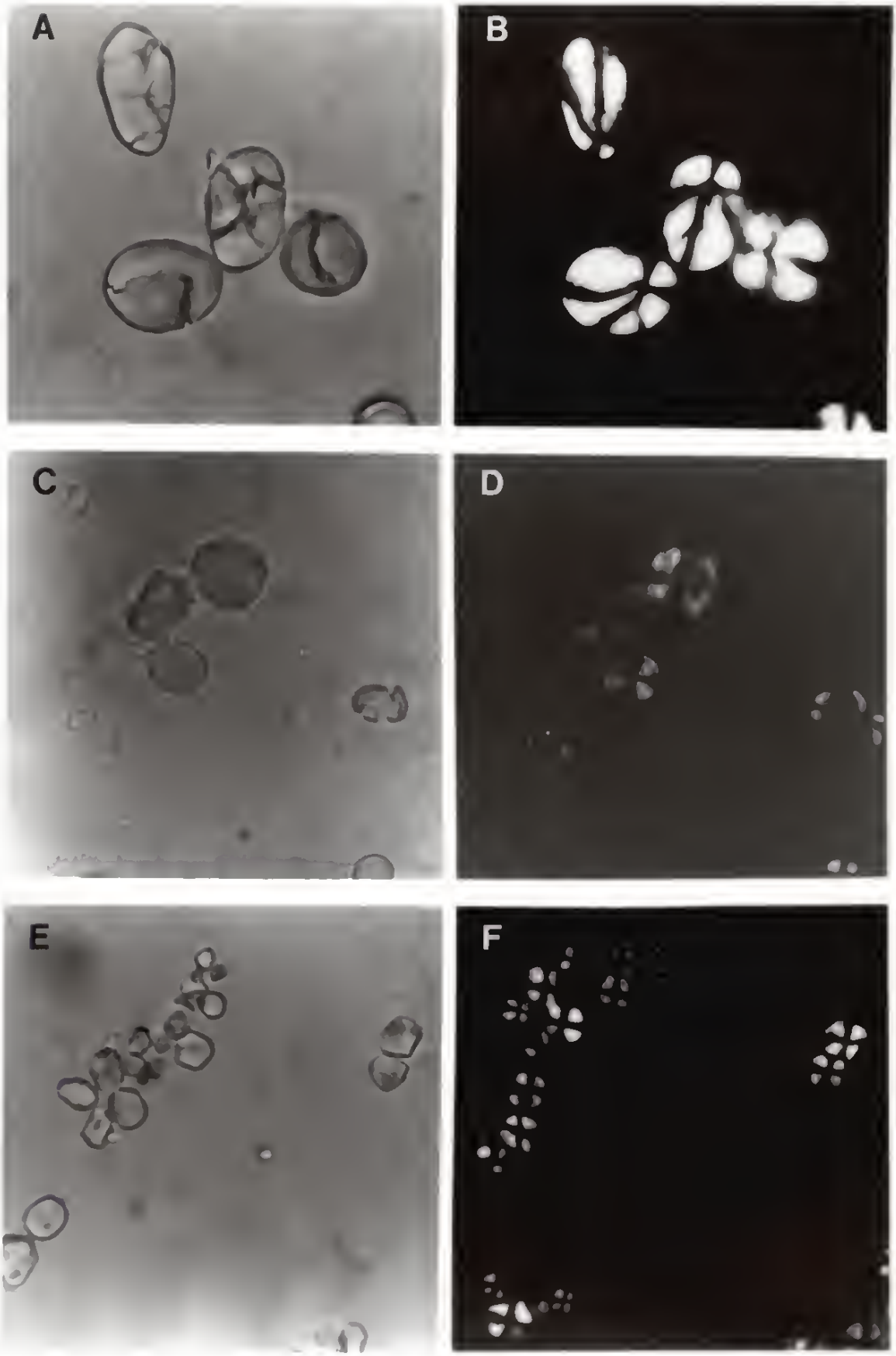

POTATO
WHEAT
CORN
SOLUBLE CARBOHYDRATE (%)
88
84
80
76
72
68
64
60
56
52
48
0
2
4
6
8
10
12
14
16
18
20
TIME (DAYS)

Figure 13. Photomicrographs of Native Starches Treated 2 Days with 16% H_2SO_4 at 38°C; 13a and 13b, Potato; 13c and 13d, Wheat; 13e and 13f, Corn. Left column brightfield illumination, right column, polarization optics.


A
B
C
D
E
F

As treatment continued, all starches continued to lose carbohydrate. By the eighth day, potato starch had become 80.60% soluble; wheat, 80.41% and corn, 78.90%. These figures are not statistically different. Microscopic examination continued to show differences in the granules and their remnant birefringence. Potato starch (Fig. 14a) granules were extensively degraded but a small percentage of the granules remained intact. The majority of the granules contained large crevices and/or missing pieces. Under polarization strong birefringence (Fig. 14b) remained even though under bright field observation the granules appeared severely damaged. Wheat starch granules (Fig. 14c) appeared less damaged than the potato starch at 8 days. Interestingly, birefringence was now lost from the great majority of the wheat starch granules (Fig. 14d). Corn starch granules seemed extensively damaged under bright field yet retained birefringence (Fig. 14e and f). This suggests that a significant amount of crystallinity remained. Corn starch (Fig. 14e and f), was unique in often displaying a radial substructure within the granule after treatment.

Over the 20 days of testing, solubilization increase but at different rates for each starch. By 20 days potato starch was 88.36% soluble; wheat, 81.69% and corn, 84.07%. There were significant differences between the amount of carbohydrate rendered soluble and the rate of solubilization. Potato starch had a faster rate of solubilization than did wheat or corn starch. Potato starch granules appeared extremely degraded (Fig. 15a). Their growth rings became very apparent and the hilum darkened. Birefringence still remained in most granule remnants (Fig. 15b) but its intensity was greatly reduced. Loss of carbohydrate from wheat starch began to slow after the 10th day (at

Figure 14. Photomicrographs of Native Starches Treated 8 Days with 16% H_2SO_4 at 38 °C; 13a and 13b, Potato; 13c and 13d, Wheat; 13e and 13f, Corn. Illumination as in Figure 13.

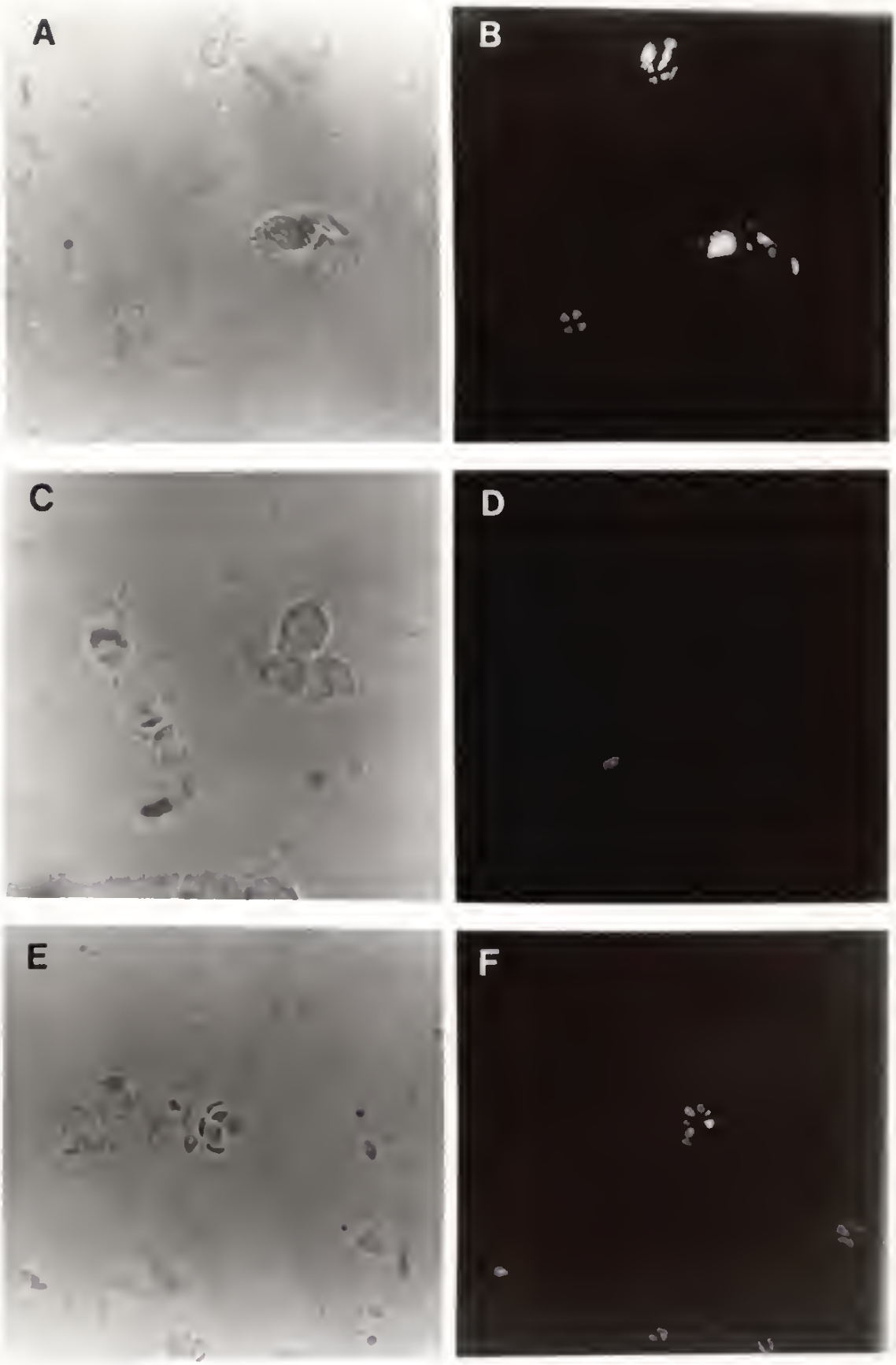
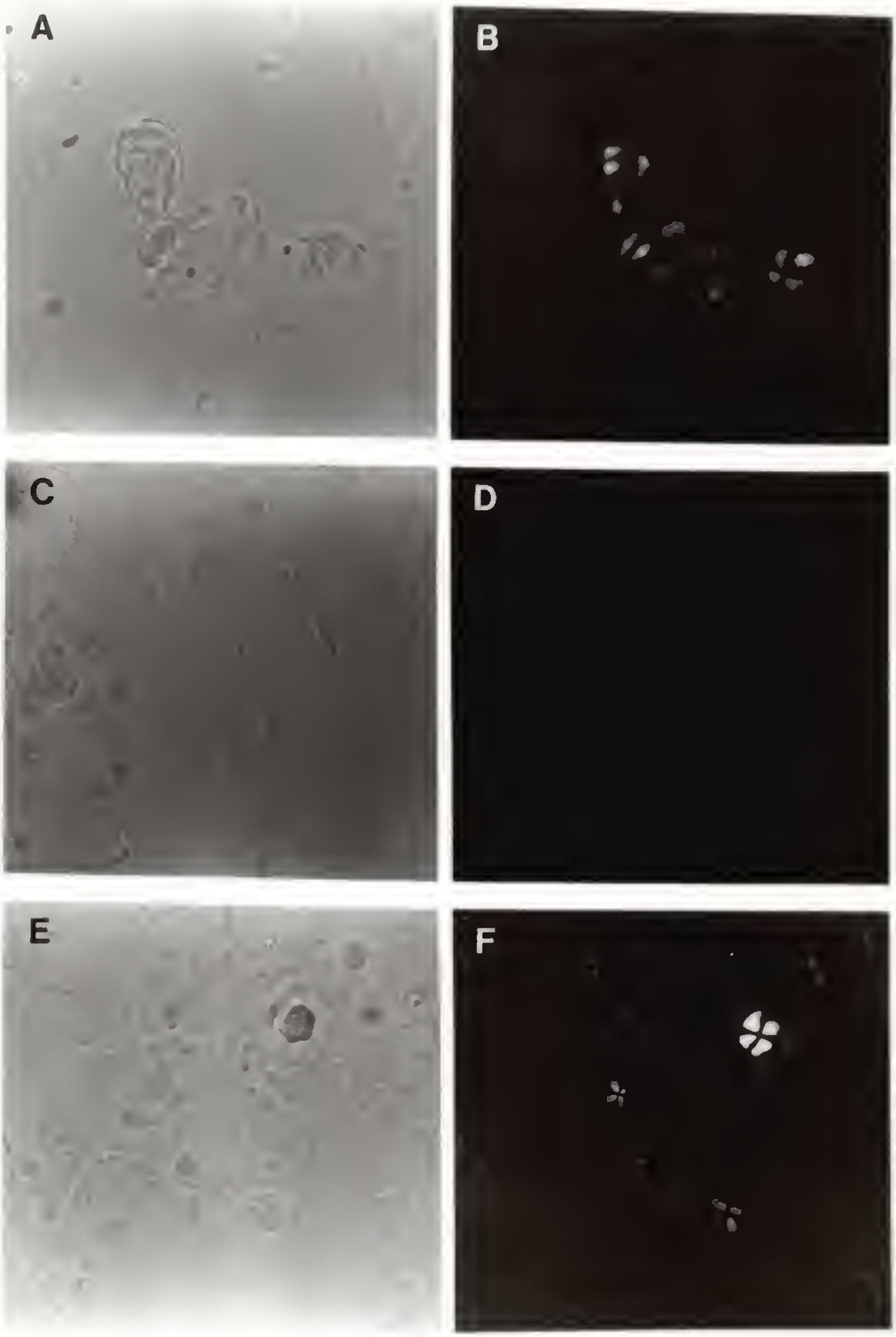

A
B
C
D
E
F

Figure 15. Photomicrographs of Native Starches Treated 20 Days with 16% H_2SO_4 at 38°C; 13a and 13b, Potato; 13c and 13d, Wheat; 13e and 13f, Corn. Illumination as in Figure 13.


A
B
C
D
E
F

81.69% soluble carbohydrate (Fig. 12)). At this point (Fig. 15c) the granules were broken, striated and fragmented. In wheat starch, birefringence was completely lost after the 10th day of treatment. This was unique to wheat starch. Corn continued to lose soluble carbohydrate to acid hydrolysis throughout the treatment. By day 20, all granules were extensively damaged and birefringence intensity was greatly reduced but still visible (Fig. 15e and f). The existence of occasional granules with birefringence suggests that some individual granules were much more acid-heat resistant than others.

At room temperature (22°C) after one week of treatment in 16% H_2SO_4 , potato starch was 66.60% soluble; wheat, 64.39% and corn, 65.22% (Fig. 16). These solubility levels are significantly lower than those for starch treated at 38°C for only 48 hours (see above). When viewing these starches under the microscope with bright field optics their appearance was relatively unchanged (Fig. 17a, c and e) from that of the native, untreated granules. Under polarization, potato starch (Fig. 17b) still appeared unaffected. Wheat and corn starch (Fig. 17d and f), on the other hand, presented another phenomenon. Granules possessing the "A" X-ray pattern lost birefringence intensity while "B" pattern starches (potato) retained strong birefringence.

Carbohydrate solubilization continued for all starches over the next 8 weeks (Fig. 18). The increase was linear and less than that observed for treatment at 38°C. The latter increased rapidly for 10 days and then plateaued. After 4 weeks of treatment, potato starch granules (Fig. 18a) were cracked, broken and in some cases fragmented yet their birefringence was intense (Fig. 18b). This holds true for the separated sections of the granules. Wheat starch granules remained intact (Fig.

Figure 16. Percent Soluble Carbohydrate for Native Starch (Potato, Wheat and Corn) Treated with 16% H_2SO_4 at 22°C.

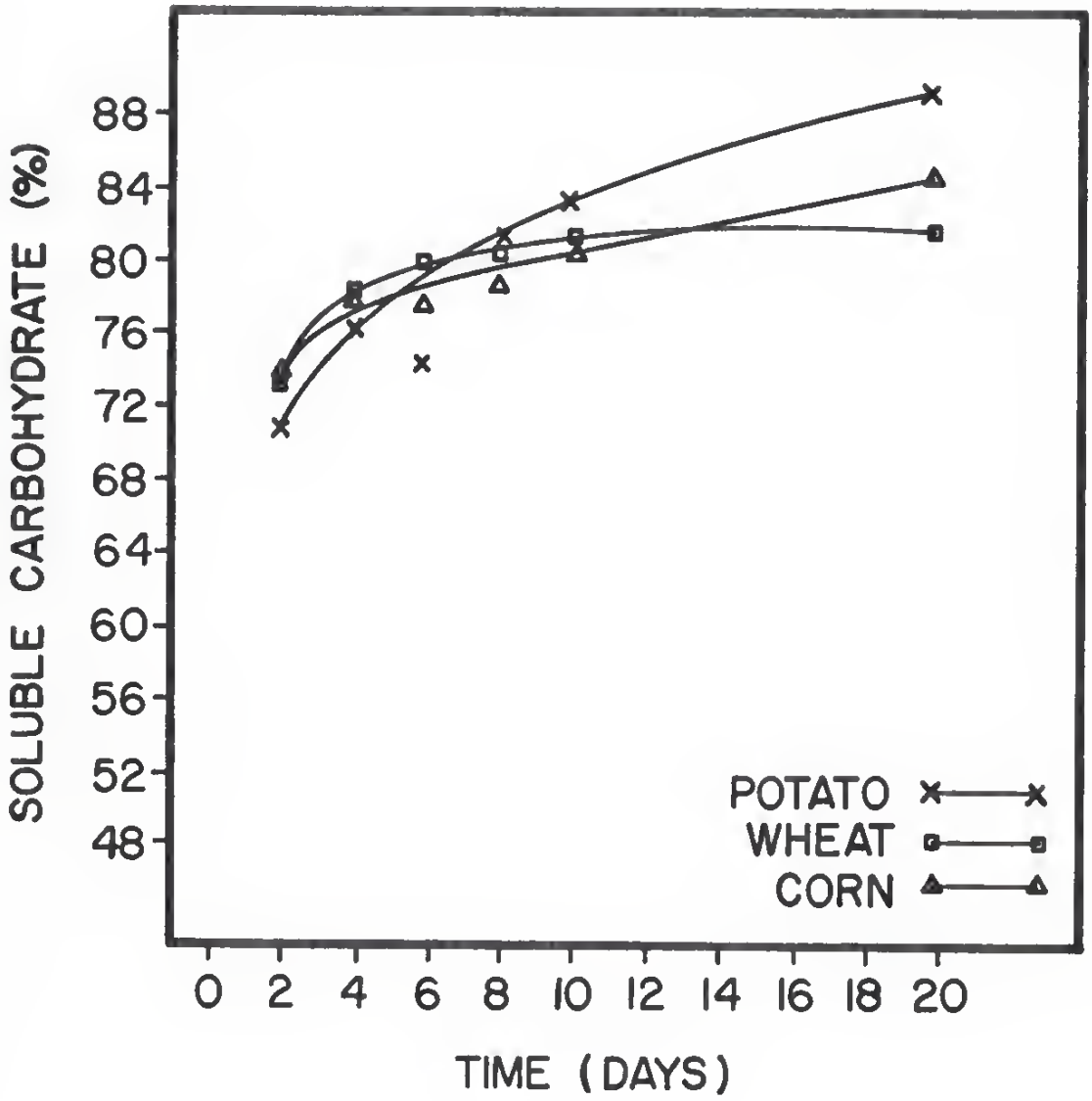

SOLUBLE CARBOHYDRATE (%)
88
84
80
76
72
68
64
60
56
52
48
0
2
4
6
8
10
12
14
16
18
20
TIME (DAYS)
POTATO
WHEAT
CORN

Figure 17. Photomicrographs of Native Starches Treated 1 Week with 16% H_2SO_4 at 22 °C; 17a and 17b, Potato; 17c and 17d, Wheat; 17e and 17f, Corn. Illumination as in Figure 13.

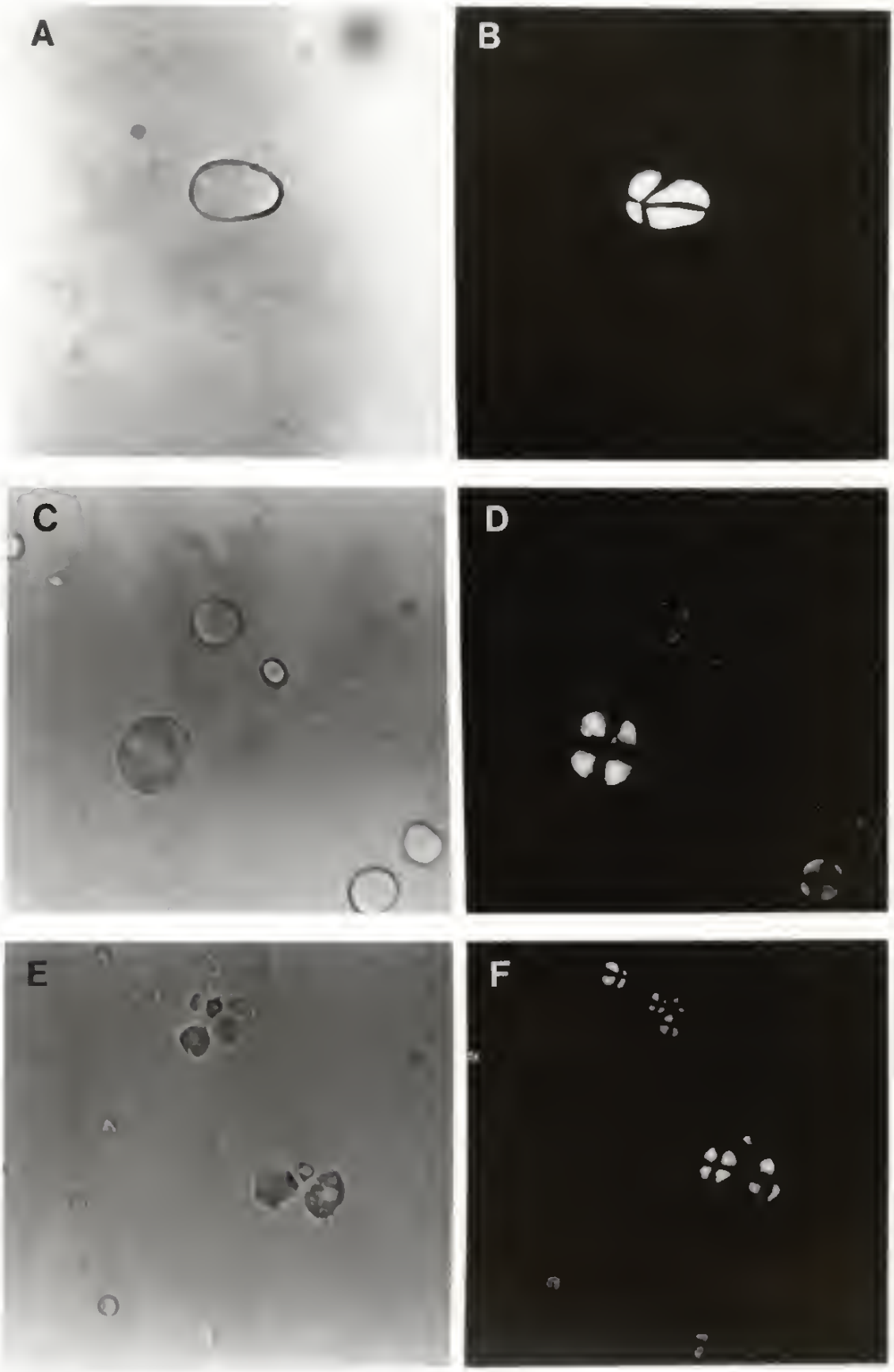
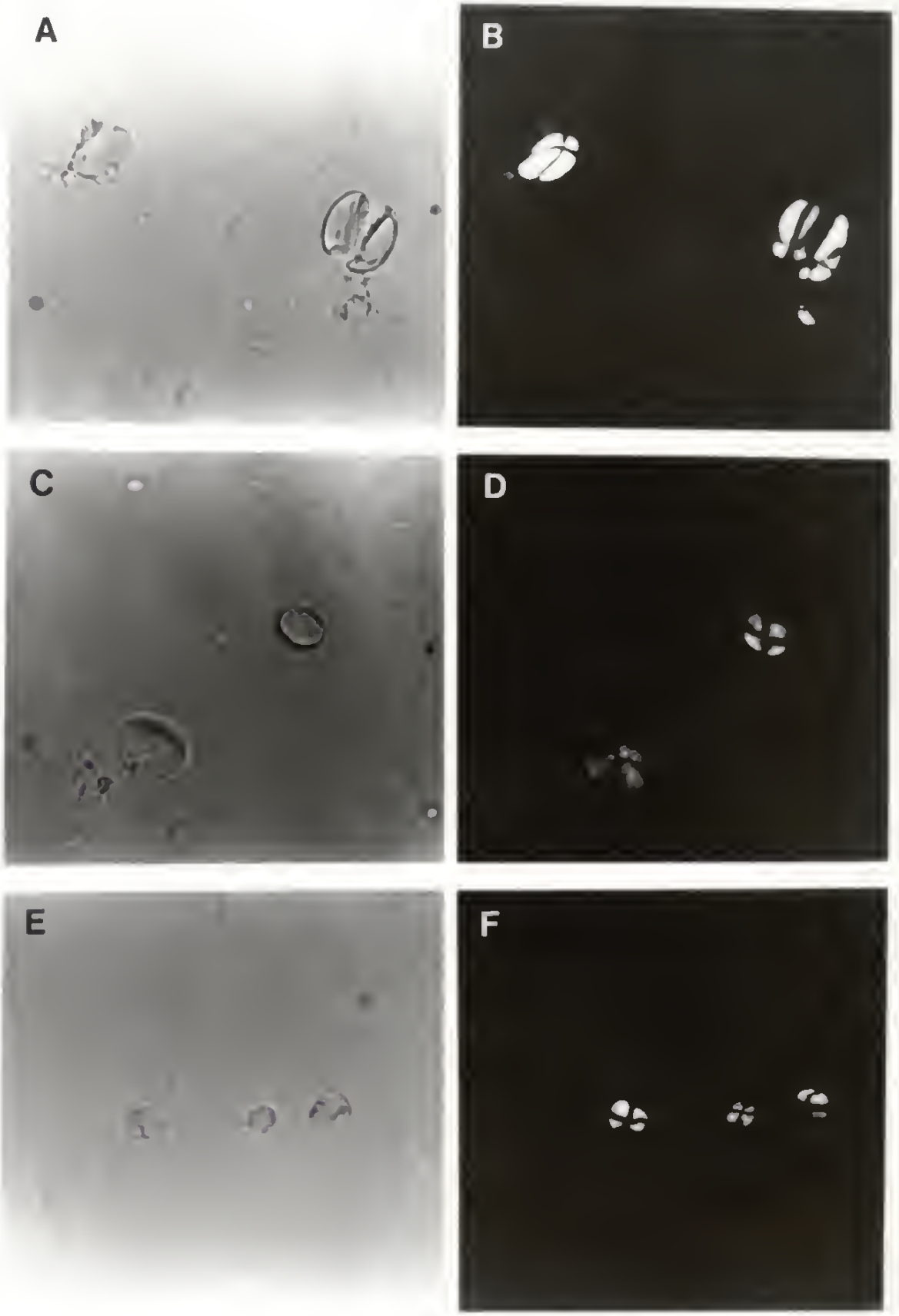

A
B
C
D
E
F

Figure 18. Photomicrographs of Native Starches Treated 4 Weeks with 16% H_2SO_4 at 22°C; 17a and 17b, Potato; 17c and 17d, Wheat; 17e and 17f, Corn. Illumination as in Figure 13.


A
B
C
D
E
F

18c and d) with only a small amount of the granules appearing broken apart. Corn starch (Fig. 18e and f), however, was beginning to show cracks in the granules although the majority of the granules appeared unaffected. Birefringence of potato and corn starch remained intense while wheat starch lost intensity.

By the 8th week of treatment the granules of potato, wheat and corn starches were extensively fragmented. Potato starch (Fig. 19a) consisted of fragments with only a small percentage of intact granules. However, these pieces and granule remnants still gave a bright birefringent image (Fig. 19b), evidence that there was still crystalline organization in what remained of the granules after hydrolysis. This is dramatically different than wheat starch, where majority of the granules remained intact (although in many irregular shapes), but lacked birefringence (Fig. 19c). The few wheat starch granules which were birefringent (Fig. 19c) possessed a broadened maltese cross along with the appearance of "growth rings." Corn starch (Fig. 19e) appeared to come apart radially and yet still gave a birefringent image (Fig. 19f) as did potato starch. The intensity of corn starch birefringence was reduced relative to that of potato.

Over the last 7 weeks of treatment at room temperature, the percent of soluble carbohydrate increased 4.28%, 9.80% and 8.67% for potato, wheat and corn starch respectively. After 20 days of treatment at 38°C, solubility increased 17.4% for potato, 8.49% for wheat, and 10.42% for corn. This increase in solubility after 20 days is very comparable to the increase after 56 days of treatment at 22°C for wheat and corn starches (Table 2). By elevating the treatment temperature 16°C, the rate of solubilization increased drastically for 10 days and then plateaued. This gave a curvilinear effect. Percent solubility

Figure 19. Photomicrographs of Native Starches Treated 8 Weeks with 16% H_2SO_4 at 22 ^{o}C; 17a and 17b, Potato; 17c and 17d, Wheat; 17e and 17f, Corn. Illumination as in Figure 13.

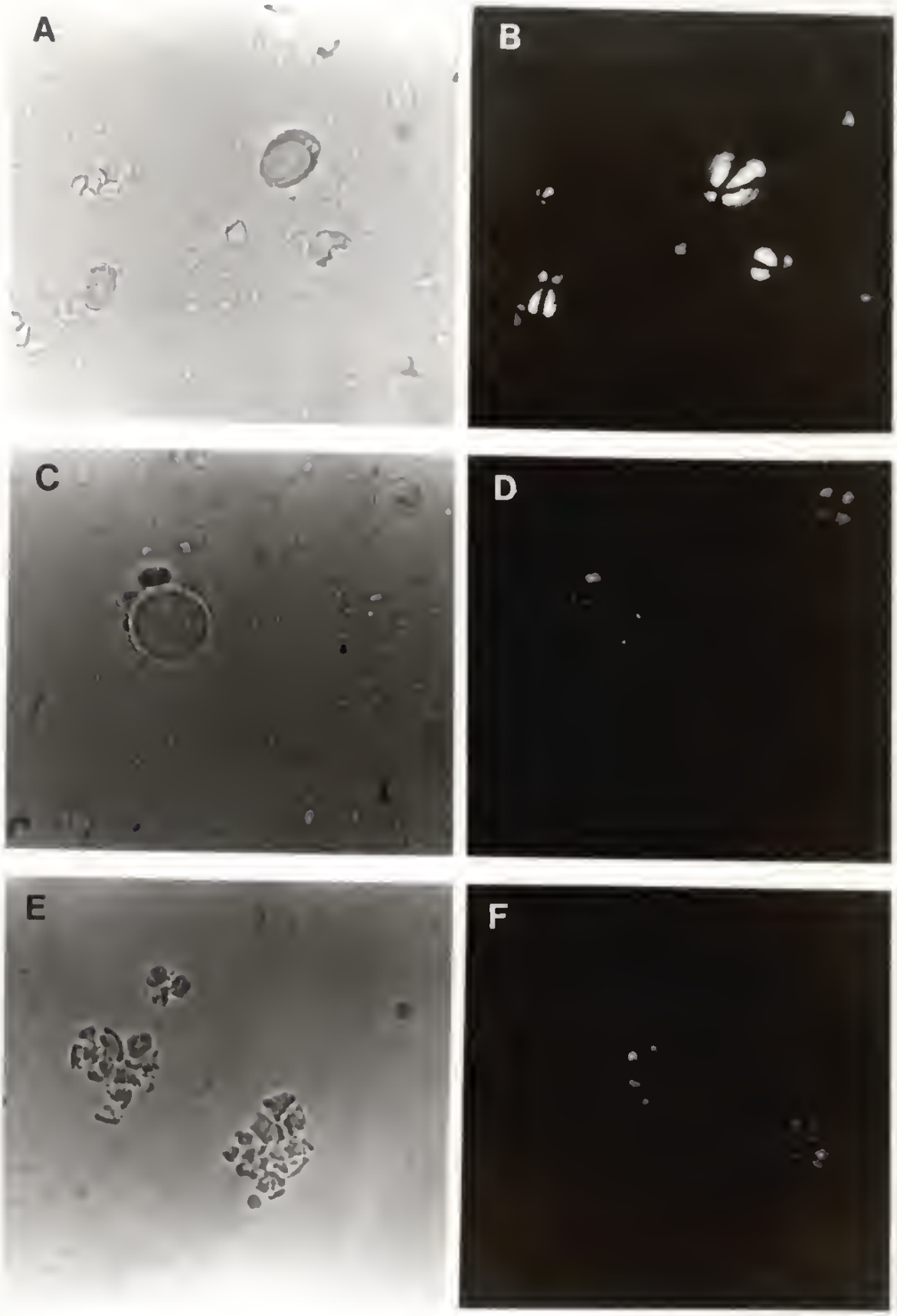

A
B
C
D
E
F

TABLE 2. COMPARISON of SOLUBILITY
(20 days, 38°C vs 56 days, 22°C)

STARCH SAMPLE	SOLUBILITY FINAL TESTING (%)	SOLUBILITY FIRST TESTING (%)	INCREASE in SOLUBILITY (%)
POTATO (22°C)	70.88 (56 days)	66.60 (7 days)	4.28
POTATO (38°C)	88.36 (20 days)	70.89 (2 days)	17.47
WHEAT (22°C)	74.73 (56 days)	64.93 (7 days)	9.80
WHEAT (38°C)	81.69 (20 days)	73.20 (2 days)	8.49
CORN (22°C)	73.89 (56 days)	65.22 (7 days)	8.67
CORN (38°C)	84.07 (20 days)	73.65 (2 days)	10.42

increased linearly for 8 weeks at 22°C. The observed differences in rate and extent of carbohydrate solubilization suggest that wheat starch was less sensitive to temperature differences than were corn and potato starches (Table 3).

ABSORPTION

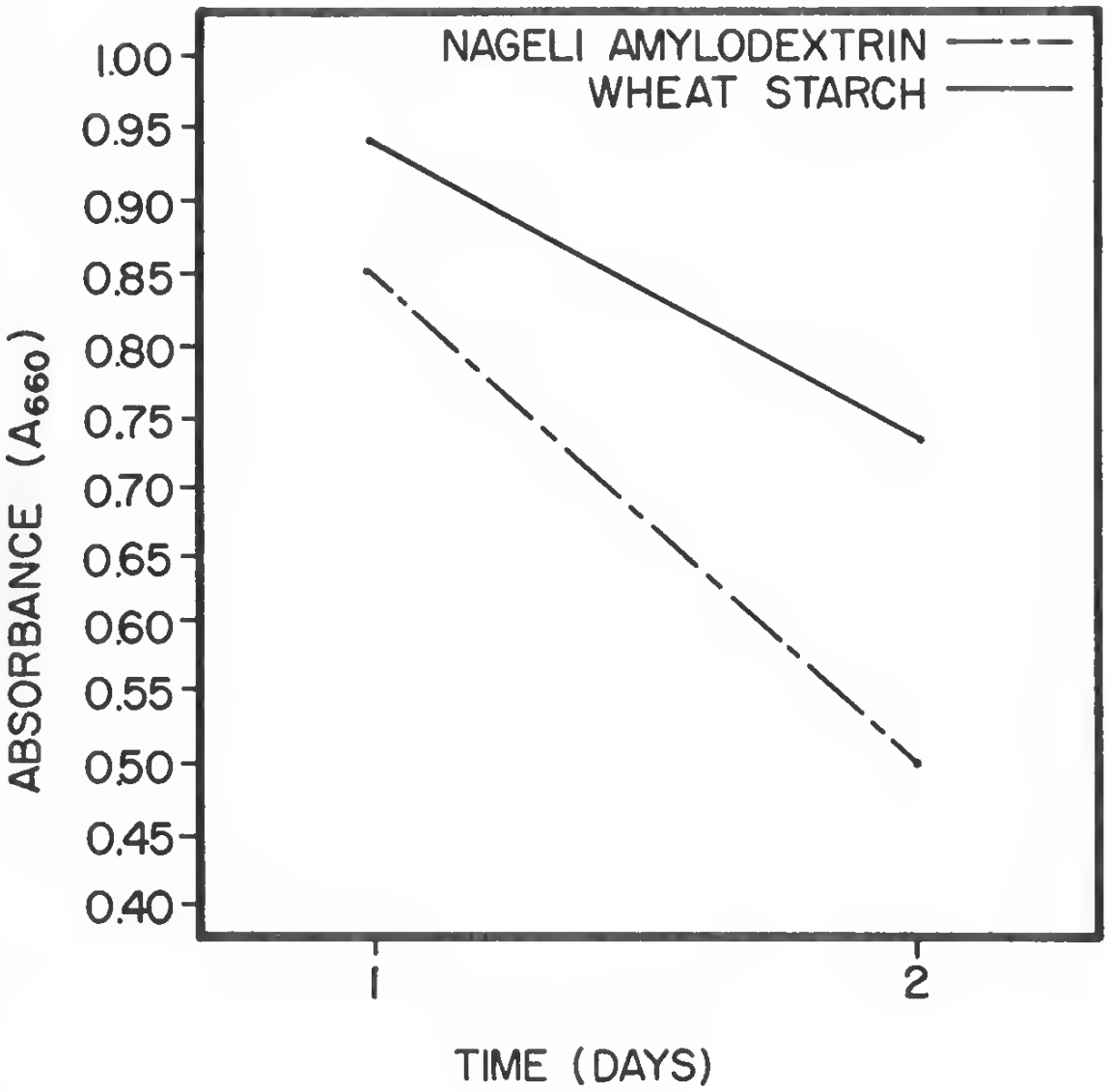
Differences were observed in the absorption of water by wheat starch and the Nageli amylodextrins produced from wheat starch. After 24 hours of treatment, the supernatent Blue Dextran solution from wheat starch had an absorbance A_{660} of 0.940 while the supernatent from the Nageli was 0.859 (Fig. 20). Since the absorbance of the 0.1% Blue Dextran solution used as initial imbibition solution was 0.766, it was clear that the samples had absorbed water from the solution. The result of this water was that the remaining supernatent was more concentrated than the original solution.

For the measurement at 24 hours, one milliliter of supernatent was removed and replaced with 1 ml. of the original 0.1% Blue Dextran solution. This resulted in a lower concentration of Blue Dextran in the solution now on the samples. In the wheat starch samples, the A_{660} of Blue Dextran solution was reduced from 0.94 to 0.87 . For the Nageli amylodextrins the reduction was from 0.859 to 0.82 . After a second 24 hours the A_{660} of the supernatents decreased to 0.731 for starch and to 0.509 for the Nageli amylodextrins. The A_{660} of these supernatents was well below the calculated absorbance of the Blue Dextran solutions present if no Blue Dextran was lost to the starch. This suggests that the samples were in fact absorbing or at least removing Blue Dextran molecules from the solution. The Nageli amylodextrins took up or bound

TABLE 3. INCREASE in SOLUBILITY (22°C vs 38°C)

STARCH SAMPLE	20 DAYS 38°C (%)	56 DAYS 22°C (%)	INCREASE in SOLUBILITY (%)
POTATO	88.36	70.88	17.48
WHEAT	81.69	74.73	6.96
CORN	84.07	73.89	10.18

Figure 20. Water Uptake of Wheat Starch and Wheat Nageli Amylodextrins as determined by A_{660} of their Supernatent Blue Dextran Solutions.


NAGELI AMYLODEXTRIN
WHEAT STARCH
1.00
0.95
0.90
0.85
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
ABSORBANCE (A660)
1
2
TIME (DAYS)

more Blue Dextran than the wheat starch. Although it was not anticipated that Blue Dextran would be able to enter the native granule, it apparently did. Absorption into the amylodextrins was not unexpected due to the physical and chemical changes resulting from acid-heat treatment. Both wheat starch and its Nageli amylodextrins were able to take up the Blue Dextran molecule during 48 hours of testing. The question remains as to whether the Blue Dextran was bound within the granules or simply held on the surface voids of the granules.

RETROGRADATION

Defatted potato, wheat, and corn starches were retrograded and the crystalline organization of the starches determined. The effect of time on the x-ray diffraction pattern of the starches was studied. We also determined the effect of retrogradation on starch solubility in acid.

X-ray Diffraction patterns of retrograded, defatted potato, wheat and corn starch were examined after 7 days and 21 days of retrogradation. Potato starch, originally a B starch, gave a very weak V pattern after 7 days of retrogradation (Fig. 21). The x-ray pattern showed primarily amorphous organization with only small maxima at 13 and 22.2. The peaks characteristic of the V pattern are 13.6 and 21.5. This starch sample was defatted with methanol extraction. Therefore, the maxima are shifted slightly due to starch complexing with the residual methanol. After 21 days, potato starch gave a stronger V pattern plus a weak retrograded A or possibly B pattern superimposed on it (Fig. 22). The separation of the peaks between 16 - 18 is characteristic of the A pattern while the separation between 24 - 26 peak is characteristic of the B pattern (Zobel 1964).

After 7 days, wheat starch gave a very weak V pattern along with

Figure 21. X-Ray Diffraction of Defatted Potato Starch After 7 Days of Retrogradation.

10
13
22.2
30
2θ

Figure 22. X-Ray Diffraction of Defatted Potato Starch After 21 Days of Retrogradation.

10
13.1
16
18
22.2
24
26
30
2θ

Figure 23. X-Ray Diffraction of Defatted Wheat Starch After 7 Days of Retrogradation.

10
11.5
21.5
30
2θ

Figure 24. X-Ray Diffraction of Defatted Wheat Starch After 21 Days of Retrogradation.

10
13.6
16.8
21.5
23.5
30
2θ

expected amorphous background (Fig. 23). Although the pattern is very weak, small peaks are seen at 11.5 and a larger peak at 21.5. In testing wheat starch after 21 days of retrogradation the V pattern was stronger with an A pattern clearly superimposed upon it (Fig. 24). A strong peak appeared at 21.5 and a weak peak at 13.6 V pattern. The A pattern was weak but but gave small peaks at 16.8 and 23.5.

Corn starch was very similar to wheat starch in the x-ray patterns it produced. At 7 days, a small peak was detected at 21.8 and an even smaller peak between 16 - 18, once again confirming a weak V pattern (Fig. 25). After 21 days retrograded wheat starch again produced the V pattern with a superimposed A pattern (Fig. 26). A very sharp peak was detected at 21.2 with a small curve at 13.0. Along with these peaks are less intense curves at 16 - 18 and 22 - 24 suggesting a weak A pattern.

Retrograded defatted potato, wheat and corn starch were also treated with 16% H_2SO_4 at 38°C. Immediately following retrogradation the samples (0 hours) were dissolved in 16% H_2SO_4 and tested for percent of soluble carbohydrate. Samples were subsequently tested for soluble charbohydrated every 48 hours. Potato starch was initially 64.87% soluble; wheat starch, 48.97% and corn starch, 53.20% (Fig. 27). Observation of the starches by bright field and polarization through microscopy, showed that birefringence was absent. The samples were, therefore, considered to have been gelatinized prior to retrogradation.

Under bright field illumination, retrograded potato starch granules were intact (Figure 28a) but deformed. Wheat starch (Fig. 28b) was also altered in shape and showed growth rings. Corn starch granules (Fig. 28c) appeared spherical instead of polygonal. These changes are

Figure 25. X-Ray Diffraction of Defatted Corn Starch After 7 Days of Retrogadation.

10
16
18
21.8
30
2θ

Figure 26. X-Ray Diffraction of Defatted Corn Starch After 21 Days of Retrogradation.

10
13
16
18
21.2
22
24
30
2θ

Figure 27. Percent Soluble Carbohydrate from Retrograded Defatted Starches (Potato, Wheat and Corn) Treated with 16% H_2SO_4 at 38°C.

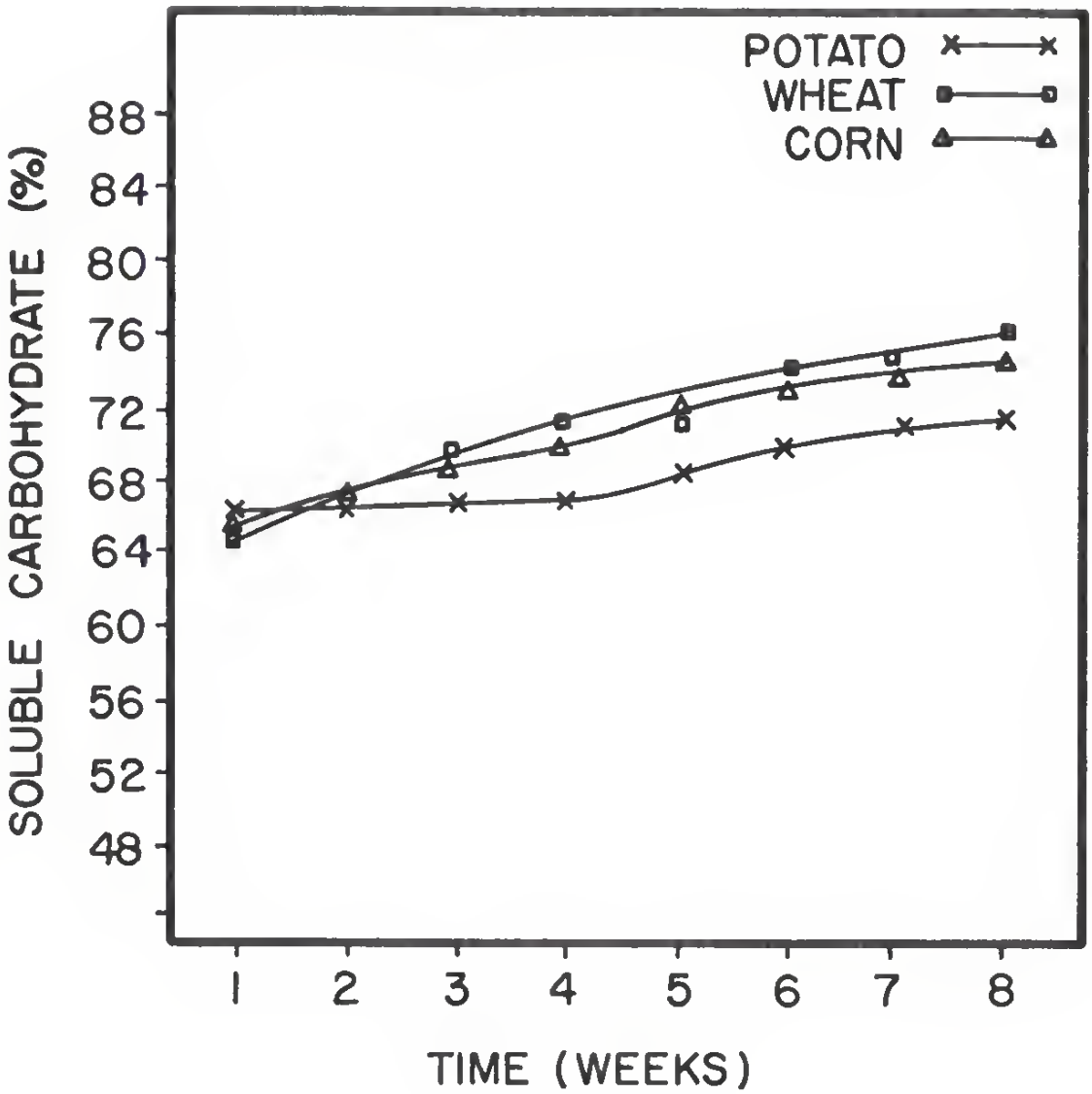

POTATO
WHEAT
CORN
SOLUBLE CARBOHYDRATE (%)
88
84
80
76
72
68
64
60
56
52
48
1
2
3
4
5
6
7
8
TIME (WEEKS)

Figure 28. Photomicrographs of Retrograded Defatted Starches Treated 0 Days with 16% H_2HSO_4 at 38°C; 28a - potato; 28b - wheat; 28c - corn.

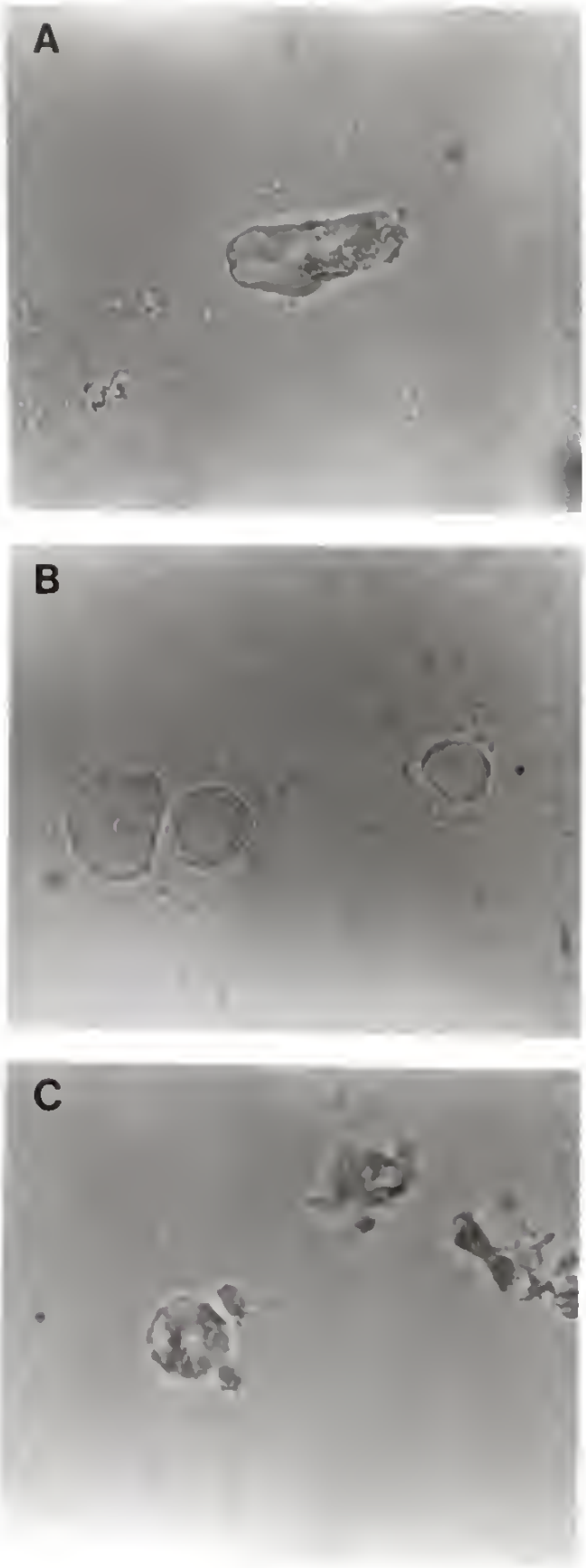

A
B
C

Figure 29. Photomicrographs of Retrograded Defatted Starches Treated for 6 Days with 16% H_2SO_4 at 38°; 29a - potato; 29b - wheat; 29c - corn. Illumination as in Figure 28.

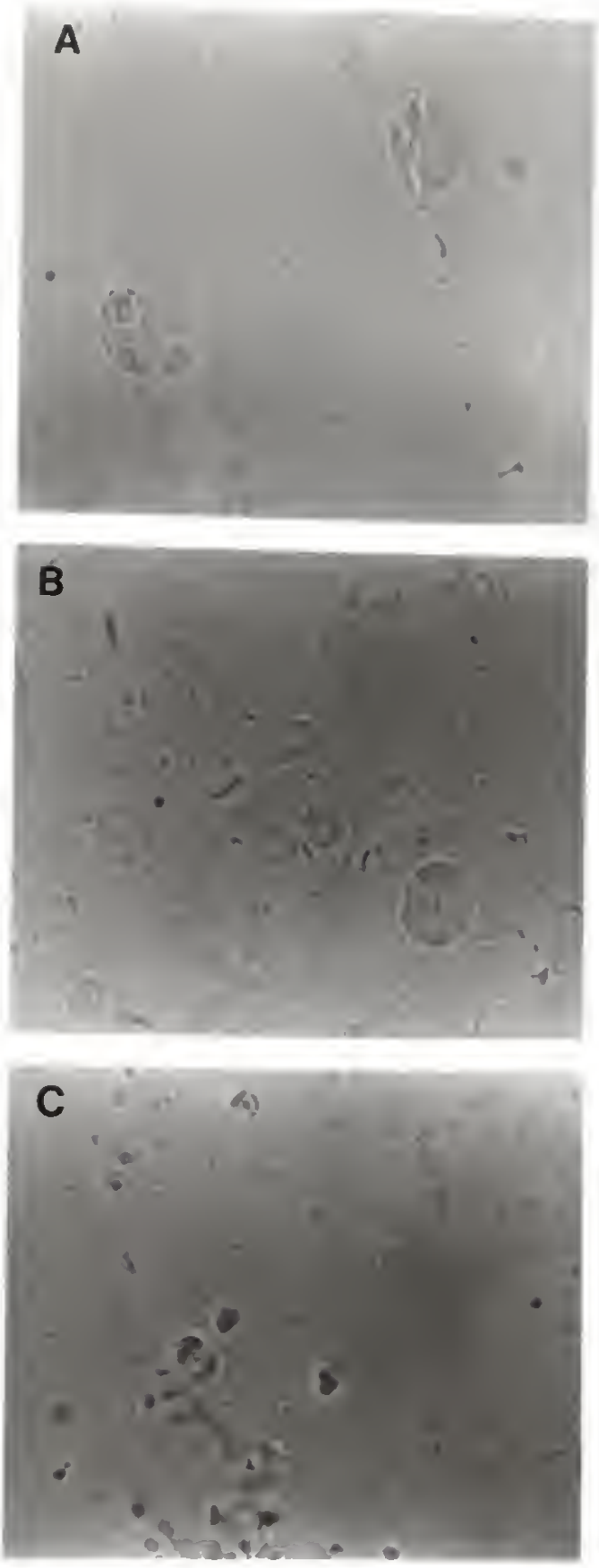
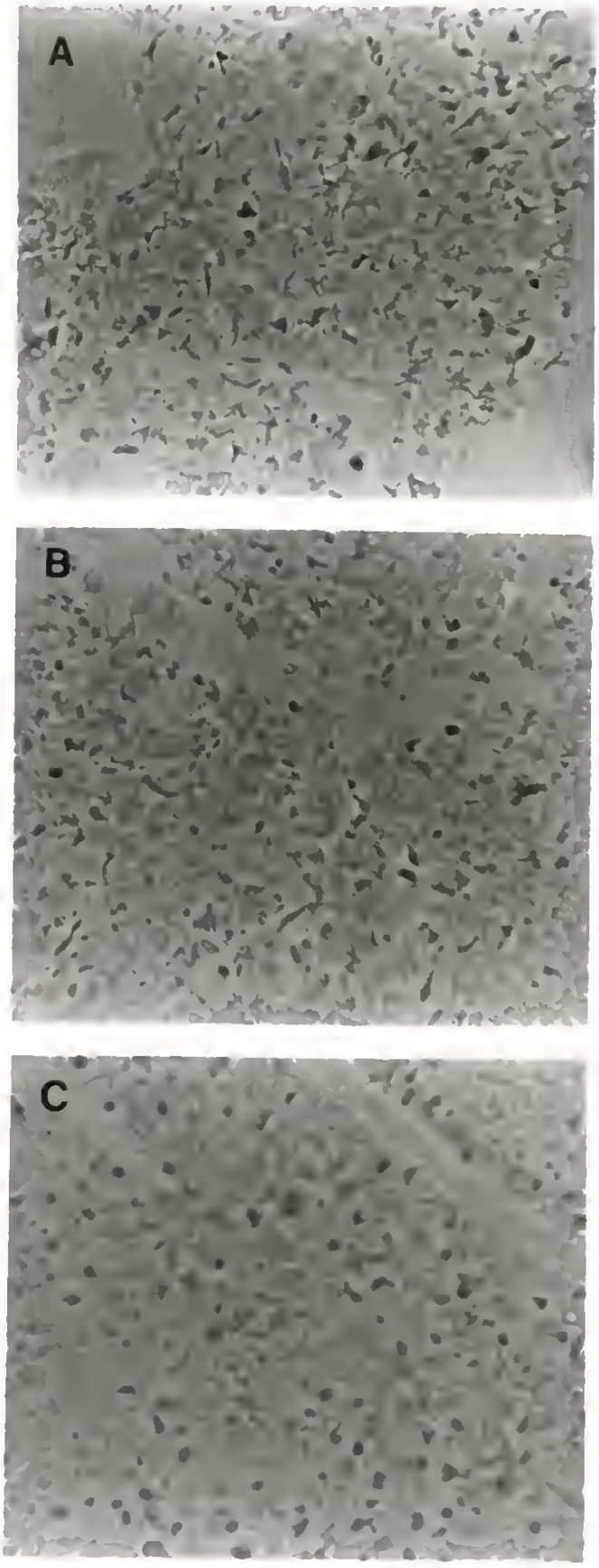

A
B
C

Figure 30. Photomicrographs of Retrograded Defatted Starches Treated 20 Days with 16% H_2SO_4 at 38°C; 30a - potato; 30b - wheat; 30c - corn. All brightfield illumination.


A
B
C

consistant with gelatinization in a limited (50%) water system.

After 6 days of hydrolysis, retrograded potato starch granules (Fig. 29a) were severely cracked and deformed. Microscopic examination of wheat starch (Figure 29b) showed that the majority of starch granules were broken into pieces. Some granules were intact but cracked. Corn starch (Fig. 29c) was very difficult to view but pieces of granules were the only structures to be seen. By the 20th day, solubility had increased by 16.51%, 27.5% and 20.53% for potato, wheat and corn respectively (Table 4). All the starches (Fig. 30) appeared as small pieces amorphous agglomerates plus a very few granules. At this point, as illustrated in Fig. 27, carbohydrate loss from starches was slowing down. Over the last 14 days potato increased 1.66, wheat 1.21 and corn 2.84. Even after retrogradation and acid-heat treatment for 20 days at 38^{o}C, the amount of carbohydrate rendered soluble was less than that solubilized from the native starches treated in a similar manner. 6.98%, potato; 5.22%, wheat and 10.34%, corn starch less than the native starch treated 20 days at 38^{o}C (Table 5).

TA8LE 4. INCREASE in SOLU8ILITY of RETROGRADED STARCHES

RETROGRADED STARCH SAMPLES	20 DAYS 38°C (%)	0 DAYS 38°C (%)	INCREASE in SOLU8ILITY (%)
POTATO	81.38	64.87	16.51
WHEAT	76.47	48.97	27.50
CORN	73.73	53.20	20.53

TABLE 5. INCREASE in SOLUBILITY (NATIVE vs RETROGRADED)

STARCH SAMPLES	NATIVE 20 DAYS 38°C (%)	RETROGRADED 20 DAYS 38°C (%)	INCREASE in SOLUBILITY (%)
POTATO	88.36	81.38	6.98
WHEAT	81.69	76.47	5.22
CORN	84.07	73.73	10.34

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BIBLIOGRAPHY

American Association of Cereal Chemists. 1975. Approved Methods of the AACC. Method 44-15, approved April 1961. The Association, St. Paul, MN.

Banks, W. and Greenwood, C.T. 1975. Starch and Its Components, Wiley, New York.

Banks, W. and Muir, D.D. 1980. Structure and Chemistry of the Starch Granule. Biochem. of Plants 3:321.

Berry, C.P., D'Appolonia, B.L. and Giles, K.A. 1971. The Characterization of Triticale Starch and Its Comparison with Starches of Rye, Durum and HRS Wheat. Cereal Chem. 48(4):415.

Biliaderis, G.C., Maurice, T.J. and Vose, J.R.1980. Starch Gelatinization Phenomena Studied by DSC. J.Food Sci. 45:1669.

Christensen, C. 1982. Storage of Cereal Grains and Their Products. 3rd Ed. Amer. Ass. of Cereal Chem., Inc., St. Paul, MN.

Collison, R. and Chilton, W.G. 1974. Starch Gelatinization as a Function of Water Content. J. Food Tech. 9:309.

Donovan, J.W. 1979. Phase Transitions of the Starch - Water System. Biopolymers 18:263.

Dreher, M.L. and Berry, J.W. 1983. Buffalo Gourd Root Starch Part I. Properties and Structure. Staerke 35:76.

Ellison, A.C. 1980. Effect of Water Content on the Gelatinization of Wheat Starch. Staerke 32:270.

Evans, I.D. and Haisman, D.R. 1982. The Effect of Solutes on the Gelatinization Temperature range of Potato Starch. Staerke 34:224.

Faubion, J.M. 1983. Personal Communication, Kansas State Univ.

French, D. 1984. Organization of Starch Granules. page 183 in: Starch : Chemistry and Technology 2nd Ed. Whistler, R.L., BeMiller, J.N. and Paschall, E.F. ed. Academic Press, New York.

Ghiasi, K., Hoseney, R.C. and Varriano-Marston, E. 1982 b. Gelatinization of Wheat Starch III. Comparison by Differential Scanning Calorimetry and Light Microscopy. Cereal Chem. 59(4):258.

Ghiasi, K., Varriano-Marston, E. and Hoseney, R.C. 1982 a. Gelatinization of Wheat Starch IV. Amylograph Viscosity. Cereal Chem. 59(4):262.

Hizukuri, S. 1961. X-Ray Diffractometric Studies on Starches. Part VI. Crystalline Types of Temperature and Concentration of Mother Liquor on Crystalline Type. Agri. Biol. Chem. 25(1):45.

Hodge, J.E. and Osman, E.M. 1976. "Carbohydrates". page 103 in: Principles of Food Science Part I. O.R. Fennema, ed. Marcel Dekker, Inc. New York.

Kainuma, K. and French, D. 1971. Nageli Amylodextrin and Its Relationship to Starch Granule Structure. I. Preparation and properties of Amylodextrins from Various Starch Types. Biopolymers 10:1673.

Kugimiya, M., Donovan, J.W. and Wong, R.Y. 1980. Phase Transitions of Amylose-Lipid Complexes in Starches: A Calorimetric Study. Staerke 32:265.

Lindquist, I. 1979. Cold Gelatinization of Starch. Staerke 31:195.

Lineback, D.R. 1984. The Starch Granule: Organization and Properties. Bakers Digest 58(2):16.

Matsukura, U., Matsunaga, A. and Kainuma, K. 1983. Structural Studies on Retrograded Normal and Waxy Corn Starches. J. Jpn. Soc. Starch Sci. 30(1):106.

Pomeranz, Y. 1971. Composition and Functionality of Wheat Flour Components. page 585 in: Wheat : Chemistry and Technology, Pomeranz, Y. ed. Amer. Ass. Cereal Chem.: St. Paul, MN.

Stevens, D.J. and Elton, A.H. 1971. Thermal Properties of the Starch/Water System I. Measurement of Heat of Gelatinization by Differential Scanning Calorimetry. Staerke 23:8.

Sterling, C. 1960. Molecular Association of Stach at High Temperature.

Staerke 12:78.

Umeki, K. and Kainuma, K. 1981. Fine Structure of Nageli Amylodextrin Obtained by Acid Treatment of Defatted Waxy-Maize Starch. Structural Evidence to Support the Double Helix Hypothesis Carbohydrate Research 96:143.

Varriano-Marston, E., Ke, V., Huang, G. and Ponte, J. Jr. 1980. Comparison of Methods to Determine Starch Gelatinization in Bakery Foods. Cereal Chem. 57(4):242.

Wendlandt, W.W. 1974. Thermal Methods of Analysis, Second Edition. P.J. Elving and I.M. Kolthoff, ed. John Wiley & Sons, New York, NY.

Whistler, R.L. 1953. Starch and Its Derivatives. page 213 in: Radleys, J.A. Starch and Its Derivatives.

Whistler, R.L. and Daniel, J.R. 1984. Molecular Structure of Starch. page 153 in: Starch: Chemistry and Technology 2nd Ed. Whistler, R.L., BeMiller, J.N. and Paschall, E.F., ed. Academic Press, New York.

Wolf, M. J. 1964. Wheat Starch page 6 in: Methods in Carbohydrate Chemistry, Vol. IV. R.L. Whistler, ed. Academic Press, New York.

Wooton, M. and Bamunuarachchi, A. 1979 a. Application of Differential Scanning Calorimetry to Starch Gelatinization I. Commercial, Native and Modified Starches. Staerke 31:201.

Wooton, M. and Bamunuarachchi, A. 1979 (b). Application of Differential Scanning Calorimetry to Starch Gelatinization II. Effect of Heating Rate and Moisture Level. Staerke 31:262.

Zobel, H.F. 1964. X-Ray Analysis of Starch Granules. page 109 in: Chemistry Vol. IV. R.L. Whistler, ed. Academic Press, New York.

Zobel, H.F. and Senti, F.R. 1959. THe Bread Staling Problem. X-Ray Diffraction Studies on Breads Containing a Cross-Linked Starch and a Heat-Stable Amylase. Cereal Chem. 36(4):441.

STUDIES ON CEREAL AND TUBER STARCHES

by

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AN ABSTRACT OF A MASTER'S THESIS

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ABSTRACT

Chemical and physical properties of cereal and tuber starches were studied by Differential Scanning Calorimetry (DSC), X-ray diffraction, and the production of Nageli amylodextrins. The gelatinization energy (enthalpy) as a function of water content over water:starch ratios of 2:1, 1:1, and 0.5:1 were determined. Millet, oat, triticale, corn, barley, and wheat starches required between 3.2 and 2.4 cal/g excess water. As water content was reduced the ΔH decreased to 2.6 and 1.8 cal/g. Tuber starches (potato and buffalo gourd) required more energy to gelatinize at all water levels than did the cereal starches tested. The gelatinization energy for waxy corn, sorghum, and barley was intermediate to the values required for the cereal and tuber starches. The production of soluble carbohydrate during Nageli amylodextrin production from potato, wheat, and corn was analyzed over time at two incubation temperatures. By elevating the temperature (22°C vs 38°C), both rate of solubilization and the total percent of carbohydrate solubilized increased. At 38°C, a bimodal effect was observed, while at 22°C a linear increase occurred. Potato and corn starch were more heat sensitive than wheat starch, thus increasing their percent of soluble carbohydrates. Water absorption by wheat starch and its Nageli amylodextrins were determined by blue dextran exclusion at both 1 and 2 days of testing the Nageli amylodextrins absorbed greater amounts of water than did the native starch. It also appeared that some Blue Dextran may be able to penetrate the granule or be adsorbed to its surface. These same starches were also retrograded and their crystalline organization determined. The effect of time (7 days vs 21

days) on the X-ray diffraction patterns were studied. After 7 days, a weak V pattern was present along with indications of amorphous areas. At 21 days, a stronger V pattern was present with a superimposed A or B pattern. The effect of retrogradation on the solubility in acid was also observed. The rate of solubilization was curvilinear and the total percent of carbohydrate solubilized from retrograded starch was less than that of the native starch tested. Appropriate photographs illustrate the effects of acid-heat treatment on starch granules.