Retrogradation of Amylopectin from Maize and Wheat Starches[1]

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ABSTRACT

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Differential scanning calorimetry was used to study retrogradation of amylopectin (AP) isolated from corn and wheat starches. Corn AP developed more crystallinity during storage (as demonstrated by higher enthalpy [ΔH] values) than did wheat AP; most of the recrystallization occurred during the first week of storage. An increase in onset temperature of melting (T_0) (annealing of the crystallites) continued during two weeks of storage. As AP concentration was increased from 25 to 45% (w/v), ΔH increased and T_0 decreased. Therefore, although more crystallites were formed at higher concentrations, those formed at lower concentrations achieved a higher degree of annealing. Retrogradation effects were determined for some common food additives: NaCl (4%, based on weight of AP); citric acid (3.5%); sodium stearoyl lactylate (0.5%); or sucrose, glucose, and fructose (100%). The ΔH of corn AP gels were not affected by any of the additives. The ΔH of wheat AP gels were not affected by sodium stearoyl lactylate or the sugars, but the ΔH of wheat AP decreased with NaCl. The rate of recrystallization was changed with citric acid. T_0 of corn AP gel was not affected by NaCl or citric acid. The T_0 of wheat AP, however, decreased with NaCl. The rate of annealing decreased with citric acid. T_0 of both amylopectins was decreased by sodium stearoyl lactylate and increased by sugars.

Starch retrogradation has been defined as "a process which occurs when the molecules comprising gelatinized starch begin to reassociate in an ordered structure" (Atwell et al 1988). Retrogradation affects the texture and acceptability of many starch-containing foods. How this process is affected by interactions between starch and other food components needs to be understood to better control the keeping quality of starchy food products.

Extent of retrogradation, and the nature of the crystallites formed, may be affected by: starch source (Orford et al 1987); concentration (Zeleznak and Hoseney 1986, Orford et al 1987, Slade and Levine 1987); storage temperature (Slade and Levine 1987, Eliasson and Ljunger 1988); salts (Morsi and Sterling 1963, Ciacco and Fernandes 1979); acids (Muhrbeck and Eliasson 1987, Russell and Oliver 1989); lipids and surfactants (Lagendijk and Pennings 1970, De Stefanis et al 1977, Germani et al 1983, Russell 1983, Batres and White 1986, Evans 1986, Hahn and Hood 1987, Eliasson and Ljunger 1988, Krog et al 1989); and sugars (Maxwell and Zobel 1978, Germani et al 1983, Slade and Levine 1987).

Although both starch amylose (AM) and amylopectin (AP) are subject to retrogradation, the AP component appears to be more responsible for long-term quality changes in foods (Miles et al 1985, Ring et al 1987). Therefore, this study has focused on AP retrogradation. The objectives were: 1) to study retrogradation of AP from maize (corn) and wheat starches, and 2) to determine the influence of various food additives on retrogradation.

MATERIALS AND METHODS

All chemicals used in this study were reagent grade. The sodium stearoyl lactylate (SSL) was obtained from Grindsted Products, Inc., Industrial Airport, KS.

Isolation of Amylopectin

A slurry of 60 g of corn starch (American Maize-Products Co., Hammond, IN) or wheat starch (Midwest Grain Products, Atchison, KS) in 3,000 ml of water was held at 85°C for 1 hr with slow stirring and then centrifuged. The AM-rich supernatant was decanted. The AP-rich precipitate was dissolved in 1 L of 1*N* KOH at 10°C (Potter et al 1953), stirred for 2 hr, and neutralized with 4*N* HCl. The solution was heated to 95°C, and thymol was added to precipitate the remaining AM (Banks and Greenwood 1967). After two days at room temperature (23 ± 1°C), the solution was centrifuged; the supernatant was decanted and mixed with an equal volume of methanol. After the mixture stood for one day at room temperature, the precipitated AP was isolated by centrifugation and blended with fresh methanol. The procedure was repeated three times. The AP was collected by filtration and dried at 40°C. Products from all batches were combined and thoroughly blended to ensure uniformity and to minimize variability in AP quality because of batch processing. The purity of the final products was determined by iodine binding capacity using potentiometric titration (Schoch 1964).

Chain Length Distribution

High-performance anion-exchange chromatography with pulsed electrochemical detection was used to compare the distribution of chain lengths of the corn and wheat AP using the method of Koizumi et al (1989). Amylopectin samples were prepared by dissolving 40 mg of AP in 20 ml of 40 m*M* acetate buffer (pH 3.8) and debranching with 20 μl of isoamylase (Hayashibara Biochemical Labs, Okayama, Japan) for 24 hr at 45°C. The reaction was stopped by boiling for 10 min. The samples were centrifuged and filtered before analysis by high-performance anion-exchange chromatography; 20 μl of solution (1 mg of AP per milliliter of solution) were injected. Analyses of both amylopectins were performed on the same day.

Differential Scanning Calorimetry

The differential scanning calorimetry (DSC) used a DSC-2 calorimeter (Perkin-Elmer, Norwalk, CT) equipped with a flexi-cooler and temperature controller (FTS Systems, Stone Ridge, NY) calibrated with indium. Data were collected and analyzed using DSC software (DARES, 1987, v1.4; Industrial Technology Research Institute, Cambridge, UK). The temperature range of the scan was 7–127°C at 10°C/min. Enthalpy (ΔH), the energy required to melt the crystalline material, was used as the index of crystallinity in the samples. ΔH was determined by measuring the area of the DSC endotherm. Onset temperature of the endothermic transition (T_0) was determined as the point at which a line extrapolated from the baseline crossed the line extrapolated from the leading edge of the endotherm peak (Russell 1987).

For control samples, AP was weighed directly into calorimeter aluminum sample pans using a Cahn 21 automatic electrobalance (Cahn Instruments, Cerritos, CA). Water was added using a microliter syringe and allowed to evaporate until the desired moisture

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content was attained. The pan was sealed quickly to prevent further moisture loss and then reweighed. Samples were heated from 7 to 127°C using the calorimeter and stored at 1°C for one day. The samples were then stored at room temperature (23 ± 1°C) for periods of one to four weeks. Subsequently, the samples were reheated in the calorimeter to evaluate retrogradation.

Samples with additives were prepared by different methods, depending on the nature and concentration of the additive. Amounts to be added were determined based on relative amounts of such additives used in baked products. Citric acid and sodium chloride were each dissolved in water and added to the sample pans using a microliter syringe to give concentrations of 3.5 and 4.0% (w/w, based on weight of AP), respectively. The starch-to-water ratio was 0.35:0.65. A solution of 3.5 g of citric acid in 65 ml of water gave pH 2.0. A mortar and pestle was used to blend SSL with AP at 0.5% (w/w, based on weight of AP). The mixture was then weighed into sample pans.

The percentage of sugar by flour weight commonly ranges from 6% in breads to more than 100% in cakes (Pyler 1988). This is equivalent to ~12.5–200% of the weight of AP in these products. Three sugars (sucrose, glucose, or fructose) were used at a level of 100% of the AP. They were dissolved in water and added as a solution to the AP in the sample pans. In additional experiments, the AP was allowed to retrograde, and then the sugars were added.

Statistical Analysis

All DSC experiments were replicated at least twice. Means and standard errors were obtained using the general linear model (SAS Institute, Cary, NC).

RESULTS AND DISCUSSION

The AP isolated from corn and wheat starches had iodine affinities of 1.9 and 1.6%, respectively. This corresponded to AM contents of ~7.3% for the corn AP and ~5.6% for the wheat AP, assuming that pure amylose has an iodine affinity of 20% (Takeda et al 1984) and that starch lipids were not present.

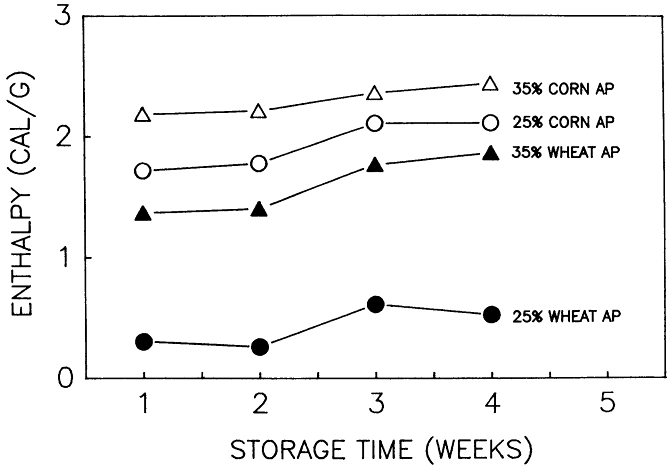

Fig. 1. Enthalpy values of retrograded corn and wheat amylopectin (AP) in gels stored at 23°C, as determined by differential scanning calorimetry.

Retrogradation of Amylopectins in Water

Most recrystallization appears to occur within the first week of storage, because ΔH increased only slightly from one to four weeks of storage at 23°C. The retrograded corn AP had higher ΔH than did wheat AP (Fig. 1), indicating that corn AP developed more crystallinity during storage. This may be explained by the fact that the degree of crystallinity in native corn starch granules is higher than that in native wheat starch granules. This is shown by higher ΔH for initial gelatinization of corn starch (Table I). Kalichevsky et al (1990) reported that the shear modulus increased faster for a gel of corn AP than it did for a gel of wheat AP, which agrees with our findings. Zobel (1984), using x-ray diffraction, also found corn starch to be more crystalline than wheat starch. When recrystallization is compared on a percentage basis (Table I), the percentage of recrystallization in corn starch was greater than that in wheat starch.

The differences between the retrogradation of the two amylopectins may also be explained by differences in their unit chain lengths (Table II). Corn AP has some very short chains (DP 4–5) and more chains of DP 15–20 than wheat AP has. Wheat AP has a greater proportion of chains in the range of DP 9–13 than corn AP has. The higher proportion of the DP 15–20 chains in the corn AP may explain its rapid retrogradation, compared to that of wheat AP.

There was an indication that the crystallites continued to anneal for up to two weeks of storage, because T_0 increased during weeks 1 and 2, with little change thereafter (Fig. 2). No differences were found between T_0 of retrograded corn AP and retrograded wheat AP at the 35% concentration level. Only a small difference (1–2°C) was found at the 25% level. This was in contrast to the T_0 temperatures of the granular starches: native corn starch melted at about 66°C, some 9°C higher than the temperature at which wheat starch melts (Table I). Melting temperature of retrograded AP crystallites was 8–22°C lower than the gelatinization temperature of native starches. This may relate to the role of the granular structure, which affects plasticization of crystallites by water during gelatinization (Levine and Slade 1987). Furthermore, retrograded AP from corn or wheat starch is the B-polymorphic crystal, containing 32 water molecules, compared to the A-crystal of both native starches containing four water molecules (Imberty and Perez 1988, Imberty et al 1988). The high water content in the B-crystals may tend to give them the same melting point.

Extent of retrogradation was dependent on concentration of AP; ΔH increased as concentration increased from 25 to 45% (Fig. 1). Zeleznak and Hoseney (1986) found that maximum ΔH occurred in wheat starch gels at 50–60% starch solids, which would correspond to 37.5–45% AP, when stored at 25°C for seven days. Minimal enthalpy resulted in gels with less than 15% or more than 80% starch. Thus, there appears to be an optimum concentration for recrystallization.

T_0 was highest at the 25% level of both corn and wheat AP (Fig. 2). At lower AP concentration or higher moisture content, the AP chains would have more mobility, thus allowing the annealing process to proceed further.

TABLE I
Gelatinization of Corn and Wheat Starches and Recrystallization After Four Weeks of Storage at 23°C

	Native Starches		Gels	
Level of Concentration, %	Initial Enthalpy (cal/g)	T_0[a] (°C)	Enthalpy After Four Weeks (cal/g)	Recrystallization (%)
Corn Starch				
25	3.14 a[b]	66.5 c	1.58 e	50.3
35	3.22 a	65.5 c	2.06 f	63.8
Wheat Starch				
25	2.71 b	57.8 d	0.77 g	28.2
35	2.64 b	57.1 d	1.40 h	53.0

[a] Onset temperature.

[b] Values with same letter are not significantly different ($P < 0.05$).

Effect of Salt, Citric Acid, and SSL on Retrogradation

The presence of 4% (w/w) sodium chloride did not significantly affect the ΔH of retrograded corn AP (Table III). However, wheat AP gels exhibited a significant decrease in ΔH with sodium chloride. The latter results are in agreement with Russell and Oliver (1989), who found that ΔH decreased as sodium chloride concentration increased in wheat starch gels. They also agree with results of Chang and Lin (1991) for rice starch. T_0 of corn AP samples containing NaCl was not significantly different than that of the control after three weeks of storage. Wheat AP samples with NaCl, however, had significantly lower T_0 after four weeks of storage.

Sodium chloride appeared to have no consistent effect on T_0 of retrograded AP. At the molarity examined in this work (0.4*M*), T_0 of raw starch was increased by about 4°C (Sandstedt et al 1960). This could reflect a difference in mechanism in each case. In recrystallization, sodium chloride could interfere with the annealing process. Less annealing is shown by the lower melting temperature. In gelatinization, sodium chloride may be acting in its role as a swelling inhibitor (Oosten 1990).

Citric acid (3.5%, w/w) had virtually no effect on retrogradation of corn AP (Table IV). However, it produced ΔH values that were significantly higher for wheat AP until the fourth week of storage. Although ΔH for the wheat control samples gradually increased with time, samples with citric acid showed a larger increase from week 1 to week 2 and a gradual decline thereafter, so that the two lines converged with time.

T_0 of corn AP was unaffected by citric acid (Table IV). However, in the wheat AP, citric acid apparently slowed annealing of the crystallites, as reflected in the change in the rate at which T_0 increased. In results similar to those with NaCl, wheat starch appears to be sensitive to ionic material, but corn starch is not.

An experiment was conducted to determine the reason for the effects of citric acid on wheat AP recrystallization. To test the effects of lower pH, the pH was reduced to 2.0 with 0.01*N* HCl.

TABLE II
Chain Length Distribution (DP) of Corn and Wheat Amylopectin (AP)[a]

DP	Height of Peak, cm Corn AP	Wheat AP
4	2.20	...
5	1.00	...
6	1.45	1.00
7	2.20	1.00
8	2.50	1.75
9	4.80	5.20
10	7.35	9.10
11	8.35	10.80
12	8.15	9.80
13	7.05	7.40
14	6.60	6.70
15	5.80	5.70
16	5.10	4.70
17	4.10	3.60
18	3.70	3.20
19	3.30	3.10
20	3.00	2.90
21	2.60	2.60
22	2.20	2.30
23	1.90	1.95
24	1.50	1.60
25	1.30	1.30

[a] Determined by high-performance anion-exchange chromatography.

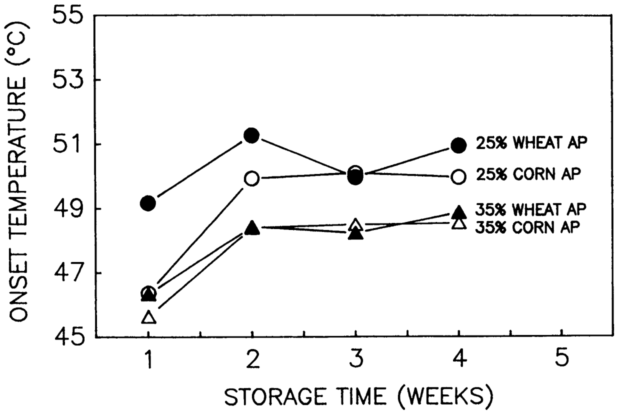

Fig. 2. Onset temperatures of retrograded corn and wheat amylopectin (AP) in gels stored at 23°C, as determined by differential scanning calorimetry.

TABLE III
Effects of Sodium Chloride[a] on Enthalpy Values and Onset Temperatures of Retrograded Corn and Wheat Amylopectin (AP) at 35% Concentration

AP at Weeks of Storage	Enthalpy Value (cal/g) Control	NaCl	Onset Temperature (°C) Control	NaCl
Corn				
1	2.19 ab[b]	2.16 ab	45.63 d	45.10 d
2	2.21 bc	2.04 a	48.40 ef	49.00 e
3	2.36 c	2.42 c	48.50 eg	47.75 f
4	2.44 c	2.18 ab	48.53 e	47.85 fg
Wheat				
1	1.37 a	1.14 c	46.33 e	45.10 d
2	1.40 a	1.09 c	48.43 gh	49.20 h
3	1.77 b	1.53 a	48.23 f–h	47.50 fg
4	1.86 b	1.29 ac	48.87 h	47.35 ef

[a] 4.0%, w/w, based on AP.

[b] Values with same letter within AP classification are not significantly different ($P < 0.05$).

TABLE IV
Effects of Citric Acid[a] on Enthalpy Values and Onset Temperatures of Retrograded Corn and Wheat Amylopectin (AP) at 35% Concentration

AP at Weeks of Storage	Enthalpy Value (cal/g) Control	Citric Acid	Onset Temperature (°C) Control	Citric Acid
Corn				
1	2.19 a[b]	2.26 a–c	45.63 e	45.35 e
2	2.21 ab	2.52 d	48.40 f	48.75 f
3	2.36 b–d	2.41 c	48.50 f	48.80 f
4	2.44 d	2.50 d	48.53 f	49.10 f
Wheat				
1	1.37 a	1.68 b	46.33 f	45.10 g
2	1.40 a	2.20 e	48.43 hi	46.00 f
3	1.77 b	1.99 de	48.23 hi	47.75 h
4	1.86 b–d	1.92 cd	48.87 i	48.25 hi

[a] 3.5%, w/w, based on weight of AP.

[b] Values with same letter within AP classification are not significantly different ($P < 0.05$).

TABLE V
Effects of Citric Acid, Hydrochloric Acid, and Sodium Citrate on Enthalpy Values and Onset Temperatures of Retrograded Wheat Amylopectin at 35% Concentration

	Weeks of Storage 1	2	3	4
Enthalpy value, cal/g				
Control	1.37 a[a]	1.40 a	1.77 b–d	1.86 c–e
Citric acid[b]	1.68 b	2.20 f	1.99 e	1.92 de
HCl	1.42 a	1.63 b	1.69 bc	1.79 b–d
Sodium citrate	1.06 f	0.98 f	1.02 f	0.41 g
Onset temperature, °C				
Control	46.66 a	48.43 cd	48.23 cd	48.87 dfg
Citric acid	45.10 b	46.00 a	47.75 ce	48.25 cd
HCl	47.40 e	48.60 df	49.45 gh	49.90 hi
Sodium citrate	48.45 cdf	49.20 f–h	50.90 i	52.50 j

[a] Values with the same letter are not significantly different ($P < 0.05$).

[b] 3.5%, w/w, based on weight of amylopectin.

Sodium citrate, at the same molar concentration ($0.1M$) as citric acid, was added to wheat AP gels to evaluate the effects of the citrate ion. Lowering the pH with HCl had no effect on ΔH (Table V), but did slightly increase T_o. Sodium citrate ($0.1M$) appeared to behave like sodium chloride ($0.1M$) and reduced the extent of retrogradation of wheat AP.

The extent of AP retrogradation was not affected significantly by SSL (Table VI). Although ΔH of control samples increased gradually over the four weeks of storage, ΔH of samples with added SSL did not increase after two weeks of storage. Similar results were found when SSL was added to native starches; differences in ΔH between control samples and those with SSL were not significant (Table VI).

The presence of SSL did affect T_o in the AP samples. Although T_o for the corn AP control samples increased during one to two weeks of storage and then remained stable, the samples with SSL showed a gradual increase in T_o for the entire four weeks of storage, finally reaching the same T_o as the control (Table VI). In the wheat AP samples, T_o of the samples with SSL remained lower than that of the control samples for the entire four weeks of storage. Contrary to effects on T_o of isolated AP, T_o of starches was not affected by SSL (Table VII).

These results indicate that 0.5% SSL does not affect the extent of recrystallization (amount of crystallites formed), but it does affect the nature of the crystallites formed when AM is not present. SSL complexes readily with AM (Krog 1971). Thus, SSL complexes with AM in the starches, thereby having no effect on the recrystallization of the AP fraction of the starch. In the isolated AP, where little AM was present, SSL interacted with AP, slowing the annealing of the developing crystallites.

Recent DSC results indicate that AP does complex with surfactants at concentrations of 2–10% (based on weight of AP). Gudmudsson and Eliasson (1990) reported that 2–3% sodium dodecyl sulfate and cetyltrimethylammonium bromide complexed with potato AP, as evidenced by a new endotherm at T_o ~105°C and by the inhibition of retrogradation. Slade and Levine (1987) found evidence of complexing of SSL (one part) with waxy maize starch (nine parts). After the mixture was heated to 120°C and cooled for 24 hr, a new endotherm was found at T_o ~70°C. In contrast, in this study, SSL was ground with the AP in a mortar to obtain a uniform mixture and then weighed in the sample pan with added water. This difference in preparation may be responsible for the different results.

TABLE VI
Effects of Sodium Stearoyl Lactylate (SSL) (0.5%, w/w) on Enthalpy Values and Onset Temperatures of Retrograded Corn and Wheat Amylopectin (AP) at 35% Concentration

AP at Weeks of Storage	Enthalpy Value (cal/g)		Onset Temperature (°C)	
	Control	SSL	Control	SSL
Corn				
1	2.19 a[a]	2.34 a–c	45.63 d	44.00 f
2	2.21 a	2.52 c	48.40 e	44.50 f
3	2.36 a–c	2.24 ab	48.50 e	47.05 g
4	2.44 bc	2.20 a	48.53 e	48.15 e
Wheat				
1	1.37 ab	1.25 a	46.33 fg	45.35 f
2	1.40 a–c	1.60 b–d	48.43 h	45.95 fg
3	1.77 d	1.52 bc	48.23 hi	46.80 fg
4	1.86 e	1.65 c–e	48.87 h	47.05 gi

[a] Values with same letter within AP classification are not significantly different ($P < 0.05$).

TABLE VII
Effects of Sodium Stearoyl Lactylate (SSL) (0.5%, w/w) on Enthalpy Values and Onset Temperatures of Retrograded Corn and Wheat Starches at 35% Concentration

Starch at Weeks of Storage	Enthalpy Value (cal/g)		Onset Temperature (°C)	
	Control	SSL	Control	SSL
Corn				
1	1.86 a[a]	1.92 a	47.85 b	46.65 c
2	1.89 a	2.00 a	48.75 bde	48.50 bd
3	1.87 a	2.10 a	49.70 e–g	49.25 d–f
4	2.06 a	2.04 a	50.25 fg	50.45 g
Wheat				
1	1.23 a	1.24 ab	47.60 de	46.80 d
2	1.25 ab	1.38 a–c	48.80 fg	48.45 ef
3	1.41 a–c	1.51 bc	49.40 fg	49.70 gh
4	1.40 a–c	1.56 c	50.45 hi	50.75 i

[a] Values with same letter within starch classification are not significantly different ($P < 0.05$).

Effect of Sugars on Retrogradation

The ΔH of AP gels containing sugars (AP-sugar-water, 1:1:2, w/w) were not significantly different from those of the controls (Table VIII). T_o of all the samples increased with increased storage time, presumably because of annealing. All the sugars significantly ($P < 0.05$) increased T_o of corn and wheat AP (Table VIII). The effects of sucrose and glucose were similar, but fructose had significantly higher T_o.

To determine whether retrogradation was affected by sugars during recrystallization or only during melting, AP gels were pre-

TABLE VIII
Effects of Sugars (100%, w/w) on Enthalpy Values and Onset Temperatures of Retrograded Corn and Wheat AP at 35% Concentration

	Weeks of Storage			
	1	2	3	4
Enthalpy value, cal/g				
Corn				
Control	2.19 a–c[a]	2.21 a–c	2.36 b–e	2.44 c–e
Sucrose	2.03 a	2.38 b–e	2.38 b–e	2.57 de
Glucose	2.22 a–c	2.57 de	2.29 a–e	2.62 e
Fructose	2.16 a–c	2.27 a–d	2.09 ab	2.26 a–d
Wheat				
Control	1.37 ab	1.40 ab	1.77 ac	1.86 cd
Sucrose	0.53 e	1.28 b	1.28 b	1.64 a–c
Glucose	1.43 a–c	1.23 b	1.55 a–c	2.22 d
Fructose	1.51 a–c	1.56 a–c	1.51 a–c	1.66 a–c
Onset temperature, °C				
Corn				
Control	45.63 a	48.40 b	48.50 b	48.53 b
Sucrose	49.05 bc	50.95 d	51.70 de	52.45 e–g
Glucose	48.70 b	51.35 d	52.25 ef	52.55 fg
Fructose	49.50 c	52.35 ef	53.15 g	54.00 h
Wheat				
Control	49.17 a	51.27 b–e	49.97 ab	50.93 bc
Sucrose	49.45 a	50.45 a–c	50.45 a–c	52.40 d–f
Glucose	49.45 a	51.10 b–d	51.45 c–e	53.10 f
Fructose	47.50 g	51.70 c–f	51.00 b–d	52.70 ef

[a] Values with the same letter within AP classification are not significantly different ($P < 0.05$).

TABLE IX
Effects of Sugars (100%, w/w) on Onset Temperatures of Retrograded Corn and Wheat AP at 35% Concentration Where AP Gels Were Stored at 23°C Before Addition of Sugar Solutions

AP at Weeks of Storage	Onset Temperature (°C)			
	Control	Sucrose	Glucose	Fructose
Corn				
1	46.90 a[a]	56.70 c	57.15 cd	58.85 ef
2	47.50 a	58.00 de	58.05 de	60.50 g
3	49.45 b	57.85 de	59.75 fg	62.70 h
4	49.55 b	59.65 fg	60.55 g	62.15 h
Wheat				
1	46.05 a	54.45 c	56.60 d	59.85 f–h
2	49.35 b	56.45 d	58.25 e	60.60 h
3	49.25 b	57.50 e	59.75 fg	61.50 i
4	49.10 b	59.30 f	60.25 gh	62.25 i

[a] Values with the same letter within AP classification are not significantly different ($P < 0.05$).

pared and stored for four weeks at 23°C. Sugar solutions were added to the retrograded gels just before heating in the calorimeter. Sugars had no significant effects on ΔH of corn or wheat AP (data not shown), but all sugars significantly increased T_0 (Table IX). In corn AP gels, sucrose and glucose increased T_0 to the same extent, whereas fructose increased T_0 significantly more than the other sugars. Similarly, in wheat AP, samples with fructose had the greatest increase in T_0, followed by glucose, and then sucrose. This demonstrates that the increase in T_0 in the presence of sugars is not an effect of crystallite annealing, because the sugars were not present during storage. Furthermore, sugars caused an increase in T_0 despite the absence of the granule structure.

The effects of sugars on retrogradation of starches were also evaluated. Enthalpy values of initial gelatinization were higher in the presence of sugars (Table X). Therefore, ΔH of the retrograded starches were compared on a percentage basis (ΔH after storage/ΔH of initial gelatinization). It was apparent that, in the corn starch samples after four weeks of storage, ΔH values in samples with sucrose were decreased somewhat; in samples with glucose they were slightly increased; and in samples with fructose they were greatly increased. Similar results were seen in the wheat starch samples, except that glucose slightly decreased the percentage of recrystallization. This is interesting in light of the fact that sugars did not affect ΔH of the isolated AP products (Table VIII).

Earlier work (Maxwell and Zobel 1978, Germani et al 1983, Chang and Lin 1991) showed that the rate of retrogradation in wheat and corn starch gels was increased by sucrose, glucose, fructose, and maltose. However, gel rigidity was reduced by glucose and sucrose. Slade and Levine (1987) used DSC to measure the inhibition of retrogradation in wheat starch gels (starch-sugar-water, 1:1:1, w/w) after eight days of storage at 25°C. They reported the order of decreasing retrogradation to be: fructose > blank > glucose > sucrose.

TABLE X
Effects of Sugars (100%, w/w) on Enthalpy Values of Corn and Wheat Starch Gels (35% Starch Solids) Stored at 23°C, as Determined by Differential Scanning Calorimetry

		Enthalpy Values		
Starch	Treatment	Initial Gelatinization (cal/g)	Stored Four Weeks (cal/g)	Four Week Recrystallization (%)
Corn	Control	3.36 a[a]	2.06 g	61.31
	Sucrose	3.69 b	2.17 g	58.81
	Glucose	3.76 b	2.44 h	64.89
	Fructose	3.52 c	2.59 h	73.58
Wheat	Control	2.63 a	1.40 g	53.23
	Sucrose	3.23 b	1.63 h	50.46
	Glucose	3.29 b	1.72 h	52.23
	Fructose	3.01 c	1.96 i	65.12

[a] Values with same letter are not significantly different ($P < 0.05$).

TABLE XI
Effects of Sugars (100%, w/w) on Onset Temperature of Native and Retrograded Corn and Wheat Starch at 35% Concentration, as Determined by Differential Scanning Calorimetry

		Onset Temperature, °C		
Starch	Treatment	Initial Gelatinization	Stored Two Weeks	Stored Four Weeks
Corn	Control	64.9 a[a]	48.8 e	50.3 g
	Sucrose	79.3 b	51.1 f	52.5 g
	Glucose	76.1 c	51.0 f	52.3 h
	Fructose	74.8 d	51.4 f	52.5 h
Wheat	Control	56.6 a	48.8 e	50.5 h
	Sucrose	71.3 b	51.0 fg	52.1 i
	Glucose	68.7 c	50.5 f	52.3 i
	Fructose	67.0 d	51.3 g	52.1 i

[a] Values with same letter within starch classification are not significantly different ($P < 0.05$).

Sugars increased the initial gelatinization temperatures in the order: sucrose > glucose > fructose (Table XI). T_0 of the recrystallized starches was increased the same amount by all the sugars.

To summarize, we found that when sugars were present during the recrystallization process, T_0 values were increased to about the same extent (2–6°C) by all the sugars. However, when sugars were added to an AP gel network or to a granular starch, T_0 values were increased to a greater extent (10–14°C), and the sugars differed in their effects.

CONCLUSIONS

Definite differences were found between corn and wheat AP with respect to extent of retrogradation, as well as their interactions with additives. Retrogradation of corn AP was unaffected by sodium chloride or citric acid. However, wheat AP gels with sodium chloride had lower ΔH and T_0 than did the controls. SSL did not affect ΔH of corn or wheat AP but did decrease T_0 in both products.

Sugars had no effect on ΔH of AP gels but did affect recrystallization of starches. T_0 was increased when sugars were present in AP or starch gels during storage, as well as when they were added to the retrograded AP gels just before heating. The increase in T_0 was greater when sugars were added to native starches or to retrograded gels than when they were present during storage.

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