Physical Characteristics of Wheat Starch Granule Gelatinization in the Presence of Cycloheptaamylose[1]

H. O. KIM and R. D. HILL, Department of Plant Science, University of Manitoba, Winnipeg, Manitoba, Canada R3T 2N2

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ABSTRACT

Cycloheptaamylose (CHA) increased the swelling power and solubility of wheat starch granules during gelatinization. At a concentration of 1.5% CHA, the swelling power of the starch doubled, and the solubility almost tripled at 95°C. The effect of CHA was reduced when the starch was partially defatted. This effect was due largely to an increase in the swelling power and solubility of the starch upon defatting. Amylose leaching was also promoted by CHA. Maximum leaching when CHA was present occurred at lower temperatures than when it was absent. The viscosity of the starch pastes increased approximately fourfold at a CHA concentration of 1.5%. Cycloheptaamylose had little or no effect at or below the gelatinization temperature of the starch on any of the above characteristics. The effects of CHA on starch granule gelatinization are consistent with CHA disrupting lipid-amylose complexes by its complexing with the lipid.

Various agents affect the properties of starch. Several researchers have shown that sugars inhibit swelling and gelatinization of starch (Bean and Yamazaki 1978, Bean et al 1978, Savage and Osman 1978, Wootton and Bamunuarachchi 1980, Spies and Hoseney 1982). Hizukuri and Takeda (1978) examined the effect of lower alcohols on starch gelatinization and found that they promoted gelatinization because of the exchange of alcohols for lipids in the amylose-lipid complex that exists in the starch granules. Surfactants, on the other hand, reduce gelatinization and swelling by preventing hydration of the starch granules (Longley and Miller 1971, Larsson 1980, Hoover and Hadziyev 1981).

Recently, Weselake and Hill (1983) reported that CHA inhibited the adsorption of wheat α-amylase to wheat starch granules and, in so doing, inhibited the release of soluble starch from starch granules because of hydrolytic action.

To assess the direct effects of CHA on starch granules, we have been investigating the swelling and pasting properties of wheat starch in the presence of CHA. Cycloheptaamylose increases the swelling and viscosity of wheat starch granules in a manner consistent with the disruption of lipid-amylose complexes within the granule.

MATERIALS AND METHODS

Starch Analysis

Commercial wheat starch (unmodified) and CHA were obtained from Sigma. Moisture content was calculated from the loss in weight after heating at 130°C for 1 hr. The moisture content of wheat starch and CHA was 10.3 and 11.6%, respectively. Amylose content was determined by the amperometric titration method of Williams et al (1970). The amylose content of the commercial wheat starch was 26.7%.

Total lipid content was determined by extraction of starch with water-saturated butanol (WSB) at 95°C for 5.5 hr, according to the method of Morrison et al (1980).

Gelatinization temperatures were determined by use of a polarizing microscope equipped with a Koefler hot stage. The rate of temperature increase was 2°C/min.

Swelling Power and Solubility

The method described by Schoch (1964) was used to determine swelling power and solubility of native and defatted wheat starch. One gram of the starch was suspended in 30 ml of double-distilled water in a tared, 50-ml centrifuge bottle. The suspension was mechanically stirred with a small stainless-steel paddle at a rate just sufficient to keep the starch completely suspended. The bottle was placed in a water bath and maintained at the desired temperature while stirring for 30 min. After centrifugation at 1,000 × *g* for 15 min, the clear supernatant was carefully drawn off by suction. Soluble carbohydrate in the supernatant was determined by the phenol-sulfuric acid method (Dubois et al 1956).

Preparation of Defatted Starch

Wheat starch was extracted four times at 40°C with 10 volumes of WSB for a total of 48 hr under N_2 atmosphere. After each extraction, the WSB-starch mixture was filtered through a Buchner funnel under reduced pressure. The combined WSB extracts were concentrated in a vacuum rotary evaporator at 60°C. The dried extract was redissolved in $CHCl_3$, filtered through Whatman No. 3 paper, redried by the rotary vacuum evaporator, and weighed.

The defatted starch was washed with double-distilled water three times and air-dried at 20°C.

Viscosity Measurements

A Brookfield model LVT with a No. 1 spindle was used. The viscosity of a suspension containing 1 g of starch in 30 ml of double-distilled water was measured at 30 and 60 rpm after heating for 30 min at specified temperatures.

RESULTS AND DISCUSSION

Swelling Power and Solubility

Because it is an oligosaccharide, cycloheptaamylose (CHA) can act as an inhibitor of swelling during gelatinization, as demonstrated for sugars (Bean and Yamazaki 1978, Bean et al 1978, Savage and Osman 1978). Alternatively, since it includes fatty acids (Schlenk and Sand 1961, Szejtli and Bánky-Elöd 1975), it can increase swelling and solubility by binding fatty acids. Figures 1 and 2 demonstrate that, for concentrations up to 1.5%, CHA increased swelling power and solubility in both native and defatted wheat starch. The effects of CHA were more pronounced as the temperature of the starch paste increased. Up to 75°C, CHA had only a slight effect on swelling power (Fig. 1), whereas the solubility of starch increased from 5% with no CHA added to 18% with 1.5% CHA (Fig. 2a). Above 75°C, swelling power and solubility of the paste were strongly affected by CHA in native wheat starch. Defatting the starch reduced the effect of CHA on swelling power by increasing the swelling of samples containing no CHA (Fig. 1b). Defatting also increased the solubility of the starch (Fig. 2b), thus reducing the effect of added CHA on solubility.

Cycloheptaamylose is more effective in increasing swelling power and solubility during the second stage of gelatinization, in which extensive hydration occurs and solubilized starch is released. This is further substantiated by the observation that CHA had only a slight effect on the gelatinization temperature of wheat starch (Table I). There was a small increase in the gelatinization

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temperature range, suggesting that at these temperatures the CHA may be restricting water entry. Solutes, such as salt and sugar, increase starch-gelatinization temperature (Derby et al (1975) because of the competition between starch and solute for available water. In our case, the change in gelatinization temperature range is small, since the CHA concentration is low (1.5%).

Amylose Leaching

Cycloheptaamylose promoted the leaching of amylose from native wheat starch granules during gelatinization (Fig. 3a) at temperatures above the gelatinization temperature. A concentration between 0.5 and 1.0% gave maximal effect except at temperatures approaching 95°C, at which all three CHA concentrations gave similar values of 82%. Defatting the wheat starch increased amylose leaching at all temperatures measured (Fig. 3b), whereas leaching of amylose was almost complete at 95°C, whether or not CHA was present. As in native wheat starch, CHA promoted amylose leaching above the gelatinization temperature in defatted starch and it had a greater effect on defatted starch than on native starch below 85°C.

It is known that lipid complexing of amylose prevents amylose leaching from starch granules (Gray and Schoch 1962, Hoover and Hadziyev 1981, Ghiasi et al 1982), possibly because of a hydrophobic interaction between the hydrocarbon chain of the fatty acid and the intrahelical spaces of amylose molecules. Cycloheptaamylose increased amylose leaching and, in this regard, it had an effect similar to defatting of wheat starch granules. There are some differences in the effect of CHA, because defatting did not completely eliminate increased leaching by CHA (Fig. 3b). It is difficult to completely remove lipid from starch granules without denaturing the starch (Morrison 1981). Our preparation contained 0.44% lipid, which is equal to the approximate one-third of the total lipid in native wheat starch. This residual lipid is probably internal starch lipid (Morrison 1981). It is, therefore, possible that the effect of CHA on defatted starch granules is due to complexing of the internal lipid by CHA.

Viscosity

The viscosity of wheat starch suspensions during gelatinization was increased by the addition of CHA (Fig. 4). Little effect was observed at temperatures below 65°C, but as temperatures increased the effect of CHA increased. At 95°C, the viscosity in the presence of 0.5% CHA was 2.5 times greater than in a sample

TABLE I
Effect of Cycloheptaamylose (CHA) on the Gelatinization Temperature of Wheat Starch Granules[a]

Fraction with No Birefringence (%)	Wheat Starch[b] (°C)	Wheat Starch[b]+ 1.5% CHA (°C)
10	53.3 ± 1.2	55.7 ± 1.4
50	60.1 ± 0.2	61.0 ± 0.5
90	62.1 ± 0.4	65.2 ± 0.6

[a]All values are means of four trials.
[b]0.1% (w/v).

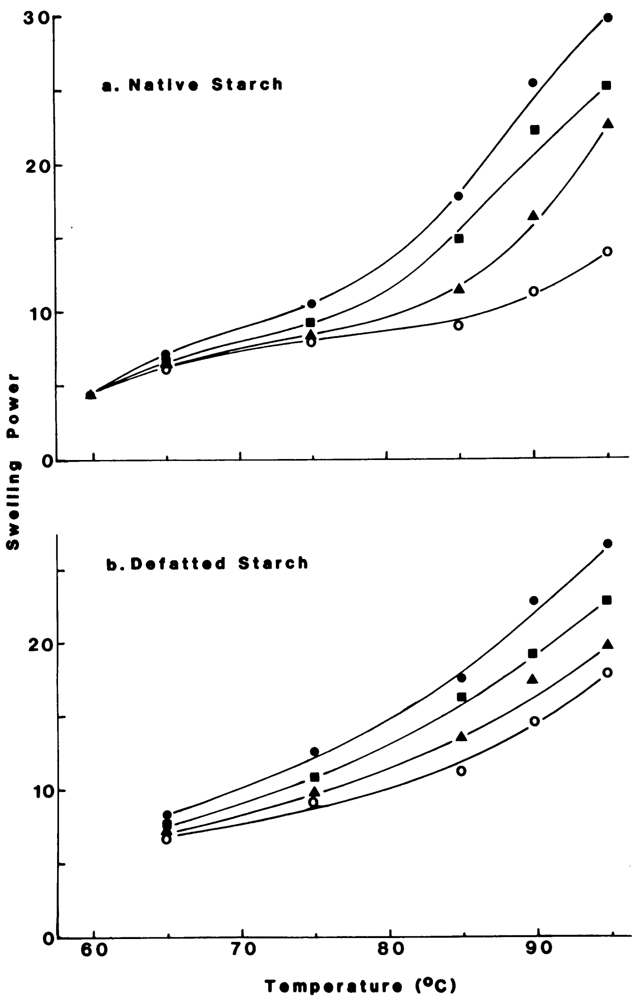

Fig. 1. Effect of cycloheptaamylose (CHA) on the swelling power of native and defatted wheat starch. o = 0% CHA, ▲ = 0.5% CHA, ■ = 1.0% CHA, and ● = 1.5% CHA.

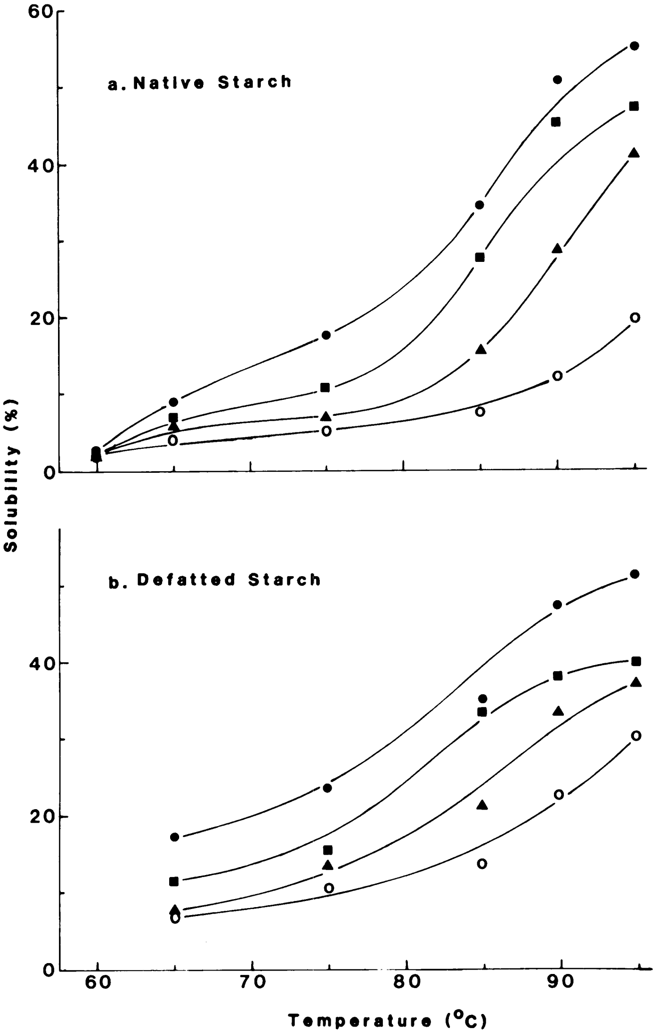

Fig. 2. Effect of cycloheptaamylose (CHA) on the solubility of native and defatted wheat starch. o = 0% CHA, ▲ = 0.5% CHA, ■ = 1.0% CHA, and ● = 1.5% CHA.

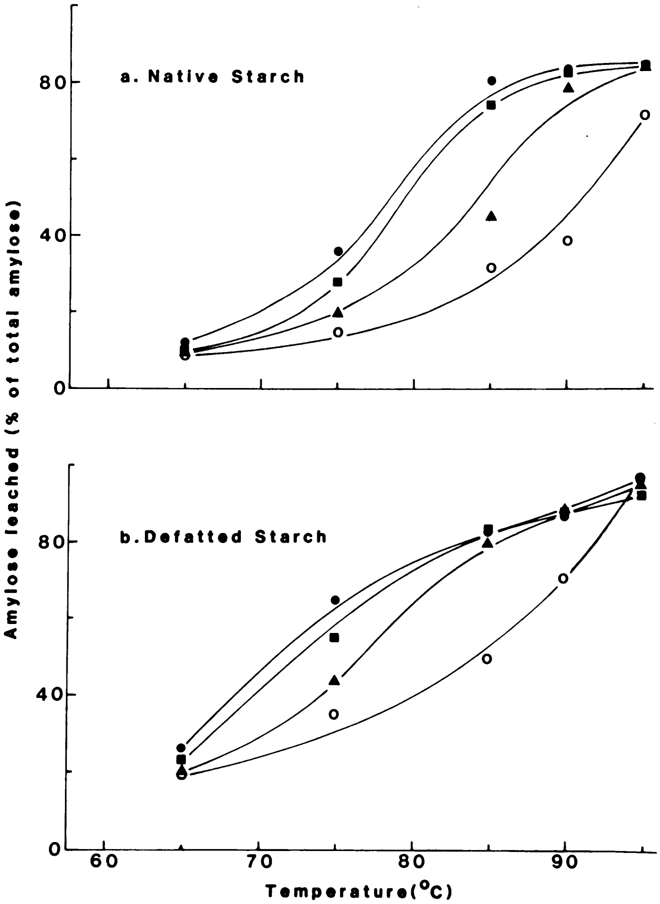

Fig. 3. Effect of cycloheptaamylose (CHA) on amylose leaching of native and defatted wheat starch. o = 0% CHA, ▲ = 0.5% CHA, ■ = 1.0% CHA, and • = 1.5% CHA.

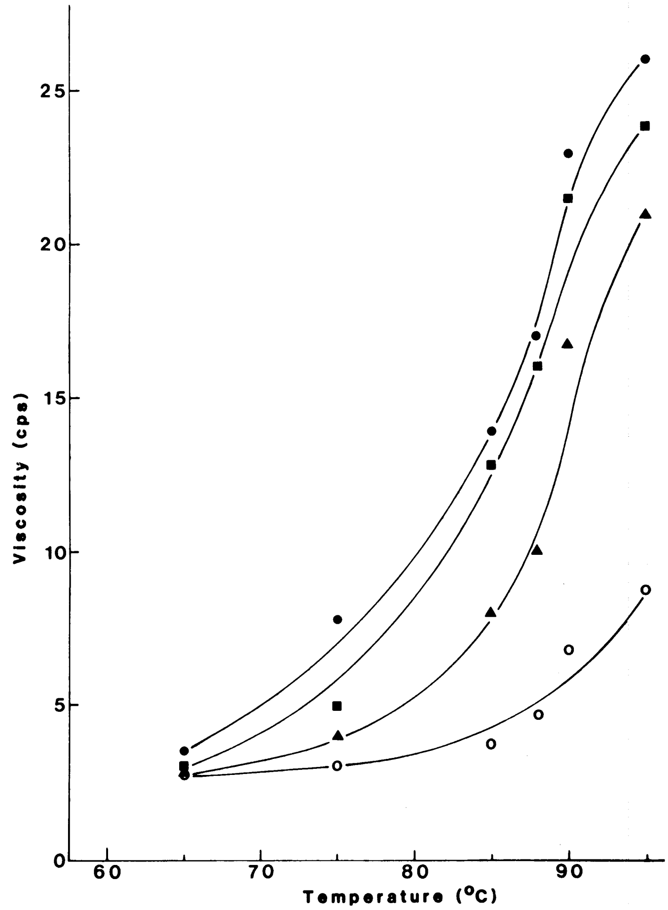

Fig. 4. Effect of cycloheptaamylose (CHA) on the viscosity of wheat starch suspensions as measured by a Brookfield viscometer. o = 0% CHA, ▲ = 0.5% CHA, ■ = 1.0% CHA, and • = 1.5% CHA.

lacking CHA. The effect of CHA appeared to approach a limit at about 1% CHA.

Swelling and solubility of starch granules have a direct effect on the viscosity of a starch suspension (Katz et al 1938). The increase in viscosity is, therefore, consistent with CHA action, which increased swelling and solubility.

DISCUSSION

Wheat starch granules contain approximately 1% lipid, with lysophospholipid accounting for more than 86% of the total lipid (Meredith et al 1978). Some of the lipid is thought to be complexed with amylose or outer chains of amylopectin as helical complexes. Up to 25% of wheat starch amylose may be bound to lipid (Wren and Merryfield 1970). These lipid-amylose complexes have a pronounced effect on the physical properties of starch pastes (Hellman et al 1954, Leach 1965, Larsson 1980). Fatty acids can form inclusion complexes with CHA (Schlenk and Sand 1961, Szejtli and Bánky-Elöd 1975). Several CHA molecules form long channels with hydrophobic cores into which a fatty acid molecule can be incorporated.

Our results suggest that CHA complexes with starch granule lipid, and, in so doing, facilitates the hydration of starch molecules during gelatinization. Cycloheptaamylose had only a slight effect on the range of gelatinization temperature (Table I), indicating that its effect probably depends upon initial hydration of the starch granule. Furthermore, its effect on swelling power and solubility was minimal near the gelatinization temperature (Figs. 1a and 2a). With defatted starch, the effect of CHA was reduced (Figs. 1b and 2b) because lipid was partially removed and the swelling and solubility of defatted starch in the absence of CHA increased. Full removal of granule lipid was not accomplished, and it was, therefore, not possible to determine whether the effect of CHA would be completely eliminated in a lipid-free starch granule.

Increases in amylose leaching (Fig. 3) and in viscosity (Fig. 4) in the presence of CHA are also consistent with lipid complexing by CHA. Conclusive evidence of the effect of CHA on lipids of starch granules may require X-ray diffraction studies to determine whether the V-type fat-amylose complex pattern (Hellman et al 1954) is changed in the presence of CHA. Alternately, it may be possible to follow endothermic transitions of amylose-lysolecithin complexes in the presence of CHA (Kugimiya et al 1980, Kugimiya and Donovan 1981).

Adding small amounts of CHA can substantially increase the swelling power and viscosity of starch suspensions and might prove useful in increasing the viscosity in systems using dilute starch pastes.

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