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Starch and amylopectin: effect of solutes on their calorimetric behavior

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The gelatinization of starches and the calorimetric behavior of amylopectins in the presence of glucose, sucrose and sodium chloride were studied by differential scanning calorimetry. Increasing concentrations of sucrose and glucose increased the gelatinization temperatures. Amaranth and waxy corn starches showed higher enthalpy values than the starch from the normal corn sample. Sucrose was more effective than glucose in increasing these values. The three starches (amaranth, waxy and normal corn) used for this study showed gelatinization endotherms in the presence of sodium chloride. However, amaranth, waxy corn and commercial potato amylopectins did not show such gelatinization endotherms; only commercial corn amylopectin did. The patterns followed by starches and amylopectin with sodium chloride were similar; the enthalpy values were lower at higher salt concentrations.

INTRODUCTION

Starch, the major storage polysaccharide of higher plants, is a polymeric mixture of essentially linear (amylose) and branched (amylopectin) glucans. Starch owes much of its functionality to these two macromolecules, as well as to their physical organization into the granular structure (French, 1984).

Starch gelatinization in the presence of small sugars has been described as mechanical relaxation processes affected by the mobility of aqueous sugar solutions. The retardation effect of concentrated sugar solutions on, for example, the glass transition temperature (T_g) governing starch gelatinization has been suggested to result from 'antiplasticization' by sugar–water cosolvents, relative to the extent of plasticization by water alone (Slade & Levine, 1991). This retardation effect has also been attributed to the capability of sugar to limit water availability to the starch granule. It has been known for decades that various sugars, including sucrose, fructose, and glucose, raise the temperature of starch gelatinization and delay the increase in viscosity (pasting), and that the effect on the gelatinization phenomenon increases with increasing sugar concentration (Chungcharoen & Lund, 1987; Paredes-López & Hernández-López, 1991; Eliasson, 1992). At the concentration used in cakes (55–60%), sucrose delays gelatinization of starch from 57 to 92°C (Kim & Walker, 1992).

The effects of different sugars on gelatinization vary; in general, monosaccharides delay gelatinization less than disaccharides — except maltose, which acts like a monosaccharide (Spies & Hoseney, 1982; Kim & Walker, 1992). The elevating effect of sugars on gelatinization temperature has been attributed in the past, in part, to an unexplained interaction called 'sugar bridges' and said to involve hydrogen bonding of sugars with the amorphous areas of starch granules (Ghiasi *et al.*, 1982; Spies & Hoseney, 1982). However, the exact reaction mechanism by which sugar delays starch gelatinization and retrogradation still remains unclear (Kohyama & Nishinari, 1991). The enthalpy of gelatinization, using differential scanning calorimetry (DSC) has been reported to be unaffected by the addition of sugars (Eliasson, 1992), but increased (Kohyama & Nishinari, 1991) as well as decreased (Chungcharoen & Lund, 1987) values have also been reported.

The effect of solutes on the calorimetric behavior of amylopectin has been studied only by Eliasson (1992), who reported that when potato amylopectin plus sucrose solution was heated in the DSC, the transition observed was not a gelatinization endotherm but rather a melting of retrograded amylopectin. Thus, the objective of the present work was to study the effect of some solutes on the calorimetric behavior, as assessed by DSC, of starches and amylopectins from different starch sources.

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MATERIALS AND METHODS

Starch isolation

Amaranth starch (waxy type, 98% amylopectin) was isolated as reported previously (Paredes-López & Hernández-López, 1992). Waxy and normal corn starches containing 98 and 72% amylopectin, respectively, were a gift from Industrializadora de Maíz, S. A. de C. V. (Guadalajara, Jal., México).

Amylopectin isolation

Amylopectins were isolated from amaranth and waxy corn starches using the methodology reported by Banks and Greenwood (1967). Commercial corn and potato amylopectins were purchased (Sigma Chemical Co., St. Louis, MO, USA); no information was provided on the type of corn and potato used to isolate these amylopectins.

Differential scanning calorimetry measurements

DSC measurements were performed on a Dupont calorimeter model 9000 with a model 910 pressure DSC (E.I. Dupont de Nemours and Co. Inc., Wilmington, DE, USA) cell base. The instrument was calibrated with indium. Gelatinization of starch and calorimetric assessment of amylopectin samples was estimated (Paredes-López & Hernández-López, 1991) as follows: the samples (2 mg) were weighed directly into DSC aluminum pans and sucrose (Sigma Chemical Co.) solutions (made up with deionized water) were added with a microsyringe to make suspensions containing 0·1, 0·2, 0·3, and 0·4 g sucrose/g total sample. The same procedure was followed for glucose (J. T. Baker S. A. de C. V., Xalostoc, México) and sodium chloride (E. Merck, Darmstadt, Germany), but in the last case the concentrations were 0·05, 0·1, and 0·2 g NaCl/g total sample. After sealing, the pans were equilibrated for 1 h at room temperature and scanned at a rate of 10°C/min from 30 to 180°C, with a sensitivity of 0·005 mcal/sec. In all measurements an empty pan was used as reference in triplicated experiments.

RESULTS AND DISCUSSION

Gelatinization of starch

DSC was used to study the effect of solutes on the gelatinization of starches (Fig. 1) and amylopectins (Fig. 2). Table 1 shows, as well, the temperature changes of starches and amylopectins as a result of this effect. All starches (Fig. 1) at high sugar concentration increased their gelatinization temperature, and the enthalpy values were also increased, whereas the control (sample without solute) exhibited lower gelatinization temperatures than the corresponding samples.

In amaranth starch, the control always showed a lower enthalpy value than all samples in the presence of sugars (Fig. 1A). This same value was usually lower for the waxy corn control than with the remaining samples with added sugars (Fig. 1B), whereas the opposite effect was observed for the normal starch samples (Fig. 1C). Amaranth starch in the presence of sugar (Fig. 1A) presented lower gelatinization temperatures but higher enthalpy values than waxy (Fig. 1B) and normal (Fig. 1C) corn starches; moreover, waxy corn starch showed gelatinization temperatures and enthalpy values usually higher than normal corn starch. The amounts of amylose and amylopectin, as well as chain distributions in the amylopectin, may play an important role in this phenomenon. Eliasson (1992) reported increases of enthalpy values for corn starches with higher amylopectin content in the presence of sucrose, but gelatinization temperatures did not show a defined trend. Kim and Walker (1992), in their gelatinization studies, anticipated that sugars would increase the enthalpy values by generating more compact structures with starch chains. However, lower enthalpy values were obtained.

It was found that gelatinization temperatures for starch in the presence of sucrose were always higher than those for glucose. Spies and Hoseney (1982) also found the same trend. They reported that sugar delays gelatinization by interacting with starch. Sugar molecules may bond with starch chains in the amorphous regions of the granule, thus effectively producing interactions between such chains. Longer sugar molecules can bridge more gaps between chains and thus produce more links than shorter molecules can. Bridges between chains restrict the flexibility of the chains, thus requiring more energy to 'strip' the crystallites. As more links are formed, flexibility is more restricted, and more energy is required to pull the crystallites apart. The increased energy requirement results in an even higher gelatinization temperature for starch.

In the present experiments the enthalpy values of both waxy starches (from amaranth and corn) tended to be higher for glucose than for sucrose; normal corn did not show a defined pattern. Further research is needed to explain this behavior.

Sodium chloride had a different and complex effect on starch gelatinization (Fig. 1). When the sodium chloride concentration increased, the enthalpy value decreased. This behavior is similar to that reported by Chungcharoen and Lund (1987) and Paredes-López and Hernández-López (1991). For the three starch samples, the gelatinization temperature was the lowest at 0·2 g NaCl/g total. As for sugars, in the presence of sodium chloride, amaranth starch (Fig. 1A) showed higher enthalpy values than waxy (Fig. 1B) and normal (Fig. 1C) corn samples.

Wootton and Bamunuarachchi (1980) reported that sodium chloride appeared to exhibit a maximum inhibitory effect on starch gelatinization at 6–9%. Evans and Haisman (1982) found that sodium chloride and calcium chloride at low concentrations slightly increased the gelatinization temperatures, but when the concentrations increased further the temperatures

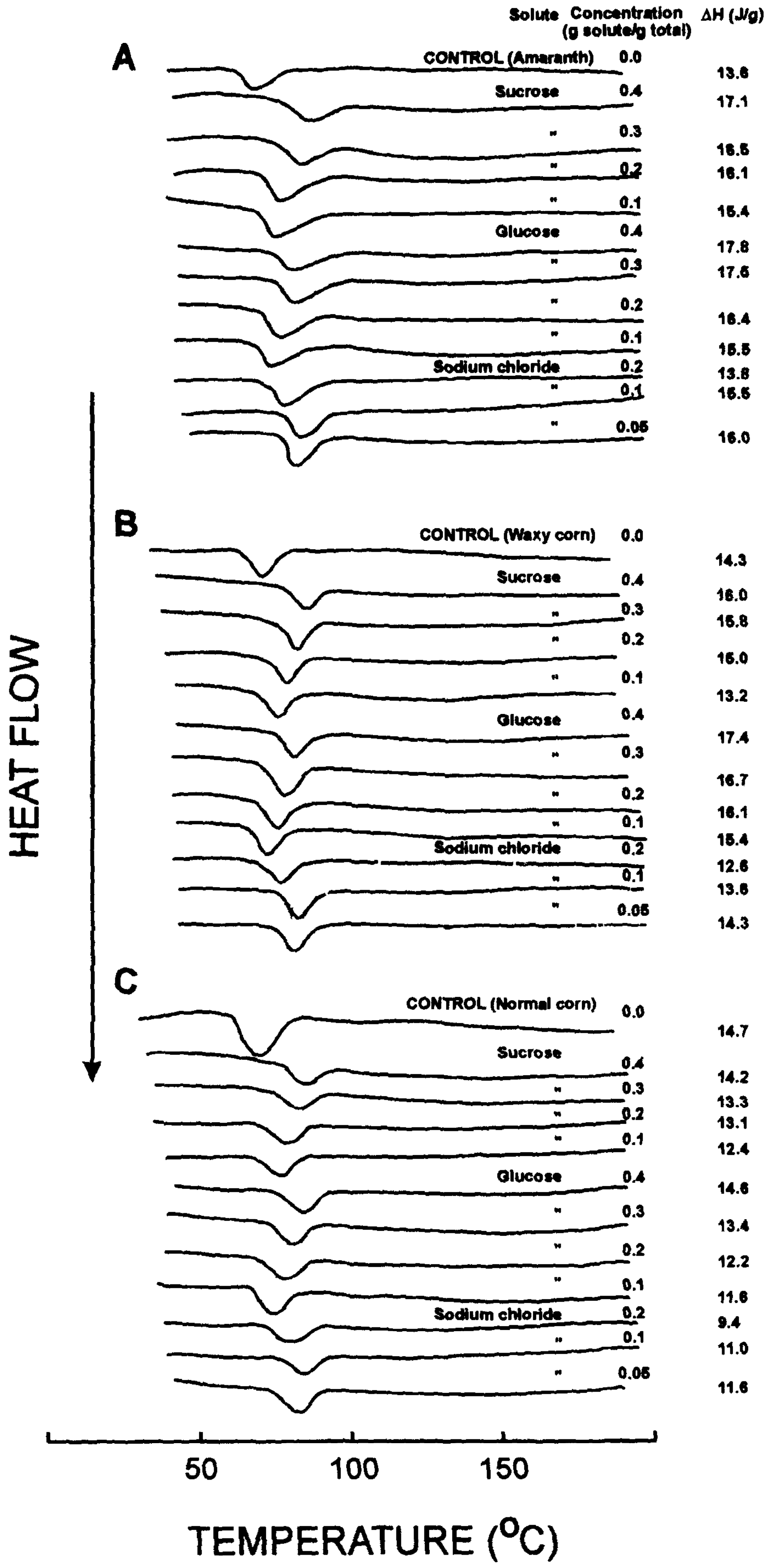

Fig. 1. Effect of sugars and sodium chloride on the gelatinization thermograms of starches by differential scanning calorimetry. A, Amaranth; B, waxy corn; C, normal corn.

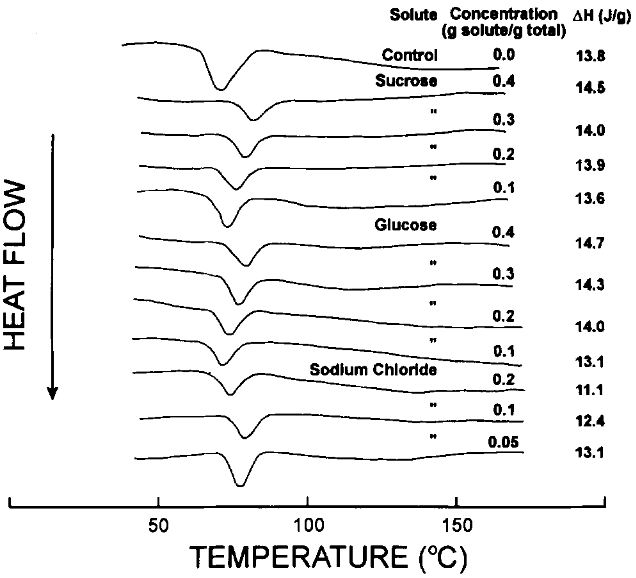

Fig. 2. Effect of sugars and sodium chloride on the calorimetric behavior of commercial corn amylopectin by differential scanning calorimetry.

decreased. Oosten (1982) suggested that starch acts as a weak acid ion-exchanger and that cations tend to protect and to stabilize the granule structure, while anions act as gelatinizing agents by rupturing hydrogen bonds. A mechanism of starch gelatinization in neutral salt solutions was proposed by Jane (1993). She reported that starch gelatinization in such salts seems to be controlled by two effects: water structure and electrostatic interaction between starch and ions. These two effects conflict with one another and result in complex patterns depending on the concentration of the salts.

Calorimetric behavior of amylopectin

The DSC thermograms of commercial corn amylopectin (Fig. 2 and Table 1) show similar gelatinization temperatures to waxy corn starch (Fig. 1B) but with usually lower enthalpy values. These results suggest that commercial corn amylopectin still had a granular structure as reported elsewhere (Paredes-López *et al.*, 1993). Amaranth, waxy corn and commercial potato amylopectin did not show endotherms with the solutes under study; such absence of endotherms may be due to structural changes during the isolating step of amylopectins (Hoseney *et al.*, 1986; Eliasson, 1992; Yuan *et al.*, 1993; Paredes-López *et al.*, 1993).

In conclusion, in the presence of sugars, amaranth starch presented lower gelatinization temperatures but higher enthalpy values than waxy and normal corn starches. The higher enthalpy values of the waxy types may be attributed to the different level and degree of

Table 1. Effect of some solutes on gelatinization temperatures of starches and amylopectins[a]

Sample and solute concentration (g solute/g total sample)	Solute			Control
	Sucrose	Glucose	Sodium chloride	
Amaranth starch				
0·4	80·6 ± 0·8	76·7 ± 0·2	—	—
0·3	78·2 ± 0·8	75·5 ± 0·5	—	—
0·2	73·6 ± 0·8	72·4 ± 0·3	73·3 ± 0·6	—
0·1	71·1 ± 0·8	69·9 ± 0·1	78·7 ± 0·1	—
0·05	—	—	77·2 ± 0·2	—
0·0	—	—	—	68·3 ± 0·4
Waxy corn starch				
0·4	86·1 ± 0·8	82·7 ± 0·2	—	—
0·3	83·6 ± 0·1	80·8 ± 0·8	—	—
0·2	79·7 ± 0·9	78·0 ± 0·7	79·2 ± 0·8	—
0·1	76·8 ± 0·4	75·8 ± 0·4	83·3 ± 0·1	—
0·05	—	—	82·2 ± 0·3	—
0·0	—	—	—	71·6 ± 0·3
Normal corn starch				
0·4	86·0 ± 0·7	86·5 ± 0·8	—	—
0·3	83·4 ± 0·8	80·8 ± 0·2	—	—
0·2	79·4 ± 0·9	77·7 ± 0·6	78·2 ± 0·9	—
0·1	76·8 ± 0·07	74·7 ± 0·0	82·5 ± 0·4	—
0·05	—	—	81·4 ± 0·5	—
0·0	—	—	—	71·2 ± 0·5
Commercial corn amylopectin				
0·4	84·9 ± 0·1	81·9 ± 0·1	—	—
0·3	82·9 ± 0·8	80·3 ± 0·6	—	—
0·2	79·5 ± 0·7	77·2 ± 0·3	77·0 ± 0·5	—
0·1	75·9 ± 0·3	74·8 ± 0·8	82·4 ± 0·1	—
0·05	—	—	80·9 ± 0·1	—
0·0	—	—	—	72·9 ± 0·3

[a]Mean values ± standard deviation.

branching of the amylopectin from those materials. With sucrose, the gelatinization temperatures were higher than with glucose but for amaranth and waxy corn samples the enthalpy values appeared to be higher in the presence of glucose than sucrose. The effect of sodium chloride was complex. When the sodium chloride concentration in the starches decreased, the enthalpy values increased. Of all amylopectins studied only the commercial corn showed a transition.

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REFERENCES

Banks, W. & Greenwood, C. T. (1967). The fractionation of laboratory- isolated cereal starches using dimethyl sulphoxide. *Starch/Stärke*, **19**, 394–8.

Chungcharoen, A. & Lund, D. B. (1987). Influence of solutes and water on rice starch gelatinization. *Cereal Chem.*, **64**, 240–3.

Eliasson, A.-C. (1992). A calorimetric investigation of the influence of sucrose on the gelatinization of starch. *Carbohydr. Polym.*, **18**, 131–8.

Evans, I. D. & Haisman, D. R. (1982). The effect of solutes on the gelatinization temperature range of potato starch. *Starch/Stärke*, **34**, 224–31.

French, D. (1984). Organization of starch granules. In *Starch: Chemistry and Technology*, eds R. L. Whistler, J. N. BeMiller & E. F. Paschall. Academic Press, New York, USA, pp. 183–247.

Ghiasi, K., Hoseney, R. C. & Varriano-Marston, E. (1982). Effects of flour components and dough ingredients on starch gelatinization. *Cereal Chem.*, **59**, 58–61.

Hoseney, R. C., Zeleznak, K. J. & Yost, D. A. (1986). A note on the gelatinization of starch. *Starch/Stärke*, **38**, 407–9.

Jane, J.-L. (1993). Mechanism of starch gelatinization in neutral salt solutions. *Starch/Stärke*, **45**, 161–6.

Kim, C. S. & Walker, C. E. (1992). Effects of sugars and emulsifiers on starch gelatinization evaluated by differential scanning calorimetry. *Cereal Chem.*, **69**, 212–17.

Kohyama, K. & Nishinari, K. (1991). Effect of soluble sugars on gelatinization and retrogradation of sweet potato starch. *J. Agric. Food Chem.*, **39**, 1406–10.

Oosten, B. J. (1982). Tentative hypothesis to explain how electrolytes affect the gelatinization temperature of starches in water. *Starch/Stärke*, **34**, 233–9.

Paredes-López, O. & Hernández-López, D. (1991). Application of differential scanning calorimetry to amaranth starch gelatinization — influence of water, solutes and annealing. *Starch/Stärke*, **43**, 57–61.

Paredes-López, O. & Hernández-López, D. (1992). Food properties of amaranth seeds and methods for starch isolation and characterization. In *Modern Methods of Plant Analysis*, eds H. F. Linskens & J. F. Jackson. Springer-Verlag, Berlin, Germany, pp. 217–39.

Paredes-López, O., Bello-Pérez, L. A. & López, M. G. (1994). Amylopectin—structural, gelatinization and retrogradation studies. *Food Chem.*, **50**, 411–17.

Slade, L. & Levine, H. (1991). Beyond water activity: recent advances based on an alternative approach to the assessment of food quality and safety. *CRC Crit. Rev. Food Sci. Nutr.*, **30**, 115–360.

Spies, R. D. & Hoseney, R. C. (1982). Effect of sugars on starch gelatinization. *Cereal Chem.*, **59**, 128–31.

Wootton, M. & Bamunuarachchi, A. (1980). Application of differential scanning calorimetry to starch gelatinization. III. Effect of sucrose and sodium chloride. *Starch/Stärke*, **32**, 126–9.

Yuan, R. C., Thompson, D. B. & Boyer, C. D. (1993). Fine structure of amylopectin in relation to gelatinization and retrogradation behavior of maize starches from three wax-containing genotypes in two inbred lines. *Cereal Chem.*, **70**, 81–9.