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Effect of polyhydroxy compounds on structure formation in waxy maize starch gels: a calorimetric study

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The effects of polyhydroxy compounds (PHCs) on structure formation in ageing waxy maize starch gels were investigated by measuring the retrogradation endotherm (ΔH) using calorimetry. Changes in retrogradation kinetics observed by addition of PHCs at a weight ratio of starch : PHC : water of 1 : 0·5 : 1·5 were solute specific. In the homologous series of glucose oligomers, maltotriose exhibited the largest inhibitory effect, while maltooctaose promoted retrogradation. Among various pentose and hexose sugars, ribose and talose, respectively, were the most effective in retarding retrogradation. Fructose led to increased rates of chain ordering, particularly at high concentrations. The results were correlated with literature data of several physicochemical properties of PHCs in solution. Strong linear relationships were shown between the effect of sugars on retrogradation endotherm and the hydration characteristics of these solutes. It was further suggested that compatibility of sugar with the water structure, as governed by the stereochemistry of the main sugar conformers in solution, is an important determinant of amylopectin stability in the composite gel matrix; i.e. PHCs which disturb very little the hydrogen-bonded network of water are also effective in inhibiting retrogradation.

INTRODUCTION

The ability of starch chains to form ordered structures in pastes, gels and baked foods during storage, a process often described by the term 'retrogradation', greatly influences the texture and shelf-life of these products. It is generally accepted that the adoption of double helical chain structures, acting as 'junction zones', followed by chain aggregation in the polymer-rich regions of the ageing gel network are the underlying molecular processes to the observed changes in structure and physical properties of starch materials (Miles *et al.*, 1985*a*,*b*; Ring *et al.*, 1987; Clark *et al.*, 1989; Gidley, 1989; German *et al.*, 1992; Wu & Eads, 1993). There is also increasing evidence that phase separation (demixing) of amylose and amylopectin may occur in an aqueous medium particularly at high water contents (Kalichevsky & Ring, 1987; Svegmark & Hermansson, 1991; German *et al.*, 1992). When phase separation occurs, the effective concentration of both polymers in their respective microdomains is raised and this influences the gelation and chain aggregation events.

Starch retrogradation kinetics have been monitored by several techniques including turbidity (Ring *et al.*, 1987) and solubility (Rosario & Pontiveros, 1983) measurements, thermal analysis (McIver *et al.*, 1968; Longton & LeGrys, 1981; Russell, 1983, 1987; Jankowski & Rha, 1986), X-ray diffraction (Katz & Van Itallie, 1930; Zobel & Senti, 1959; l'Anson *et al.*, 1988), Fourier Transform IR (Wilson & Belton, 1988; Goodfellow & Wilson, 1990), Raman spectroscopy (Bulkin *et al.*, 1987), NMR (Lechert & Hennig, 1976; Wynne-Jones & Blanshard, 1986; Gidley, 1989; German *et al.*, 1992; Teo & Seow, 1992; Wu & Eads, 1993) and various rheological tests (Kim & D'Appolonia, 1977; Wong & Lelievre, 1982; Miles *et al.*, 1985*a*,*b*; Clark

et al., 1989; l'Anson *et al.*, 1988; Biliaderis & Zawistowski, 1990; Mita, 1992). These methods measure different physicochemical properties and, therefore, are sensitive to various elements of structure in the ageing gels. For example, chain reordering of amylopectin, as monitored by calorimetry, was related with the slow developing modulus component of starch gels (Ring *et al.*, 1987; Biliaderis & Zawistowski, 1990). On the other hand, development of crystallinity (long-range order) is a much slower process, as followed by X-ray diffraction. Furthermore, the mechanical properties of starch gels, determined by either large deformation testing or small strain oscillatory rheometry, are dependent on chain entanglement density and crystallinity.

Starch retrogradation is affected by moisture, lipids and other food constituents (Kulp & Ponte, 1981; Zeleznak & Hoseney, 1986; Biliaderis, 1991, 1992). While monoacyl lipids have long been known to retard the process, the effects of salts and sugars are more complex and less well understood. Maxwell and Zobel (1978), using large deformation mechanical tests, showed a marked increase in the rate of firming of starch gels by fructose, a slight increase by glucose and essentially no effect for sucrose (wheat starch : sugar : water at 1 : 1 : 1). Similar rheological studies by Germani *et al.* (1983) indicated that maltose and sucrose were more effective in increasing the firming rate of corn starch gels than glucose. In both these studies, however, the elastic moduli of sugar-containing gels were lower than for pure starch gels. l'Anson *et al.* (1990), using X-ray diffraction and rheological tests, concluded that sugars reduce firmness and crystallinity development in wheat starch gels (starch : sugar : water at 1 : 1 : 1); the effectiveness of the three sugars examined was in the order of ribose > sucrose > glucose. In a subsequent study, Cairns *et al.* (1991*a*) reported that both ribose and xylose continuously reduced starch crystallization with increasing sugar concentration. In contrast, gels containing fructose showed higher crystallinity than pure starch gels. The unusual behaviour of fructose, as promoter of amylopectin crystallization, was also observed by Slade and Levine (1988) using calorimetry. These authors suggested that sugars act as antiplasticizers, thus reducing chain mobility and crystallization rate of starch gels, in the order of xylose > maltose > glucose > galactose > control gel > fructose (wheat starch : sugar : water at 1 : 1 : 1). Obviously, the results obtained for fructose cannot be interpreted on the basis of the antiplasticization theory. Recent calorimetric studies on sweet potato starch gels indicated that fructose prevented retrogradation although not as effectively as glucose or sucrose (Kohyama & Nishinari, 1991). On the basis of viscoelastic responses (creep compliance) of gels containing sugars, at relatively low sugar concentration (2·57% w/w), Katsuta *et al.* (1992*a*, *b*, *c*) and Miura *et al.* (1992) have shown that the ability of sugars to impede retrogradation is related with the mean number of equatorial hydroxyl groups; solutes with large numbers of equatorial —OH groups were effective in inhibiting retrogradation. The relative ranking of sugars in decreasing the rate of retrogradation was: maltotriose > maltose > sucrose > glucose > fructose > xylose, ribose > control gel. Among monosaccharides, hexoses were more effective in retarding retrogradation than pentoses, which contradicts the findings of earlier works (l'Anson *et al.*, 1990; Cairns *et al.*, 1991*a*, *b*).

Overall, considerable confusion appears to exist in the published literature with respect to the role of sugars on starch retrogradation. A complete description of a mechanism by which these solutes affect chain ordering and aggregation processes in starch gels requires further investigation. The present article describes a systematic calorimetric study of the effect of various polyhydroxy compounds (PHCs) on amylopectin chain reordering in waxy maize starch gels. The results presented here, might be used to throw more light onto the relation between solvent structure and stability of starch hydrogels.

EXPERIMENTAL

Materials

A commercial sample of waxy maize starch was obtained from National Starch and Chemical Corp. (Bridgewater, NJ). Oligomers of glucose (tetramer to heptamer, G4–G7) were products of Boehringer Mannheim Canada Ltd. (Laval, PQ); maltooctaose (G8) was isolated from a starch hydrolysis product by gel permeation chromatography; fructose, glucose and sucrose were products of Mallinckrodt (Paris, KY). All other PHCs (ribose, xylose, methyl-β-xylopyranoside, arabinose, talose, galactose, 3-O-methyl-D-glucopyranoside, sorbitol, lactose, maltose, trehalose, cellobiose, gentiobiose, isomaltose, maltitol, lactitol and maltotriose) were obtained from Sigma Chemical Co. (St Louis, MO). All reagents were of analytical grade.

Preparation of starch gels and DSC analysis

Calorimetric measurements of ageing starch/PHC gels were carried out using a DuPont 9900 thermal analyser equipped with a 910 DSC high pressure cell. Starch samples (3·0–3·3 mg) were suspended in aqueous PHC solutions and hermetically sealed in coated aluminium pans. The suspensions were first heated to 135°C to gelatinize the granules under pressure (1400 kPa, with N_2), cooled slowly (5°C min^{-1}) to room temperature and stored for a designated period (9, 12, 18, 24, 48, 72, 96 and 144 h) at 6°C. The samples were subsequently analysed with DSC (20–135°C min^{-1}). The instrument was calibrated with indium and all conditions and

analysis of the endothermic transition (ΔH in J/g) were as previously described (Biliaderis *et al.*, 1985).

Statistical analysis — relationships with hydration properties

The magnitude of retrogradation endotherm (ΔH) was taken as an indicator of chain reordering in gels. Data presented are means of at least triplicate measurements; analysis of variance and differences among means were determined using the Duncan's multiple range test. Differences between sugars and their respective alcohol derivatives were assessed by paired t-tests. The three-dimensional plots for the effect of sugar concentration on retrogradation were generated using the Systats software package (Evanston, IL), and a distance weighted least-squares (DWLS) smoothing function was applied to fit a surface through the data points. The levels chosen for the two independent variables were: (a) sugar level (X) in the starch : PHC : water ($1 : X : 1{\cdot}5$ w/w) mixture was adjusted at 0·1, 0·3, 0·5, 0·7 and 0·9; (b) storage periods at 6°C were 12 h, 1, 2, 3, 4, 6, 8 and 10 days.

The retrogradation data were related with the hydration characteristics and other physicochemical properties of the PHCs. Values for the following parameters were taken or calculated from published literature data: (a) hydration number, n_h (Galema & Hoiland, 1991); (b) isentropic partial molar compressibilities (K_2^o, $cm^3\ mol^{-1}\ bar^{-1}$; Galema & Hoiland, 1991); (c) rotational correlation times, τ_c^h/τ_c^o, and dynamic hydration number, n_{DHN} (Uedaira *et al.*, 1989, 1990); relative mobility, $(T - T_g')/(T_m - T_g)$ (Slade & Levine, 1988). A modified dynamic hydration number, n^*_{DHN}, was also calculated based on the following relationship developed by Uedaira *et al.* (1989) for determining $n_{DHN} : n_{DHN} = n_h\,[k(\tau_c^h/\tau_c^o) - 1]$, where n_h is the coordination number (number of water molecules close to the sugar). In the case of n^*_{DHN}, as a coordination number the value of hydration number (n_h) derived from the ultrasound experiments of Galema and Hoiland (1991) was used, since it better reflects the hydration cosphere of the solute.

RESULTS AND DISCUSSION

Glucose oligosaccharides

The effects of the homologous glucose oligosaccharide series on amylopectin retrogradation are shown in Fig. 1 and Table 1. The development of ordered structures in waxy maize starch gels increased rapidly during the first few days of storage at 6°C, and was followed by a

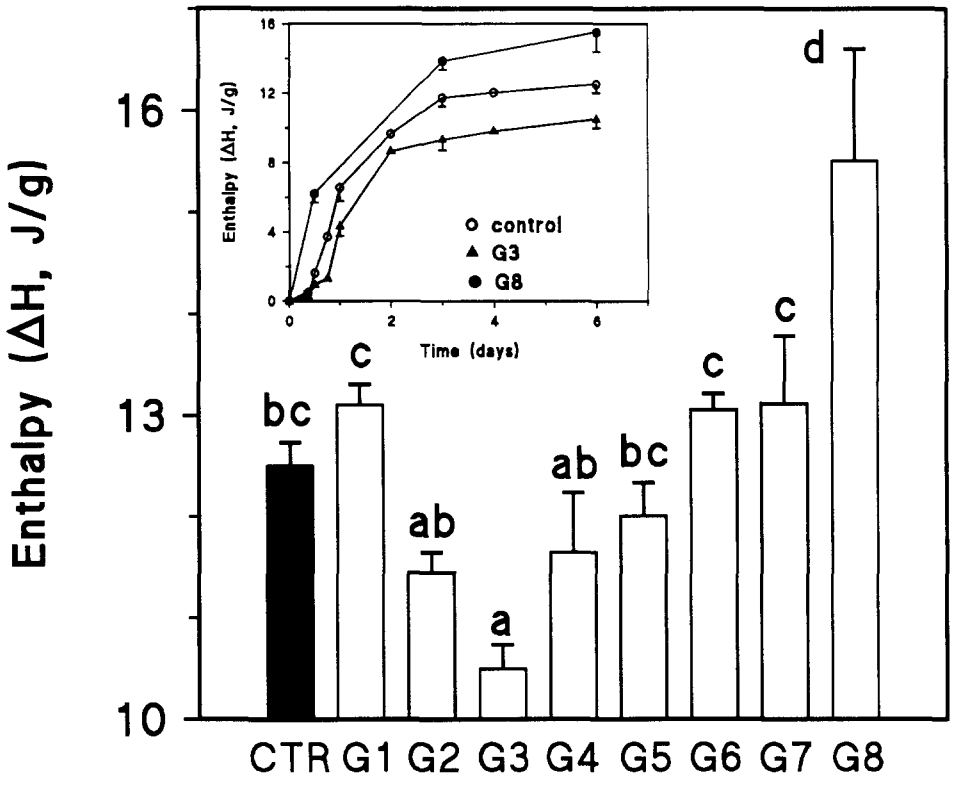

Fig. 1. Effect of glucose oligosaccharides (G1–G8) on retrogradation (ΔH) of waxy maize starch gels stored at 6°C for 6 days; starch : oligosaccharide : water at 1 : 0·5 : 1·5, w/w. Inset: kinetics of structure development for maltotriose (G3)- and maltooctaose (G8)-containing gels. Control gel (CTR) had starch : water at 1 : 1·5. Data are means ± SD ($n = 3$); bars followed by the same letter are not significantly different ($p < 0{\cdot}05$).

Table 1. The effect of glucose oligomers on retrogradation (ΔH) of waxy maize starch gels stored at 6°C

Oligomer[a]	Transition enthalpy (J/g)[b]							
	9 h	12 h	18 h	24 h	48 h	72 h	96 h	144 h
Control	$0.5 \pm 0.2^{a,b,c}$	1.6 ± 0.1^{a}	$3.7 \pm 0.4^{c,d}$	$6.5 \pm 0.8^{c,d}$	9.7 ± 0.3^{c}	11.7 ± 0.1^{c}	$12.0 \pm 0.1^{c,d,e}$	$12.5 \pm 0.2^{b,c}$
Glucose	1.9 ± 0.1^{e}	4.1 ± 0.6^{b}	6.5 ± 0.5^{d}	9.8 ± 0.1^{f}	11.3 ± 0.5^{d}	11.9 ± 0.5^{c}	$12.4 \pm 0.2^{d,e}$	13.1 ± 0.1^{c}
Maltose	0.3 ± 0.1^{a}	1.3 ± 0.1^{a}	1.5 ± 0.1^{a}	$5.2 \pm 0.2^{a,b}$	5.9 ± 0.4^{a}	8.6 ± 0.7^{a}	$10.2 \pm 0.2^{a,b}$	$11.5 \pm 0.1^{a,b}$
Maltotriose	0.3 ± 0.2^{a}	0.9 ± 0.8^{a}	1.3 ± 0.3^{a}	4.3 ± 0.6^{a}	8.7 ± 0.5^{b}	9.3 ± 0.6^{a}	9.9 ± 0.4^{a}	10.5 ± 0.2^{a}
Maltotetraose	$0.5 \pm 0.2^{a,b}$	1.5 ± 0.1^{a}	3.4 ± 0.1^{b}	$5.2 \pm 0.2^{a,b}$	$9.1 \pm 0.1^{b,c}$	10.4 ± 0.3^{b}	10.6 ± 0.2^{b}	$11.7 \pm 0.6^{a,b}$
Maltopentaose	$0.7 \pm 0.1^{b,c}$	1.2 ± 0.6^{a}	3.3 ± 0.4^{b}	$5.7 \pm 0.4^{b,c}$	$8.8 \pm 0.8^{b,c}$	10.6 ± 0.4^{b}	$11.7 \pm 0.1^{c,d}$	$12.0 \pm 0.3^{b,c}$
Maltohexaose	0.8 ± 0.1^{c}	4.2 ± 0.2^{b}	4.8 ± 0.4^{c}	7.8 ± 0.1^{e}	9.2 ± 0.7^{c}	12.0 ± 0.1^{c}	11.6 ± 0.3^{c}	13.1 ± 0.2^{c}
Maltoheptaose	1.2 ± 0.1^{d}	3.3 ± 0.5^{b}	6.3 ± 0.7^{d}	$7.5 \pm 0.8^{d,e}$	9.9 ± 0.5^{c}	12.5 ± 0.1^{c}	12.6 ± 0.1^{e}	13.1 ± 0.7^{c}
Maltooctaose		6.2 ± 0.1^{c}				13.9 ± 0.1^{d}		15.5 ± 1.1^{d}

[a]Oligomers were incorporated at a ratio of 1:0·5:1·5 (w/w) for starch : oligomer : water mixtures.
[b]Means ± SD ($n = 3$); values followed by the same letter (column) are not significantly different ($p < 0.05$).

slower phase of ΔH growth (Fig. 1). After six days of storage the addition of glucose, maltose and the oligomers G4–G7 did not significantly suppress the development of the retrogradation endotherm (starch : PHC : water at 1:0·5:1·5, w/w). In contrast, maltotriose (G3) significantly retarded retrogradation whereas maltooctaose (G8) promoted the process. The relative ranking of glucose oligosaccharides in altering the retrogradation rate varied slightly with the storage time (Table 1). Also, the larger differences in the responses of these sugars were observed within the first day of storage. Overall, it appears that oligomers with DP 1–3 reduce retrogradation in the order of G1 < G2 < G3, the G4–G7 have relatively little influence, and G8 strongly promotes structure development in waxy maize starch gels.

Glucose disaccharides and sugar alcohols

The results obtained for disaccharides varying in their glucosidic linkage are summarized in Fig. 2. Cellobiose (β 1 → 4) and trehalose (a 1 → 1), at 1 day, were found to retard retrogradation more than maltose (a 1 → 4), gentiobiose (β 1 → 6) and isomaltose (a 1 → 6). Up to 2 days storage, trehalose was the most effective disaccharide in retarding retrogradation. The binary trehalose–water system is interesting in that its T_g is much higher than other disaccharides (maltose, sucrose), particularly in the sugar concentration range of 10–40% mole/mole (Green & Angell, 1989). This behaviour has been connected with the excellent glass-forming ability of this sugar which is important in the tolerance to desiccation of cryptobiotic organisms (Green & Angell, 1989; Roser, 1991). These differences among the disaccharides diminished over longer storage periods. A comparison between some sugars and their respective sugar alcohols was also made (Fig. 2). Only sorbitol seemed to retard amylopectin retrogradation more effectively than glucose, particularly within the first 2 days of storage. Between the disaccharides maltose, lactose and their respective sugar alcohols, no significant differences were found.

Pentoses versus hexoses

The effects of added pentoses and hexoses on retrogradation are summarized in Fig. 3. Generally, pentoses reduced significantly structure development in the ageing gels, with ribose exhibiting the strongest effect. Xylose, methyl-β-D-xylopyranoside and arabinose were less effective in this respect. Among hexoses, talose, galactose and 3-O-methyl-D-glucopyranose significantly retarded retrogradation, whereas glucose (at short storage periods) and fructose were structure-promoting solutes. As a group, pentoses were more inhibitory to retrogradation than hexoses. It is noteworthy, however, that arabinose behaved more like a hexose and talose like a pentose. The relative ranking of the monosaccharides in inhibiting structure formation in ageing gels was: ribose > xylose, talose > methyl-β-D-xylopyranoside > arabinose > galactose > 3-O-methyl-D-glucopyranose > water alone, glucose > fructose.

Sugar concentration effects

The effects of varying concentration of fructose, ribose and sucrose on the magnitude of retrogradation endotherm are shown in Fig. 4. Addition of fructose at high concentrations (>7·5% w/w) accelerated the retrogradation of amylopectin; interestingly, this solute seemed to exert an inhibitory effect when added at low concentration (<7·5% w/w). Ribose had an opposite effect; the gels showed a descending level of structure with ascending ribose concentration. For sucrose, at low concentrations (<7·5% w/w), there was a reduction in the kinetics of ΔH development. At concentrations above 7·5% (w/w), the kinetics of chain ordering remained relatively independent of the weight fraction of this solute.

Retrogradation and hydration characteristics of PHCs

The retrogradation data for various PHCs added in waxy maize starch gels clearly show that the responses of the system are rather solute specific. This has prompted the authors to seek possible relationships between retrogradation and some physicochemical properties of these solutes. Some of these relationships are illustrated in Fig. 5 and the corresponding correlation coefficients for several storage periods are summarized in Table 2.

In Fig. 5(a), the relationship between ΔH of retrogradation endotherm at 2 days storage and hydration number (n_h) of the PHCs is shown. The hydration numbers are data reported by Galema and Hoiland (1991) using ultrasound experiments on sugar solutions of low concentration. The n_h is indicative of the number of water molecules that are disturbed by the presence of the carbohydrate solute; the smaller the number, the better the compatibility of the PHC with the three-dimensional hydrogen-bonded structure of water. For monosaccharides the hydration numbers show a strong correlation with the ΔH. This would imply that the better the compatibility of a solute (e.g. ribose, xylose) with the water structure, the smaller the tendency of starch chains to form ordered domains. A similar trend is also seen between retrogradation and isentropic partial molar compressibility values (K_2^o) of these solutes (Fig. 5(b)). This parameter expresses the compressibility of the hydration layer surrounding a solute. Pure water has a molar compressibility of $+9{\cdot}17 \times 10^{-4}$ cm^3 mol^{-1} bar^{-1}, while for small molecular weight carbohydrates the partial molar compressibilities range between -4×10^{-4} and -34×10^{-4} cm^3 mol^{-1} bar^{-1} (Galema & Hoiland, 1991); the more negative the K_2^o, the more disturbed the hydration layer around the solute is, compared to pure water. Again, the retrogradation data show that the kinetics are enhanced with solutes showing a poor fit with the structure of water (large negative K_2^o values). The disaccharides do not seem to follow these relationships (Fig. 5(a) and (b)). For disaccharides and oligosaccharides, the hydration numbers cannot be simply interpreted since in addition to the sugar moieties,

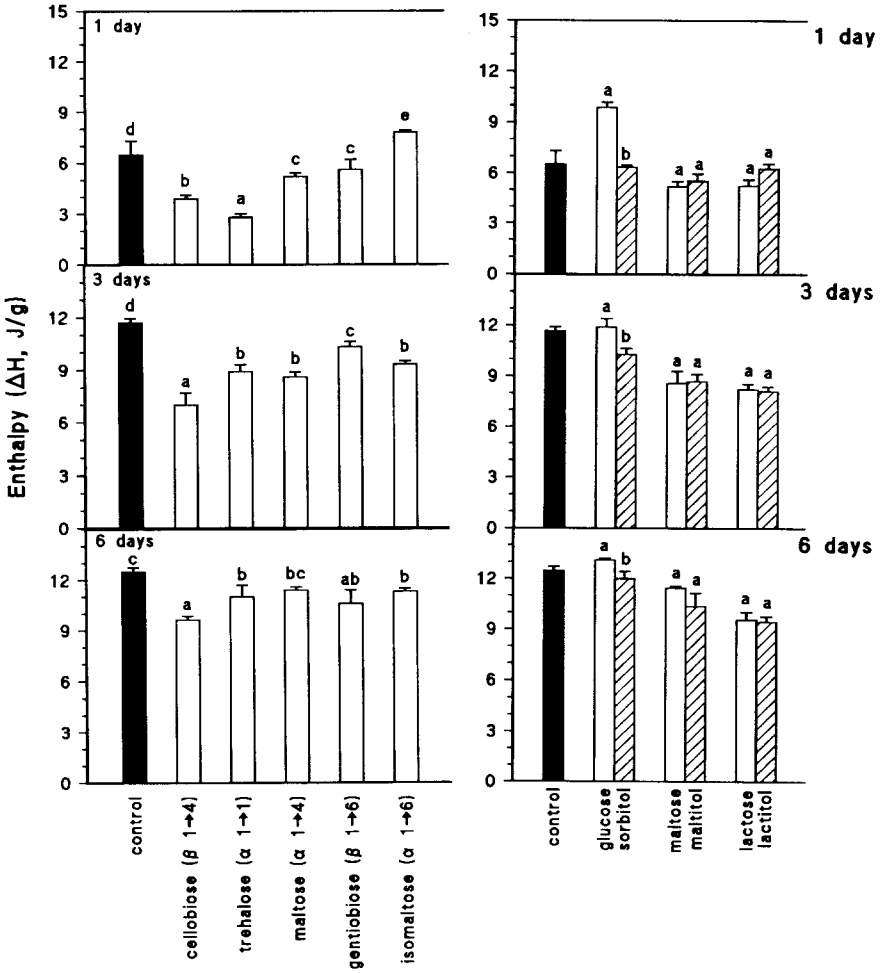

Fig. 2. Effect of glucose disaccharides (left) and comparison of sugars and sugar alcohols (right) on retrogradation (ΔH) of waxy maize starch gels stored at 6°C. Starch : sugar : water at 1 : 0·5 : 1·5, w/w (control gel had starch : water at 1 : 1·5, w/w). Data are means ± SD ($n = 3$); bars followed by the same letter are not significantly different ($p < 0{\cdot}05$).

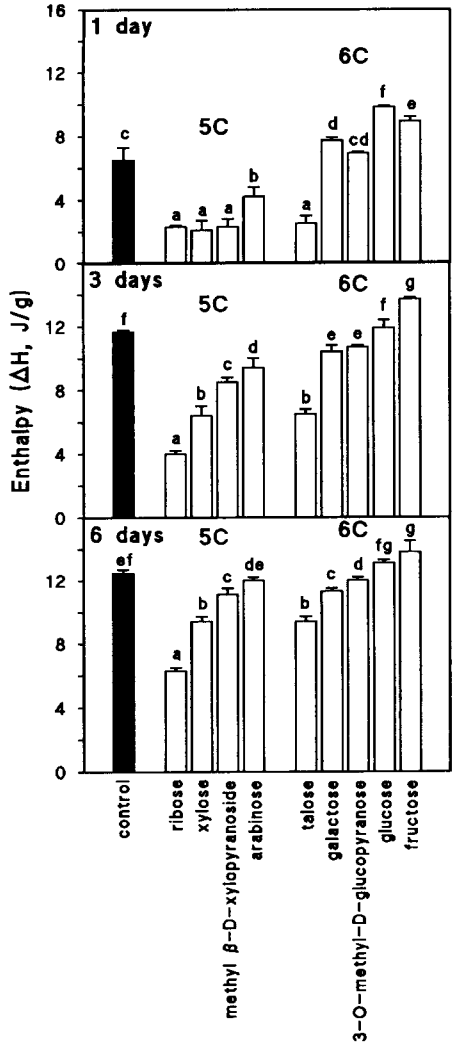

Fig. 3. Effect of pentoses and hexoses on retrogradation (ΔH) of waxy maize starch gels. Conditions are as those in Fig. 2.

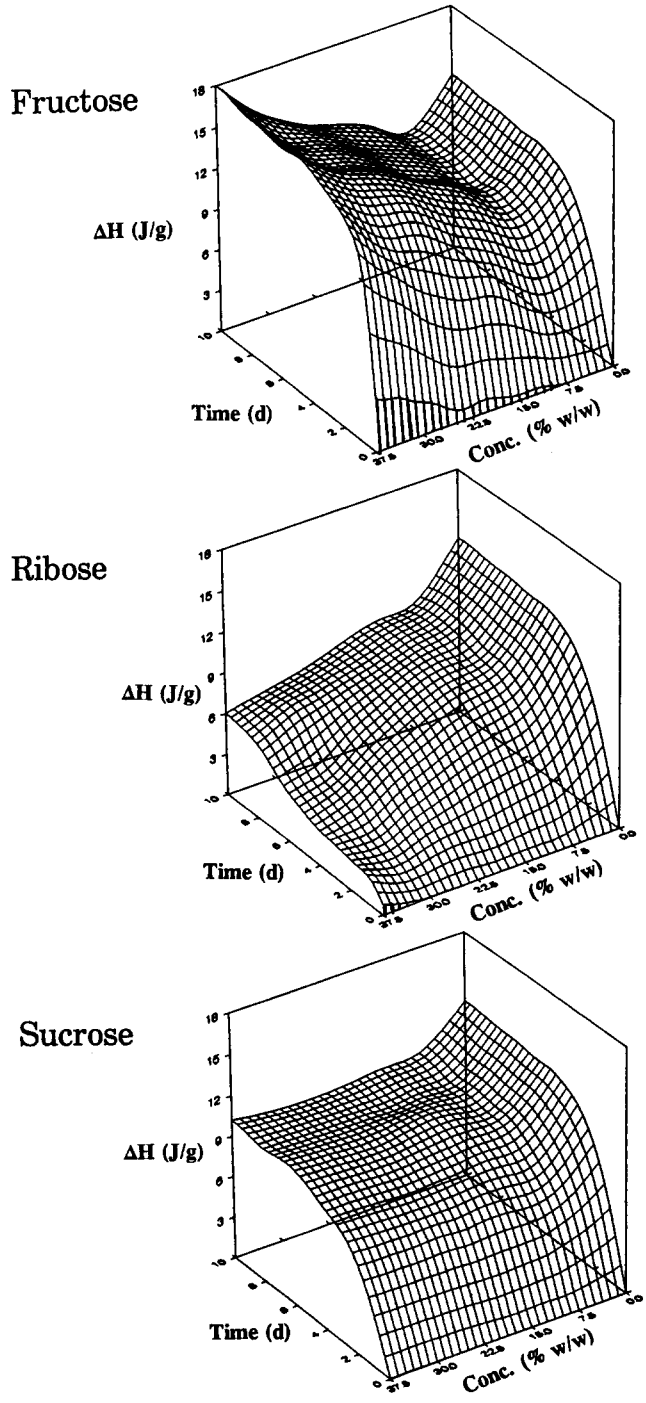

Fig. 4. Effect of sugar concentration on retrogradation (ΔH) of waxy maize starch gels stored at 6°C. Starch : sugar : water at 1 : X : 1·5, w/w, where X varied between 0·1 and 0·9. The sugar concentration is expressed as a percentage of the polyol solution.

conformational aspects related to glucosidic linkages also contribute to changes in water dynamics.

A fairly good linear relationship also holds between ΔH and the ratio of rotational correlation times of water in the sugar solution over that of pure water, τ_c^h/τ_c^o. The τ_c^h/τ_c^o values for some of the PHCs examined in the present study were published by Uedaira *et al.* (1989, 1990) based on measurements of spin-lattice relaxation times of ^{17}O. The parameter τ_c^h/τ_c^o reflects the microviscosity (structure) around the solute molecule as it describes the relative restriction in motion of water in the polyol solution; the higher the ratio, the more structured (more disturbed) the water molecules are in the hydration cosphere of the solute. The observed linear correlation between ΔH and τ_c^h/τ_c^o (Fig. 5(c)) further supports the argument that the tendency of amylopectin chains to retrograde is in some way connected with the solute compatibility with the water structure. Similar strong relationships were also shown between retrogradation and the dynamic hydration numbers, n_{DHN} and n^*_{DHN} (Table 2). As argued by Uedaira *et al.* (1989, 1990), these parameters express the dynamic state of water molecules in the solute's hydration cosphere, i.e. solutes with a large dynamic hydration number exhibit stronger interactions with water (the hydration layer is more structured than for pure water). Again, amylopectin retrogradation is favoured

in aqueous environments of solutes with large n_{DHN} or n^*_{DHN}.

Finally, the retrogradation data were plotted against 'relative mobility', a parameter introduced by Slade and Levine (1988). According to these authors, this parameter is related with the rotational diffusion time of the solute and is defined as the difference between storage temperature and T'_g (glass transition temperature of the freeze-concentrated aqueous solution) normalized by the difference $T_m - T_g$ of the dry solute. For 13 different solutes tested in the present study, a positive relationship between ΔH and relative mobility was found (Fig. 5(d) and Table 2), although the data are more scattered than for the relationships discussed above.

As evidenced by the magnitude of the correlation coefficients given in Table 2, strong relationships exist

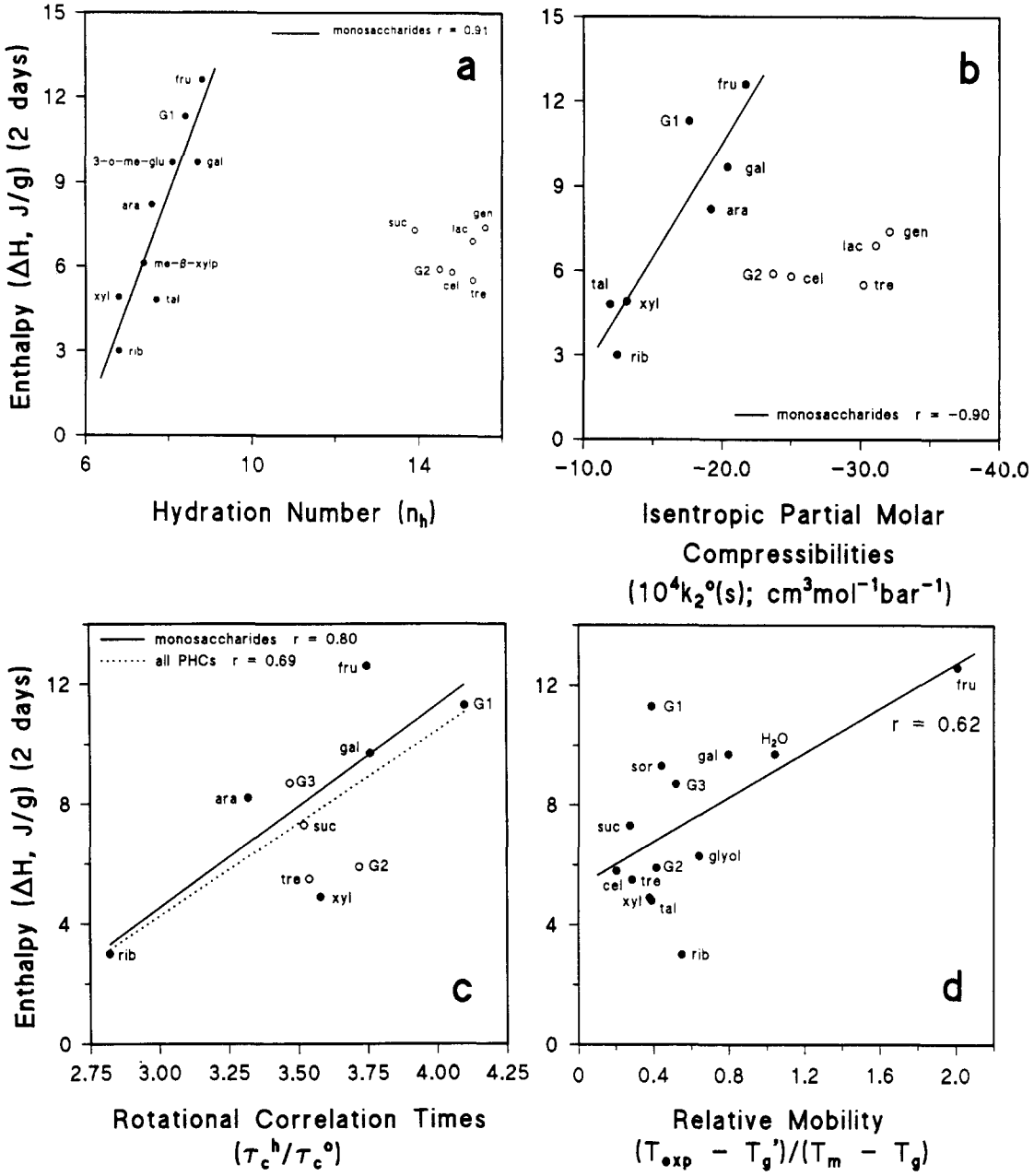

Fig. 5. Relationships between retrogradation (ΔH) of waxy maize starch gels at 6°C after 2 days storage; starch : PHC : water at 1:0·5:1·5, w/w, and hydration characteristics of polyhydroxy compounds. Hydration numbers and isentropic partial molar compressibilities were reported by Galema and Hoiland (1991), rotational correlation times were published by Uedaira *et al.* (1989, 1990), and relative mobility values were calculated from data published by Slade and Levine (1987, 1988). Abbreviations for PHCs: rib = ribose, G1 = glucose, G2 = maltose, G3 = maltotriose, 3-O-me-glu = 3-O-methyl-D-glucopyranose, me-β-xylp = methyl-β-D-xylopyranoside, ara = arabinose, tal = talose, xyl = xylose, gal = galactose, fru = fructose, cel = cellobiose, lac = lactose, gen = gentiobiose, tre = trehalose, suc = sucrose, sor = sorbitol, glyol = glycerol.

Table 2. Relationships between the effect of polyols on retrogradation of waxy maize starch gels (ΔH at specified storage time) and selected physicochemical properties of aqueous polyol solutions

Parameter	References	D.F.	Correlation coefficient (r)				
			12 h	1 day	2 days	3 days	5 days
Hydration number (n_h)							
Monosaccharides	Galema & Hoiland (1991)	8	0·85****	0·90****	0·91****	0·89****	0·80***
Disaccharides		5	−0·05	−0·32	−0·03	0·66	0·22
Both		14	−0·18	−0·12	0·02	0·02	0·05
Isentropic partial molar compressibilities ($cm^3\ mol^{-1}\ bar^{-1}$)							
Monosaccharides	Galema & Hoiland (1991)	6	−0·82**	−0·80**	−0·90***	−0·89***	−0·84***
Disaccharides		4	−0·39	−0·09	0·64	−0·62	−0·22
Both		11	−0·16	−0·19	−0·17	−0·37	−0·11
Rotational correlation times (τ_c^h/τ_c^o)							
Monosaccharides	Uedaira *et al.* (1989)	5	0·60	0·80**	0·80**	0·80**	0·81**
Di/trisaccharides	Uedaira *et al.* (1990)	3	−0·01	0·62	−0·65	−0·10	0·68
Both		9	0·49	0·74***	0·69**	0·76***	0·80**
Dynamic hydration number (n_{DHN})							
Monosaccharides	Uedaira *et al.* (1989)	5	0·60	0·80**	0·80**	0·80**	0·81**
Di/trisaccharides	Uedaira *et al.* (1990)	3	0·13	0·41	0·79	0·68	0·06
Both		9	−0·32	−0·09	0·05	0·12	0·14
Dynamic hydration number (n^*_{DHN})							
Monosaccharides	As described in methods	5	0·82**	0·94***	0·93***	0·91***	0·87**
Di/trisaccharides		2	−0·69	0·35	−0·94*	0·95**	0·99**
Both		8	−0·15	0·07	0·06	0·24	0·32
Relative mobility $(T_{exp} - T_g')/(T_m - T_g)$	Slade & Levine (1988)	13	0·64**	0·56**	0·62**	0·64**	0·52**

*significant at $p < 0·1$; **significant at $p < 0·05$; ***significant at $p < 0·01$; ****significant at $p < 0·001$.

between the extent of retrogradation and hydration characteristics of the PHCs (particularly monosaccharides) at all storage periods. These observations provide support for the notion that compatibility of small carbohydrate solutes with the water structure is of crucial importance in determining conformational stability of starch polymers in an aqueous environment. Monosaccharides which fit well in the water structure (e.g. ribose) also seem to retard polymer chain reordering. In contrast, solutes which greatly disturb the structure of water appear to facilitate conformational ordering and aggregation of starch molecules.

Among small molecular size carbohydrates, differences in their compatibility with water are attributed to the stereochemistry of their anomeric forms in solution. According to the works of Galema and co-workers (Galema & Hoiland, 1991; Galema *et al.*, 1990, 1992), compatibility is governed by the nearest or the next nearest neighbour oxygen distances in the molecule compared to the relevant oxygen distances in liquid water. The findings of their studies also indicated that the most crucial structural feature for compatibility of monosaccharides is the relative position of OH(4) and OH(2) groups. The results of Fig. 3 indicate that talose behaved more like a pentose, while arabinose resembled the responses of most hexoses. These observations are consistent with the compressibility values for these two sugars reported by Galema and Hoiland (1991). As it turns out, talose with axial OH(2) and OH(4) fits into water structure best among hexoses, thus having a hydration layer with the least disturbed structure compared to pure water (Table 3). Arabinose, on the other hand, with axial OH(4) and equatorial OH(2), brings about a larger disturbance in the hydrogen-bonded network of water. All other pentoses, which have OH(4) in equatorial and OH(2) in either equatorial (e.g. ribose, xylose) or axial positions show better compatibility with the water structure. The keto-hexose fructose disturbs the hydration layer more than glucose and this is probably because the —CH(OH) group is situated at the anomeric centre (Galema & Hoiland, 1991). A strong perturbation of water structure caused by fructose, as compared to glucose and sucrose, is also deduced from deconvolution of Roman spectra of D-fructose solutions (Mathlouthi & Seuvre, 1988). For glucose oligosaccharides (G1–G3), Uedaira *et al.* (1989, 1990) reported progressively decreasing τ_c^h/τ_c^o values from glucose (3·76) to maltotriose (3·47), which implies that maltotriose has a less disturbing effect on water structure than maltose or glucose. These findings are consistent with the retrogradation data of the present study (Table 1 and Fig. 1) according to which maltotriose is the most effective glucose oligosaccharide in impeding retrogradation. The promoting effect of maltooctaose may be attributed to decreased polymer miscibility among components in the composite gel. This would lead to demixing and a higher concentration of amylopectin in its own microphase. According to the calorimetric studies of Longton and LeGrys (1981) and Zeleznak and Hoseney (1986), starch retrogradation increases with increasing weight ratios of starch/water between 0·1 and 1·5, whereas the reverse trend is seen at ratios above 1·5.

Table 3. Conformation of sugar, hydration number and retrogradation data for representative pentoses and hexoses

Sugar	Main conformer[a]	Hydration number, n_h[b]	ΔH (J/g)[c]	
			18 h	48 h
Ribose	1e 2e 3a 4e	6·8	1·9 (3·7)[d]	3·0 (9·7)[d]
Xylose	1e 2e 3e 4e	6·8	1·2	4·9
Arabinose	1a 2e 3e 4a	7·6	3·3	8·2
Talose	1a 2a 3a 4a 6e	7·7	1·1	4·8
Galactose	1e 2e 3e 4a 6e	8·7	7·1	9·7
Glucose	1e 2e 3e 4e 6e	8·4	6·5	11·3
Fructose	1e 2a 3e 4e 5a	8·8	8·2	12·6

[a]Denotes axial (a) or equatorial (e) hydroxyl groups.
[b]Source: Galema and Hoiland (1991).
[c]Retrogradation data (starch:sugar:water at 1:0·5:1·5, w/w) following storage at 6°C. Data are means of at least triplicate measurements; c.v. <8% in all cases.
[d]Numbers in parentheses are the enthalpy values of control gels (starch:water at 1:1·5, w/w).

Role of PHCs in starch retrogradation

In the light of the above considerations and experimental findings of the present study, one could envisage several contributing effects to understand the role of PHCs in starch retrogradation. First, these solutes would tend to reduce the effective water concentration due to formation of a hydration layer around their molecules. Using the published hydration numbers for some PHCs, estimates of the amount of available 'mobile' water in the gels at a specified composition of the ternary starch–PHC–water system can be calculated. Assuming a monolayer hydration cosphere only and a weight ratio starch : sugar : water of 1:0·5:1·5, the ratio of starch to 'available' water for fructose ($n_h = 8·8$) and ribose ($n_h = 6·8$), two extreme solutes in their responses, would be 0·99 and 0·91, respectively. These numbers are still within the range of 0·1–1·5 where retrogradation increases with increasing weight ratio of starch : water (Zeleznak & Hoseney, 1986); the corresponding ratio for pure waxy maize starch gels used in the present study was 0·67. It seems, from these assumptions, that both sugars must promote retrogradation if their action is entirely related to changes in 'available' water. Obviously the similar changes in starch : 'available' water ratio for both sugars cannot account for the large differences in the retrogradation kinetics observed for these solutes. Also, the antiplasticization theory for PHCs proposed by Slade and Levine (1987) can only partially explain the retarding effect sugars have on retrogradation. These authors claimed that incorporation of PHCs in an aqueous medium decreases chain mobility and diffusion in the water/solute-plasticized amylopectin matrix; i.e. PHCs elevate the T_g of the composite medium compared to water alone. This theory cannot explain the profound accelerating effect some solutes (e.g. fructose) have on retrogradation kinetics if one assumes a homogeneous solvent–polymer–cosolute composite matrix.

Another factor which seems to play a dominant role in the kinetics of starch retrogradation, as evidenced by the findings of the present study, is related to solute compatibility with the water structure. This notion is supported by the strong relationships between retrogradation and hydration characteristics of the PHCs (Fig. 5). The results indicated that the poorer a small carbohydrate solute fits into the structure of water, the more it enhances retrogradation. Although the exact mechanism by which these effects are brought about is not clear, it is conceivable that solute compatibility may affect solvent composition and microviscosity in the vicinity of polymer chains. Monosaccharides which cause very little disturbance in the water structure (e.g. ribose) may have greater access to the hydration layer of starch chains since the distances between hydroxyl groups in their ring structures resemble those of water. Consequently, the polymer would experience a localized environment of increased viscosity (i.e. strong antiplasticizing effect compared to water alone). This would reduce translational motions and thereby retard chain ordering and aggregation. In contrast, PHCs which greatly disturb the 'normal' water structure (e.g. fructose) and form strong hydration layers around them could be more excluded from the vicinity of the polymer hydration cosphere. For such solutes, the influence from increasing the effective polymer concentration (due to more selective partioning of the solute) could become greater than the generally expected antiplasticizing effect of the sugar. This in turn would result in enhanced retrogradation kinetics. Further studies on water–solute–starch interactions would be required to test this postulate.

CONCLUSION

On the basis of the kinetic data for starch retrogradation presented herein and the relationships found

with the hydration characteristics of PHCs, the authors submit that chain ordering of amylopectin in sugar-containing starch gels is governed by the compatibility of the sugar with the water structure. Clearly, solutes which cause little perturbation in the hydrogen-bonded network of water have a stabilizing effect on the polymer, thus significantly retarding retrogradation. Although the precise reasons for such responses are not clear as yet, the findings of this work require special consideration in developing a more systematic approach to modify and control the mechanical properties and storage stability of starch-based products. In designing a small carbohydrate solute as an effective antistaling agent, emphasis must be placed on the stereochemistry of its dominant conformer(s) in solution, particularly as it relates to water structure.

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