ELSEVIER

Carbohydrate Research 280 (1996) 157–169

CARBOHYDRATE RESEARCH

Note

Effect of *n*-alkyl glucosides on waxy maize and wheat starch retrogradation

Costas G. Biliaderis [a,1], Dale J. Prokopowich [a], Mark R. Jacobson [b,2], James N. BeMiller [b,*]

[a] *Department of Food and Nutritional Sciences, The University of Manitoba, Winnipeg, MB R3T 2N2, Canada*
[b] *Whistler Center for Carbohydrate Research and Department of Food Science, Purdue University, West Lafayette, IN 46907-1160, USA*

Received 19 October 1994; accepted in revised form 2 August 1995

Keywords: *n*-Alkyl α-D-glucopyranosides; Retrogradation; Starch gels; Surfactants

The gelatinization of starch when granules are heated in the presence of water and the formation of ordered molecular structures during storage of products containing gelatinized or pasted starch granules (often described by the term retrogradation) greatly affect the texture and shelf-life of starch-containing foods. Retrogradation is believed to be a major contributor to staling of baked products, although staling is a complex phenomenon in which many factors and processes are involved [1–4]. Staling, with all accompanying changes in texture and sensory attributes, is responsible for the decreased acceptance of bakery items by consumers. Because of the economic and scientific interest in staling, much effort has been devoted to establish a fundamental description of this phenomenon in terms of physicochemical changes and interactions among constituents. Most investigations of bread staling have focused on starch retrogradation and the factors influencing the kinetics of this process.

The processes of chain ordering and crystallization between and/or within starch molecules are facilitated by water plasticization (increasing molecular mobility) of the amorphous starch matrix produced by gelatinization. It is generally accepted that the

* Corresponding author. Tel. (317)-494-6171; Fax (317)-494-7953.
[1] Current address: Department of Food Science and Technology, Aristotle University, Thessaloniki, Greece 540 06.
[2] Current address: Nestlé Research and Development Center in Connecticut, New Milford, CT 06776-5528, USA.

SSDI 0008-6215(95)00296-0

crystallization of amylose that has leached from swollen granules occurs rapidly and is generally essentially complete by the time the baked product has cooled to room temperature, while the staling process takes place over a time period measured in days and is associated with amylopectin crystallization. It is believed that adoption of double helical structures and chain aggregation are the underlying molecular events that effect the changes associated with amylopectin retrogradation [5–7]. However, it is often difficult to link the molecular processes occurring during gelation and retrogradation with the mechanical properties of the system, i.e., the kinetics of retrogradation and firming are not always correlated [4]. Moreover, the factors that influence chain ordering and the mechanical properties of starch gels are not fully known. Besides moisture and starch composition (amylose/amylopectin ratio, granular lipids, etc.) [8,9], other constituents also affect the rate of retrogradation. For example, monoglycerides and other emulsifiers have long been known for their antifirming action [10] and, thus, are frequently used in bread formulations to improve crumb softness and extend the shelf-life of the product. Monoacyl lipids form inclusion complexes with starch molecules and thereby prevent interchain associations; it is likely that texture modification is controlled by this interaction [11]. Amylopectin–lipid complexes have been studied far less than amylose–lipid complexes, due in part to only relatively recent direct evidence of their interaction, despite considerable indirect evidence of amylopectin–lipid interactions from research that has shown that monoacyl lipids modify the properties of amylopectin pastes [12]. In addition, due to a lack of agreement in the limited existing results, it is difficult to draw any conclusions as to the optimal lipid acyl chain length for amylopectin complexing [13–15]. Sugars and other polyhydroxy compounds also affect chain ordering and the physical properties of starch gels, although such effects are not well understood [16–21]. Generally, sugars reduce firmness and starch crystallinity; an

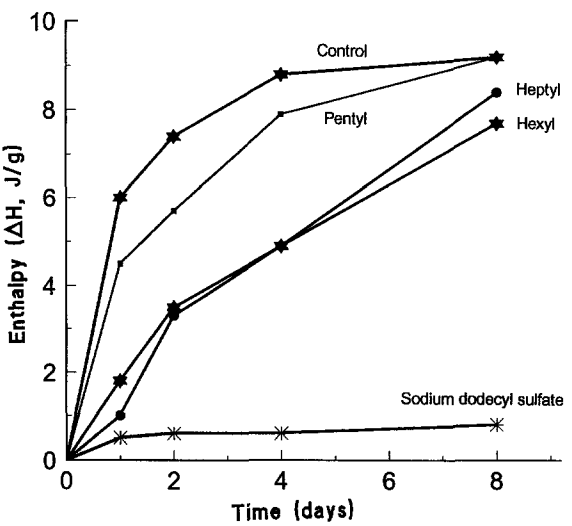

Fig. 1. Effect of added *n*-alkyl α-D-glucopyranosides on the retrogradation endotherm (ΔH) of 40% (w/w) waxy maize starch gels (4.5 mg starch in 5.5 μL of 0.305 M glucoside or SDS) stored at 4°C.

exception is D-fructose, which is often reported to promote structure development in ageing starch gels [17–19,21].

Because of the significance of starch retrogradation to the quality of starch-based products, there is a continuing interest in exploring new possibilities to control the rate of retrogradation. The present study was undertaken to investigate the effect on the kinetics of starch retrogradation of a series of *n*-alkyl D-glucosides differing both in the chain length of the aliphatic group and in anomeric configuration. The presence in their molecular structures of both an alkyl group (which may complex with starch molecules) and a glucosyl unit (compatible with the starch matrix) has prompted us to test the potential of these compounds as retrogradation inhibitors. The time-dependent changes in structure of the composite starch-glucoside gels were followed by calorimetry and small strain dynamic rheometry.

1. Results and discussion

Calorimetric measurements.—Calorimetry has proved to be a convenient tool to quantify the extent of chain ordering in starch gels and baked products [9], i.e., the enthalpy of the endothermic transition is proportional to the degree of retrogradation. The effects of added *n*-alkyl D-glucosides and SDS on amylopectin retrogradation of waxy maize starch gels are shown in Figs. 1 and 2; DSC data are summarized in Table 1. The solution concentration of alkyl glucosides used (305 mM) is well above their critical micelle concentrations which range from 0.19 mM to about 70 mM [22]. Depending on the molecular weight of each alkyl glucoside, the amount of glucoside

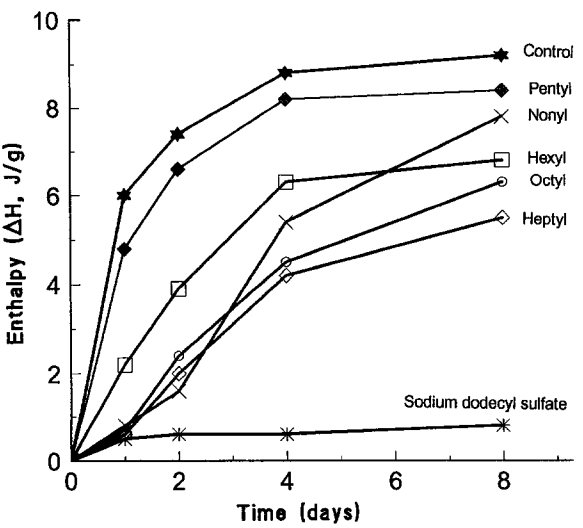

Fig. 2. Effect of added *n*-alkyl β-D-glucopyranosides on the retrogradation endotherm (ΔH) of 40% (w/w) waxy maize starch gels (4.5 mg starch in 5.5 μL of 0.305 M glucoside or SDS) stored at 4°C.

Table 1
Effect of *n*-alkyl glucopyranosides on the retrogradation endotherm (ΔH) of 40% (w/w) waxy maize starch gels [a] stored at 4°C

Sample	Storage time (days)			
	1	2	4	8
Control	6.0+0.5 [b]	7.4+0.5	8.8+0.1	9.2+04
+ α-pentyl	4.5+0.5	5.7+0.5	7.8+0.3	9.2+0.5
+ α-hexyl	1.8+0.5	3.5+0.5	4.9+0.3	7.7+0.3
+ α-heptyl	1.0+0.5	3.3+0.4	4.9+0.4	8.4+0.4
+ α-octyl	glucoside melting/dissolving endotherm at 41°C			
+ α-nonyl	glucoside melting/dissolving endotherm at 45°C			
+ β-pentyl	4.8+0.4	6.6+0.3	8.2+0.2	8.4+0.4
+ β-hexyl	2.2+0.4	3.9+0.2	6.3+0.5	6.8+0.4
+ β-heptyl	0.6+0.1	2.0+0.4	4.2+0.5	5.5+0.5
+ β-octyl	0.7+0.3	2.4+0.4	4.5+0.2	6.3+0.3
+ β-nonyl	0.8+0.1	1.5+0.1	5.4+0.4	7.8+0.4
+ β-dodecyl	glucoside melting/dissolving endotherm at 45°C			
+SDS	0.6+0.1	0.6+0.1	0.6+0.2	0.8+0.1

[a] Starch gels consisted of 4.5 mg starch in 5.5 μL of 0.305 M glucoside or SDS solution.
[b] Mean+S.D. (J/g).

based on the weight of starch (dwb) ranged between 10.5% (butyl) and 14.6% (dodecyl), but was constant on a mole ratio basis. These levels are well above those commonly used (ca. 0.5% w/w of flour) for crumb softener and dough strengthener surfactants [23]. Using much lower concentrations than used in this study, namely, 0.5% of the weight of amylopectin, Ward et al. [24] found that amylopectin recrystallization was not affected by SSL. At concentrations above 1–2% (w/w of starch), monoglycerides are known to interact with both amylose and amylopectin, substantially reducing the rate of retrogradation [25–27]. The development of ordered structures in waxy maize starch gels was reduced by the addition of glucosides, although the responses were less pronounced than those given by the anionic detergent SDS. The relative effectiveness of glucosides in inhibiting retrogradation seemed to depend on the chain length of the alkyl group. After eight days of storage at 4°C, glucosides with intermediate chain lengths in their alkyl groups (6–8 carbon atoms) were the most effective in inhibiting structure formation. This behavior is likely connected with the ability of these compounds to complex with amylopectin chains. Huang and White [15] found that the monoglyceride with the shortest acyl chain (out of those with C_{12}–C_{18} fatty acyl chain lengths) formed the greatest number of complexes with waxy maize starch. The complexing may be due to interactions with the outer chains of amylopectin, association of which is believed to be the primary process involved in amylopectin retrogradation [7]. There were minor differences in the relative ranking of the alkyl α- and β-D-glucopyranosides as retrogradation inhibitors (e.g., heptyl vs. hexyl glucosides, Figs. 1 and 2). For the higher chain length β-D-glucopyranosides (*n*-octyl, *n*-nonyl, and *n*-dodecyl), sharp melting

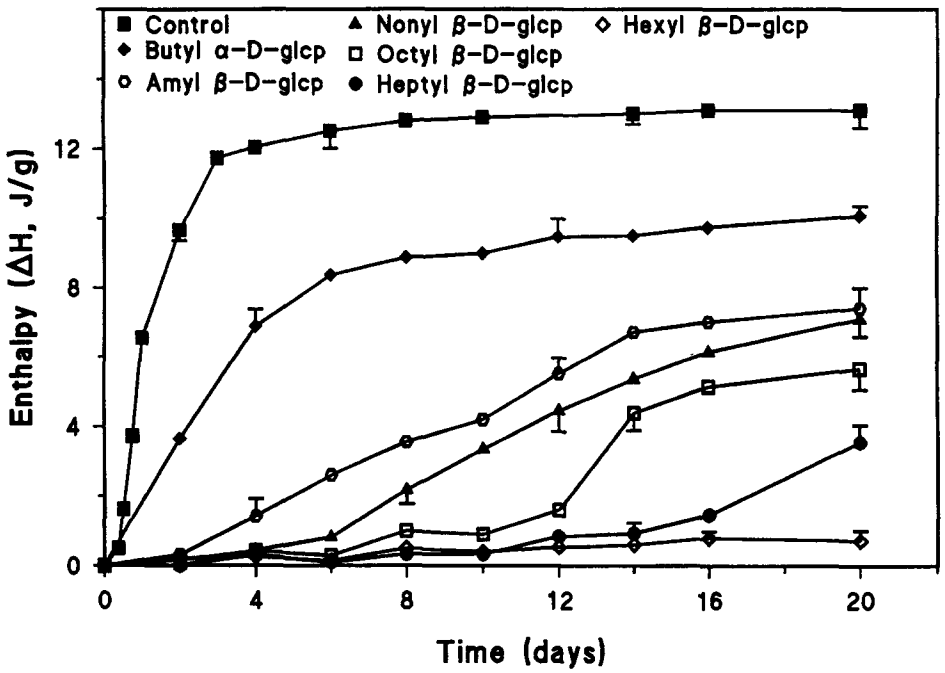

Fig. 3. Effect of added *n*-alkyl D-glucopyranosides on the retrogradation endotherm (ΔH) of waxy maize starch gels (starch:glucoside:water at 1.0:0.2:1.5 w/w; control gel, starch:water at 1.0:1.5 w/w) stored at 6°C.

transitions were found in the thermal profiles of the composite gels, indicating the melting of crystalline forms of these compounds (Table 1). These transitions, in the temperature range 39–46°C, overlap with the amylopectin retrogradation (staling) endotherm, limiting the use of calorimetry to quantify the extent of retrogradation in such gels. For the same reason, it was not possible to assess the inhibitory effect of GMS and SSL to chain ordering of amylopectin at comparable surfactant concentrations.

In a separate study, greater concentrations of glucosides (starch:glucoside:water ratio of 1.0:0.2:1.5, w/w) were employed and the waxy maize starch gels were stored at 6°C (Fig. 3). The most effective ligands in retarding retrogradation over the entire storage period were the *n*-hexyl and *n*-heptyl β-D-glucopyranosides. The effect of varying concentration of two β-glucosides on the extent of retrogradation was further assessed (Fig. 4). The gels showed a descending level of structure with increasing glucoside concentration. *n*-Hexyl β-D-glucopyranoside effected a greater reduction in rate of ΔH development than did the corresponding *n*-pentyl glucoside.

Rheological evaluation.—Dynamic rheometry is another useful means to monitor structure development in starch gels. It allows continuous assessment of the viscoelastic properties as reflected by the G′ (storage modulus) and G″ (loss modulus) without altering the structural elements of the gel network [28]. The latter is satisfied when measurements are made in the linear viscoelastic region of the specimen (i.e., when stress is proportional to strain). According to previous studies on concentrated starch

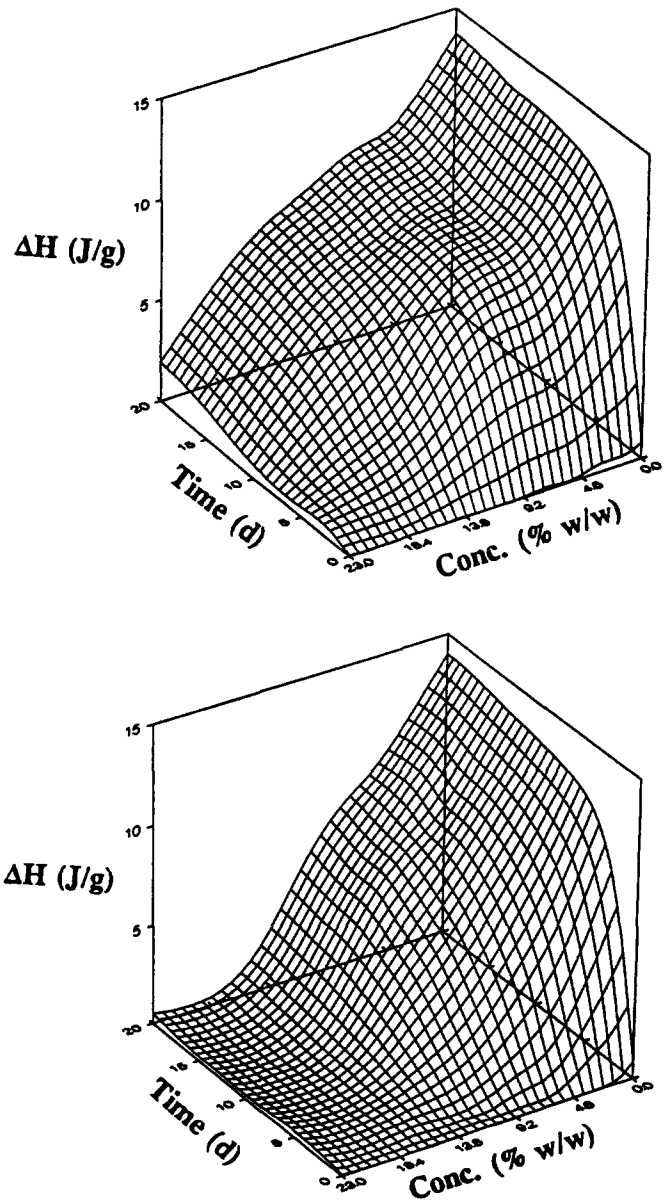

Fig. 4. Effect of glucoside concentration on retrogradation endotherm (ΔH) of waxy maize starch gels stored at 6°C for 20 days. The level of glucoside (x) in the weight ratio of starch:glucoside:water of 1.0:x:1.5 varied between 0.05 and 0.45. The solution concentration of glucoside is expressed as % (w/w): (top) *n*-pentyl β-D-glucopyranoside; (bottom) *n*-hexyl β-D-glucopyranoside.

gels (> 30% solids) [11,29], testing at strains < 2.0% meets the requirement for linear viscoelasticity and was employed in this study.

A comparison of G′ development in waxy maize starch gels containing pentyl or

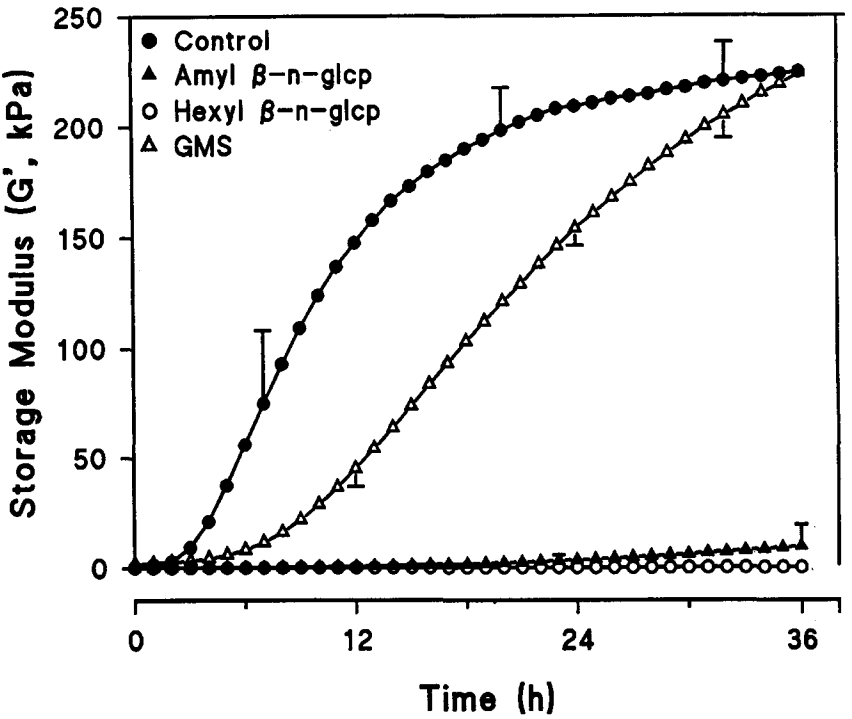

Fig. 5. Effect of added *n*-alkyl β-D-glucopyranosides or GMS on storage modulus (G′) of waxy maize starch gels stored at 8°C. The surfactants were incorporated at a weight ratio of 1.0:0.2:1.5 in the starch:surfactant:water mixture.

hexyl β-D-glucosides or GMS (starch:emulsifier:water ratio of 1.0:0.2:1.5, w/w) stored at 8°C is given in Fig. 5. At such high levels of added glucosides, the gel network development was suppressed dramatically by the alkyl β-glucosides as compared to GMS. G′ values are generally considered to reflect crosslinking density arising either from simple interchain entanglements or larger structural domains (e.g., crystallites) [28]. In the presence of large amounts of glucosides, interchain associations in the polysaccharide gel matrix seem to be reduced. However, at lower glucoside levels (2% w/w of starch), the gel-firming kinetics were not suppressed as effectively and the responses were similar to those produced by GMS (Fig. 6). For these gels, the G′–time profiles indicated that the moduli did not reach pseudoplateau values during the first 36 h of storage (8°C) as observed with the control. The rheological data of similar experiments on wheat starch gels are shown in Fig. 7. Contrary to the typical sigmoid G′–time curve of amylopectin, the G′ profiles of wheat starch gels showed a steady increase in modulus with time. All emulsifiers tested (at 2% w/w of starch) slightly reduced the kinetics of G′ development. The retarding effect on firming was far less than that observed for waxy maize starch, presumably because wheat starch contains amylose which dominates the gel network properties [11,28]. The initial rigidity of the SSL-containing gel was greater than for the control wheat starch gel, confirming

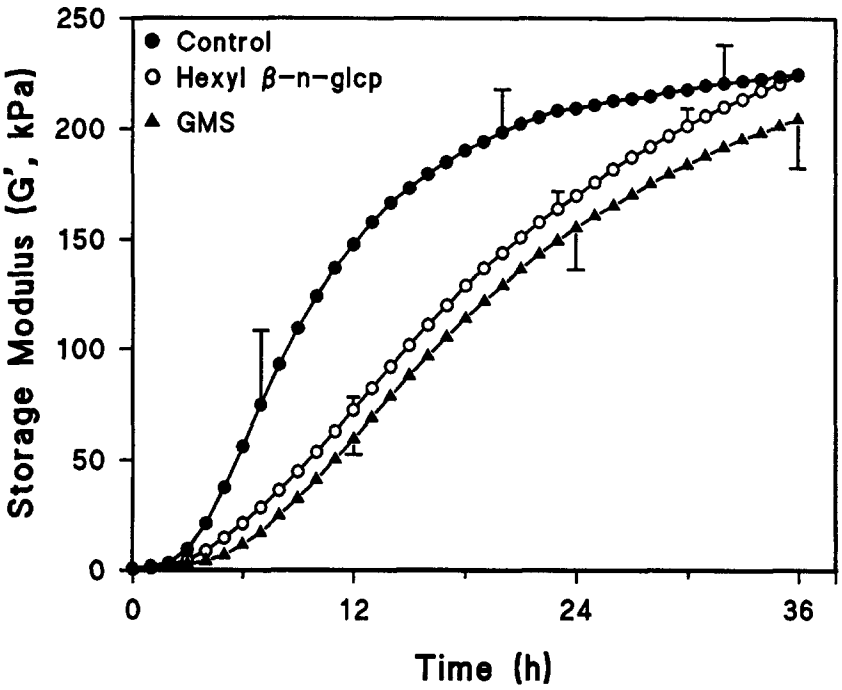

Fig. 6. Effect of added *n*-hexyl β-D-glucopyranoside and GMS (at 2.0% w/w of starch) on storage modulus (G') of 40% (w/w) waxy maize starch gels stored at 8°C.

previous findings for wheat starch gels fortified with ionic emulsifiers [11]. Overall, the rheological properties of the gels indicated that *n*-alkyl D-glucosides are as effective as other commonly used emulsifiers in retarding firmness of waxy maize and wheat starch gels.

2. Experimental

Materials.—Butyl, pentyl (amyl), hexyl, heptyl, octyl, nonyl, and dodecyl β-D-glucopyranosides were obtained from Sigma Chemical Co. (St. Louis, MO). Pentyl, hexyl, heptyl, octyl, and nonyl α-D-glucopyranosides were prepared by the method of Wing and BeMiller [30] with the following modifications: (A) the 1-nonyl α-D-glucopyranoside reaction mixture was heated at its reflux temperature for 96 h; (B) solutions were neutralized with Amberlite IRA-400 (OH^-) anion-exchange resin; (C) following alcoholysis, product isolations were accomplished by the various methods described for the specific products.

Sodium dodecyl sulfate (SDS) (99%) was obtained from Bio-Rad Laboratories (Richmond, CA). Sodium stearoyl 2-lactate (SSL) was obtained from Patco Products (Kansas City, MO). Waxy maize and wheat starches were obtained from A.E. Staley Manufacturing Co. (Decatur, IL) and Ogilvie Mills (Midland, ON), respectively. α-D-

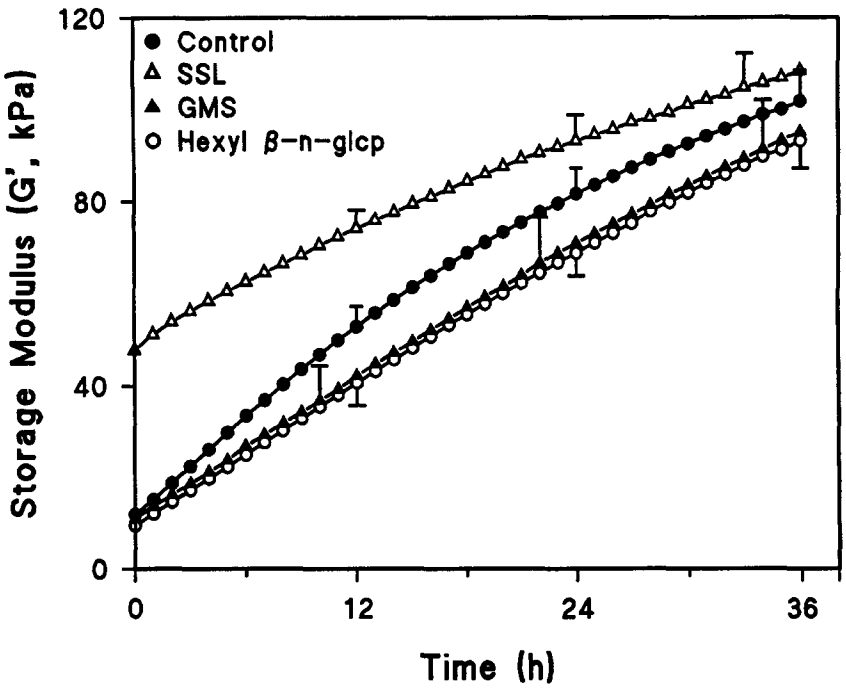

Fig. 7. Effect of added *n*-hexyl β-D-glucopyranoside, GMS, and SSL (at 2.0% w/w of starch) on storage modulus (G') of 40% (w/w) wheat starch gels stored at 8°C.

Glucopyranose, 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, 1-nonanol, D_4-methanol, tetramethylsilane (NMR grade), Amberlite XAD-4 hydrophobic resin, and Amberlite IRA-400 anion-exchange resin were obtained from Aldrich Chemical Co. (Milwaukee, WI). β-Glucosidase (3542 units/mg) was obtained from ICN Biochemicals (Irvine, CA). Acetic anhydride, ethanol, and ethyl ether were obtained from J.T. Baker Inc. (Phillipsburg, NJ). All chemicals were used as obtained.

General methods.—Thin-layer chromatography (TLC) was done using Silica Gel-60 plates (EM Separations, Gibbstown, NJ) and 3:1 (v/v) chloroform:ethanol. Uncorrected melting points were obtained using a Fisher–Johns melting-point apparatus. (Note: The melting point given for 1-octyl α-D-glucopyranoside does not agree with those in the literature, but does correspond with the temperature of a phase-transition to a liquid crystalline state [31]. Since other α-D-glucopyranosides have been found to be mesogenic [31], melting points recorded may reflect similar phase transitions.) Fast atom bombardment (FAB) mass spectra were recorded on a Kratos MS50 mass spectrometer using a DTT/DTE matrix. ^{1}H-NMR spectra were recorded using a General Electric QE-300 NMR spectrometer on samples dissolved in D_4-methanol containing tetramethylsilane.

1-Pentyl α-D-glucopyranoside.—Product was crystallized by dissolving the syrup in ethyl acetate and cooling the solution to −10°C. Crystals were recovered by filtration

and washed with cold ethyl acetate. Product was recrystallized in ethyl ether at −20°C, collected by filtration, and washed with cold ethyl ether. Crystals were dried in a vacuum oven at 40°C overnight; yield 1.93 g (11.6%); mp 81–83°C; NMR (CD_3OD): ^1H, δ 4.76 (H-1, $J_{1,2}$ 3.7 Hz); FABMS: m/z 251 [M + 1]; $[\alpha]_D^{25}$ +131.5° (c 1.0, MeOH).

1-Hexyl α-D-glucopyranoside.—The solution was evaporated under reduced pressure, with water added occasionally to remove 1-hexanol by azeotropic distillation. Product was crystallized by dissolving the syrup in ethyl acetate and cooling the solution to −20°C. Crystals were recovered by filtration and washed with cold ethyl acetate. Product was recrystallized in ethyl ether at −20°C, recovered by filtration, and washed with cold ethyl acetate. Crystals were dried in a vacuum oven at 40°C overnight. NMR analysis indicated that some β-glucoside was present, so the product was dissolved in 400 mL of a 0.1 M acetate buffer, pH 5.0, and a solution of 760 units of β-glucosidase in 100 mL of H_2O was added. The mixture was held at 37°C for 2 days, then evaporated under reduced pressure to approximately 100 mL. The concentrated solution was added to a column (47.5 cm × 50 mm i.d., 425 mL) of Amberlite XAD-4 resin. The column was eluted with 1 L of H_2O, 1 L of 25% ethanol, 2 L of 50% ethanol, then 1 L of 75% ethanol; 10-mL fractions were collected. Fractions containing product (determined by TLC) were combined and evaporated under reduced pressure to a syrup. The syrup was dissolved in ethyl acetate, and hexanes were added to incipient turbidity. The mixture was cooled to 4°C and seeded with 1-hexyl α-D-glucopyranoside (from a previous small volume crystallization). Crystals were collected by filtration, washed with cold ethyl acetate, and dried in a vacuum oven at 40°C overnight; yield 4.11 g (23.4%); mp 65–66°C; NMR (CD_3OD): ^1H, δ 4.76, (H-1, $J_{1,2}$ 3.7 Hz); FABMS: m/z 265 [M + 1]; $[\alpha]_D^{25}$ +130.7° (c 1.0, MeOH).

1-Heptyl α-D-glucopyranoside.—The syrup was evaporated under reduced pressure, with water added occasionally during evaporation to remove 1-heptanol by azeotropic distillation. Product was crystallized by dissolving the resulting syrup in ethyl acetate and cooling the solution to −10°C. Crystals were recovered by filtration and washed with cold ethyl acetate. Product was recrystallized in ethyl ether at 5°C initially, then at −5°C, recovered by filtration, and washed with cold ethyl acetate. Crystals were dried in a vacuum oven at 40°C overnight; yield 3.65 g (19.7%); mp 52–54°C; NMR (CD_3OD): ^1H, δ 4.76 (H-1, $J_{1,2}$ 3.7 Hz); FABMS: m/z 279 [M + 1]; $[\alpha]_D^{25}$ +127.0° (c 1.0, MeOH).

1-Octyl α-D-glucopyranoside.—The syrup was dissolved in 60 mL of methylene chloride, and the solution was applied to a column (38 cm × 50 mm i.d., 390 mL) of Silica Gel 60 (EM Separations, Gibbstown, NJ). The column was eluted with 2400 mL of a 2:1 (v/v) methylene chloride–ethanol solution. After the solvent front eluted (i.e., after 500 mL), 50-mL fractions were collected. Those containing product (determined by TLC) were combined and evaporated under reduced pressure to a syrup. The resulting syrup was dissolved in 100 mL of methylene chloride. Hexanes were added to incipient turbidity, and the solution was seeded with 1-octyl α-D-glucopyranoside and cooled to −10°C to crystallize. Crystals were collected by filtration and washed with cold ethyl acetate. Product was recrystallized in ethyl acetate at −10°C, collected by filtration, and washed with cold ethyl acetate. Crystals were dried in a vacuum oven at 40°C overnight;

yield 4.64 g (23.8%); mp 71–73°C; NMR (CD_3OD): ^1H, δ 4.76 (H-1, $J_{1,2}$ 3.7 Hz); FABMS: m/z 293 [M + 1]; $[\alpha]_D^{25}$ +116.0° (c 1.0, MeOH).

1-Nonyl α-D-glucopyranoside.—A solution in methylene chloride was applied to a column (40 cm × 50 mm i.d., 390 mL) of Silica Gel 60. The column was eluted with 1.0 L of methylene chloride, then with 1300 mL of a 1:1 (v/v) methylene chloride–ethanol solution; 50-mL fractions were collected. Fractions containing product (determined by TLC) were combined and evaporated under reduced pressure to a syrup, which was held 48 h in a vacuum oven at 60°C and < 25 mm Hg pressure in the presence of paraffin shavings to remove residual 1-nonanol. The syrup was then dissolved in 70% ethanol, and the solution was evaporated under reduced pressure to incipient turbidity. The mixture was cooled slowly to 5°C and seeded with previously prepared 1-nonyl α-D-glucopyranoside. Crystals were collected by filtration and washed with cold water. Product was recrystallized in ethyl ether and hexanes (added to incipient turbidity) at −20°C, collected by filtration, washed with cold water, and dried in a vacuum oven at 40°C. NMR analysis indicated that some β-glucoside was present, so the crystals were dispersed in 400 mL of 0.1 M acetate buffer, pH 5.0, and a solution of 760 units of β-glucosidase in 100 mL of H_2O was added. The mixture was kept at 37°C for 2 days, then stirred at room temperature for 1 day. The mixture was evaporated under reduced pressure to approximately 100 mL, heated on a steam bath, then filtered while hot. Crystallization occurred upon cooling to 4°C. Crystals were collected by filtration, washed with cold water, and dried in a vacuum oven at 40°C overnight; yield 3.19 g (15.6%); mp 69–70°C; NMR (CD_3OD): ^1H, δ 4.74 (H-1, $J_{1,2}$ 3.7 Hz); FABMS: m/z 307 [M + 1]; $[\alpha]_D^{25}$ +114.6° (c 1.0, MeOH).

Preparation, storage and analysis of starch gels.—Two separate calorimetric studies were conducted to assess the inhibitory role of glucosides on starch retrogradation. First, a DuPont 910 differential scanning calorimeter equipped with a high-pressure cell was used to make calorimetric measurements of ageing starch–glucoside gels. Starch samples (3.0–3.3 mg) were suspended in aqueous glucoside solutions/dispersions (at a specified glucoside concentration) to obtain a ratio of starch:water of 1.0:1.5 (w/w). Since SSL and GMS were insoluble in water, these emulsifiers were first dissolved in 95% ethanol and mixed with the starch granules (at a specified weight ratio of starch/lipid); the ethanol was then removed under vacuum at 60°C [11]. Aqueous starch granule suspensions with or without added emulsifiers were hermetically sealed in polymer-coated aluminum pans and heated to 135°C under pressure (1400 kPa with N_2) to gelatinize the granules. After cooling, the gels were stored at 6°C. Aged gels were analyzed with the DuPont calorimeter as described elsewhere [32]. In a separate study, 4.5 mg of waxy maize starch (11.7% moisture [33]) and 5.5 μL of a 0.305 M solution of a glucoside or SDS [3] were mixed in a 40-μL aluminum DSC pan (Mettler ME-27311). The pans were sealed, and the starch was gelatinized in an oven at 100°C for 20 min. The pans were then stored at 4°C until analyzed with a Mettler 30 DSC equipped with a TC-11 processor. The area of the retrogradation endotherm (ΔH in J/g starch) was

[3] 0.305 M is the molar concentration equivalent to the ratio of SSL to starch given by a SSL:wheat starch ratio of 1:9 (w/w), using 71% for the amount of starch in a 70% extraction flour [34].

taken as the indicator of chain ordering (amylopectin) in ageing gels; data represent means of at least three measurements.

The effect of glucoside concentration (for pentyl and hexyl β-D-glucopyranosides) on retrogradation of waxy maize starch was also examined. Three-dimensional plots (ΔH vs. glucoside concentration and time) were generated using the Systats software package (Evanston, IL); a distance weighted least-squares smoothing function was applied to fit a surface through the data points. The levels chosen for the two independent variables were: (a) glucoside level (x) in the starch:glucoside:water mixture (1.0:x:1.5, w/w) was varied as follows: 0.05, 0.10, 0.20, 0.30, and 0.45; (b) storage periods at 6°C were 12 h and 1, 2, 4, 6, 8, 10, 12, 14, 16, and 20 days.

The mechanical properties of waxy maize and wheat starch gels, with and without added emulsifiers, were measured by small strain oscillatory rheometry using a Bohlin VOR Rheometer (Bohlin Rheology, Edison, NJ), operated with parallel plate geometry (30 mm diameter) and a torque element of 93.2 g · cm. Gels were prepared for rheological examination as described elsewhere [11,35].

The kinetic aspects of structure development were probed at 0.2 Hz, 10% amplitude (< 2.0% strain) and 8°C; data were collected for 36 h at 15-min intervals, and means of triplicate measurements were calculated. Storage modulus (G′) values were used to evaluate changes in rigidity of the ageing gels.

References

[1] K. Kulp and J.G. Ponte Jr, *CRC Crit. Rev. Food Sci. Nutr.*, 15 (1981) 1–48.
[2] H. Levine and L. Slade, in H. Faridi and J.M. Faubion (Eds.), *Dough Rheology and Baked Product Texture*, Van Nostrand Reinhold/AVI, New York, 1990, p 157.
[3] R.C. Hoseney, M.L. Martin, and H. He, in D.J. Martin and C.W. Wringley (Eds.), *Cereals International 91*, Royal Australian Chemical Institute, Parkville, Vic., Australia, 1991, pp 99–106.
[4] D.R. Lineback, in D.J. Martin and C.W. Wringley (Eds.), *Cereals International 91*, Royal Australian Chemical Institute, Parkville, Vic., Australia, 1991, pp 64–69.
[5] M.J. Miles, V.J. Morris, and S.G. Ring, *Carbohydr. Polym.*, 4 (1984) 73–77.
[6] M.J. Miles, V.J. Morris, P.D. Orford, and S.G. Ring, *Carbohydr. Res.*, 135 (1985) 271–281.
[7] S.G. Ring, P. Colonna, K.J. I'Anson, M.T. Kalichevsky, M.J. Miles, V.J. Morris, and P.D. Orford, *Carbohydr. Res.*, 162 (1987) 277–293.
[8] K.J. Zeleznak and R.C. Hoseney, *Cereal Chem.*, 63 (1986) 407–411.
[9] C.G. Biliaderis, in V.R. Harwalkar and C.-Y. Ma (Eds.), *Thermal Analysis of Foods*, Elsevier Applied Science, London, 1990, p 169.
[10] T. Riisom, N. Krog, and J. Eriksen, *J. Cereal Sci.*, 2 (1984) 105–118.
[11] C.G. Biliaderis and J.R. Tonogai, *J. Agr. Food Chem.*, 39 (1991) 833–840.
[12] A.-C. Eliasson and K. Larsson, *Cereals in Breadmaking*, Marcel Dekker, New York, 1993, pp 171–201.
[13] J. Langendijk and H.J. Pennings, *Cereal Sci. Today*, 15 (1970) 354–356, 365.
[14] L.V. Batres and P.J. White, *JAOCS*, 63 (1986) 1537–1540.
[15] J.J. Huang and P.J. White, *Cereal Chem.*, 70 (1993) 42–47.
[16] J.L. Maxwell and H.F. Zobel, *Cereal Foods World*, 23 (1978) 124–128.
[17] L. Slade and H. Levine, in S.S. Stivala, V. Crescenzi, and I.C.M. Dea (Eds.), *Industrial Polysaccharides*, Gordon and Breach Science, New York, 1987, pp 387–430.
[18] P. Cairns, M.J. Miles, and V.J. Morris, *Carbohydr. Polym.*, 16 (1991) 355–365.
[19] P. Cairns, K.J. I'Anson, and V.J. Morris, *Food Hydrocolloids*, 5 (1991) 151–153.
[20] M. Miura, A. Nishimura, and K. Katsuta, *Food Structure*, 11 (1992) 225–236.

[21] C.G. Biliaderis and D.J. Prokopowich, *Carbohydr. Polym.*, 23 (1994) 193–202.
[22] M.D. Womack, D.A. Kendall, and R.C. MacDonald, *Biochim. Biophys. Acta*, 733 (1983) 210–215.
[23] R.C. Hoseney, *Principals of Cereal Science and Technology*, American Association of Cereal Chemists, St. Paul, MN, 1986, pp 207–208.
[24] K.E.J. Ward, R.C. Hoseney, and P.A. Seib, *Cereal Chem.*, 71 (1994) 150–155.
[25] N. Krog, S.K. Olesen, H. Toernaes, and T. Joensson, *Cereal Foods World*, 34 (1989) 281–285.
[26] E. Mettler, J.-M. Brummer, and W. Seibel, in D.J. Martin and C.W. Wringley (Eds.), *Cereals International 91*, Royal Australian Chemical Institute, Parkville, Vic., Australia, 1991, pp 79–89.
[27] S.K. Olesen, in D.J. Martin and C.W. Wringley (Eds.), *Cereals International 91*, Royal Australian Chemical Institute, Parkville, Vic., Australia, 1991, pp 90–98.
[28] C.G. Biliaderis, in R.J. Alexander and H.F. Zobel (Eds.), *Developments in Carbohydrate Chemistry*, American Association of Cereal Chemists, St. Paul, MN, 1992, pp 87–135.
[29] C.G. Biliaderis and B.O. Juliano, *Food Chem.*, 48 (1993) 243–250.
[30] R.E. Wing and J.N. BeMiller, *Carbohydr. Res.*, 10 (1969) 441–448.
[31] E. Barrall, B. Grant, M. Oxsen, E.T. Samulski, P.C. Moews, J.R. Knox, R.R. Gaskill, and J.L. Haberfeld, *Org. Coat. Plast. Chem.*, 40 (1979) 67–74.
[32] C.G. Biliaderis, C.M. Page, L. Slade, and R.R. Sirett, *Carbohydr. Polym.*, 5 (1985) 367–389.
[33] *Approved Methods of the AACC*, Method 44-40, approved April 1961, reviewed October 1976 and October 1982, American Association of Cereal Chemists, St. Paul, MN, 8th ed., 1983.
[34] E. Ziegler and E.N. Greer, in Y. Pomeranz (Ed.), *Wheat Chemistry and Technology*, American Association of Cereal Chemists, St. Paul, MN, 2nd ed., 1971, pp 115–199.
[35] C.G. Biliaderis and J. Zawistowski, *Cereal Chem.*, 67 (1990) 240–246.