Reactions of Oligosaccharides. III. Hygroscopic Properties[1]

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ABSTRACT

The hygroscopicities of a series of D-glucose polymers of DP_3 through DP_7 plus a sample of DP_{11} were determined to correlate the humectant properties of corn starch hydrolysates with their carbohydrate composition. This was achieved by exposing the dried samples to relative humidity (r.h.) environments of 25, 56, 75, and 90% at 75°, 86°, and 100°F. and measuring the weight gain every 24 hr. Also included in this study were samples of glucose, fructose, maltose, sucrose, sucrose/glucose (50:50 blend), sucrose/maltose (50:50 blend), and lactose. Results showed that the oligosaccharides have similar moisture adsorptive powers whereas the mono- and disaccharides vary considerably in their hygroscopicities, particularly at the high r.h. levels.

The term "hygroscopicity" refers to the property of moisture adsorption which occurs under normal atmospheric conditions. The ability of many food products to adsorb or desorb moisture when exposed during storage to atmospheres of differing relative humidities (r.h.) can cause undersirable results. For example, hard candies become sticky when exposed to high r.h. environments, and texture changes occur in fondants, jams, and jellies by loss of moisture at the r.h. levels to which they are normally exposed. Various humectants such as sorbitol, glycerin, propylene glycol, invert sugar, and corn syrups are used to counteract such problems.

Corn syrups are used in the confectionery and baking industries, and the humectant properties of a number of these have been examined (1). Included in that study were low conversion (32 DE acid-converted),[2] regular conversion (42 DE acid-converted), high maltose (42 DE acid-enzyme-converted), high conversion (63 DE acid-enzyme-converted), and extra-high conversion (71 DE acid-enzyme-converted) syrups. These samples were evaluated at 30, 60, and 90% r.h. at temperatures of 38°, 60°, 77°, and 100°F. The authors postulated that, although the corn syrups are classified by DE and by the type of conversion, the carbohydrate composition is the determining factor for the specific humectant property of a syrup. Consequently, knowledge of the hygroscopicities of the component sugars is needed to predict the behavior of the finished product.

Basically two procedures have been previously used to determine the hygroscopicities of sugars and sugar mixtures. Browne (2) exposed a number of dried sugar samples in weighing bottles to atmospheres of 60 and 100% r.h. at 20°C. and measured the weight gain as percent moisture adsorbed. Dittmar (3) used known concentrations of sulfuric acid solutions to give controlled r.h. environments and measured the hygroscopicities at 25°C. of sucrose, fructose, invert sugar, and sucrose-invert sugar mixtures. Using the same measuring technique with saturated salt solutions instead of sulfuric acid solutions to give constant r.h. environments, Sokolovsky (4) determined the hygroscopic properties of saccharose, maltose, lactose, and caramel at 43, 62.7, 81.8, and 88.8% r.h. and 25°C. The second procedure, adopted by Whittier and Gould (5), involved measuring the vapor pressures of saturated equilibrated solutions of sucrose, glucose, galactose, and

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[2]DE (Dextrose Equivalent) is a measure of the reducing sugar content of a sweetener calculated as dextrose and expressed as a percentage of the total dry substance.

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lactose at 25°C. and calculating the r.h. levels corresponding to each pressure. From this the hygroscopic tendency of each sugar was determined.

The technique used in this study was essentially the same as that used by Sokolovsky in which saturated salt solutions (6) were prepared in desiccators to give the required r.h. levels. Dried sugar samples were exposed to the different r.h. environments under controlled temperature conditions. A series of D-glucose polymers from DP_3 to DP_7 plus a sample of DP_{11} (henceforth these oligosaccharides will be designated as G_3, G_4, G_5, G_6, G_7, and G_{11}) were previously isolated in this laboratory (7). These, along with other mono- and disaccharides, were examined for their hygroscopic properties.

MATERIALS AND METHODS

Relative Humidity Chambers

Saturated salt solutions of potassium acetate, sodium dichromate, sodium chloride, and zinc sulfate heptahydrate were prepared in separate desiccators to give r.h. levels of 25, 56, 75, and 90%, respectively.

Oligosaccharides

The D-glucose polymers G_3, G_4, G_5, G_6, G_7, and G_{11} were lyophilized to constant weight. The homogeneity of G_3 through G_7 was established by thin-layer chromatography (TLC) (Fig. 1) at the 98% purity level. The linear nature of these oligosaccharides was indicated by hydrolysis with crystalline β-amylase (Nutritional Biochemicals Corp., Cleveland, Ohio). Such treatment of G_4 and G_6 at pH 5.0 in 0.1M acetate buffer yielded only maltose. G_5 and G_7 yielded mainly maltose with trace amounts of glucose and maltotriose as shown by TLC. That these are linear malto-oligosaccharides was further substantiated by periodate oxidation. As in the method of Potter and Hassid (10) 3 moles of formic acid were liberated per mole of G_3, G_4, G_5, G_6, and G_7 oxidized. Because insufficient quantities of G_{11} were available, structural data were not obtained.

Other Sugars

Crystalline samples of reagent grade glucose, fructose, sucrose, maltose, and lactose were vacuum-oven-dried to constant weight. Samples of sucrose/glucose (50:50 blend) and sucrose/maltose (50:50 blend) were lyophilized to constant weight. Moisture determinations by Karl-Fischer titration showed the vacuum-oven-dried samples to contain less than 0.2% moisture. The lyophilized samples of sucrose/glucose (50:50 blend) and sucrose/maltose (50:50 blend) contained 6.5% moisture. Lyophilized samples of G_3 and G_4 contained 4.4 and 4.8% moisture, respectively. Insufficient quantities of the higher oligosaccharides were available for such moisture determination but presumably they possessed approximately 5% moisture.

Procedure

The hygroscopicities of the above carbohydrates were measured by placing the samples in weighing bottles with ground glass stoppers (weights ranged from 100 to 200 mg.), exposing them to 25% r.h. at 75°F. (24°C.), and re-weighing the samples every 24 hr. until there was no further weight gain. This weight gain was calculated as percent moisture adsorbed on the basis of the initial sample weight. Upon

equilibration at 25% r.h. the samples were transferred to the 56% r.h. chamber and the measurements repeated. The same process was performed at 75 and 90% r.h. After reaching final equilibrium moisture content at 90% r.h., the samples were subsequently exposed to the successively lower environments of 75, 56, and 25% r.h.

This same study was repeated at 86°F. (30°C.) and 100°F. (38°C.). The desiccators were placed in an incubator to maintain temperature control to within ± 1.0°F.

RESULTS AND DISCUSSION

The hygroscopic data obtained in these experiments are summarized 'in Fig. 2 (A, B, and C) and Fig. 3 (A, B, and C). The oligosaccharide G_6 was not available when this study began and is not in Fig. 2, A.

The oligosaccharides G_3, G_4, G_5, G_6, G_7, and G_{11} showed very similar
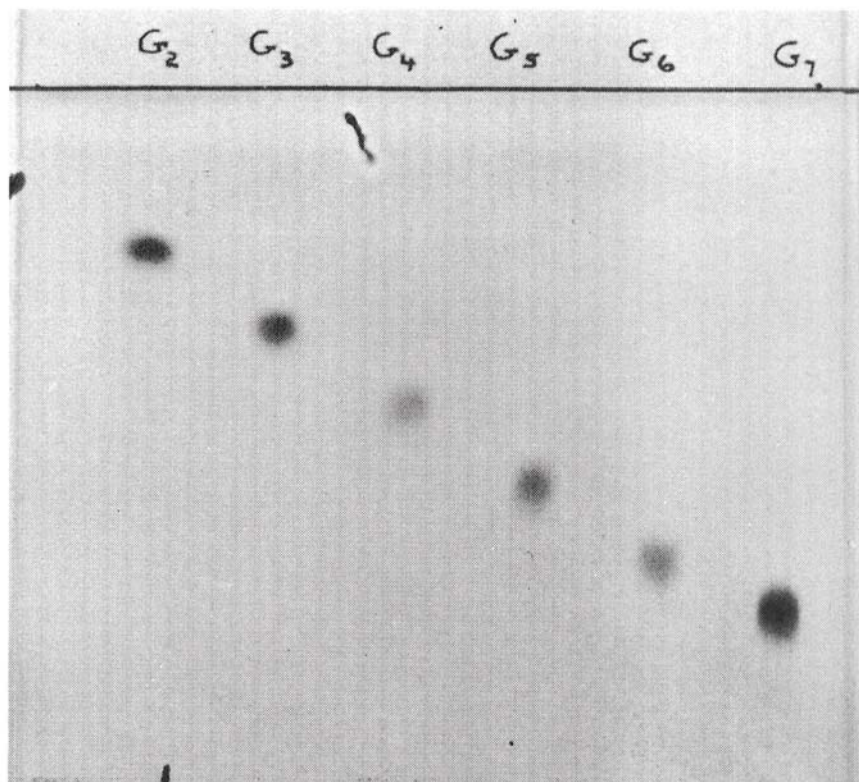

Fig. 1. A thin-layer chromatoplate showing the separation of D-glucose polymers. Spot identification: G_1, glucose; G_2, maltose; G_3, maltotriose; G_4, maltotetraose; G_5, maltopentaose; G_6, maltohexaose; G_7, maltoheptaose. Adsorbent is silica gel H (E. Merck, Darmstadt, Germany) impregnated with 0.02M sodium acetate as described by De Stefanis and Ponte (8) but without calcium sulfate. The plate was developed two successive times in chloroform: acetic acid: water (10:79:11) and visualized with DPA (9).
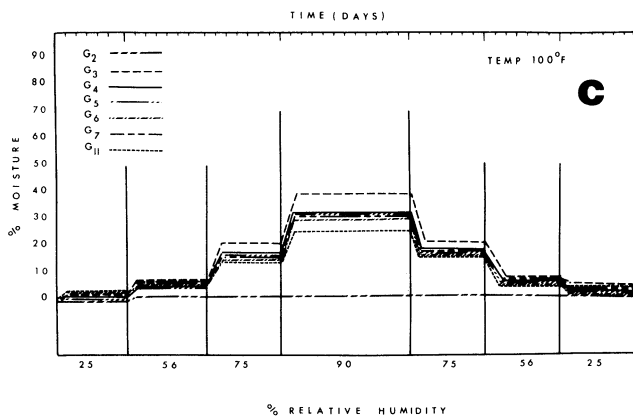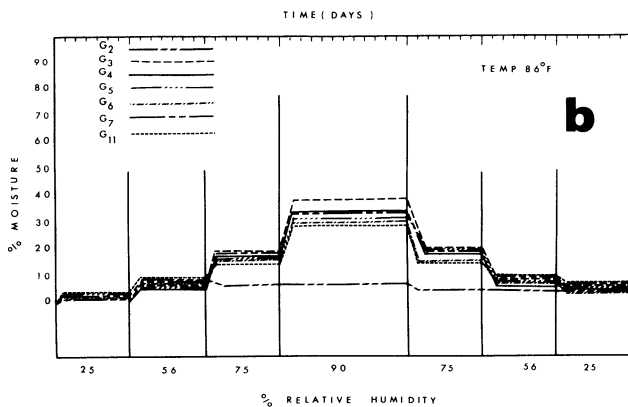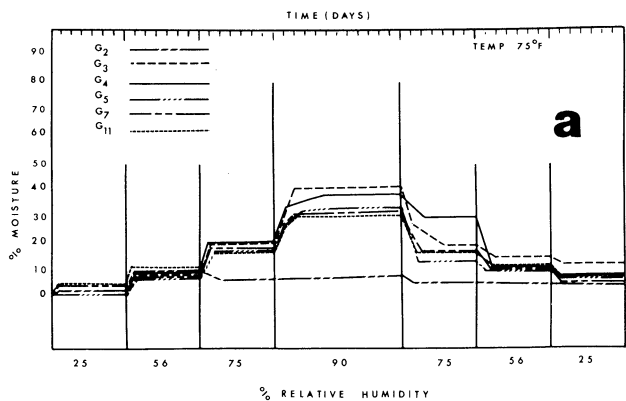
Fig. 2. Hygroscopicities of oligosaccharides stored under varying relative humidities. A, 75° F.; B, 86° F.; C, 100° F.
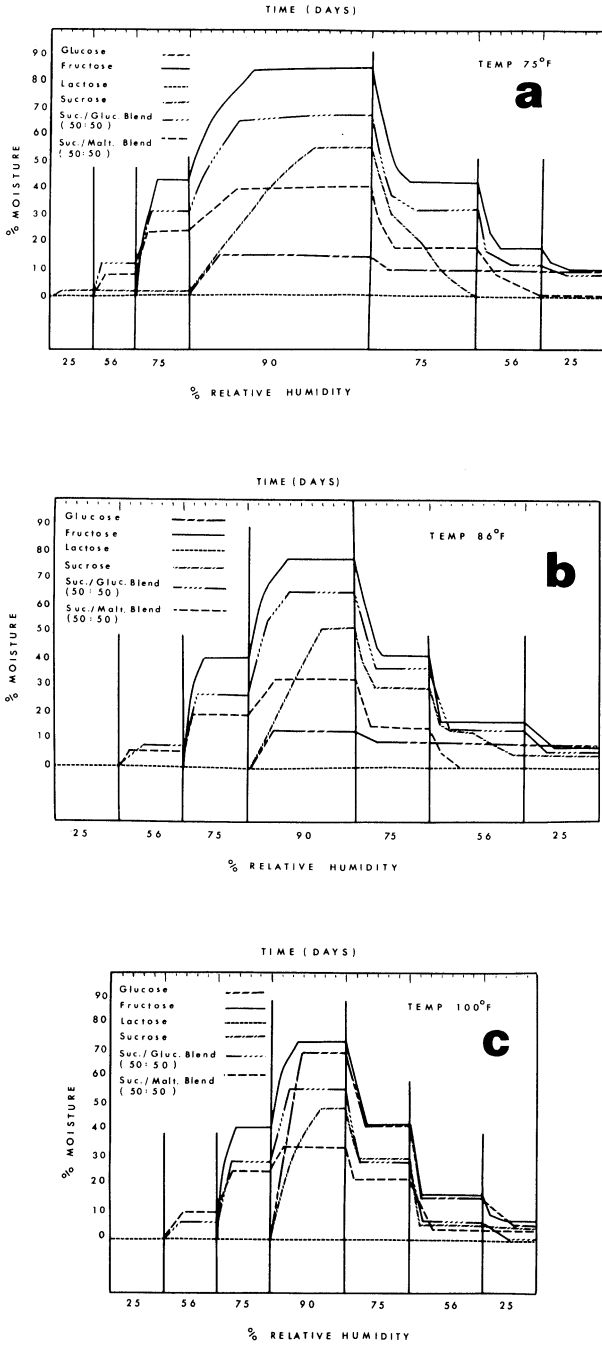
Fig. 3. Hygroscopicities of two mono- and disaccharides and two blends stored under varying relative humidities. A, 75° F.; B, 86° F.; C, 100° F.

moisture adsorption values over the range of r.h. environments and storage temperatures used. As can be seen from Fig. 2 the curves followed well-defined stepwise patterns. The only significant spread in hygroscopicities appeared at 90% r.h. where the lower oligomer G_3 adsorbed as much as 10% more moisture than G_{11} at 75 and 86°F. and up to 14% more at 100°F. All these oligosaccharides formed clear syrups at 75% r.h. at the three storage temperatures used except G_{11} which did not do so until exposed to 90% r.h.

As shown in Fig. 2, B and C, moisture losses from the oligosaccharides, after equilibration at 90% r.h. and subsequent exposure to the successively lower r.h. environments, followed patterns that were essentially the mirror images of the adsorption curves at their equilibrium points. At the storage temperature of 75°F. (Fig. 2, A), however, there was somewhat of a greater spread in moisture loss values at 75% r.h.

The above results agree with the generally recognized phenomenon that the lower the DE of a corn syrup, and consequently the higher the content of high-molecular-weight oligosaccharides, the less hygroscopic the syrup.

With respect to the individual oligosaccharides G_2, G_3, G_4, G_5, G_6, G_7, and G_{11}, the pattern of moisture adsorption at 90% r.h. and 75°, 86°, and 100°F. suggests some interesting theoretical possibilities. The listing below relates the moisture adsorptive powers of these carbohydrates:

$$75°F.: \ G_3 > G_4 > G_5 = G_7 > G_{11} > G_2$$

$$86°F.: \ G_3 > G_4 = G_7 > G_5 > G_6 > G_{11} > G_2$$

$$100°F.: \ G_3 > G_4 = G_5 = G_7 > G_6 > G_{11} > G_2$$

The change in position of G_7 at 86°F. was due to its increased moisture adsorbance as G_5 remained approximately the same. The slightly greater ability of G_7 to pick up moisture is possibly related to destruction of the helical content of G_7 (11), whereas the difference at 100°F. may be caused by mobility and flexibility between non-helical chains. Maltose (G_2) has much lower ability to adsorb moisture than the higher oligomers. This could be a function of intermolecular hydrogen bond formation yielding aggregates. For G_3 and above steric hindrance may prevent such aggregation.

The other mono- and disaccharides showed widely differing moisture adsorptive powers, particularly at the higher r.h. environments. The two sugars in this study which showed the best humectant properties were maltose and lactose. The moisture gain by maltose did not exceed 10%. Lactose did not adsorb more than 0.5% moisture over the whole range of r.h. environments and storage temperatures used.

Glucose showed little or no tendency to adsorb moisture until exposed to 90% r.h. It equilibrated between 17 and 18% moisture at this r.h. at 75° and 86°F. At 100°F., however, there was a dramatic change. Figure 3, C shows that glucose picked up a considerable amount of moisture at 90% r.h., finally equilibrating at 69% moisture as a free-flowing liquid. Its subsequent desorption curve followed very closely that of fructose.

Fructose, unlike glucose, picked up moisture at 75% r.h. It equilibrated between 41 and 43% moisture at all three storage temperatures as a clear syrup. The large

rise in moisture content continued at 90% r.h. with equilibrium moisture content occurring at 85.1, 78.6, and 72.7% at 75°, 86°, and 100°F., respectively. On passing from 75 to 90% r.h. the fructose changed from a clear viscous syrup to a free-flowing liquid.

Sucrose, like glucose, did not adsorb significant amounts of moisture until placed in the 90% r.h. environment whereupon it equilibrated between 50 and 56% moisture at all three storage temperatures.

The hygroscopic properties of sucrose, glucose, and maltose changed, however, when 50:50 blends of sucrose/glucose and sucrose/maltose were evaluated. The lyophilized blends picked up significant amounts of moisture at 56% r.h. at all three storage temperatures. The results ranged from 6.6 to 12.5% moisture for sucrose/glucose and 6.0 to 10.2% moisture for sucrose/maltose. At 75% r.h. the sucrose/glucose blend adsorbed 2.7, 8.6, and 6.1% more moisture than the sucrose/maltose blend at 75°, 86°, and 100°F., respectively. The higher moisture adsorption by the sucrose/glucose blend continued at 90% r.h. It equilibrated at 67.8, 54.5, and 55.6% moisture whereas the sucrose/maltose blend equilibrated at 40, 33.5, and 34.3% moisture and 75°, 86°, and 100°F., respectively. In the process of adsorbing moisture the sucrose/glucose blend formed a clear syrup at 56% r.h., deposited some crystalline material at 75% r.h., and returned to a clear syrup at 90% r.h. at both storage temperatures of 75° and 86°F. At 100°F., however, the sample formed a colorless syrup at 56% r.h. and remained as such through 75 and 90% r.h. The sucrose/maltose blend formed a heterogeneous syrup/solid at 56, 75, and 90% r.h. and 75° and 86°F. At 100°F. a clear syrup was formed at 75 and 90% r.h.

A correlation of the hygroscopic properties of these monosaccharides, disaccharides, and blends showed the following sequence at 90% r.h.

75°F.   Fructose > Sucrose/Glucose > Sucrose > Sucrose/Maltose > Glucose
         > Lactose

86°F.   Fructose > Sucrose/Glucose > Sucrose > Sucrose/Maltose > Glucose
         > Lactose

100°F.   Fructose > Glucose > Sucrose/Glucose > Sucrose > Sucrose/Maltose
         > Lactose

At 75° and 86°F. the sucrose/glucose blend adsorbs more moisture than either sucrose or glucose. It is possible that the sucrose and glucose by themselves form dimers, trimers, etc. In the blend, however, these interactions are partially inhibited because of the competition of the hydrogen bonding sites between the two sugars. This competition would allow the blend to interact more strongly with water. At 100°F. the aggregation of sucrose and glucose would be essentially destroyed, hence the sequence glucose > sucrose/glucose > sucrose. Note that glucose also surpasses sucrose in its ability to adsorb moisture at 100°F. With the breakdown in the aggregation of glucose and sucrose as compared to the lower temperatures of 75° and 86°F., the moisture adsorption powers of the two sugars may now be a function of their configurations. Consequently, the destruction of the hydrogen bonds between sugar units must be involved in the increase in the ability of the particular sugar to hydrogen bond with water molecules.

TABLE I.   FINAL SUGAR-MOISTURE EQUILIBRATION TIMES AT 90% r.h.

Sample	Time (Days)		
	Storage Temp. 75°F.	Storage Temp. 86°F.	Storage Temp. 100°F.
Sucrose	14	7	4
Sucrose/glucose (50:50 blend)	7	4	2
Sucrose/maltose (50:50 blend)	7	4	2
Fructose (crystalline)	6	6	2

The effect of storage temperature on moisture equilibration times with respect to fructose, sucrose, sucrose/glucose blend, and sucrose/maltose blend is shown in Table I. The samples of sucrose, sucrose/glucose, and sucrose/maltose when exposed to 90% r.h. at 86°F. reached equilibrium moisture content in approximately half the time it took at 75°F. Again at 100°F. it took roughly one half the time it took these samples to equilibrate at 86°F. Fructose had the same moisture equilibration times at this r.h. level and 75° and 86°F., but when stored at 100°F. it took one third this time to reach its moisture equilibrium.

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