Note

Fundamental studies on the interaction of alkaline-earth metals with carbohydrates
I. Reaction of D-glucose and maltose with the hydroxides of barium, calcium, and strontium

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The reaction between simple carbohydrates and alkali-metal salts[1] and hydroxides[2] to give complexes has been studied by many workers Rendleman[2,3] isolated complexes by precipitation from nonaqueous and partially aqueous media The products derived from alkali-metal hydroxides were not crystalline Mackenzie and Quin[4] were able to isolate compounds of calcium hydroxide with sucrose and with D-glucose, and Herzfeld[5] prepared 1 1 maltose–calcium hydroxide Several workers[6–8] have studied the interaction of carbohydrates with alkaline and alkaline-earth metal salts, but the results are not without ambiguity

The present investigation was undertaken with the intention of preparing adducts of D-glucose and maltose with alkaline-earth metal hydroxides The utilization of such adducts may be useful in the isolation of oligosaccharides from industrial wastes Metal hydroxide–sugar complexes may play an important biological role in the transport of the metal hydroxides across cell membranes[9]

We have established standard procedures for the preparation of 1:1 adducts of D-glucose and maltose with the hydroxides of barium, calcium, and strontium The curves indicating the yield of adduct corresponding to different molar proportion of sugar clearly established that the yield is highest when the components are mixed in 1 1 molar proportion Analysis of the adducts of different fractions for the metal atom showed that the composition of the adducts is the same (namely, 1 1) in all cases All of the adducts were hygroscopic, and none could be crystallized They decomposed when exposed to the air for more than 10 min

(Previous studies[3] had indicated the formation of adducts at a higher ratio of metal to sugar, but the composition reported for the adducts by different authors varied and the ratio also differed with different metals)

The shape of the curves relating pH to volume of sugar solution is that of a typical titration curve, and it, too, indicates that the adducts have a 1 1 composition

It is interesting that the adducts of D-glucose and maltose are extremely hygroscopic, in comparison to the hydroxides of the alkaline-earth metals.

EXPERIMENTAL

Paper chromatography was performed in 8 2 1 (*v*/*v*) ethyl acetate–pyridine–water The spray reagent used was ammoniacal silver nitrate for sugars, and 1% violuric acid solution for the metal hydroxides Measurements of pH were made with a Cambridge pH-meter.

Reaction of D-*glucose and maltose with barium hydroxide and with strontium hydroxide — Method A* A solution (44 mM) of the sugar in 80% methanol was added in 10-ml portions to 44 mM base in 80% methanol at 5°, a precipitate formed immediately After 30 min, the precipitate was collected by centrifugation, washed once with 99% ethanol, dried under vacuum, and weighed Analysis of the product for the particular metal showed that one molecule of the metal hydroxide was attached to one molecule of D-glucose or maltose, and the proportion of base used had no influence on the composition of the final product The pH of the mother liquor was recorded The results are summarized in Fig 1

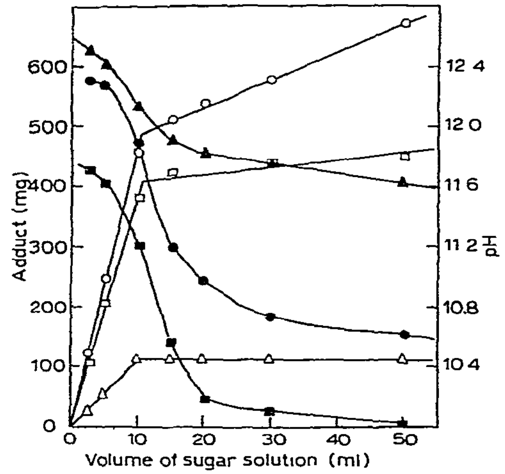
In the case of maltose, the mother liquor of each fraction was analyzed both for the metal atom and for maltose The fraction containing 0 5 molar equivalent of the hydroxides did not contain any hydroxide in the mother liquor, as revealed by testing with sulfuric acid and with maltose solution This fraction contained maltose in the mother liquor, and this maltose could be precipitated by the addition of barium hydroxide solution The fraction containing the components in the ratio of 1.1 contained neither the hydroxide nor maltose. The fractions containing higher molar equivalents of the hydroxide contained an excess of the hydroxide in the mother liquor, because more adduct could be precipitated by the addition of maltose solution

Method B Reaction at constant volume The reactions were conducted under the same conditions and in the same medium (80% methanol) as just described Different proportions (namely, 1.7, 1 3, 3 5, 1 1, 5 3, 3 1, and 7 1) of sugar and base solutions were mixed together, the total volume being kept constant The adducts formed were collected as before, and the pH value of each mother liquor was determined The results are summarized in Figs 2 and 3

Blank experiments were also performed, in which a solution of strontium hydroxide or barium hydroxide was added to 80% methanol, and the pH values of the solutions were recorded, the results are given in Fig 4

Preparation of the adduct In preliminary experiments, attempts were made to prepare the adducts in methyl sulfoxide, *N*,*N*-dimethylformamide, *p*-dioxane, methanol, ethanol, or water, or in mixtures of them at various concentrations The most suitable medium was found to be 80% methanol, in which both of the components (the sugar and the hydroxide) are soluble As the hydroxides are insoluble in nonaqueous solvents, it was not possible to perform studies with completely nonaqueous media

A solution (44 mM) of each of the components in 80% methanol (500 ml each) was prepared, these were mixed together at 5° in a 2-liter Erlenmeyer flask, with stirring, and a precipitate formed immediately The mixture was allowed to stand for



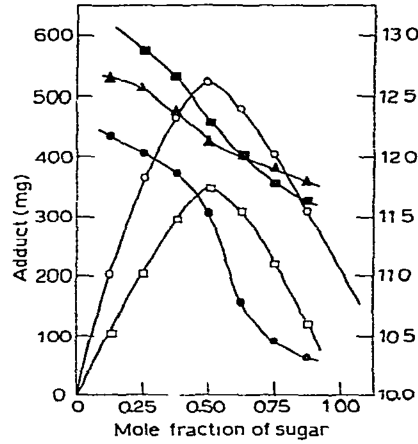
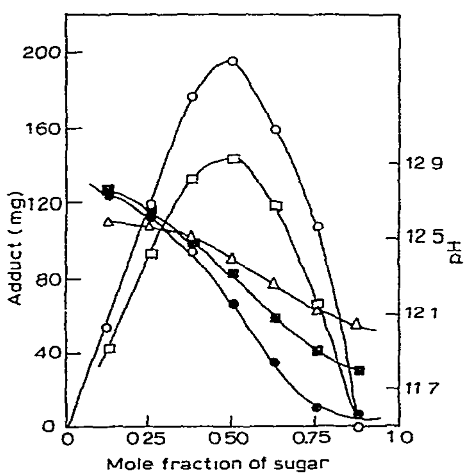


Fig 1 Interaction of D-glucose and maltose with different hydroxides, the amount of hydroxide being kept constant Amount of adduct (hollow points) and pH (dark points) *vs* volume of sugar (○ and ●, Maltose and barium hydroxide, □ and ■, maltose and strontium hydroxide, △ and ▲, D-glucose and barium hydroxide)

Fig 2 Interaction of maltose with different hydroxides by the constant-volume method Amount of adduct (hollow points) and pH (dark points) *vs* mole fraction of sugar (○ and ●, with barium hydroxide, □ and ■, with strontium hydroxide, ▲, with calcium hydroxide)



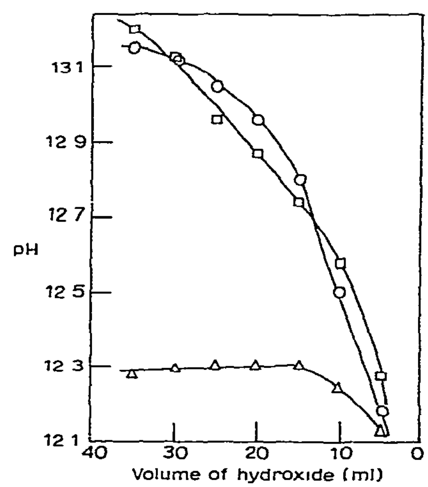


Fig 3 Interaction of D-glucose with different hydroxides by the constant-volume method Amount of adduct (hollow points) and pH (dark points) *vs* mole fraction of sugar (○ and ●, with barium hydroxide, □ and ■, with strontium hydroxide, ▲, with calcium hydroxide)

Fig 4 Blank experiments with different hydroxides by the constant-volume (40 ml) method (△, calcium hydroxide, □, strontium hydroxide, and ○, barium hydroxide)

30 min at 5°, and the product was collected under suction on a Büchner funnel, washed twice with 99% ethanol, and dried over phosphorus pentaoxide under vacuum for two days The results are summarized in Table I

TABLE I

ANALYTICAL DATA FOR THE ADDUCTS

Compound	*Formula*	*Yield (%)*	*Analysis*					
			Calc			*Found*		
			C	*H*	*Metal*	*C*	*H*	*Metal*
Maltose–barium hydroxide	$C_{12}H_{22}O_{11}$ $Ba(OH)_2$	98 0	28 2	4 7	26 7	27 8	5 1	26 8
Maltose–strontium hydroxide	$C_{12}H_{22}O_{11}$ $Sr(OH)_2$	83 8			18 1			18 0
Maltose–calcium hydroxide	$C_{12}H_{22}O_{11}\cdot Ca(OH)_2$	68 0			9 6			9 8
D-Glucose–barium hydroxide	$C_6H_{12}O_6$ $Ba(OH)_2$	62 4	20 6	4 0	39 1	20 4	4 4	38 6
D-Glucose–strontium hydroxide	$C_6H_{12}O_6$ $Sr(OH)_2$	53 0			25 7			25 2
D-Glucose–calcium hydroxide	$C_6H_{12}O_6$ $Ca(OH)_2$	65 0			15 6			16 3

Acetylation of the maltose–barium hydroxide adduct with pyridine and acetic anhydride gave octa-*O*-acetylmaltose, as revealed by t l c on Silica Gel G with 1 1 ether–chloroform

Paper chromatogaphy of the maltose–barium hydroxide adduct for 24 h showed two spots, one for the sugar and one for the hydroxide

Reaction of D-*glucose and maltose with calcium hydroxide* — As a saturated solution of calcium hydroxide in water is 25 mM, the experiments were conducted in aqueous solution, with 25 mM sugar solution and a saturated solution of calcium hydroxide The constant-volume method was applied as before (total volume, 20 ml) As no precipitate appeared in aqueous solution, 20 ml of distilled acetone was added to each flask A blank experiment with calcium hydroxide (see Fig 4) was performed simultaneously. A precipitate appeared in all of the flasks (including the blanks), but they were not collected because of the small quantity of the materials involved. The pH values were measured in each case

In the preparative procedure, D-glucose (5 g) or maltose (10 g) was shaken with an excess of calcium hydroxide (6 g) in water (200 ml) for 1 h, and filtered Acetone (300 ml) was added to the filtrate The adduct precipitated out It was collected on a Büchner funnel, washed successively with 80% acetone and acetone, and dried *in vacuo* Yield· 4 4 g (from D-glucose) and 7.5 g (from maltose)

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