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Note

Fundamental studies on the interaction of carbohydrates with alkaline-earth metals.

Part III. Reaction of D-glucose and maltose with the hydroxides of Ba^{2+}, Ca^{2+}, Mg^{2+}, and Sr^{2+} in presence of ethylenediamine and 2-aminoethanol

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The conditions of preparation of adducts of alkaline-earth metal hydroxides with carbohydrates have been extensively studied in this laboratory[1,2]. Adducts of carbohydrate derivatives with the alkaline-earth metal ions have also been reported[3,4]. In a separate study, the probability of association of carbohydrates with ethylenediamine has been described[5,6]. (There had been a preliminary report that, on working in the presence of ethylenediamine, other kinds of adducts between a carbohydrate and an alkaline-earth metal hydroxide may be formed[7].)

In view of our investigations on the formation of carbohydrate–alkaline-earth metal ion adducts, as well as on the association of ethylenediamine with the carbohydrates, we have now extended the first kind of study to adduct formation in the presence of ethylenediamine and 2-aminoethanol.

EXPERIMENTAL

Materials. — The carbohydrates used were of AnalaR (BDH) quality. The alkaline-earth metal chlorides and hydroxides were either of AnalaR (BDH) or Pro Analysi (Merck) grades. The other chemical compounds used were also of analytical grade.

Method of analysis. — The analyses for calcium and magnesium were performed by titration with (ethylenedinitrilo)tetraacetic acid (EDTA). Barium and strontium were estimated by the chromate and oxalate methods[8]. In some instances, the metals were also estimated by neutralizing their hydroxides with an excess of standard hydrochloric acid, and back-titrating the excess of acid with standardized alkali (phenolphthalein as indicator).

The chloride ion was estimated by titrating with standardized silver nitrate with dibromofluorescein as the adsorption indicator.

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*Dedicated to Dr. Louis Long, Jr., in honour of his 70th birthday.

The presence of nitrogen was qualitatively tested for by the sodium (metal) fusion method. Quantitative analysis for nitrogen was made microanalytically (see Table I).

TABLE I

ANALYTICAL RESULTS FOR THE ADDUCTS

Compound[a]	*Color*	*Found*		*Metal*		*Ratio of carbohydrate to* $M(OH)_2$
		N (%)	*Cl* (%)	*Calc.*	*Found*	
D-Glucose–$Ca(OH)_2$						
(D)	white	—	—	15.6	15.1	1:1
(DE_D)	white	—	—	24.3	23.4	1:2
(IE_D)	white	3.3	3.8	24.3	24.0	1:2
(DE_A)	white	—	—	15.6	15.2	1:1
D-Glucose–$Ba(OH)_2$						
(D)	yellowish	—	—	39.1	39.2	1:1
(IE_D)	yellowish	7.76	2.2	52.3	51.5	1:2
(DE_A)	brownish	—	—	25.7	25.1	2:1
D-Glucose–$Sr(OH)_2$						
(IE_D)	yellowish	—	1.5	41.2	40.4	1:2
(DE_A)	brownish	—	—	18.1	18.3	2:1
D-Glucose–$Mg(OH)_2$						
(IE_D)	yellowish	—	9.1	10.1	11.2	1:1
Maltose–$Ca(OH)_2$						
(D)	brownish	—	—	9.6	9.5	1:1
(DE_D)	yellowish	—	—	16.2	15.7	1:2
(IE_D)	yellow	—	—	16.2	15.9	1:2
(DE_A)	brownish	—	—	9.6	9.5	1:1
Maltose–$Ba(OH)_2$						
(DE_D)	yellow	—	—	26.7	26.3	1:1
(IE_D)	yellow	1.7	1.4	26.7	26.0	1:1
(DE_A)	yellow	—	—	15.8	15.0	2:1
Maltose–$Sr(OH)_2$						
(IE_D)	white	—	—	18.1	18.9	1:1
(DE_A)	brownish	—	—	10.0	10.5	2:1
Maltose–$Mg(OH)_2$						
(IE_D)	white	—	4.5	10.4	11.0	1:2

[a] D indicates direct reaction; DE_D, direct reaction in the presence of ethylenediamine; IE_D, indirect reaction in presence of ethylenediamine; and DE_A for direct reaction in the presence of 2-aminoethanol.

Method of preparation. — The association of D-glucose and maltose with the hydroxides of Ba^{2+}, Ca^{2+}, Mg^{2+}, and Sr^{2+} was investigated under three conditions of reaction, as described.

(*A*) *Reaction of* D-*glucose and maltose with calcium hydroxide.* This is a direct reaction between the carbohydrate and the hydroxide, already reported[1,2]. However, as the experimental conditions now used are different, we performed two experiments to compare the results now obtained with our past results.

In an Erlenmeyer flask, the carbohydrate was dissolved in the minimum quantity of 20% aqueous methanol. To the solution was added calcium hydroxide powder, with stirring, until the molar composition was 1:1. The mixture was then shaken vigorously, and a viscous, milky substance appeared at the bottom of the flask; on further shaking, this was transformed into a white precipitate. This was kept overnight in a refrigerator, and then further precipitation was caused by adding a little methanol to the solution. The precipitate was filtered off under suction, washed thoroughly with aqueous methanol and acetone, dried under vacuum, and analyzed for calcium (see Table I).

(*B*) *Reaction of* D-*glucose and maltose with calcium hydroxide and with barium hydroxide in the presence of amine.* This set of experiments was the same as the previous one, except that the carbohydrates and the bases interacted directly in the presence of an equimolar concentration of amine. The solutions were agitated gently for only 5 min, and kept for 1 h at 30° and, thereafter, overnight in the refrigerator.

During filtration and washing, 20% aqueous methanol was found to dissolve a part of the product; thereafter, only acetone was used in washing (to remove traces of the adhering amine). The samples were dried, tested for the presence of nitrogen, and analyzed for the respective metal ion (see Table I).

(*C*) *Reaction of* D-*glucose and maltose with barium, calcium, magnesium, and strontium hydroxides (generated in the solution from the corresponding chlorides) in the presence of amine.* This set of experiments was similar to that discussed under subheading (*B*), differing only in the form of the hydroxides used; these were generated in the solution by adding sodium hydroxide to their chlorides, to give an "indirect" reaction between the respective carbohydrates and metal hydroxides.

To an equimolar mixture of the carbohydrate, the amine, and the alkaline-earth metal chloride was slowly added an alcoholic solution of 0.1M sodium hydroxide to generate the alkaline-earth metal hydroxide. When the mixture became permanently turbid, only a little more of the alkali solution was added. The reaction was allowed to take place for 2 h, with gentle warming for the first 5 min, and then at room temperature, and the suspension was kept overnight in a refrigerator. Further precipitation was caused by adding ethanol–acetone. The samples were dried, tested for the presence of nitrogen, and analyzed for the metal ions. The nitrogen content was determined whenever considered necessary, and the content of chloride ion was also determined (see Table I).

Paper chromatography of the adducts. — Chromatographic examination of the products was performed on Whatman No. 1 paper with 8:2:1 ethyl acetate–pyridine–water, for 18–20 h. Ammoniacal silver nitrate and violuric acid sprays were used for the identification of the carbohydrates and the metal hydroxides, respectively.

RESULTS

Some of the isolated compounds are white, and some are yellowish or brownish. They are fairly stable at room temperature in a desiccator. The adducts formed in presence of 2-aminoethanol are more stable than those obtained in the presence of ethylenediamine.

The adducts are soluble in water and decompose readily therein; consequently, reliable paper-chromatographic identification of the freshly prepared samples was not possible. Nevertheless, aged samples showed new spots on the paper; their R_F values are given in Table II. It may be seen from this Table that the composition of the direct-reaction products is 1:1; this agrees with previous reports from this laboratory[1,2].

TABLE II

R_F VALUES OF COMPONENTS OF THE AGED[a] ADDUCTS

Carbohydrate	*Metal hydroxide*	*Medium*	R_F[b]
D-Glucose	$Ca(OH)_2$	water	0.22
	$Ba(OH)_2$		0.05
	$Ca(OH)_2$	ethylenediamine–water	0.42
	$Ba(OH)_2$		0.203
	$Sr(OH)_2$		0.447, 0.10
	$Mg(OH)_2$		0.33
Maltose	$Ca(OH)_2$		0.36
	$Ba(OH)_2$		0.28
	$Sr(OH)_2$		0.18
Glucose	$Ca(OH)_2$	2-aminoethanol–water	0.69
	$Ba(OH)_2$		0.67
	$Sr(OH)_2$		0.65
Maltose	$Ca(OH)_2$		0.59

[a]Products from water and from ethylenediamine–water media were aged for one year. Those from 2-aminoethanol–water medium were aged for 2 months. [b]The $Ba(OH)_2$ adduct of D-glucose gave two distinct spots; two R_F values are, therefore, given. R_F stands for R_G and R_M as the case may be (where the mobility of D-glucose is 19.4 cm and that of maltose is 9.8 cm).

In the presence of ethylenediamine, D-glucose and maltose accepted more calcium hydroxide than that which would correspond to the 1:1 ratio, but the maltose–$Ba(OH)_2$ compound had a 1:1 composition. The indirect reactions between the pairs, D-glucose–$Mg(OH)_2$, maltose–$Ba(OH)_2$, and maltose-$Sr(OH)_2$, in the presence of this amine, yielded a 1:1 adduct in each case. Such reactions between the pairs, D-glucose–$Ba(OH)_2$, D-glucose–$Ca(OH)_2$, D-glucose–$(SrOH)_2$, maltose–$Ca(OH)_2$, and maltose–$Mg(OH)_2$ were all 1:2 adducts.

The adducts formed in the presence of 2-aminoethanol are 2:1 for the reactions of D-glucose and maltose with $Ba(OH)_2$ and $Sr(OH)_2$; those with $Ca(OH)_2$ are of 1:1 composition.

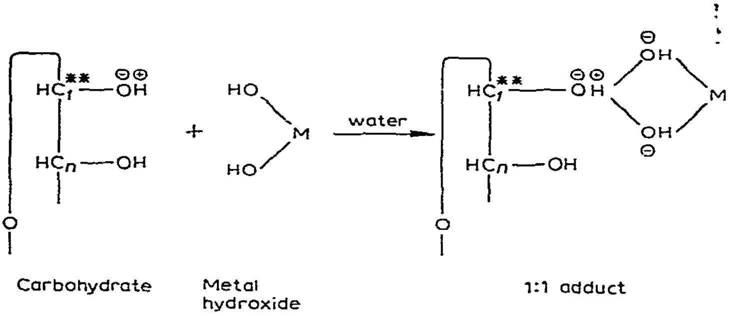
DISCUSSION

It is clear that the compositions of the adducts formed depend on the composition of the generating solution. The presence of ethylenediamine, in some instances, causes the carbohydrates to consume more of a metal hydroxide, whereas 2-aminoethanol has less influence.

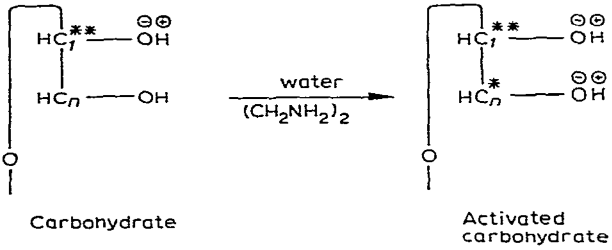
In some of the compounds prepared by using ethylenediamine, the presence of some of the amine, as well as of the metal chloride, was observed; these may be adhering impurities, or they themselves may participate in the adduct formation. At this stage, no justification for the presence of the metal chlorides in the adducts can be given. However, it may be noted that, as association of carbohydrates with ethylenediamine is possible^{5,6}, and adducts of alkaline-earth metal chlorides with ethylenediamine are also formed^{3}, ethylenediamine may, under some conditions, form a bridged compound between a carbohydrate and a metal chloride.

The lack of effect of 2-aminoethanol on the adduct formation is noteworthy. Presence of even a trace of this amine in the adducts was not observed. The non-association thereof with the carbohydrates has been reported from this laboratory^{5,6}. It was, therefore, anticipated that 2-aminoethanol would have no activation effect on the formation of adducts by the carbohydrates.

The effects of ethylenediamine and 2-aminoethanol may be represented in the following Schemes, in which the active centers in the carbohydrate are marked with asterisks. The hydroxyl group attached to such an active center is considered more acidic (having a more dissociative hydrogen atom) than others; this is also shown by conductometric studies^{9}.

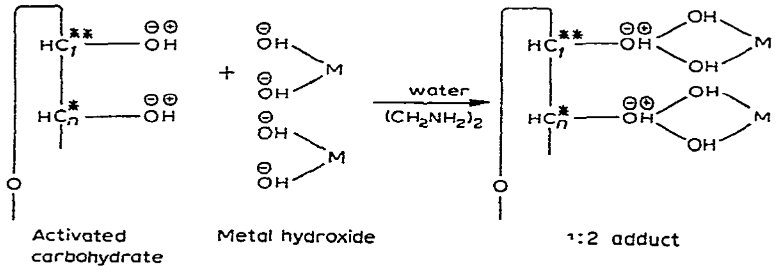


SCHEME I

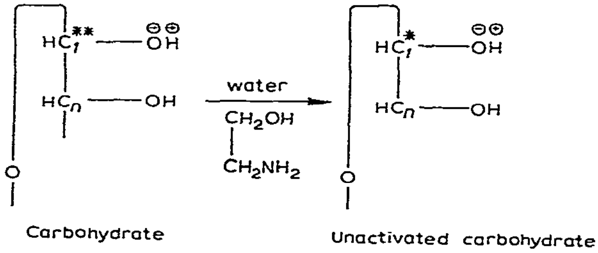


SCHEME IIa

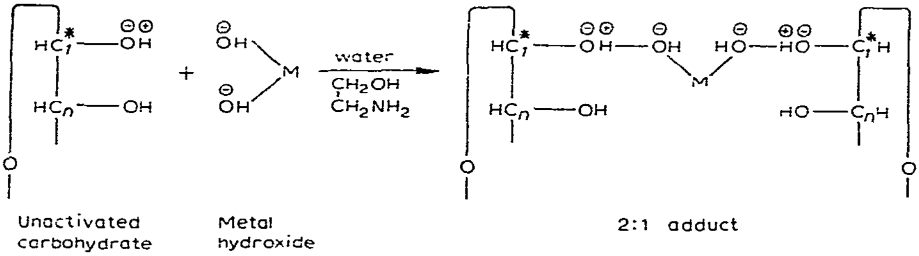
In these schemes, C-1 is considered to be the most active, and is marked with two asterisks. In the presence of 2-aminoethanol, the activation is lessened, and the atom is marked with one asterisk. The C_n centers refer to any centers other than C-1.



SCHEME IIb



SCHEME IIIa



SCHEME IIIb

The paper-chromatographic studies of the aged adducts reveal new components. However, in some instances, a trace of the parent carbohydrate was also evident. Some breakdown of the adducts on the paper was therefore envisaged. The new spots may be the proposed adducts. (They might also be degradation products of the carbohydrates, formed during the long association of the sugars with the bases, but appearance of only one such product, without tailing of the front, does not favor this supposition). In this connection, it may be mentioned that, after prolonged storage, an adduct prepared in the presence of sodium hydroxide produced long tailing on the paper; this had a dense section at almost the same position as the spot afforded by a product prepared in the absence of sodium hydroxide. On storage, the D-glucose–$Ba(OH)_2$ adduct showed two new spots on the paper; this may indicate two types of adduct or two degradation products, but here, also, absence of tailing militates against the concept of degradation.

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