Note

Fundamental studies on the interaction of alkaline-earth metals with carbohydrates
II. Behavior of some disaccharides towards the hydroxides of barium, calcium, and strontium*

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(Received March 15th, 1972, accepted for publication, May 1st, 1972)

In a previous communication[1], we discussed the interaction of D-glucose and maltose with the hydroxides of barium, calcium, and strontium Both sugars form 1.1 adducts with these hydroxides Even though maltose has two D-glucose residues in its molecule, it engages only one molecule of the hydroxides per molecule These findings gave rise to the following questions What is the behavior of oligosaccharides and polysaccharides towards these hydroxides? Is the reducing end responsible for the adduct formation, and, if so, what will be the behavior of sugars devoid of a reducing group? And, finally, what is the mode of attachment of the metal atom to the sugar moiety?

In an attempt to answer the first two questions, we studied the interaction of several disaccharides, both reducing and nonreducing, and of amylose and amylopectin We found that all of the disaccharides studied form 1 1 adducts with the hydroxides of barium, calcium, and strontium Several ratios (1 7, 1 3, 3 5, 1.1, 5·3, 3 1, and 7.1) of the reactants in 80% methanol (acetone–water, in the case of calcium) were mixed, the volume being kept constant (40 ml) The precipitate formed in each experiment was weighed, and the pH of the mother liquor from each precipitate was measured The amount of adduct was found maximal at the ratio of 1 1 The slope of the curve for pH *vs* volume of sugar was also found maximal at the 1 1 ratio With α,α-trehalose, no precipitate formed, but the curve for pH *vs* volume of sugar had a similar shape, the adduct was, however, precipitated by adding 40 ml of acetone, and was collected by centrifugation Fig 1 shows the curves for the interaction of melibiose and barium hydroxide, as a typical example

It is interesting that, although sucrose and α,α-trehalose have no reducing group, each gives a 1.1 adduct Maltitol[2], which has no reducing group but contains a D-glucitol residue, also gives a 1 1 adduct The weight of carbohydrate–barium hydr-

*Part of a paper presented before the Carbohydrate Section, 8th International Symposium on the Chemistry of Natural Products, New Delhi, India, February, 1972

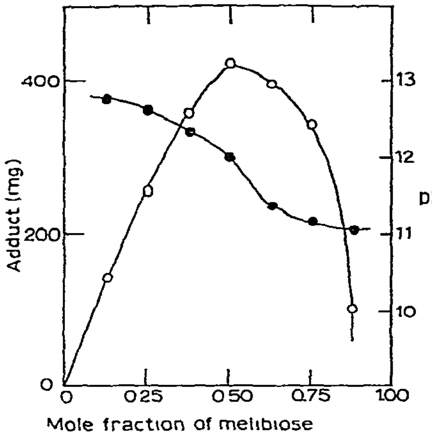

Fig 1 Interaction of melibiose with barium hydroxide by the constant-volume method Amount of adduct (hollow points) and pH (dark points) *vs* mole fraction of sugar

oxide adduct and the corresponding pH value of the mother liquors for the 1 1 ratio (total vol 40 ml) of the reactants are given in Table I The yield of adduct varied, probably due to differences in solubility. Where the solubility is high, the pH of the mother liquor is also high

TABLE I

WEIGHT OF CARBOHYDRATE–BARIUM HYDROXIDE ADDUCT, AND THE CORRESPONDING pH VALUES FOR THE 1 1 RATIO (TOTAL VOL 40 ml) OF THE REACTANTS

Carbohydrate	*Weight of adduct (mg)*	*pH*
Cellobiose	349 8	11 78
D-Glucose	150 2	12 08
Lactose	327 8	11 90
Maltitol	299 2	11 20
Maltose	386 2	11 60
Melibiose	359 6	11 24
Sucrose	343 4	11.50
α,α-Trehalose	0 0	12 50

It was also found that amylose and amylopectin form adducts with the hydroxides of barium, calcium, and strontium when a 1% solution of the polysaccharides in 0 5M sodium hydroxide (10 ml) is added at room temperature to 250 ml of a saturated solution of calcium hydroxide, of 0 05M strontium hydroxide, or of 0 05M barium hydroxide The adduct was precipitated in each case, and was collected by centrifugation, followed by washing with methanol, and drying Analysis for the metal atom showed that, in each adduct, there was one metal atom for every two D-glucose (or related) residues

Thus, both for the disaccharides and polysaccharides studied, one metal atom is attached in some way to two D-glucose (or derived) residues. The reducing end is, however, not necessary for adduct formation. It is premature at this stage to discuss the mode of attachment of the metal atom. Sugars that have three adjacent hydroxyl groups in axial–equatorial–axial relationship[3] give adducts with alkaline-earth metals, but none of the carbohydrates studied have such an orientation in a single unit.

Most of the metals were determined by acid–base titration. First an excess of acid was added, and the amount of acid consumed was determined by titration with base. For the adducts of amylose and amylopectin, the metals were determined by the gravimetric[4] or by the EDTA method[4]. The sugars were determined by the phenol–sulfuric acid method[5]. The analytical results are summarized in Table II.

TABLE II

ANALYTICAL DATA FOR DIFFERENT ADDUCTS

Adduct[a]	*Metal* (%)		*Sugar* (%)	
	Found	*Calc*	*Found*	*Calc*
With barium hydroxide				
Cellobiose	26.0	26.7	68.1	66.7
D-Glucose	39.1	39.1	54.0	51.2
Lactose	25.8	26.7	69.2	66.7
Maltitol	25.7	26.7	67.5	66.7
Maltose	26.8	26.7	71.5	66.7
Melibiose	27.1	26.7	66.0	66.7
Sucrose	26.5	26.7	69.0	66.7
α,α-Trehalose	27.2	26.7	70.1	66.7
With calcium hydroxide				
Cellobiose	10.3	9.6	82.9	82.2
D-Glucose	16.3	15.6	72.6	70.8
Lactose	10.2	9.6	84.0	82.2
Maltitol	10.3	9.6	83.8	82.2
Maltose	9.8	9.6	83.8	82.2
Melibiose	10.1	9.6	83.2	82.2
Sucrose	10.1	9.6	82.4	82.2
α,α-Trehalose	10.5	9.6	83.5	82.2
With strontium hydroxide				
Cellobiose	18.5	18.1	75.1	73.8
D-Glucose	25.2	25.7	61.0	59.8
Lactose	17.2	18.1	74.5	73.8
Maltitol	18.5	18.1	75.6	73.8
Maltose	18.0	18.1	76.2	73.8
Melibiose	17.8	18.1	74.0	73.8
Sucrose	17.5	18.1	74.6	73.8
α,α-Trehalose	18.9	18.1	75.8	73.8

[a]Adducts of D-glucose and maltose have already been reported[1]. They are included here only for comparison.

ACKNOWLEDGMENTS

Financial assistance by the U S D A under PL-480 grant No FG-In-365 (UR-A7-(10)-144) is gratefully acknowledged Our thanks are due Mr. B Mukherjee for technical assistance

REFERENCES

1 N Roy and A K Mitra, *Carbohyd Res*, 24 (1972) 175
2 P Karrer and J Buchi, *Helv Chim Acta*, 20 (1937) 86
3 S J Angyal and K P Davies, *Chem Commun*, (1971) 500
4 A. I Vogel, *A Text Book of Quantitative Inorganic Analysis*, Longmans, London, 1962
5 J E. Hodge and B T Hofreiter, *Methods Carbohyd. Chem*, 1 (1962) 388