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Complexes between Glycosides and Cadoxen

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The reactions between cadoxen, a solution of cadmium hydroxide in aqueous ethylene diamine, and some glycosides have been investigated. From the differences in optical rotation observed between solutions of the glycosides in cadoxen and in aqueous ethylene diamine, it was concluded that complexes are formed between cadmium and adjacent hydroxyls in the glycosides. Methyl β-D-glucopyranoside showed no electrophoretic mobility in cadoxen and reduced its conductivity, which proved that the complexes are uncharged.

The solubility of cellulose in cadoxen depends upon complex formation involving the C-2 and C-3 hydroxyls of the glucose residues.

Cadoxen, a solution of cadmium hydroxide (6 % as Cd) in 28 % aqueous ethylene diamine, was introduced as a solvent for cellulose by Jayme and coworkers [1]. The cellulose solutions are colourless and fairly stable, and therefore cadoxen has definite advantages over other cellulose solvents. In the present paper, studies on the reaction between cadoxen and some glycopyranosides are reported.

The reaction between another cellulose solvent, cuprammonium (copper(II) hydroxide in aqueous ammonia), and glycosides has been studied by Reeves [2]. He found that it gave cyclic complexes with adjacent hydroxyls in sixmembered rings, as example for cellulose with the hydroxyls in the 2- and 3-positions. The complex formation is accompanied by a large shift in the optical rotation, and from the signs and magnitudes of these shifts, Reeves was able to draw conclusions regarding the conformations of the glycosides studied. Reeves and Bragg [3] have also shown that the diol : copper ratio is 1:1.

The optical rotations of some glycosides were determined in cadoxen and in 28 % aqueous ethylene diamine. The determinations were made at 578, 546, 436, and 364 mμ. Measurements were also made at 313 mμ, but due to the relatively strong absorption of cadoxen and of some of the glycosides, these

Table 1. Rotational shifts for some glycopyranosides.

	Substance	Rotational shift *			
		578 mμ	546 mμ	436 mμ	364 mμ
a	Methyl α-D-glucoside	+ 45	+ 49	+ 71	+ 105
b	Methyl β-D-glucoside	+ 23	+ 14	+ 29	+ 44
c	Methyl 2-*O*-methyl-α-D-glucoside	+ 74	+ 85	+ 142	+ 223
d	Isopropyl 2-deoxy-β-D-glucoside	+ 63	+ 74	+ 137	+ 245
e	Methyl 3-deoxy-β-D-glucoside	+ 4	+ 1	+ 7	+ 9
f	Methyl 4-*O*-methyl-β-D-glucoside	− 73	− 86	− 158	−291
g	Methyl 4-*O*-benzyl-β-D-glucoside	− 61	− 71	−133	−238
h	Methyl 4,6-*O*-ethylidene-β-D-glucoside	−115	−132	−235	−392
i	Benzyl β-D-xyloside	+ 23	+ 25	+ 47	+ 68
j	Benzyl4-*O*-methyl-β-D-xyloside	− 76	− 86	−157	−288
k	Benzyl α-D-arabinoside	+ 61	+ 71	+ 137	+ 249

* Rotational shift = ([α] Cadoxen − [α] aqueous ethylene diamine) × (molecular weight/100).

measurements were less reliable and are not included. The shifts in molecular rotation due to complex formation are summarised in Table 1. Except for the magnitudes of the shifts, the results are identical with those obtained by Reeves [2] in his studies of the same or similar substances in cuprammonium. The glucosides and xyloside which can give complexes with either the 2,3- or the 3,4-hydroxyls (a, b, and i) show small positive shifts. Those which can give complexes only with the 2,3-hydroxyls (f, g, h, and j) show strong negative shifts. The glucosides which can give complexes only with the 3,4-hydroxyls (c and d) show strong positive shifts. The 3-deoxy-D-glucoside (e) which has no pair of adjacent hydroxyls, shows insignificant shifts, probably reflecting the experimental error. Finally the D-arabinoside (k), in which, according to Reeves, the two competing complexes should both give positive contributions to the optical rotation, shows strong positive shifts. It could therefore be concluded that glycopyranosides form a similar type of complex with cadoxen as they do with cuprammonium, that is 5-membered cyclic complexes with adjacent hydroxyl groups.

In agreement with these results cellulose dissolved in cadoxen shows negative optical rotation. The specific rotation was determined at three concentrations and was found to decrease somewhat at higher concentrations (Table 2). The values in Table 2 were determined about 1 h after the cellulose had been dissolved. The changes in optical rotation after the solutions had been kept

Table 2. Specific rotation of cellulose in Cadoxen.

Conc. of cellulose, %	[α]			
	578 mμ	546 mμ	436 mμ	364 mμ
0.402	−53.5	−62.0	−115.8	−202.0
1.023	−53.6	−63.1	−112.4	−199.3
2.101	−49.5	−57.4	−107.8	−189.7

for 24 h were small, except for those determined at 364 mμ, which had decreased (in absolute values) considerably. As the turbidity of the solutions affect the measurements, especially at the lower wave-lengths, it is difficult to decide whether this decrease indicates degradation or slight differences in state of solution.

The electrophoretic mobilities of methyl β-D-glucopyranoside and some reducing sugars in cadoxen (at pH 12) was studied. The sugars showed slight mobilities, similar to those observed by Frahn and Mills [3] on electrophoresis in aqueous sodium hydroxide. The glucoside did not move, indicating that the complex is unchanged. In agreement with this result the conductivity of a cadoxen solution was decreased on addition of methyl β-D-glucopyranoside. Uncharged complex would correspond to a diol : cadmium ratio of 1:1.

EXPERIMENTAL

The cadoxen solution was prepared according to Jayme *et al.*[1] The optical rotations were determined with a Perkin Elmer 141 photoelectrical polarimeter, which gives readings to ± 0.001°. The substances (Table 1), some of which were available only in small quantities, were dissolved to about 0.2 % solutions and the rotations measured in a 10 cm micro tube (vol. ≃1 ml). For the cellulose solutions, a 10 cm ordinary tube (vol. ≃ 6 ml) was used. Whatman Cellulose Powder, Standard Grade, was used, and a correction for the moisture content was made. The temperature, approximately 22°, was not thermostatically controlled. The paper electrophoresis was run in 10 % cadoxen in water (0.55 % Cd). For the conductometric measurements a mixture of cadoxen solution and water (1:1) was used.

REFERENCES

1. Jayme, G. and Neuschäffer, K. *Naturwiss.* **44** (1957) 62.
2. Reeves, R. E. *Advan. Carbohydrate Chem.* **6** (1951) 107.
3. Reeves, R. E. and Bragg, P. *J. Org. Chem.* **66** (1961) 3487.
4. Frahn, J. L. and Mills, J. A. *Australian J. Chem.* **12** (1959) 65.

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