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COMPLEXES BETWEEN POLYHYDROXY COMPOUNDS AND COPPER(II) IONS

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ABSTRACT

Several polyhydroxy compounds have been shown to form cationic complexes with copper(II) ions. Paper electrophoresis in copper(II) acetate and basic copper(II) acetate solutions, and chromatography on the Cu^{2+} form of a cation-exchange resin are useful methods for the resolution of mixtures and identification of polyhydroxy compounds.

INTRODUCTION

The partially filled set of d-orbitals of the copper(II) ion confers, among other characteristic properties, the ability to form co-ordination complexes[1]. Pertinent examples of complexes with chelating ligands are those of glycosides of aldoses[2] and aminodeoxyaldoses[3] formed in cuprammonium solutions. In an effort to extend the range[4] of simple methods for the separation of carbohydrates and related compounds, we have investigated the paper electrophoresis in copper(II) acetate and basic copper(II) acetate solutions of a number of polyhydroxy compounds, and the chromatography of selected compounds on the Cu^{2+} form of a cation-exchange resin.

RESULTS AND DISCUSSION

The compounds examined electrophoretically are listed in Table I. D-Glucitol (sorbitol) was used as a standard for the comparison of rates of migration, and 5-hydroxymethyl-2-furaldehyde as a non-migrating marker for correction of electro-osmosis. Hence, the migration rates are expressed as M_S values. The symbols Cu_{Ac} and Cu_{BAc} refer to copper(II) acetate and basic copper(II) acetate solutions, respectively. Migration was always towards the cathode.

It is impracticable to discuss in detail all the applications of this method of electrophoresis, since these will vary with the individual problems encountered. However, the results show that, in general, tetritols, pentitols, hexitols, and reduced disaccharides of D-glucose (except laminaribiitol) form cationic complexes with the copper(II) ion, but, under the conditions described here, reducing sugars (except D-ribose, D-xylose, and D-gulose) do not. It is further interesting to note that each of

TABLE I

ELECTROPHORETIC MOBILITIES OF ALDITOLS IN COPPER(II) ACETATE AND BASIC COPPER(II) ACETATE SOLUTIONS

Compound	M_S (Cu_{Ac})	M_S (Cu_{BAc})	*Non-migrating compounds:* M_S (Cu_{Ac}) *and* M_S (Cu_{BAc}) <0.1
Erythritol	0.24	<0.1	Glycerol
L-Threitol	0.7–0.9	0.20	L-Arabinose
L-Arabinitol	0.5–1.0	0.87	D-Lyxose
Ribitol	0.20	0.17	D-Galactose
Xylitol	1.35	1.20	D-Glucose
Allitol	0.25	0.36	
D-Altritol	0.5–1.0	0.89	D-Mannose
Galactitol	1.03	1.00	D-Fructose
D-Glucitol	1.00	1.00	L-Sorbose
L-Iditol	0.6–1.3	1.15	Sucrose
D-Mannitol	1.00	0.88	Kojibiose
Kojibitol	0.53	0.39	Sophorose
Sophoritol	0.30	0.29	Nigerose
Nigeritol	0.34	0.16	Laminaribiose
Maltitol	0.72	0 54	Maltose
Cellobiitol	0.27	0.18	Cellobiose
Isomaltitol	0.88	0.72	Isomaltose
Gentiobiitol	0.92	0.88	Gentiobiose
D-Ribose	0.15	<0.1	Laminaribitol
D-Xylose	0–0.3	<0.1	
D-Gulose	0.37	<0.1	

the four pairs of α- and β-isomers of reduced disaccharides of D-glucose can be resolved by this method.

It is tedious to apply electrophoretic techniques to preparative work, unless a special apparatus is used. However, that complexing of polyhydroxy compounds with copper(II) ions can easily be used when larger quantities of materials are involved is illustrated by the successful resolution of mixtures on Amberlite IR-120 (Cu^{2+}) resin (Table II). The results indicate that chromatography on this resin resolves mixtures which can also be resolved by paper electrophoresis in copper(II) acetate or basic copper(II) acetate solutions.

EXPERIMENTAL

Paper electrophoresis. — Electrophoresis was carried out on sheets (10 cm wide) of Whatman No. 3 filter paper. The electrolytes consisted of freshly prepared 5% aqueous copper(II) acetate monohydrate, $Cu(CH_3CO_2)_2 \cdot H_2O$ (pH 5.1), or 5% aqueous basic copper(II) acetate, $Cu(CH_3CO_2)_2\ CuO \cdot 6H_2O$ (pH 5.1–5.3). Electrophoretograms were prepared by applying a voltage of *ca.* 60 volts/cm for *ca.* 2 h. Compounds were detected by treating the dried paper with a saturated solution of potassium permanganate in acetone. Under the conditions used, D-glucitol had mobilities of 2.65×10^{-5} and 2.21×10^{-5} $cm^2\ volt^{-1} sec^{-1}$ in aqueous copper(II) acetate and aqueous basic copper(II) acetate, respectively.

TABLE II

CHROMATOGRAPHY OF ALDITOLS ON AMBERLITE IR-120(Cu^{2+}) RESIN

Components of mixture	*Weight (mg)*	*Size of column (cm)*	*Eluent*[a] *(ml)*	*Effluent containing pure sample (ml)*	*Extent of separation*	*Recovery (mg)*
D-Glucose	200	4 × 33	730(10)[c],1080(10)[g]	31–210	Complete	
D-Glucitol	200			1611–1810		
D-Mannose	100	2.5 × 36	3000(50)[b],500(500)[g]	1–1500	Complete	
D-Mannitol	100			3000–3500		
Cellobiitol	100	2.5 × 36	1750(25)[d]	1–500	Partial	
Maltitol	100			1000–1750		
Maltitol	100	4 × 33	1850(10)[e],450(10)[f],	51–1850	Complete	80
Isomaltitol	100		2000(100)[g]	2051–4300		95
Ribitol	200			1–100	Partial	132
D-Arabinitol	200	2.5 × 36	1625(25)[c]	251–700	Partial	107
Xylitol	200			976–1625		122

[a]Figures in parenthesis are the volumes (ml) of individual fractions collected; [b]water; [c]0.2% $CuAc_2 \cdot H_2O$; [d]0.4% $CuAc_2 \cdot H_2O$; [e]1% $CuAc_2 \cdot H_2O$; [f]1.25% $CuAc_2 \cdot H_2O$; [g]2.5% $CuAc_2 \cdot H_2O$.

Chromatography. — Columns of Amberlite IR-120 (H^+) resin were treated with 2.5% aqueous copper(II) acetate monohydrate (2–4 l). The mixtures of polyhydroxy compounds dissolved in 2.5% aqueous copper(II) acetate monohydrate (2 ml) were run into the columns and the whole allowed to stand overnight. The effluents were analysed by paper electrophoresis in copper(II) acetate solution (see above). Fractions from which the solute was recovered were treated with gaseous hydrogen sulphide, filtered, and evaporated under reduced pressure. Other details are shown in Table II.

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