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Note

Interactions of aqueous solutions of sugars with alumina

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Many polybasic acids and metal salts are well known to interact with carbohydrates or structurally related compounds in aqueous solution[1–9]. This paper describes such an interaction occurring between aluminium oxide and aqueous solutions of monosaccharides.

During passage of a solution of several monosaccharides through a column of alumina, different monosaccharides are retarded to different extents. A similar effect is observed in thin-layer chromatography on alumina (Table I).

TABLE I

RELATIVE MOBILITIES OF MONOSACCHARIDES ON ALUMINAS HAVING VARIOUS BASICITIES

Alumina system (≃ *pH*)	*Acidic Column B*[a] (*3.5*)	*Thin layer* (*5.5*)	*Neutral (I) Column B* (*6.5*)	*Neutral (II) Columns B, C* (*7.2*)	*Basic Column B* (*10*)
	M_{CHD}[b] ±3	R_{CHD}[b] ±2	M_{CHD} ±3	M_{CHD} ±3	M_{CHD} ±3
Cyclohexane-1,4-diol (CHD)	100	100	100	100	100
L-Rhamnose	80	77	73	62	44
D-Glucose	75	75	73	70	61
D-Xylose	75	71	69	60	50
L-Arabinose	75	65	66	53	48
D-Galactose	75	65	66	53	48
D-Mannose	75	64	51	36	24
D-Lyxose		70	46		
D-Gulose		49[c]	34		
D-Allose		32[c]	20		
D-Altrose		57[c]	18		
D-Fructose	61	36[c]	13	6	1
L-Sorbose		53[c]	8		
L-Idose		40[c]	7		
D-Talose		18[c]	7		
D-Ribose	51	17[c]	3	3	1

[a]For column dimensions, see Experimental. [b]M_{CHD} and R_{CHD} are the mobilities relative to cyclohexane-*cis,trans*-1,4-diol (R_F 0.77 ±0.02; $V_P/V_T = 0.48 \pm 0.02$, V_P = peak effluent volume, V_T = total bed volume). Since the amounts of rare sugars at our disposal were small, their mobilities were determined in only two experiments. [c]Streak.

The extent of retardation depends on the basicity of the alumina. For neutral alumina, it was found to be proportional to the electrophoretic mobilities of monosaccharides in alkaline arsenite[3] (Fig. 1). This kind of interaction is generally regarded as resulting from complex formation between a metal atom and suitably oriented hydroxyl groups. The observed similarity suggests that sugar–alumina interactions may likewise be explained in terms of complex formation. Apparently, all monosaccharides containing three adjacent hydroxyl-groups with either an *ax,eq,ax*-orientation in the preferred pyranoid conformation[10], or possessing high, equilibrium concentrations of furanoses[10], are strongly retarded (Table I, allose to ribose). If an *ax,eq,ax*-orientation of vicinal hydroxyl groups can be achieved only by ring inversion to the less-favourable conformation, interaction becomes pronounced only with alumina of higher basicity. This is the situation with rhamnose, mannose, lyxose, and gulose. Sugars lacking the required orientation, *i.e.*, glucose, xylose, arabinose, and galactose, are retarded only to a minor degree.

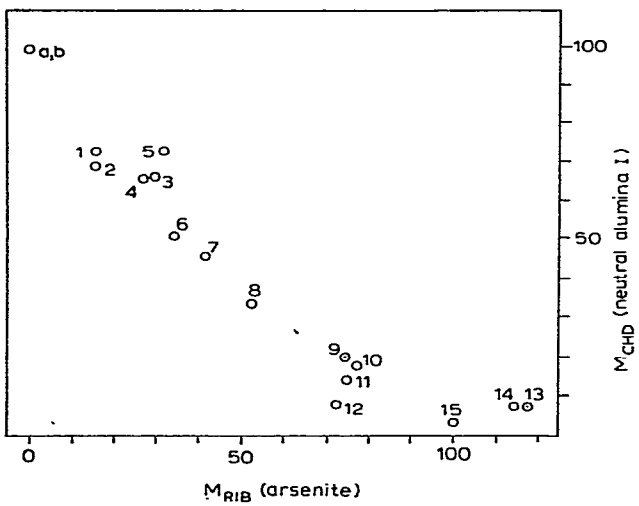

Fig. 1. Complexing of sugars with alumina and arsenite. Relative mobilities (M_{CHD}) on neutra. (pH $\simeq$ 6.5) alumina *vs.* relative electrophoretic mobilities (M_{RIB}) in alkaline (pH 9.6) arsenite[3] a Cyclohexane-1,4-diol; b butane-1,4-diol; 1 D-glucose; 2 D-xylose; 3 L-arabinose; 4 D-galactose; 5 L-rhamnose; 6 D-mannose; 7 D-lyxose; 8 D-gulose; 9 D-allose; 10 D-altrose; 11 D-fructose; 12 L-sorbose; 13 D-talose; 14 L-idose; 15 D-ribose. M_{CHD} for cyclohexane-1,4-diol = 100; M_{RIB} for ribose = 100.

By proper choice of alumina, this effect can be used to achieve separation of sugars easily and quickly, on a preparative as well as an analytical scale.

EXPERIMENTAL

Acidic, neutral (2 different lots), and basic alumina for column chromatography were obtained from Woelm, Eschwege, Germany; and thin layers of alumina on

plastic foil from Macherey and Nagel, Düren, Germany. The following sugars and sugar derivatives were generous gifts from the Chemisches Staatsinstitut, University of Hamburg: D-lyxose, D-allose, L-sorbose, penta-*O*-acetyl derivatives of D-altrose, D-talose, L-idose, and D-gulose·$CaCl_2$·$2H_2O$. The free sugars were regenerated from their derivatives by standard methods.

Columns were prepared by filling with aqueous suspensions of alumina, and operated mainly by gravity elution. Column dimensions were *A*, 120 × 9 mm (7.5 cm^3); *B*, 500 × 20 mm (157 cm^3); and *C*, 820 × 17 mm (185 cm^3). Columns were charged with up to 3 (*A*), or 150 mg (*B*) of sugars, either singly or in mixtures. Samples were applied to the columns in 0.5 (*A*, *C*) or 1 ml (*B*) of water. Column *A*, charged with alumina previously titrated to pH 5[12], was used to effect the separation of D-glucose and D-mannose from D-fructose.

Deionized water was passed through column *C* by means of a pulseless, piston-type pump (LDP 13 A, Labotron, Munich, West Germany) at a flow-rate of 80 ml/h. Effluent sugars were detected with a differential refractometer (R4, Waters Messtechnik GmbH., Frankfurt, West Germany), using an UR 400 recorder (Vitatron, Dieren, The Netherlands). The quantity of sugars applied to this column varied between 0.5 and 17 mg. When a saturated, aqueous solution of chloroform was passed through column *C*, the retention times of chloroform and cyclohexane-*cis*, *trans*-1,4-diol (used as a standard) were identical.

The retention behaviour of various monosaccharides on this column is shown in Fig. 2. Due to the permanent contamination of the effluents with traces of dissolved alumina, rather large amounts of the more strongly retarded sugars were required for detection by the refractometer; for example, D-fructose and D-ribose could not be detected.

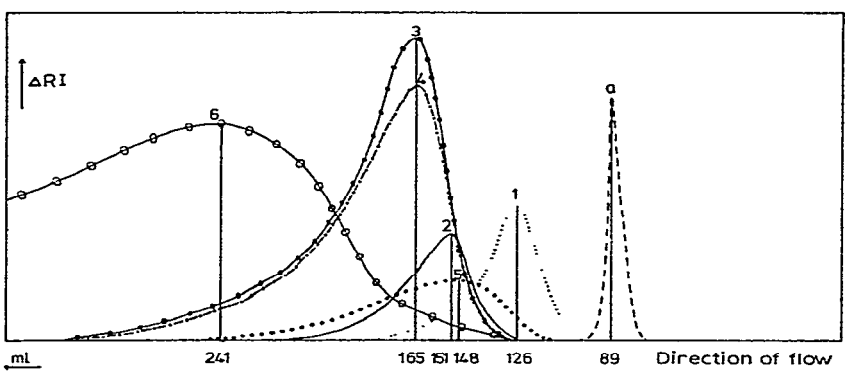

Fig. 2. Column chromatography of monosaccharides on neutral alumina (pH ≃ 7.2); column dimensions, 820 × 17 mm; bed volume, 185 cm^3; solvent, deionized water; flow rate, 80 ml/h; detector, differential refractometer. a Cyclohexane-*cis*,*trans*-1,4-diol (0.5 mg; a saturated aqueous solution of chloroform yielded a peak having exactly the same position; 1 D-glucose (1.1 mg); 2 D-xylose (1.6 mg); 3 L-arabinose (4 mg); 4 D-galactose (4 mg); 5 L-rhamnose (2 mg); 6 D-mannose (10 mg).

The compositions of gravity-flow effluents of alumina columns were monitored by t.l.c. on silica gel (Merck) with ethyl acetate–acetone–water (40:50:10)[11], and detection with diphenylamine–aniline–phosphoric acid[11] or with Tollens' reagent.

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REFERENCES

1 J. Böeseken, *Rec. Trav. Chim.*, 61 (1942) 82.
2 A. B. Foster, *Advan. Carbohyd. Chem.*, 12 (1957) 81.
3 J. L. Frahn and J. A. Mills, *Aust. J. Chem.*, 12 (1959) 65.
4 H. Weigel, *Advan. Carbohyd. Chem.*, 18 (1963) 61.
5 A. S. Perlin and E. Von Rudloff, *Can. J. Chem.*, 43 (1965) 2071.
6 H. J. F. Angus, E. J. Bourne, F. Searle, and H. Weigel, *Tetrahedron Lett.*, (1964) 55.
7 E. J. Bourne, D. H. Hutson, and H. Weigel, *J. Chem. Soc.*, (1960) 4252.
8 G. R. Barker and D. F. Shaw, *J. Chem. Soc.*, (1959) 584.
9 S. J. Angyal and K. P. Davies, *Chem. Commun.* (1971) 500.
10 S. J. Angyal, *Angew. Chem.*, 81 (1969) 172; *Angew. Chem. Int. Ed. Engl.*, 8 (1969) 157.
11 E. Bancher, H. Scherz, and K. Kaindl, *Mikrochim. Acta*, (1964) 1043.
12 L. Birkofer, C. Kaiser, and M. Donike, *J. Chromatogr.*, 22 (1966) 303.