Reactions of saccharides catalyzed by molybdate ions. VI.* Epimerization of aldotetroses

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Epimerization of both D-erythrose and D-threose catalyzed by molybdate ions gives an equilibrium mixture of D-erythrose and D-threose in the ratio 3 : 4. The complexing of D-erythrose with molybdate ions reflects itself in the change of its specific rotation.

Transformation of reducing saccharides in basic media — the Lobry de Bruyn—Alberda van Ekenstein reaction — has been known for a longer time [1]. In alkaline solutions an aldose is preferably transformed into 2-ketose and epimeric aldose. In more concentrated solutions of alkali the changes are greater and lead also to formation of the so-called saccharinic acids. The transformation in pyridine is important for the preparation of 2-ketoses or for the inversion of the C-2 hydroxyl group of aldonic acids.

In acidified water solutions under catalytic action of molybdate ions, the aldoses epimerize and equilibrium mixtures are formed in which the epimeric aldose with *trans* relationship of the hydroxyl groups at C-2 and C-3 [2, 3] predominates. Each pair of epimeric aldoses has a characteristic composition of equilibrium mixture. For instance, from the equilibrium mixture of epimerized L-mannose [4] and L-rhamnose [5, 6], L-glucose and L-chinovose were obtained in a particularly simple manner, by fractional crystallization. This communication is one of the papers in a series dealing with the epimerization of aldoses and with the behaviour of tetroses.

Molybdate complexes of D-erythrose and L-threose have been ascertained by electrophoreses (pH 5) [7, 8]. Their different mobilities enabled to use electrophoresis as a simple method for separation of both sugars [7]. We found that D-erythrose and D-threose epimerize in water solution of molybdate ions (80°C, 2 hours) forming an equilibrium mixture of tetroses in which D-threose predominates. The ratio of D-erythrose to D-threose is about 3 : 4 at equilibrium. Contrary to the transformation of D-erythrose in pyridine [9], the epimerization of this sugar catalyzed by molybdate ions is not accompanied by formation of D-*glycero*-tetrulose.

Specific rotation of D-erythrose (−38.6°) showed a remarkable change (+12.6°) due to the complexing with molybdate ions; however, almost no change was recorded with D-threose. This phenomenon may be accounted for by the fact that D-erythrose (Scheme 1; *I*) possesses the carbonyl group and the hydroxyl groups at C-2 and C-3 in such a steric arrangement (*Ia*) which is altered by the complex formed (*II*). In the case of D-threose (*III*, *IIIa*), the formation of the complex (*IV*) does not cause any apparent changes in the conformation of the ligand, and, consequently, any significant change in specific rotation. Similar absolute values of specific rotation of the molybdate

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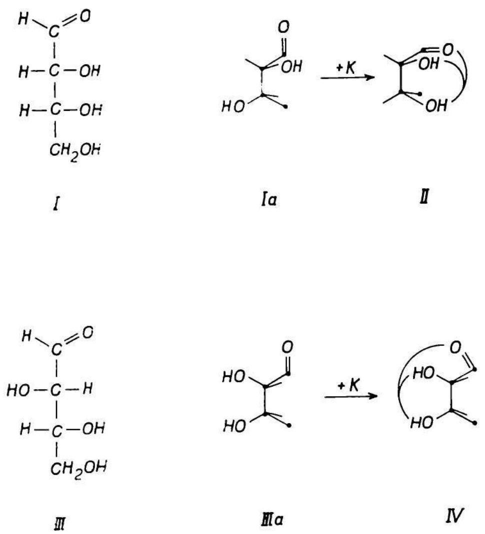
* For Part V see Ref. [5].



Scheme 1

complexes of D-erythrose (+12.6°) and D-threose (−11.6°) suggest that one complex spatially resembles the mirror image of the other one. From the above said it follows that the epimerization of D-erythrose or D-threose gives preferably D-threose, *i.e.* the epimer forming energetically a more favourable complex.

Experimental

D-Erythrose and D-threose used were prepared by oxidation of D-glucose and D-galactose with lead tetraacetate [10]. The purification of thus obtained tetroses and the fractionation of epimerization mixtures was carried out by chromatography on a Cellulose F (Whatman) column (100 × 4.6 cm) in ethyl acetate—acetic acid—4% boric acid in water (9 : 1 1 v/v). The control of D-erythrose and D-threose purity as well as the estimation of their ratios during epimerization were done by chromatography on Whatman No. 1 paper in the above quoted solvent system for 16—18 hours. Sugars (D-threose, R_T 1.00; D-*glycero*-tetrulose, R_T 1.35; D-erythrose, R_T 2.00) were detected with the aniline phthalate reagent [11]. Specific rotations of water solutions of tetroses were measured after 24 hours on a Bendix—Ericsson type 143 A automatic polarimeter.

Epimerization of D-erythrose and D-threose

A mixture of D-erythrose or D-threose (2 g), molybdenic acid (50 mg) in water (100 ml) was heated at 80°C for 2 hours. The reaction mixture was then filtered and deionized with Dowex 1 (OH^- form, *ca.* 1 g), the filtrate was concentrated *in vacuo* (40°C) and fractionated on a Cellulose column. Fractions containing individual tetroses were pooled and evaporated under reduced pressure. The residues were dissolved and evaporated three times with anhydrous methanol.

The epimerization of D-erythrose gave: D-erythrose, 0.53 g, $[\alpha]_D^{24}$ −39.1° (*c* 1.2); D-threose, 0.74 g, $[\alpha]_D^{24}$ −12.2° (*c* 1.6).

The epimerization of D-threose gave: D-erythrose, 0.58 g, $[\alpha]_D^{24}$ $-38.0°$ (c 1.3); D-threose, 0.77 g, $[\alpha]_D^{24}$ $-13.0°$ (c 1.4).

Specific rotations of the starting tetroses in water, D-erythrose $[\alpha]_D^{25}$ $-38.0°$ (c 1.0) and D-threose $[\alpha]_D^{25}$ $-13.0°$ (c 1.4), showed following values after dilution with equal volume of 4% water solution of molybdenic acid within 4 minutes: D-erythrose $[\alpha]_D^{25}$ $+12.6°$, D-threose $[\alpha]_D^{25}$ $-11.6°$. Ref. [9] gives for D-erythrose $[\alpha]_D^{24}$ $-40.6°$ (c 1.0, water) and for D-threose $[\alpha]_D^{20}$ $-13.0°$ (c 1.0, water).

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