Reactions of Saccharides Catalyzed by Molybdate Ions. IV.* Epimerization of Aldopentoses

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Epimerization of aldopentoses in water solution catalyzed by molybdenic acid leads to the formation of equilibrium mixtures of all four aldopentoses. In the equilibrium mixture, which is characteristic for each epimeric pair of pentoses (D-arabinose : D-ribose — 6 3, D-xylose : D-lyxose — 10 9), the epimer having *trans* arrangement of the C-2 and C-3 hydroxyl groups predominates. Small amounts of the complementary pair of epimeric pentoses in the equilibrium mixture are explained by the inversion of the hydroxyl group at C-3 due to the formation of the molybdate complex with the hydroxyl groups at C-2 and C-4 of D-ribose and D-xylose in the conformation 1C.

Investigation of the epimerization of individual aldopentoses in water solution molybdenic acid has shown that the reaction leads to the equilibrium of all four aldopentoses. A characteristic equilibrium ratio is obtained for each pair of epimeric aldopentoses Thus the epimerization of ribose or arabinose gives arabinose and ribose as the ma components in the ratio 6 : 3. The same reaction with xylose or lyxose ends at the ratio 10 : 9 (Table 1). During the epimerization of each aldopentose small amounts the complementary pair of aldopentoses are also formed. The mechanism of the epimerization is associated with the formation of transitory molybdate complexes of pentoses [1] involving the hydroxyl groups at C-1 and C-3 according to *Bayer* and *Voelter* [2]. Th formation of the complementary pair of epimeric pentoses suggests that a transitor molybdate complex is also formed between the hydroxyl groups at C-2 and C-4 of D-ribos (*III*) and D-xylose (*IV*) in the conformation 1C (Scheme 1). The complexing of molybda with the C-1 and C-3 hydroxyl groups is probably preferred by the hemiacetal hydroxy group which is sufficiently electronegative to form a coordination bond with the centra molybdenum atom. The condition for the complexing with the hydroxyl groups at C and C-3 is fulfilled by α,D-arabinose (*I*), α,D-ribose (*II*) in the conformation C1 and b β,D-xylose (*V*) and β,D-lyxose (*VI*) in the conformation 1C. During the formation of th epimeric pair of aldoses such epimer is preferentially formed which possesses *trans* arrangement of the hydroxyl groups at C-2 and C-3 (arabinose, xylose). This points to th fact that the complexes of aldoses having *cis-cis* relationship of the hydroxyl groups (1 ax, 2 eq, 3 ax) are richer in energy, which has been proved also by spectral methods elsewhere [3, 4].

The electronegativity of the hydroxyl groups of aldoses is lower at C-2 and C-4 tha at C-1 and C-3. Therefore, it may be assumed that the probability for the complexing with molybdate is lesser with the hydroxyl groups at C-2 and C-4. This proposal is support

* For Part III. see *Chem. Zvesti* **26**, 187 (1972).

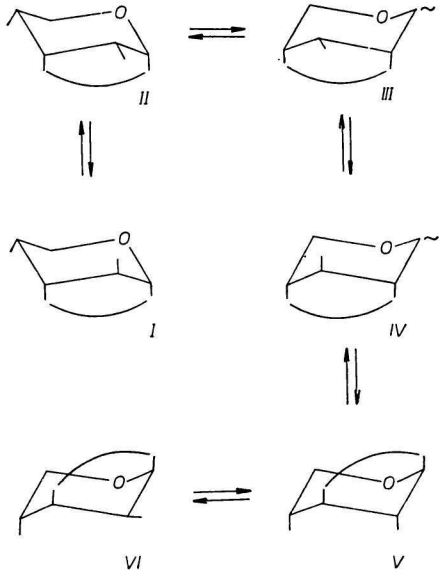
Table 1

Compounds formed by epimerization of pentoses determined by gas—liquid chromatography as per-*O*-(trifluoroacetyl)alditols

Compound [%]	Relative retention time*	Epimerized pentoses			
		ribose	arabinose	xylose	lyxose
erythrose	0.38	0.15	0.15	3.4	8.7
threose	0.46	1.6	—	—	—
anhydropentoses	0.58	0.05	0.3	—	—
	0.65	3.2	0.1	3.0	6.1
	0.73	0.9	—	1.0	2.5
	0.78	1.0	0.2	—	—
ribose	0.86	31.3	26.8	1.6	2.0
arabinose	1.00				
		59.9	68.5	41.5	37.9
lyxose	1.00				
xylose	1.11	1.8	3.8	49.3	42.8
arabinose**	—	58.3	65.1	3.2	4.0
lyxose**	—	1.6	3.4	38.3	33.9

* Retention time relative to that of D-arabinose (t_r = 9.3 min).

** Values calculated from the equilibrium ratio of ribose : arabinose (1 : 2) and xylose : lyxose (10 : 9) estimated by paper chromatography.



Scheme 1.

I, α,D-arabinose; *II*. α,D-ribose; *III*. D-ribose; *IV*. D-xylose; *V*. β,D-xylose; *VI*. β,D-lyxose.

ed by the finding that the inversion of the C-3 hydroxyl group, in comparison with tha of the C-2 hydroxyl group, occurs in much smaller extent.

It is also interesting to note that the epimerization of pentoses is accompanied b partial splitting the bond between C-1 and C-2 which results in the formation of short aldoses. D-Threose was observed in the case of D-ribose and D-erythrose in the case D-xylose and, particularly, of D-lyxose. Also the formation of anhydropentoses is interes ing. However, it needs further and more detailed study to explain these points of the ep merization.

Experimental

The compounds formed during the epimerization of pentoses were identified as per-(-(trifluoroacetyl) derivatives by gas—liquid chromatography with a Hewlett—Packar 5750 G chromatograph using a two-column system and a flame-ionization detecto The columns (6 ft × 1/4 in) were packed with 5% XE-60 on EMBACEL (AW) (60–8 mesh) and run with nitrogen at a temperature rise programmed from 150 to 180°C (2°/min Quantitative evaluation was done with a Hewlett—Packard 3370 A integrator. Th reaction mixtures were also examined by chromatography on Whatman No. 1 pape with butanol—ethanol—water (5 : 1 : 4 v/v). The chromatograms were detected wit the diphenylamine reagent [5] and evaluated by direct scanning with an ERI-10 densito meter (Zeiss, Jena).

Epimerization of pentoses

Determination of components by chromatography

A mixture of a pentose (2 g; D-ribose, D-arabinose, D-xylose or D-lyxose), molybden acid (200 mg) in water (20 ml) was heated for 6 hours at 90°C. The solution was the deionized (Amberlite 45), filtered and made up to 50 ml with water. An aliquot of th solution was used for paper chromatographic determination of the sugar component Another part of the solution (10 ml) was treated with $NaBH_4$ (35 mg), deionized (Dowe 50) and after the removal of boric acid evaporated to dry residue which was subjecte to gas—liquid chromatography analysis after trifluoroacetylation [6] (Table 1).

Isolation of anhydrosugars

A solution of D-ribose (5 g) and molybdenic acid (0.5 g) in water (50 ml) was heate for 8 hours at 90°C. The reaction mixture was evaporated under reduced pressure t a syrup which was dissolved in methanol (50 ml), treated with charcoal, concentrate to a half volume and allowed to crystallize at room temperature. Crystalline D-arabino (1.9 g) was filtered off and the mother liquor was chromatographed on a Cellulose colum (130 × 4 cm) with butanol—ethanol—water (5 1 4 v/v) to give D-arabinose (1.1 R_A 1.00), a fraction having R_A 1.27 (0.2 g), D-ribose (1.4 g, R_A 1.52) and a second unknow fraction with R_A 3.37 (0.2 g).

The fraction having R_A 1.27 was shown on paper chromatography (10-day develop ment) to contain D-xylose and D-lyxose in the ratio 3 2.

The fraction with R_A 3.37 was first hydrolyzed with 1 N-HCl (3 hours, 90°C) and th chromatographic examination of the hydrolyzate revealed the presence of D-ribos the fraction with R_A 1.27, and D-arabinose in the ratio 10 : 1 1.

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