

13. Heusser, H., Engel, C., Herzig, P. T. and Plattner, P. A. *Helv. Chim. Acta* **23** (1950) 2229.
14. Engel, C. *J. Am. Chem. Soc.* **78** (1956) 4727.
15. Venus-Danilowa, E. D. *J. Gen. Chem. USSR* **11** (1941) 847; *Chem. Abstr.* **36** (1942) 4094.
16. Aston, J. G. and Greenburg, R. B. *J. Am. Chem. Soc.* **62** (1940) 2590.
17. Morrell, R. S. and Bellars, A. E. *J. Chem. Soc.* **85** (1904) 345.
18. Rappe, C. *Arkiv Kemi* **21** (1963) 503.

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Crystallographic Data on N,N,N',N'-Tetrakis(2-aminoethyl)ethylene-diamine Pentahydrochloride = [Penten,5HCl], Hydroxy-Penten-Cobalt(III) Iodide and Hydroxy-Penten-Cobalt(III) Perchlorate

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Gauss, Moser and Schwarzenbach¹ prepared "penten", 5HCl in connection with investigations of metal complexes with polyamines. Crystallographic data on this compound (1) and on the cobalt(III) complexes [Co(OH)penten]I₂ (2) and [Co(OH)penten](ClO₄)₂ (3) were obtained from rotation and Weissenberg photographs recorded with CuK α radiation and from precession photographs recorded with

CuK α and MoK α radiation. The densities of the crystals were measured by the flotation method.

The crystals of all three compounds are monoclinic; from systematic absences (1) and (2) must have the space group $P2_1/c$ (No. 14, C_{2h}^5), although (3) has space group $P2$ (No. 3, C_2^1) or Pm (No. 6, C_s^1) the reflections $h0l$ with $l = 2n + 1$ and $0k0$ with $k = 2n + 1$ are very weak and so (2) and (3) are nearly isomorphous.

Detailed studies of these three compounds are in progress.

The crystals were kindly supplied by professor G. Schwarzenbach, Zürich.

1. Gauss, W., Moser, P. and Schwarzenbach, G. *Helv. Chim. Acta* **35** (1952) 2359.

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A Conversion of D-Glucose to D-Mannose under Acidic Conditions

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In an attempt to prepare D-mannofuranose pentaacetate, 2,3:5,6-di-O-isopropylidene-D-mannose was treated with a mixture of acetic acid, acetic anhydride and sulphuric acid at room temperature. When the deacetylated product was investigated by paper chromatography, however, it gave two spots, which corresponded to D-glucose and D-mannose. By fractionation of the mixture these two sugars were

Table 1.

	(1)	(2)	(3)
Formula	C ₁₀ H ₃₃ N ₆ Cl ₅	CoC ₁₀ H ₂₉ N ₆ OI ₂	CoC ₁₀ H ₂₉ N ₆ O ₉ Cl ₂
Formula wt.	414.7	562.2	507.2
D_m (g·ml ⁻¹)	1.34	2.07	1.71
D_x (g·ml ⁻¹)	1.35	2.07	1.71
Space group	$P2_1/c$	$P2_1/c$	
Z (calc.)	4	4	4
a (Å)	10.19	10.52	10.57
b (Å)	23.18	15.31	15.99
c (Å)	9.96	11.31	11.76
β (°)	120.0	98.4	98.4
V (Å ³)	2037	1802	1966

isolated in pure states in the relative proportions 8:2.

Rearrangements of cyclitol acetates and acetylated carbohydrates under acidic conditions have recently been reported in the literature. Fletcher and co-workers studied the epimerisation of cyclitol¹ and 1,5-anhydro-glycitol² acetates in liquid hydrogen fluoride. Angyal and co-workers³ studied the epimerisation of cyclitol acetates in 95 % acetic acid containing 1.5 % sulphuric acid at 100°. In these reactions a system containing three adjacent *O*-acetyls is rearranged from the *cis-trans* (I) to the *trans-cis* (IV) configuration. When no deacetylation takes place, the reaction is reversible. According to the proposed mechanism,^{2,3} a seven-membered ring (II) is formed between the two *O*-acetyl groups in the *cis*-position. This ring is then opened, with inversion, by attack of the *O*-acetyl group in the *trans*-position, with formation of a five-membered ring (III). The epimerisation of acylated sugars in liquid hydrogen fluoride,^{4,5} of D-quinic acid in 95 % acetic acid containing 1.5 % sulphuric acid⁶ and of acetylated 6-deoxy-6-iodo-aldehydo-sugars in acetic anhydride and zinc chloride⁷ are related reactions. It is probable that the conversion of lactose octaacetate to a neolactose derivative on treatment with phosphorus pentachloride and aluminium chloride and other conversions studied by Hudson and Richtmyer⁸ also proceed by a similar mechanism.²

The epimerisation of the D-mannofuranose derivative mentioned above is obviously another example of the same re-

arrangement, as any cyclic sugar acetate, in one of its anomeric forms, should have the *cis-trans* or *trans-cis* arrangement at the three *O*-acetyls at C-1, C-2, and C-3. The acetolysis of a number of furanosidic and pyranosidic sugar derivatives was therefore investigated under the same conditions (Table 1). In all examples the final product was a mixture of fully acetylated sugars, which was deacetylated and studied by paper chromatography. As can be seen from Table 1, no rearrangement was observed for the pyranosides, in agreement with numerous previous observations that acetolysis and anomerisation are not accompanied under these conditions by epimerisation. The three D-mannofuranose derivatives all yielded about 80 % of D-glucose. The phenyl-β-D-glucofuranoside yielded a trace of D-mannose but apart from that no epimerisation was observed for the other furanosides studied.

Acetolysis of furanosidic isopropylidene derivatives of D-glucose and D-xylose has been used as a preparative method for the synthesis of their furanosidic acetates.^{9,10} Under these conditions little or no conversion into pyranosidic acetates was observed. A chromatographic investigation of the product from the acetolysis of 2,3:5,6-di-*O*-isopropylidene-D-mannose also revealed that no pyranosidic acetates had been formed.

It is easily understood why the furanosidic acetates should be rearranged more readily than those of the pyranosides. The formation of the seven-membered ring (II), the attack from behind by the *trans-O*-acetyl group and the formation of the five-membered ring (III) should all be facilitated in the furanose form but not in the pyranose. Only one of the anomeric acetates, the one with the *cis-trans*- or *trans-cis* arrangement at the three *O*-acetyls at C-1, C-2, and C-3, can be rearranged. The stability of the furanosidic acetates of D-glucose, D-galactose, D-xylose and L-arabinose, compared to that of D-mannose, could be due to the low concentration of this anomer in the equilibrium mixture of the former acetates. Nothing is known, however, about these equilibria. Another possible reason for the above results is that all the sugars investigated, except D-mannose, had the *trans*-arrangement at C-2 and C-3 and represent the energetically-favoured epimer. It is probable that the furanosidic acetates of their epimers, e.g. ribose, lyxose and

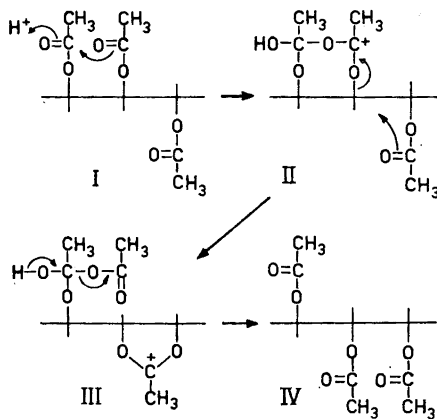


Table 1. Reaction of sugar derivatives with acetic acid, acetic anhydride and sulphuric acid.

	Product after deacetylation
2,3:5,6-Di- <i>O</i> -isopropylidene-D-mannose	80.5 % D-glucose, 19.5 % D-mannose
1,5,6-Tri- <i>O</i> -acetyl-2,3- <i>O</i> -isopropylidene-D-mannose	80.1 % D-glucose, 19.9 % D-mannose
Methyl β -D-mannofuranoside	73.0 % D-glucose, 27.0 % D-mannose
Phenyl β -D-glucufuranoside	D-glucose, traces of D-mannose
3,5,6-Tri- <i>O</i> -acetyl-1,2- <i>O</i> -isopropylidene-D-glucose	D-glucose
Phenyl β -D-galactofuranoside	D-galactose
Phenyl β -D-xylofuranoside	D-xylose
Phenyl α -L-arabinofuranoside	L-arabinose
2,3,4,6-Tri- <i>O</i> -acetyl-ethyl- β -D-mannoside	D-mannose
Methyl α -D-mannopyranoside	D-mannose
Methyl β -D-glucopyranoside	D-glucose

talose, would undergo the same rearrangement.

Experimental. The sugar derivative (1 g) was dissolved in a mixture of glacial acetic acid (30 ml) and acetic anhydride (4 ml). Concentrated sulphuric acid (1.5 ml) was added with stirring and external cooling with ice. The solution was kept for 60 h at room temperature and then poured into ice-water (100 ml). The aqueous solution was shaken with chloroform (2 \times 20 ml) and the chloroform solution was washed successively with water, saturated aqueous sodium hydrogen carbonate solution and water. It was then concentrated to a syrup. This syrup, which contained the corresponding sugar acetates, was deacetylated¹¹ by dissolving it in 10 ml water and 80 ml methanol and treating with 15 ml 45 % aqueous trimethylamine. The solution was kept overnight and then concentrated under reduced pressure. The resulting syrup was investigated by paper chromatography, using ethyl acetate-pyridine-water, 8:2:1, and Whatman No. 1 filter paper. D-Glucose, m.p. 143–5° and D-mannose, m.p. 128–31° were isolated from the reaction mixture obtained from 2,3:5,6-di-*O*-isopropylidene-D-mannose by chromatographic separation on Whatman No. 3 filter paper in the same solvent mixture. The quantitative determinations were made according to Saeman *et al.*¹² and chromatography of the acetates on dimethyl sulphoxide-impregnated paper in isopropyl ether was according to Wickberg.¹³

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- Hedgley, E. J. and Fletcher, Jr., H. G. *J. Am. Chem. Soc.* **84** (1962) 3726.
- Hedgley, E. J. and Fletcher, Jr., H. G. *J. Am. Chem. Soc.* **85** (1963) 1615.
- Angyal, S. J., Gorin, P. A. J. and Pittman, M. *Proc. Chem. Soc.* **1962** 337.
- Pedersen, C. and Fletcher, Jr., H. G. *J. Am. Chem. Soc.* **82** (1960) 945.
- Pedersen, C. *Acta Chem. Scand.* **16** (1962) 1831.
- Gorin, P. A. J. *Can. J. Chem.* **41** (1963) 2417.
- Micheel, F. and Böhm, R. *Tetrahedron Letters* **1962** 107.
- Richtmyer, N. K. *Advan. Carbohydrate Chem.* **1** (1945) 37.
- Börjeson, H., Jerkeman, P. and Lindberg, B. *Acta Chem. Scand.* **17** (1963) 1705.
- Jerkeman, P. and Lindberg, B. *Acta Chem. Scand.* **17** (1963) 1709.
- Whelan, W. J. *Private communication*.
- Saeman, J. F., Moore, W. E., Mitchell, R. L. and Millet, M. A. *Tappi* **38** (1954) 336.
- Wickberg, B. *Methods in Carbohydrate Chem.* Vol. **1** (1962) 31.

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