

Action of Strong Acids on Acetylated Glycosides

XI.* Transglycosidation of Mannosides

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The investigation of the transglycosidation reaction in the hexose series has hitherto concerned glucosides and galactosides (Parts III¹ and VI² resp.). In the present paper a similar study with mannosides is reported. As the mannosides of simple alcohols, except methanol, as well as their acetates, are difficult to obtain in a crystalline state, the investigation has been rather limited. Crystalline ethyl β -mannopyranoside tetraacetate, m.p. 132–133°, was prepared in a low yield by treatment of mannose with ethanolic hydrogen chloride and subsequent acetylation. The crystalline substance has not previously been reported in the literature, although a sirup containing different ethyl mannosides has been prepared by Levene and Sobotka³. The identity of the product was evident from the similarity of its specific rotation (-49° in chloroform) to that of methyl β -mannopyranoside tetraacetate (-50° in the same solvent).

β -Mannose pentaacetate, in a mixture of sulfuric acid, acetic anhydride and acetic acid, was transformed into the equilibrium mixture of α - and β -acetate at a rate which was practically identical with that shown by β -glucose pentaacetate. Ethyl β -mannoside tetraacetate was treated similarly. The initially rapid change in optical rotation which occurred indicated transglycosidation into the α -form, by analogy with the behaviour of other glycosides studied. This reaction proceeded 61 times faster than the isomerisation of β -glucose pentaacetate. The corresponding ratios for the ethyl β -glucoside and ethyl β -galactoside tetraacetates are 15 and 31 respectively. For the latter glycosides the rotation passed through a maximum and the final rotation was much lower than if α - and β -pentaacetates were the only products of acetolysis, indicating the formation of heptaacetate. For the mannoside, however, the

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final rotation differed very little from the value calculated under the assumption that only pentaacetates were formed.

Methyl β -mannoside tetraacetate was transformed in a good yield into the α -mannoside by the action of titanium tetrachloride in chloroform.

EXPERIMENTAL

Ethyl β -mannoside tetraacetate. Mannose (25 g) in absolute ethanol (250 ml) containing hydrogen chloride (1.0 g) was boiled on the steam bath for one hour. When cold the solution was neutralized with silver carbonate, filtered through a layer of Celite and concentrated to a sirup. The sirup was refluxed with acetic anhydride (100 ml) and sodium acetate (10 g) for one hour. The solution was then poured into ice water (1 500 ml) and extracted with chloroform (3×100 ml). The extract was washed with sodium hydrogen carbonate solution and water, dried over calcium chloride and concentrated under reduced pressure. The residue was dissolved in hot methanol (100 ml) and on cooling semi-crystalline material (4.6 g) separated. Further recrystallizations from the same solvent yielded pure ethyl β -mannoside tetraacetate (1.3 g), m.p. 132–133° (uncorr.) $[\alpha]_D^{20} -49^\circ$ (Chloroform, $C = 2$).

$C_{16}H_{24}O_{10}$ (376.4)	Calc.	C 51.1	H 6.42
	Found	» 50.8	» 6.36

Transglycosidation of methyl β -mannoside tetraacetate. Methyl β -mannoside tetraacetate (4.7 g) was dissolved in absolute chloroform (100 ml) and titanium tetrachloride (2.3 g) in chloroform (50 ml) was added. The mixture was refluxed for 5 hours on a glycerol bath, kept at 70°, and when cold poured into ice-water. The chloroform solution was washed with water several times, dried over calcium chloride and concentrated. The residue was dissolved in hot 50 % methanol and on cooling yielded the α -mannoside (3.0 g, 64 %), m.p. 62–63° alone or in admixture with an authentic specimen of methyl α -mannoside tetraacetate.

Kinetic determinations. The experimental conditions for the kinetical determinations were the same as in the preceding papers (compare Part III ¹). Sulfuric acid of concentration 0.03 C was used and the solvent was acetic anhydride-acetic acid, 10 : 3. The temperature was maintained at 20° C. The specific rotation of ethyl β -mannoside tetraacetate was initially -48° , passed through a maximum of $+46^\circ$ and finally decreased to about $+45^\circ$ (all values calculated for ethyl mannoside tetraacetate).

SUMMARY

The transglycosidation reaction has been studied for some mannosides.

Ethyl β -mannoside tetraacetate has been prepared in a pure crystalline state.

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REFERENCES

1. Lindberg, B. *Acta Chem. Scand.* **3** (1949) 1153.
2. Asp, L., and Lindberg, B. *Acta Chem. Scand.* **4** (1950) 1386.
3. Levene, P. A., and Sobotka H. *J. Biol. Chem.* **67** (1926) 759.

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