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# Action of Strong Acids on Acetylated Glycosides

## VII *. Transglycosidation of Xylosides

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The present paper deals with an investigation of the transglycosidation reaction with xylosides. The course of this reaction with glucosides and galactosides has been discussed in previous communications [1, 2] in which it was shown that acetylated alkyl $\beta$-glucosides and $\beta$-galactosides can be transformed into the respective $\alpha$-forms by the action of strong acids, such as titanium tetrachloride, boron trifluoride or sulfuric acid. The velocity of this reaction is increased by electron repelling and decreased by electron attracting groups in the aglycone. The galactosides are transformed about twice as rapidly as the corresponding glucosides.

The xylosides have now been found to react in the same way, the only difference observed being that the reactions are much faster than for the hexosides, in fact about 50 times faster than for the corresponding glucosides. The kinetic determinations, the results of which are summarized in Table 1, were carried out in acetic anhydride-acetic acid, 10 : 3, with sulfuric acid as catalyst. From the values of the final rotations, which were much lower than if only $\alpha/\beta$-xylose tetraacetate were formed by the acetolysis, it can be concluded that xylose hexaacetate is also formed. This is in agreement with the results found for glucosides and galactosides. All $k$-values are relative, the value for the transformation of $\beta$-glucose pentaacetate into the equilibrium mixture of $\alpha/\beta$-acetates being taken as unity.

In each kinetic experiment a parallel run was made with the $\beta$-acetate, using the same catalyst solution. As the velocity constants of the individual reactions studied varied by several powers of ten, different concentrations of sulfuric acid were used. The velocities of transformation and of transglyco-

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*Table 1. Relative velocity constants for the transglycosidation and acetolysis of some acetylated xylose and glucose derivatives.*

| | β-Penta-acetate | β-Ethyl glycoside | | β-*iso*-Propyl glycoside | | β-Chloroethyl glycoside | |
|---|---|---|---|---|---|---|---|
| | | $k_{\text{transglyc.}}$ | $k_{\text{acetolysis}}$ | $k_{\text{transglyc.}}$ | $k_{\text{acetolysis}}$ | $k_{\text{transglyc.}}$ | $k_{\text{acetolysis}}$ |
| Xylose | 30 | 1 120 | 68 | 2 300 | 105 | 68 | 110 |
| Glucose | 1 | 15 | 0.07 | 50 | 0.08 | 0.4 | 0.03 |
| Xylose/Glucose | 30 | 75 | 970 | 46 | 1 300 | 170 | 3 600 |

sidation of sugar acetates vary to rather different extents with changes in the concentration of the catalyst, and therefore the values obtained are not strictly comparable.

It can be seen from Table 1 that transglycosidation occurs much more rapidly with xylosides than with glucosides. In the case of acetolysis the differences are still greater, the xylosides being acetolyzed at least 1 000 times faster than the corresponding glucosides. The ratio $k_{\text{transglyc}}/k_{\text{acetolysis}}$ for a xyloside is too small for the observed maximum in optical rotation to be used as a final value for the transglycosidation reaction. This maximum has therefore to be obtained by extrapolation, which makes the determinations rather inaccurate. In view of the errors thus introduced, together with the systematical errors discussed above, the results must be regarded as being only semi-quantitative. From the rotations of the pure α- and β-derivatives, the percentage of α-isomer in the equilibrium mixture can be calculated. The values for xylose tetraacetate and ethyl xyloside triacetate are both about 90 %.

The transglycosidation of ethyl β-xyloside triacetate by the action of titanium tetrachloride in chloroform was investigated as a preparative method; under conditions similar to those employed in the previous experiments with hexosides, a 45 % yield of ethyl α-xyloside triacetate was obtained.

## EXPERIMENTAL

### Ethyl β-xyloside triacetate

Ethyl β-xyloside triacetate was prepared by the mercuric acetate method. A solution of xylose bromide triacetate (6.78 g) and mercuric acetate (3.03 g) in a mixture of absolute benzene (40 ml) and ethanol (16 ml) was boiled on the steam bath for 15 minutes. After cooling, the solution was washed several times with water, dried over calcium chloride and concentrated under reduced pressure. The crystalline residue was recrystallized from ethanol. Yield 3.1 g (51 %). M. p. 106—107° *. $[\alpha]_D^{20}$ $-62°$ (Chloroform, C = 2)

$C_7H_{11}O_5(OCCH_3)_3$ (304.3) Calc. Acetyl 42.4
Found Acetyl 42.0

### *iso*-Propyl β-xyloside triacetate

*iso*-Propyl β-xyloside triacetate was prepared by the mercuric acetate method as described above and in a yield of 62 %. It was recrystallized from ethanol. M. p. 119—120°. $[\alpha]_D^{20}$ $-61°$ (Chloroform, C = 2)

$C_8H_{13}O_5$ $(OCCH_3)_3$ (318.3) Calc. Acetyl 40.6
Found Acetyl 41.0

### β-Chloroethyl β-xyloside triacetate

β-Chloroethyl β-xyloside triacetate was also prepared by the same method as the ethyl β-xyloside and recrystallized from ethanol. Yield 49 %. M. p. 136—137°. $[\alpha]_D^{20}$ — 56° (Chloroform, C = 2). Coles, Dodds and Bergeim[3] report the melting point as 137° but give no value for the optical rotation.

### Ethyl α-xyloside triacetate

Titanium tetrachloride (1.8 g) was added to a solution of ethyl β-xyloside triacetate (3 g) in absolute chloroform (90 ml). The solution became strongly yellow, but in contradistinction to the behaviour in similar reactions, no precipitate was formed. The solution was boiled for two minutes on the steam bath, then cooled, thoroughly washed with water, dried over calcium chloride and finally concentrated under reduced pressure. When the residue was crystallized from ethanol, a small amount of unchanged starting material (0.4 g) was recovered. The mother liquors were concentrated and the residue dissolved in light petroleum. From this solution crystals of the α-xyloside, m. p. 38—39°, slowly separated. Yield 1.4 g. The melting point was unchanged by further recrystallizations from the same solvent. $[\alpha]_D^{20}$ + 100°. (Chloroform, C = 2)

$C_7H_{11}O_5$ $(OCCH_3)_3$ (304.3) Calc. Acetyl 42.4
Found Acetyl 42.4

### Kinetic determinations

The experimental conditions for the kinetic determinations were the same as in the preceding papers. (Compare Part III [1]). For the transglycosidation and acetolysis runs sulfuric acid of approximate concentration 0.004 C and 0.02 C respectively was used. A typical run is given in Table 2.

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* All melting points uncorrected.

*Table 2. Transglycosidation of ethyl β-xyloside triacetate. β-Xylose tetraacetate and ethyl β-xyloside triacetate, 0.5 g of each, dissolved in 20 ml of 0.0043 C sulfuric acid in acetic anhydride-acetic acid, 10 : 3. t = 20°. Rotations determined in 2 dm tubes. (The table gives only a part of the observed values.)*

| Time min | β-Xylose tetraacetate | | Ethyl β-xyloside triacetate | |
|---|---|---|---|---|
| | $\alpha_D$ | $k$ | $\alpha_D$ | $k$ |
| 0 | − 1.12° | | − 3.08° | |
| 4 | − 1.00 | 0.0028 | + 1.82 | 0.116 |
| 8 | − 0.91 | 24 | + 3.46 | 0.111 |
| 12 | − 0.75 | 28 | + 3.62* | |
| 16 | − 0.63 | 29 | + 3.59 | |
| 20 | − 0.48 | 31 | + 3.36 | |
| 24 | − 0.34 | 31 | + 3.16 | |
| 30 | − 0.19 | 30 | + 2.86 | |
| ∞ | + 3.80 | | + 0.50 | |
| | Mean value 0.0030 | | Mean value 0.112 | |

* The final value for the transglycosidation, calculated by extrapolation, is 4.40°.

## SUMMARY

The transglycosidation of some xylosides with sulfuric acid and titanium tetrachloride has been investigated. The reaction is much faster than that of the corresponding hexosides investigated, but otherwise perfectly analogous.

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## REFERENCES

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