

## Action of Strong Acids on Acetylated Glycosides

### XII.\* Transglycosidation of Arabinosides

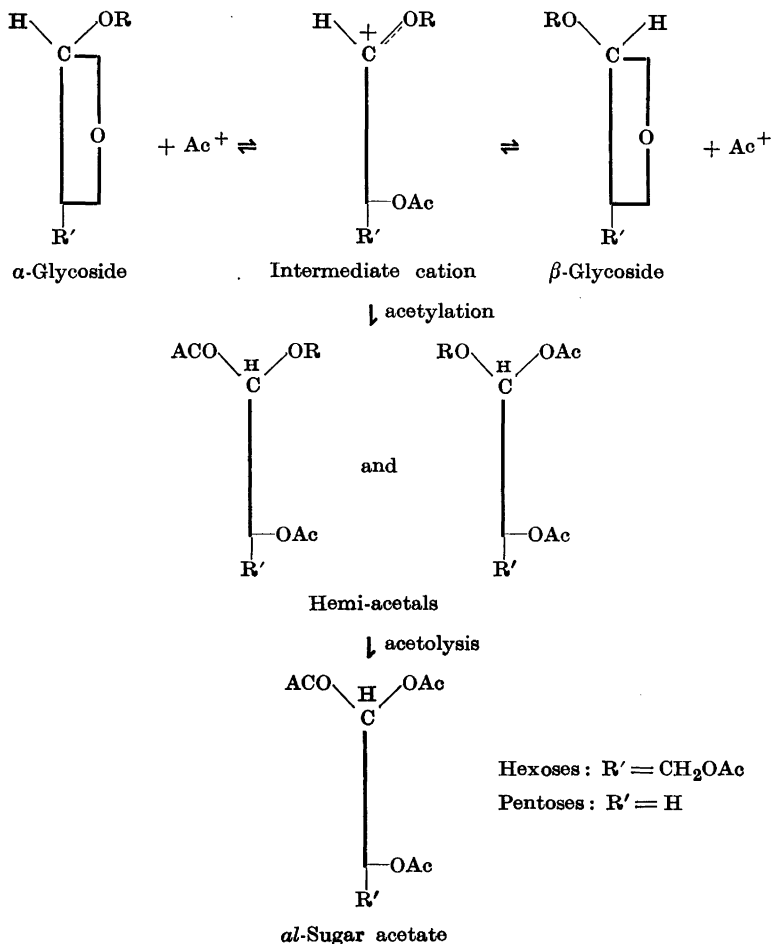
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Montgomery, Hann and Hudson<sup>1</sup> have reported some interesting studies on the action of catalyzed acetylation mixtures upon the  $\alpha$  and  $\beta$  methyl D-arabinopyranoside triacetates. From reaction mixtures containing strong catalysts (4 % sulfuric acid) they were able to isolate arabinose hexaacetate together with small amounts of  $\beta$ -arabinose tetraacetate. With weaker catalysts (0.16 % sulfuric acid or zinc chloride) the two arabinose methyl hemiacetal pentaacetates could be isolated from the reaction mixture. With sulfuric acid as catalyst it was also demonstrated that for the acetylated methyl  $\alpha$ -arabinoside, transglycosidation into the  $\beta$ -form preceded the transformation into the *al*-sugar derivatives. The transglycosidation and the formation of an open-chain sugar acetate are in agreement with the results obtained for other sugars, as reported in the preceding papers of the series. The formation of the hemiacetals is also consistent with the theory developed in Part III<sup>2</sup> for the analogous reactions with glucosides, as illustrated by the following.

(This scheme is analogous to that put forward in Part III, but is extended to include the acetylation of the intermediate cation as a separate step.) The hemiacetal derivatives should accumulate in the reaction mixture only when the rate at which they are formed is higher than that of their acetolysis. It is reasonable to assume that the rate of acetolysis is little affected by the structure of the sugar. The formation of the hemiacetals, however, passes through the same intermediate as the transglycosidation reaction, and structural relationships which favour one of the reactions should also favour the other. It seems therefore quite understandable that these hemiacetals have not been isolated in the glucose series, since transglycosidation reaction is about 50 times slower for glucosides than for arabinosides (see below).

\* Part XI, *Acta Chem. Scand.* 6 (1952) 947.



The present investigation has been confined to a study of the transglycosidation reaction with arabinosides. Methyl glycosides are transglycosidated rather slowly compared to those of other aliphatic alcohols, and the side and consecutive reactions interfere considerably. For this reason ethyl and *iso*-propyl glycosides have been preferred in these investigations. In the arabinose series these glycosides, in their acetylated form have not previously been described in the literature. Ethyl  $\alpha$ -L-arabinoside triacetate, m.p. 73–74° (uncorr.),  $[\alpha]_{\text{D}}^{20} + 7^\circ$  (chloroform,  $C = 2$ ) was prepared by the mercuric acetate method. An attempt was also made to prepare the *iso*-propyl arabinoside, but the product was non-crystalline. The transformation of  $\alpha$ -L-arabinose tetraacetate to the equilibrium mixture of  $\alpha$ - and  $\beta$ -forms and the transglycosidation of

ethyl  $\alpha$ -L-arabinoside triacetate were studied kinetically in acetic anhydride-acetic acid, with sulfuric acid as catalyst. The reactions were 26 and 780 times faster respectively than the standard reaction, namely the transformation of  $\beta$ -glucose pentaacetate into the equilibrium mixture. The corresponding values for the sugar acetates and ethyl glycosides hitherto investigated are summarized in Table 1.

Table 1. Relative velocity constants for the transformation of sugar acetates and ethyl glycopyranoside acetates into the equilibrium mixtures of  $\alpha$ - and  $\beta$ -forms;

	Acetate	Ethyl glycoside
Glucose	1	15
Galactose	2.5	31
Mannose	1	60
Xylose	30	1 120
Arabinose	26	780

The arabinose and xylose derivatives show very similar behaviour and are distinguished from the hexose derivatives by their high reactivity. The pentosides are also less stable than the hexosides in the acetylation mixture. While the former are irreversibly transformed into other products at a rate more than 100 times faster than that of the standard reaction, the corresponding rate for the latter is only about 0.1.

#### EXPERIMENTAL

*Ethyl  $\alpha$ -L-arabinoside triacetate.* A solution of arabinose bromide triacetate (6.78 g) and mercuric acetate (3.03 g) in a mixture of absolute benzene (40 ml) and ethanol (16 ml) was refluxed for 15 minutes. After cooling, the solution was washed several times with water, dried over calcium chloride and concentrated under reduced pressure. The oily residue was crystallized from methanol, giving a product (4.2 g, 69 %) which melted at 67–69°. Two further recrystallizations from the same solvent yielded the pure substance, m.p. 73–74° and  $[\alpha]_D^{20} + 7^\circ$  (chloroform,  $C = 2$ )

$C_7H_{11}O_5$  (OCCH)<sub>3</sub> (304.3) Calc. Acetyl 42.4  
Found » 42.0

*Kinetic determinations.* The experimental conditions for the kinetic determinations were the same as in the preceding papers (compare Part III<sup>2</sup>). For the transglycosidation runs sulfuric acid of approximate concentration 0.004 C was used in acetic anhydride-acetic acid, 10 : 3, at a temperature of 20°. The specific rotation of the ethyl  $\alpha$ -L-arabinoside triacetate changed from the initial value of + 8° to the maximum value of + 97° and finally decreased to – 26° (all values calculated for ethyl arabinoside triacetate).

## SUMMARY

The transglycosidation of ethyl  $\alpha$ -L-arabinoside triacetate has been investigated and the mechanism of the reaction discussed.

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## REFERENCES

1. Montgomery, E. M., Hann, R. H., and Hudson, C. S. *J. Am. Chem. Soc.* **59** (1937) 1124.
2. Lindberg, B. *Acta Chem. Scand.* **3** (1949) 1153.

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