

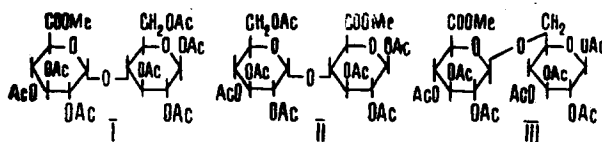
ACETOLYSIS OF ALDOBIURONIC AND PSEUDOALDOBIURONIC ACIDS

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The high resistance of aldobiuuronic acids to acid hydrolysis is well known [1], while pseudoaldobiuronic acids are hydrolyzed at the same rate as the neutral analogs corresponding to them [2, 3]. It was of interest to study the behavior of these acids in the acetolysis process. Previously [4], in an investigation of the acetolysis of neutral disaccharides we found definite differences in the rates of decomposition of the glycosidic linkages during hydrolysis and acetolysis. It could be assumed that such differences would also be observed in the behavior of the aldobiuuronic and pseudoaldobiuronic acids.

The kinetics of acetolysis was studied on the methyl esters of the heptaacetates of maltobiuronic (I), pseudomaltobiuronic (II), and gentiobiuronic (III) acids.



The acids themselves decompose during acetolysis with decarboxylation, leading to the formation of xylose derivatives. Only the methyl esters of the acids mentioned take part in a double-decomposition reaction without partial decarboxylation (Fig. 1). On comparing the results obtained for acetolysis with

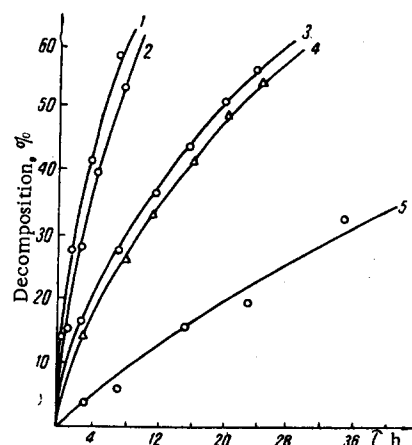


Fig. 1. Acetolysis curves of acetylated disaccharides: 1) gentiobiiose; 2) methyl gentiobiuronate; 3) maltose; 4) methyl pseudomaltobiuronate; 5) methyl maltobiuronate.

literature data on hydrolysis [1-3], it can be seen that in acetolysis the stabilizing influence of the carboxy group on the glycosidic linkage is considerably weaker. As in the case of hydrolysis, pseudomaltobiuronic acid (II) decomposes on acetolysis at the same rate as its neutral analog. Consequently, the uronic acid residue in the aglycone does not affect the strength of the glycosidic linkage. On acetolysis, substance (I) decomposes more slowly than maltose, but the differences in the reactivities of these compounds are considerably less than on hydrolysis [3]. The acetolysis of (III) takes place only slightly slower than the acetolysis of gentiobiiose, while the ratio of the rate constants of the hydrolysis of gentiobiiose and gentiobiuronic acid is 7.1 [1].

The stabilizing influence of the carboxy group is less for acetolysis than for hydrolysis, which is probably explained by a difference in the mechanisms of these processes.

EXPERIMENTAL

Paper chromatography was performed on Filtrak FN-2 paper in the ethyl acetate-pyridine-water-acetic acid (5:5:3:1) system. The compounds investigated were synthesized as described previously (maltobiuronic acid and its methyl ester [5, 6],

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pseudomaltobiuronic acid and its methyl ester [3], and methyl gentiobiuronate [7]). The melting points and analyses of these compounds agreed well with those given in the literature. The acetolysis process was studied by the method described previously [8]. The disaccharides were treated at 40°C with a mixture of acetic anhydride and acetic acid (1:1 by volume) in the presence of sulfuric acid at a concentration of 2 M.

SUMMARY

1. The acetolysis of three methyl esters of aldobiuronic acids has been studied.
2. The presence of a carboxy group in the glycone stabilizes the glycosidic linkage, and a carboxy group in the aglycone does not affect the strength of the glycosidic linkage in comparison with the neutral analog.
3. The stabilizing influence of the uronic acid residues in the glycone is more pronounced for a 1,4-glycosidic linkage than for a 1,6-linkage.

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