INFLUENCE OF THE TYPE OF BOND ON THE RATE OF ACETOLYSIS OF NEUTRAL DISACCHARIDES

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In spite of the wide preparative use of acetolysis for the fragmentation of polysaccharide chains, the influence of the type of bond and its configuration and also of the monosaccharide composition on the rate of acetolysis has not been studied systematically on simple oligosaccharide models.

We previously [1] suggested a method for measuring the rate of acetolysis and, with maltose as example, we investigated the influence of the composition of the acetolysis mixture and of the nature of the catalyst on the rate of cleavage of the glycosidic bond. In the present paper we give information on the acetolysis of 15 other oligosaccharides.

Acetolysis was performed in a mixture of acetic anhydride and acetic acid (1 : 1) in the presence of sulfuric and perchloric acids, except for the case of cellobiose which was performed in acetic anhydride because of its poor solubility. The sequence of reactivities of the disaccharides was the same for perchloric acid as for sulfuric acid.

Japanese workers [2] have considered the acetolysis of a number of glucobioses with α-glycosidic links between the monosaccharide residues. They found the following dependence of the rate of acetolysis on the nature of the bond between the monosaccharide residues: 1,6 $\gg$ 1,4 > 1,3 > 1,2 > 1,1.

We have studied the acetolysis of α-linked glucobioses in a different acetolysis mixture (Fig. 1a). However, the dependence of the activity on the type of bond remained the same: 1,4 > 1,2 > 1,1.

For glucobioses with β-glycosidic linkages the dependence of the reactivity is different (see Fig. 1b): 1,1 > 1,6 > 1,3 > 1,4 > 1,2. The greatest difference in the acetolysis of the glucobioses differing only in the configuration of the glycosidic linkage is found for the 1,1-linkage.

Disaccharides containing galactose residues are decomposed on acetolysis more rapidly than the corresponding glucobioses, the rate of acetolysis increasing particularly strongly when there is a galactose residue at the reducing end; i.e., the following rule is observed (see Fig. 1a): Glu $1\xrightarrow{\alpha}2$Gal > Gal $1\xrightarrow{\alpha}2$Glu > Glu $1\xrightarrow{\alpha}2$ Glu.

Figure 1c shows the results of the acetolysis of five oligosaccharides with a 1,6-linkage. The differences in the rates of hydrolysis of these oligosaccharides are small, but they all undergo acetolysis considerably faster than maltose in which the glycosidic bond involves the second alcoholic hydroxyl. Consequently, the lability of the 1,6 linkage is determined by the nature of the linkage and does not depend on the nature of the sugars connected by the glycosidic linkage.

The high reactivity of the 1,6 linkage possibly depends on different acetolysis mechanisms. Two points of view exist concerning the site of attack of the acetoxonium ion (CH_3CO^+): 1) attack by the cation takes place at the glycosidic oxygen atom, forming cyclic sugar acetates; and 2) attack by the cation takes place at the cyclic oxygen atom; acetates of the aldehyde forms of the sugars are produced [3]. In view of this, it was of interest to investigate the composition of the monosaccharide fraction formed in the acetolysis of a number of glucobioses. We studied the acetolysates of a number of glucobioses by gas-liquid

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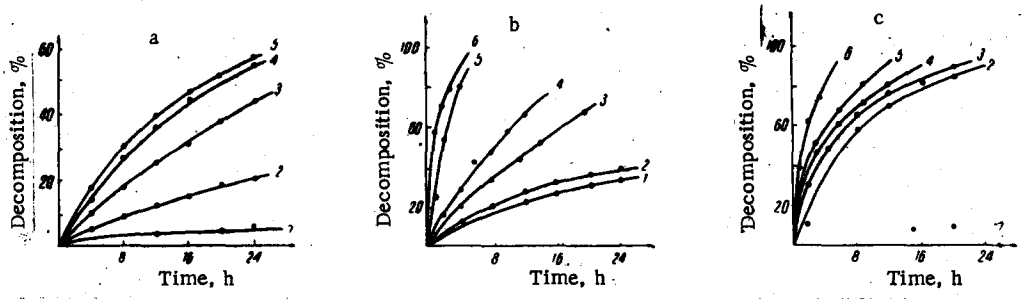

Fig. 1. Acetolysis curves of disaccharides. a-c). α-linkages in a mixture of acetic anhydride and acetic acid (1: 1) at a concentration of H_2SO_4 of 2 M. 1) trehalose (α-D-glucopyranosyl α-D-glucopyranoside); 2) kojibiose [O-α-D-glucopyranosyl-(1 → 2)-D-glucopyranose]; 3) O-α-D-galactopyranosyl-(1 → 2)-D-glucopyranose; 4) maltose (O-α-D-glucopyranosyl-(1 → 4)-D-glucopyranose]; 5) O-α-D-glucopyranosyl-(1 → 2)-D-galactopyranose. b) With β-linkages (under the same conditions). 1) Sophorose [O-β-D-glucopyranosyl-(1 → 2)-D-glucopyranose]; 2) cellobiose [O-β-D-glucopyranosyl-(1 → 4)-D-glucopyranose] (acetolysis was performed in Ac_2O); 3) laminaribiose [O-β-D-glucopyranosyl-(1 → 3)-D-glucopyranose]; 4) lactose [O-β-D-galactopyranosyl-(1 → 4)-D-glucopyranose]; 5) gentiobiose [O-β-D-glucopyranosyl-(1 → 6)-D-glucopyranose]; 6) β,β-Trehalose (O-β-D-glucopyranosyl β-D-glucopyranoside). c) With 1,6-linkages [$(CH_3CO)_2O$-CH_3COOH (1: 1); H_2SO_4 0.5 M]. 1) Maltose (given for comparison); 2) methyl gentiobiuronate; 3) primeverose [O-β-D-xylopyranosyl-(1 → 6)-D-glucopyranose]; 4) gentiobiose [O-β-D-glucopyranosyl-(1 → 6)-D-glucopyranose]; 5) epigentiobiose [O-β-D-glucopyranosyl-(1 → 6)-D-glucopyranose]; 6) melibiose [O-α-D-galactopyranosyl-(1 → 6)-D-glucopyranose].

chromatography. The ratios of the penta- and heptaacetates of glucose in the acetolysis of glucobioses are given below.

Disaccharide	Pentaacetate	Heptaacetate
α,α-Trehalose	3	1
β,β-Trehalose	5	1
Kojibiose	35	1
Sophorose	12.5	1
Maltose	35	1
Cellobiose	14.5	1
Gentiobiose	5	1

As can be seen, the differences in the ratios of the penta- and heptaacetates for the glucobioses are considerable. The greatest amounts of heptaacetate are found for gentiobiose and β,β- and α,α-trehaloses. The first two disaccharides possess a high reactivity.

Consequently, the reactivity of the disaccharides is due to the ease of opening of the ring in the glycone. The high proportion of heptaacetate in the acetolysate of α,α-trehalose can be explained by the difficult accessibility of the glycosidic oxygen, while in gentiobiose and β,β-trehalose it is more accessible.

EXPERIMENTAL

Acetolysis was performed by the method described previously [1] at 40 ± 0.1°C. The model compounds were synthesized by known methods. Their melting points and analyses agreed well with those given in the literature [4].

To determine the ratio between the penta- and heptaacetates, acetolysis was performed for three days at 40°C on 30 mg of the full acetates of the disaccharides in 0.3 ml of acetolysis mixture. The acetolysate was poured into water and extracted with chloroform, and the extract was washed with water, dried with sodium sulfate, and evaporated. The monosaccharide fraction was chromatographed in a Tswett-2 chromatograph [OKBA (Experimental Design Bureau for Automation), Dzerzhinsk] with a flame-ionization

detector. The carrier gas was nitrogen at a rate of 33 ml/min. The rate of feed of hydrogen was 33 ml/min and of air 300 ml/min. Stainless-steel column (1 m × 0.3 cm), filled with 20% of E-301 (by weight) on Chromosorb W (45-60 mesh); temperature 210°C.

SUMMARY

1. For glucobioses with a β-glycosidic linkage the following sequence of rates of acetolysis according to the type of bond has been found: 1,1 > 1,6 > 1,3 > 1,4 > 1,2.

2. It has been established that when a glucose residue in a disaccharide is replaced by a galactose residue, the resistance of the glycosidic linkage to acetolysis decreases.

3. The high reactivity of disaccharides having 1,6-glycosidic linkages has been explained.

4. The ratios of penta- and heptaacetates from some glucobioses have been determined by the GLC method.

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