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ACETOLYSIS OF DISACCHARIDE DERIVATIVES

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ABSTRACT

The acetolysis of aldobi-itols and aldobionic acids containing α- and β-(1→2), α- and β-(1→4), and β-(1→6) linkages has been studied. Cleavage of the (1→4)- and (1→6)-linked derivatives occurred more slowly than for the parent disaccharides. The reverse situation was found for (1→2)-linked aldobi-itols and methyl esters of aldobionic acids.

INTRODUCTION

Like acid hydrolysis, acetolysis can be used to fragment carbohydrate chains to give oligosaccharides[1]. Acetolysis may give oligosaccharides that are absent from, or appear in traces in, partial acid hydrolysates. The different specificity of the above methods is apparent in the fragmentation of polysaccharides containing (1→6) linkages since such linkages are extremely labile to acetolysis and relatively resistant to acid hydrolysis[2,3]. We have described[3] the acetolysis of disaccharides, and we now report on the behaviour of certain acyclic disaccharide derivatives, namely aldobi-itols and aldobionic acids.

EXPERIMENTAL

Acetolysis. — The previously described, quantitative procedure[4] was used which involved a mixture (1:1) of acetic anhydride and acetic acid in the presence of sulphuric acid (2 mol./l) at 40°. Cellobiose and its derivatives were acetolysed in acetic anhydride. Aliquots were analysed every 4 h.

Disaccharide derivatives. — The following aldobi-itol nona-acetates were obtained by the reduction of disaccharides with sodium borohydride[5] and subsequent acetylation with pyridine–acetic anhydride: sophoritol nona-acetate (58.2%), m.p. 151–152°, $[\alpha]_D^{20}$ −16° (*c* 0.79, chloroform) (lit.[9] m.p. 151–152°, $[\alpha]_D^{20}$ −21°); kojibi-itol nona-acetate (32.5%), m.p. 95.5–96°, $[\alpha]_D^{20}$ +79.8° (*c* 1.1) (Found: C, 50.12; H, 6.07. $C_{30}H_{42}O_{20}$ calc.: C, 49.86; H, 5.81%); maltitol nona-acetate (60.2%), m.p. 83–84°, $[\alpha]_D^{20}$ +84.2° (*c* 1.2) (lit.[10] $[\alpha]_D^{20}$ +86°); cellobi-itol nona-acetate (63.8%), m.p. 105.5–106°, $[\alpha]_D^{20}$ +14.2° (*c* 0.94) (lit.[11] m.p. 105–107°, $[\alpha]_D^{20}$ +18.8°); gentiobi-itol nona-acetate (55.4%), m.p. 80.5–81°, $[\alpha]_D^{20}$ −10° (*c* 0.79) (Found: C, 50.06; H, 6.12%).

The following cellobionic acid octa-acetate derivatives were obtained: nitrile[6] (51.5%), m.p. 100–102°; amide[7] (75.7%), m.p. 164.5–165.5°.

Cellobionic acid methyl ester octa-acetate was synthesised as follows. (*a*) Ethereal diazomethane was added in small portions to a solution of cellobionic acid octa-acetate[7,8] (0.4 g, m.p. 138–139°) in chloroform until the yellow colour persisted. The mixture was stirred at 20° for 12 h and then evaporated, and the residue was crystallized from ethanol to give the product (0.2 g), m.p. 178.5–179.5°, $[\alpha]_D^{20}$ +6° (*c* 0.6).

(*b*) Cellobiose (1 g) was dissolved in water (46 ml) containing barium benzoate (1.75 g) and cooled to 0°. Bromine (0.2 ml) was then added, and the mixture was kept in the dark and shaken at regular intervals at 20° for 48 h. The excess bromine was removed by aeration. 0.5M Sulphuric acid (7 ml) was added to the mixture, the precipitate was removed by centrifugation, and the supernatant was neutralised with basic lead carbonate and filtered. The solution was deionised with Dowex-50(H^+) resin and extracted with chloroform. The residual, acidic, aqueous solution was neutralised with silver carbonate, filtered, and evaporated to dryness. The residue was treated with dry methanol (100 ml), and methyl iodide (2 ml) was added dropwise. The mixture was stirred in the dark for 2 h, filtered, and evaporated, and the syrupy residue was acetylated with a mixture of acetic anhydride (5 ml) and pyridine (6.5 ml) for 48 h at 20°. The product was isolated in the conventional manner and crystallized from ethanol.

The aldobionic acid derivatives in Table I were obtained by this procedure.

TABLE I

ALDOBIONIC ACID METHYL ESTER OCTA-ACETATES

Aldobionic acid	*Yield* (%)	*M.p.* (*degrees*)	$[\alpha]_D^{22}$ (*chloroform*)	*Found*[a]	
				C	*H*
Kojibionic	25.0	90–91	+102°	49.47	5.86
Sophoronic	26.1	136–136.5	+8.7°	49.17	5.70
Cellobionic	33.2	178.5–179.5	+7.8°	49.32	5.81
Gentiobionic	24.8	151–152	−3.8°	49.64	5.92

[a] $C_{29}H_{40}O_{20}$ calc.: C, 49.15; H, 5.65%.

RESULTS AND DISCUSSION

The data for the acetolysis of disaccharides and their acyclic derivatives are shown in Figs. 1–4. The results in Figs. 1 and 2 show that the presence of an acyclic aglycon group stabilises the glycoside linkage in the acetolysis of (1→4)-linked disaccharide derivatives. Thus, maltitol is more stable than maltose (Fig. 2).

All the acyclic derivatives of cellobiose are degraded more slowly than the parent disaccharide (Fig. 1). The presence of different functional groups in the acyclic aglycon group does not seriously affect the reaction rate.

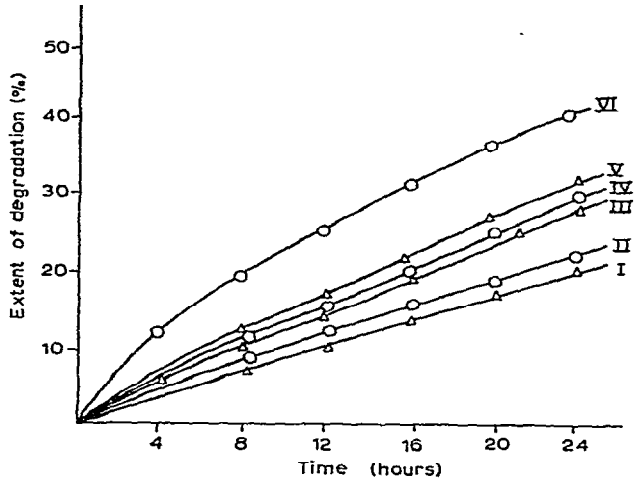

Fig. 1. Acetolysis of cellobiose and its derivatives: I cellobionic acid methyl ester, II cellobionic acid, III cellobi-itol, IV cellobionic acid nitrile, V cellobionic acid amide, VI cellobiose.

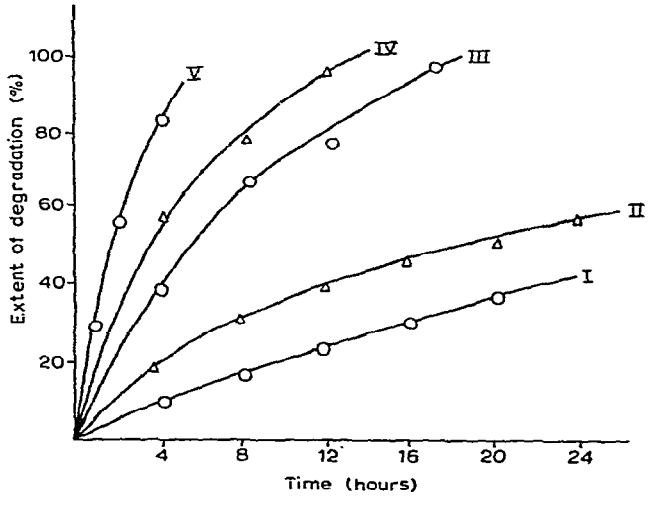

Fig. 2. Acetolysis of maltose and gentiobiose and their derivatives: I maltitol, II maltose, III gentiobi-itol, IV gentiobionic acid methyl ester, V gentiobiose.

Fig. 2 also shows the acetolysis results for the acyclic derivatives of a (1→6)-linked disaccharide. Gentiobi-itol and gentiobionic acid methyl ester are degraded more slowly than gentiobiose, although their reactivity is higher than that of disaccharides with linkages involving a secondary hydroxyl group. Hence, for (1→6)- and (1→4)-linked disaccharides, the transition to acyclic derivatives increases the stability of the glycoside bond towards acetolysis. The reverse dependency was observed for (1→2)-linked compounds which were characterized by more-rapid degradation of aldobionic acid methyl esters and aldobi-itols than of the parent

disaccharides (Figs. 3 and 4). In these series, the esters are degraded more quickly than the corresponding alcohols.

Studies in progress are intended to define the origin of the stability differences noted above.

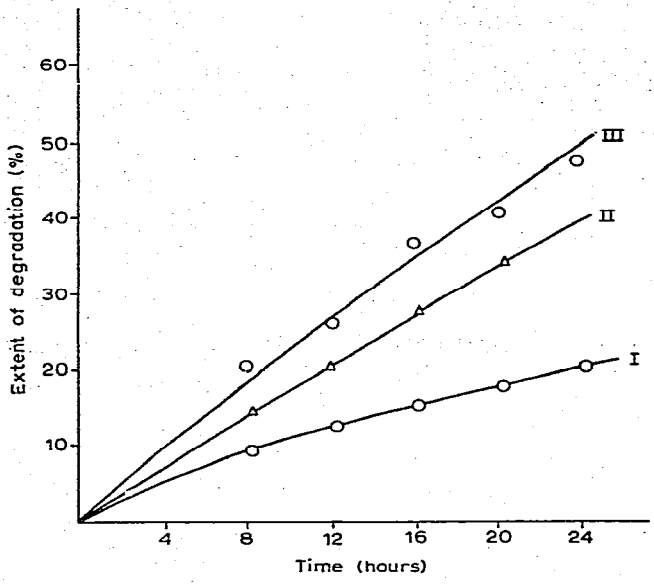

Fig. 3. Acetolysis of kojibiose and its derivatives: I kojibiose, II kojibi-itol, III kojibionic acid methyl ester.

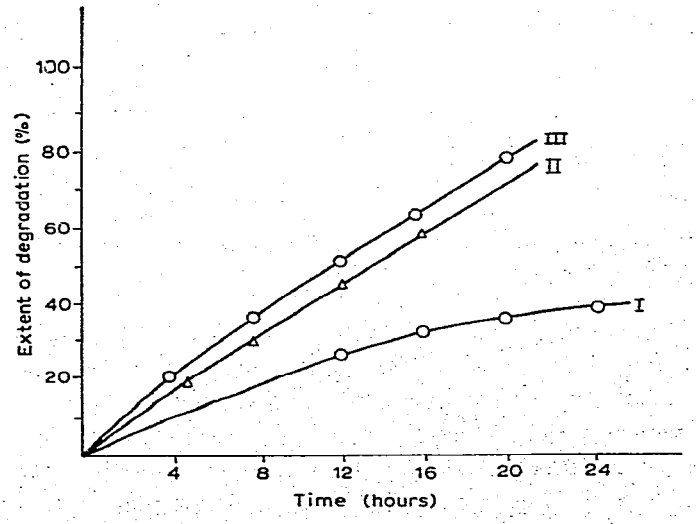

Fig. 4. Acetolysis of sophorose and its derivatives: I sophorose, II sophoritol, III sophoronic acid methyl ester.

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