Carbohydrate Research, 34 (1974) 227–232

TREATMENT OF ETHYL 4-*O*-METHYL-β-D-GLYCOPYRANOSIDES WITH OXYGEN–ALKALI

HÅKAN KOLMODIN

Department of Engineering Chemistry, Chalmers University of Technology, S-402 20 Göteborg (Sweden)

(Received September 6th, 1973; accepted for publication, January 29th, 1974)

ABSTRACT

Treatment of ethyl 4-*O*-methyl-β-D-glucopyranoside and ethyl 4-*O*-methyl-β-D-xylopyranoside with oxygen–alkali reveals that oxidation of the primary hydroxyl group in the glucoside is of minor importance. The results indicate that the main reaction route, after the oxidation of a secondary hydroxyl group to a keto group, is the elimination of the substituent on C-4.

INTRODUCTION

During the bleaching of paper pulp with oxygen, severe degradation of the cellulose molecules takes place as reflected by a decrease in the degree of polymerization[1]. The end-wise oxidative degradation of polysaccharides during treatment with oxygen–alkali, leading to the formation of aldonic acid end-groups, has been demonstrated to take place *via* D-glucosone (D-*arabino*-hexosulose) end-groups[2]. It is probable that the depolymerization of polysaccharides during treatment with oxygen–alkali occurs after the introduction of carbonyl groups along the polysaccharide chains. Cellulose contains three possible sites per D-glucose residue for the introduction of carbonyl groups, whereas only two possibilities exist in xylan. The introduction of a carbonyl group at any position will give rise to an alkali-labile product which will result in elimination of the adjacent sugar unit.

In their study of acidic end-groups in hydrocellulose after treatment with oxygen–alkali, Samuelson and Stolpe[3] did not find any uronic acids and concluded that no oxidation took place at C-6 of the D-glucose residues. However, Minor and Sanyer[4] found that primary alcohols were much more readily oxidized by oxygen in an alkaline medium than were secondary alcohols. These results were taken as a proof that the D-glucose residues in the cellulose chains are rapidly attacked at position 6, and that a β-elimination at C-4 takes place before carboxyl groups are formed.

Studies of the degradation of xylans[5] with oxygen–alkali showed that a decrease in the length of the polysaccharide chains occurred. Since there are no primary hydroxyl groups in xylan chains, the oxidative attack was assumed to involve positions 2 or 3 of the xylose residues.

The acids of low molecular weight isolated after degradation of xylan[5] and hydrocellulose[2] with oxygen–alkali have been studied in this laboratory. Although the acids originating from xylan have one carbon atom less than those derived from hydrocellulose, the products are essentially the same in type. This indicates that similar reaction routes, starting with oxidation of secondary hydroxyl groups, are responsible for the formation of these acids.

The purpose of the present investigation was to use simple model compounds to elucidate further whether primary or secondary hydroxyl groups in polysaccharides are the main points for oxidation during treatment with oxygen–alkali. Furthermore, by using ethyl 4-*O*-methyl-*β*-D-aldosides, an attempt was made to determine whether positions 1 and/or 4 of an oxidised sugar unit in a polysaccharide are involved in chain scission.

EXPERIMENTAL

The purity of the synthesized substances was determined by g.l.c. of their trimethylsilyl (TMS) derivatives. Their identities were confirmed by mass spectrometry[6,7].

Ethyl 4-O-methyl-β-D-xylopyranoside. — Ethyl 4-*O*-methyl-*β*-D-xylopyranoside, prepared by essentially the method of Hough and Jones[8], had m.p. 98°, $[\alpha]_D^{25}$ −78° (*c* 1, water) (Found: C, 50.0; H, 8.2; O, 41.5. $C_8H_{16}O_5$ calc.: C, 50.0; H, 8.4; O, 41.6%).

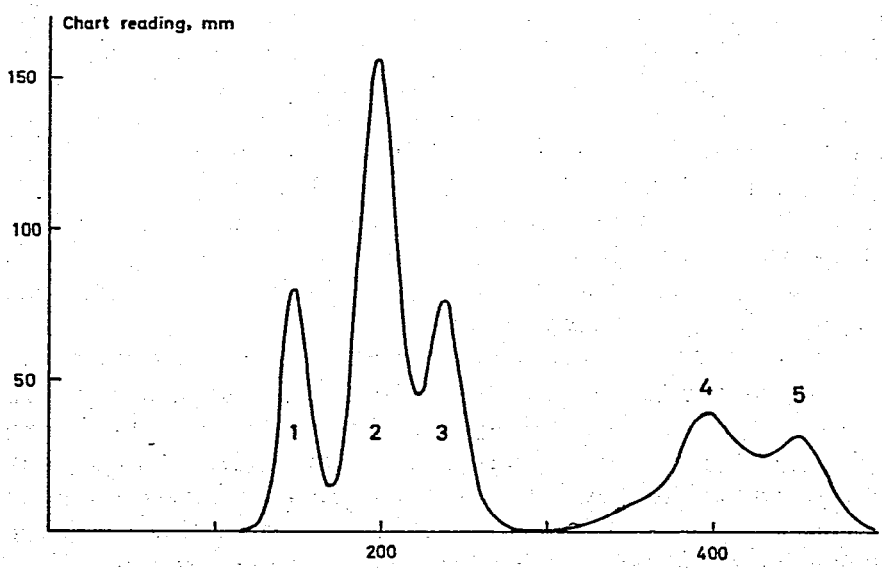

Fig. 1. Chromatograph of reaction products (1 g) obtained after methylation and deacetylation of ethyl 2,3,4-tri-*O*-acetyl-*β*-D-glucopyranoside. Ethyl 3,4-di-*O*-methyl-*β*-D-glucopyranoside (1), ethyl 4-*O*-methyl-*β*-D-glycopyranoside (2), ethyl 3-*O*-methyl-*β*-D-glucopyrano side (3), ethyl 2-*O*-methyl-*β*-D-glucopyranoside (4), ethyl *β*-D-glycopyranoside (5). Column (20 × 800 mm) of Dowex-1 × 8 (HO^-) resin (100-200 mesh) eluted with distilled water at 0.65 ml.min^{-1}. Analysis with Varian RI-detector.

Ethyl 2,3-anhydro-β-D-ribopyranoside, an intermediate in the synthesis, was methylated by the Kuhn procedure[9].

Ethyl 4-O-methyl-β-D-glucopyranoside. — Essentially the route recently described by Rowell[10] was followed. The product obtained by methylation and deacetylation of ethyl 2,3,4-tri-*O*-acetyl-β-D-glucopyranoside was ethyl 4-*O*-methyl-β-D-glucopyranoside (1 g), m.p. 129° (from ethyl acetate), $[\alpha]_D^{25}$ −24° (*c* 1, water); lit.[10] m.p. 133°, $[\alpha]_D^{20}$ −29.2°.

When the syrupy material obtained from the mother liquors of the above product was eluted from Dowex-1 x8 (HO^-) resin (100–200 mesh) with water[11] (Fig. 1), ethyl 4-*O*-methyl-β-D-glucopyranoside (1 g), ethyl 3,4-di-*O*-methyl-β-D-glucopyranoside (0.3 g), ethyl 3-*O*-methyl-β-D-glucopyranoside (0.3 g), and ethyl 2-*O*-methyl-β-D-glucopyranoside (0.2 g) were obtained. These products were identified by mass spectrometry of their TMS derivatives. These results demonstrate that, besides the O-4→O-6 and the O-3→O-4 acyl migrations reported by Rowell[10], other migrations also take place. Some loss of acetyl groups also occurs, which gives rise to the 3,4-di-*O*-methyl derivative.

Degradation of glycosides. — Degradation was carried out in a reactor (Fig. 2) made of Teflon (a) immersed in a glass cylinder (b) through which polyethylene glycol at 110° was circulated. The sample, consisting of 0.5 mmole of the glycoside dissolved

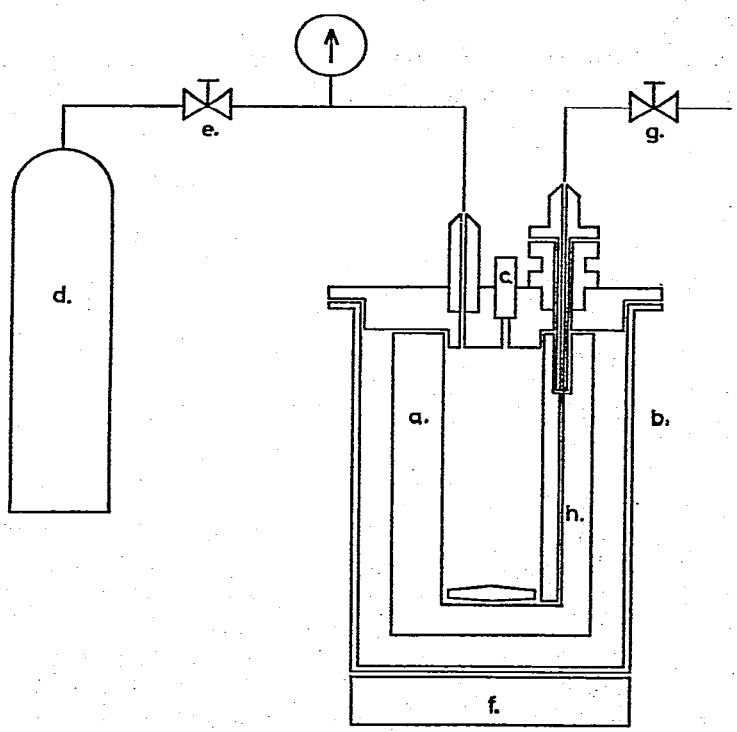

Fig. 2. Reactor used in the degradation experiments of ethyl 4-*O*-methyl-β-D-glycosides.

in 25 ml of 1.25M sodium hydroxide, was introduced through a hole at the top of the reactor, which then was closed with a Teflon plug (c). Oxygen was delivered from a gas cylinder (d) *via* a valve (e) into the reactor, and kept in contact with the solution with the aid of a magnetic stirrer (f). By opening the valve (g), the oxygen pressure inside the reactor (6 bar) forced the reaction solution from the bottom of the reactor through the channel (h) in the reactor wall, thus making it possible to withdraw samples from the reactor.

Samples withdrawn from the reaction solution were analyzed[12] for their methanol and ethanol contents by gas chromatography on Porapak QS at 140°.

Sodium ions were removed by passing the samples through a column of cation exchanger in the H^+ form. After neutralization with sodium hydroxide, samples were applied to a column (6 × 500 mm) of Dowex-1 x8 (HO^-) resin (23–40 μm) and eluted with distilled water. Automatic recording of the effluent by a Varian RI detector permitted the remaining glycoside to be determined.

RESULTS AND DISCUSSION

In earlier studies of oxygen bleaching[1,5], it had been assumed that treatment of polysaccharides with oxygen–alkali led to the introduction of carbonyl groups along the polysaccharide chains. The presence of a keto group at position 3 in a sugar unit gives rise to a β-alkoxy elimination at C-1, whereas a carbonyl group at position 2 or 6 gives elimination at C-4 (Fig. 3).

By studying the rate at which methanol and ethanol are produced during treatment of ethyl 4-*O*-methyl-β-D-xylopyranoside and ethyl 4-*O*-methyl-β-D-gluco-

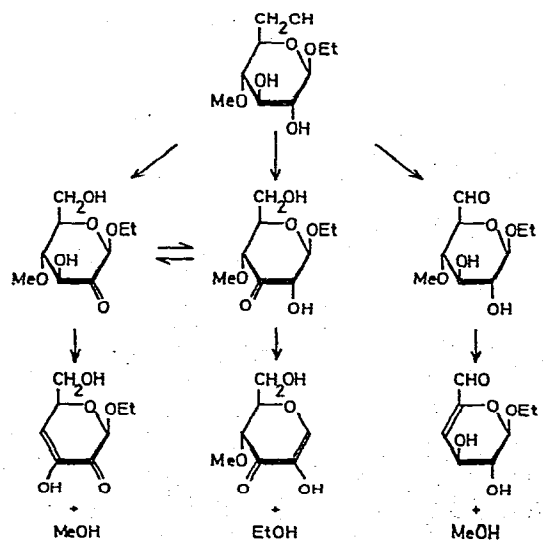

Fig. 3. Possible oxidation routes for ethyl 4-*O*-methyl-β-D-glucopyranoside, and consecutive reactions for the oxidation products.

pyranoside with oxygen–alkali, as well as their degradation rates, it should be possible to identify the position of the carbonyl groups in the oxidized glycosides.

The rate of formation of methanol is 15% greater than that of ethanol for each type of glycoside. The total amount of ethanol and methanol obtained from ethyl 4-*O*-methyl-β-D-glucopyranoside under a particular set of conditions was greater than that from the xylose derivatives (Fig. 4). The fact that the relative amounts of ethanol and methanol are the same in both experiments suggests that oxidation at C-6 in the glucopyranoside is of little importance since such oxidation would lead to an increased rate of formation of methanol compared to that of ethanol (Fig. 3). The somewhat higher reactivity of the glucoside must be attributed to factors other than oxidation of the primary hydroxyl group.

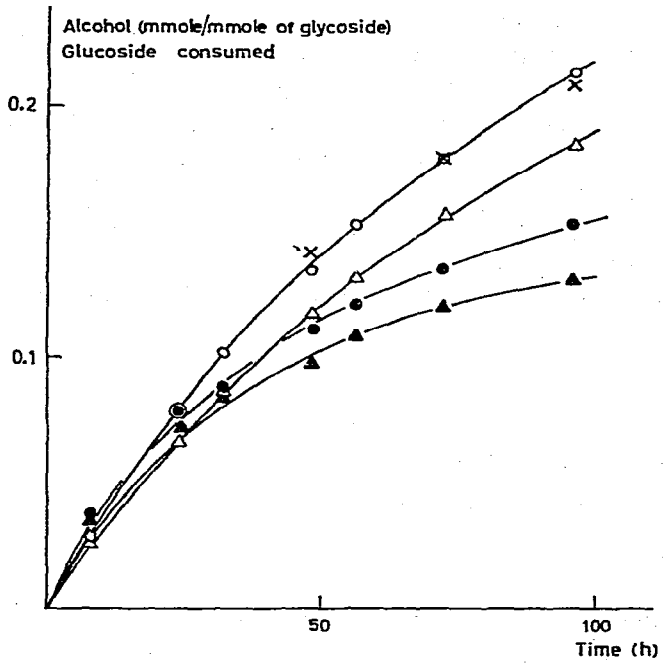

Fig. 4. Formation of ethanol (△) and methanol (○) from ethyl 4-*O*-methyl-β-D-glucopyranoside, and ethanol (▲) and methanol (●) from ethyl 4-*O*-methyl-β-D-xylopyranoside on treatment with oxygen–alkali; ×, consumption of ethyl 4-*O*-methyl-β-D-glucopyranoside.

Blank experiments, in which oxygen was replaced by nitrogen, showed that only minor amounts of methanol and ethanol are formed after 100 hours.

After 96 hours, the amounts of ethyl 4-*O*-methyl-β-D-gluco- and -xylo-pyranoside which had reacted were 21 and 18%, respectively. This observation suggests that oxidation of the primary hydroxyl of the glucopyranoside is of little or no importance.

Within experimental error, the amount of methanol formed from ethyl 4-*O*-methyl-β-D-glucopyranoside and the xylose analogue after reaction for 96 hours is equal to the consumption of the corresponding glycoside (Fig. 4). The fact that one mole of methanol is produced for each mole of glycoside consumed suggests that the primary reaction step of the oxidized glycoside leads to elimination of MeO-4. The formation of ethanol probably occurs during subsequent reactions of the oxidized and modified glycosides.

Methyl β-D-*arabino*-hexopyranosid-2-ulose rearranges[13] into methyl β-D-*ribo*-hexopyranosid-3-ulose in alkaline medium, which then reacts further by elimination of the substituent at C-1. Treatment of the 3-keto derivative of methyl 4-*O*-methyl-β-D-glucopyranoside with alkali indicates that elimination at C-4 is of great importance[14]. These results indicate that the formation of ethanol cannot be ascribed entirely to initial oxidation at C-3, and that it should not be assumed that a carbonyl group formed at position 2 exclusively gives elimination at C-4.

It is concluded that treatment of ethyl 4-*O*-methyl-β-D-glucopyranoside with oxygen–alkali leads to oxidation of the secondary hydroxyl groups. Elimination at C-4 seems to be favoured but it is not possible from the present data to determine whether the C-2 or C-3 position is the site of the oxidation step, since the 2-keto and 3-keto derivatives are rapidly interconverted[14].

The results reported herein support the conclusions drawn in studies of cellulose[1] and xylan[5] that the depolymerization of these polysaccharides during treatment with oxygen–alkali starts with oxidation of secondary hydroxyl groups and is followed by β-alkoxy elimination at C-4.

ACKNOWLEDGMENT

The financial support of 1959 Års Fond for Teknisk och Skoglig Forskning samt Utbildning is gratefully acknowledged.

REFERENCES

1 H. KOLMODIN AND O. SAMUELSON, *Sv. Papperstidn.*, 73 (1970) 93.
2 H. KOLMODIN AND O. SAMUELSON, *Sv. Papperstidn.*, 75 (1972) 369.
3 O. SAMUELSON AND L. STOLPE, *Tappi*, 52 (1969) 1709.
4 J. L. MINOR AND N. SANYER, *J. Polym. Sci., Part C*, 36 (1971) 73.
5 H. KOLMODIN AND O. SAMUELSON, *Sv. Papperstidn.*, 76 (1973) 71.
6 G. PETERSSON AND O. SAMUELSON, *Sv. Papperstidn.*, 71 (1968) 77.
7 G. PETERSSON AND O. SAMUELSON, *Sv. Papperstidn.*, 71 (1968) 731.
8 L. HOUGH AND J. K. N. JONES, *J. Chem. Soc.*, (1952) 4349.
9 R. KUHN, H. TRISCHMANN, AND I. LÖW, *Angew. Chem.*, 67 (1955) 32.
10 R. M. ROWELL, *Carbohyd. Res.*, 23 (1972) 417.
11 P. W. AUSTIN, F. E. HARDY, J. G. BUCHANAN, AND J. BADDILEY, *J. Chem. Soc.*, (1963) 5350.
12 R. N. BAKER, A. L. ALENTY, AND J. F. ZACK, *J. Chromatogr. Sci.*, 7 (1969) 312.
13 O. THEANDER, *Acta Chem. Scand.*, 12 (1958) 1887.
14 O. THEANDER, *Tappi*, 48 (1965) 105.