The Oxidation of Glycosides

XII *. Oxidation of Methyl 4,6-*O*-benzylidene-β-D-galactopyranoside with Chromium Trioxide

EILEEN BRIMACOMBE **, JOHN S. BRIMACOMBE **, BENGT LINDBERG and OLOF THEANDER

Träkemiska avdelningen, Svenska Träforskningsinstitutet, Stockholm Ö, Sweden

In previous investigations the formation of oxo-glycosides by chromium trioxide oxidation of the anomeric methyl glucopyranosides and some of their derivatives [1,2], and of methyl β-xylopyranoside [3] has been studied. The yield of a single oxo-glycoside has never exceeded *ca.* 5 %. The oxidation studies have now been extended to methyl β-D-galactopyranoside protected at $C_{(4)}$ and $C_{(6)}$ by a benzylidene group.

Two products predominated in the neutral oxidation mixture after removal of the benzylidene group. They showed characteristics of oxoglycosides: high mobility on hydrogen sulphite electrophoresis, strong reducing reaction with silver nitrate-sodium ethoxide reagent and characteristic colour reactions with anisidine hydrogen chloride and resorcinol-hydrochloric acid reagents. The two oxidation products and unreacted methyl galactoside, the main component in the reaction mixture, were eluted from a carbon-Celite column with similar ethanol concentration and the R_F-values of the three components were similar. This made preparative separation difficult.

The structure of the oxo-galactosides was proved by identifying the sugars obtained on reduction with Raney-nickel and hydrolysis. One of the oxo-galactosides (obtained in *ca.* 0.9 % yield) gave, on such treatment, talose and galactose thus proving it to be methyl β-2-oxo-galactoside (I). The other (*ca.* 0.7 %) gave gulose and galactose, thus proving it to be methyl β-3-oxo-galactoside (II). Both I and II were obtained in an amorphous state and could not be crystallised. The 3-oxo-compound had the lower R_F-value of the two and was also eluted somewhat more readily from the carbon column. Both gave elongated spots on paper chromatograms contrasting with the sharp round spots obtained with the corresponding oxo-glucosides. The oxo-galactosides were quite labile and a small amount of glucose was obtained in the products of II, after reduction and hydrolysis, possibly indicating that epimerisation took place.

In the fractions first eluted from the column were small amounts of a component chromatographically indistinguishable from lyxose. The presence of this sugar is analogous to the formation of arabinose in the oxidation of methyl glucoside [2] and indicates cleavage between $C_{(1)}$ and $C_{(2)}$.

Experimental. Melting points are corrected. Distillations were carried out under reduced pressure (bath temperature < 35°). Whatman 1 filter papers were used for paper chromatography and electrophoresis except for preparative separations, which were made on Whatman 3 MM filter papers previously washed with water.

Irrigants and buffer used:

A. Ethyl acetate — acetic acid — water, 3:1:3
B. Butanol — ethanol — water, 10:3:5
C. Butanol — pyridine — water, 6:2:5
D. Hydrogen sulphite buffer [4] (50°) pH 4.7, 0.1 M

Oxidation and fractionation of the products. Methyl 4,6-*O*-benzylidene-β-D-galactopyranoside (50 g) in acetone (3 l) was oxidised with chromium trioxide (26.5 g) and the reaction mixture worked up and fractionated essentially as previously described for the oxidation of methyl 4,6-*O*-ethylidene-β-D-glucopyranoside [2].

The neutral mixture obtained, after removal of the protecting benzylidene group, contained unreacted methyl galactoside as the main component. The majority of this was removed by crystallisation from ethanol. Of the expected reaction products 2-oxo-galactoside (I) and 3-oxo-galactoside (II) predominated. Of the minor components one was indistinguishable from lyxose. Two separations on carbon-Celite columns using gradient elution resulted in only partial fractionation of the unreacted methyl galactoside, I and II. The 3-oxo-compound was eluted at a somewhat lower concentration of ethanol than was the 2-oxo-compound. Subfractionation on thick filter paper (solvent A) was attempted but was rendered

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** Present address: Chemistry Department, The University of Birmingham, Birmingham 15, England.

difficulty by the fact that the compounds gave elongated spots and had similar migrations ($R_{Galactose}$-values: methyl β galactoside: 1.74, I ~ 2.0 and II ~ 1.6). After two fractionations on thick filter paper I and II were obtained *ca.* 80 % pure (most of the impurity being the unreacted methyl galactoside). The bulk of the two fractions was reduced, but further fractionation of aliquots of I and II on thick filter paper gave amorphous but chromatographically pure products. From these fractionations the total yield of I and II could be estimated as *ca.* 0.9 % and 0.7 %, respectively.

Characterisation of the oxo-galactosides. The oxo-galactosides gave strong reducing reactions with silver nitrate-sodium ethoxide reagent, characteristic orange-brown colourations with anisidine hydrogen chloride and orange-grey colourations with resorcinol-hydrochloric acid reagent.

The oxo-galactosides dissolved in 70 % aqueous ethanol were reduced by refluxing for 5 h with excess of Raney-nickel [5]. The product was hydrolysed with 0.5 N sulphuric acid for 17 h and the sugars obtained fractionated by chromatography on thick filter papers (solvent C). Talose and galactose only were obtained from I, and gulose and galactose from II, together with small amounts of glucose.

Part of the isolated gulose was reduced with sodium borohydride at pH 9.5. The product obtained, after deionisation, was chromatographically indistinguishable from D-gulitol. The acetylated (acetic anhydride/pyridine) product, after recrystallisation from aqueous ethanol, had the same R_F-value as authentic D-gulitol hexacetate on chromatographing on dimethylsulphoxide impregnated paper using *iso*propyl ether-light petroleum (1:1) as irrigant [6], and m.p. and mixed m.p. 98–99°.

Talose was characterised by paper chromatographic data (*e.g.*, $R_{Galactose}$-values in solvent C: talose: 1.52, gulose: 1.29 and glucose 1.15), and as its methylphenylhydrazone, m.p. 147–149° after recrystallisation from aqueous methanol (literature value [7], 154°).

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Alkaline Decomposition of Some Quaternary Phosphonium Compounds Containing Oxygen

GUNNAR AKSNES

Chemical Institute, University of Bergen, Bergen, Norway

The alkaline decomposition of aliphatic and aromatic quaternary phosphonium compounds with hydroxides and alkoxides results in the formation of hydrocarbons, ethers and phosphine oxides [1-3]. The alkaline decomposition of some oxygen-containing phosphonium compounds is reported in this paper.

The phosphorus analogs of choline(I) and choline acetate (II) were found to decompose in the following ways: