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Note

Oxidation of dextran T40 with bromine in the presence of borate

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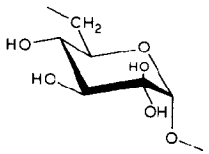
Glycosiduloses are useful intermediates for the synthesis of amino sugars and other carbohydrate derivatives[1–3]. When glycosides and polysaccharides are treated with aqueous bromine, secondary alcohol functions are oxidised to keto groups[4–7], but the yield of glycosylulose residues is limited because of further oxidative cleavage to dicarboxylic acid residues.

Carbohydrates containing suitably oriented hydroxyl groups form complexes with boric acid[8]. In aqueous solution, glycosiduloses are in equilibrium with their hydrated forms. The hydrated forms of the glycosylulose residues of oxidised dextran[7] (*e.g.*, **1**) contain *cis*-oriented vicinal hydroxyl groups, which is the feature most favourable for the formation of borate complexes[8]. The possibility of protecting the glycosylulose residues in bromine-oxidised dextran from further oxidation to dicarboxylic acid residues was therefore investigated by performing the reaction in the presence of borate.



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Dextran T40 was oxidised with various amounts of bromine in the presence of sodium metaborate. At pH >7, the glycosylulose residues were degraded to some extent[9], and, at pH <7, the reaction rate was low. The reactions were therefore performed at pH 7. When the reaction was complete (after 24 h), inorganic material was removed from the oxidised polysaccharide by dialysis, and part of each product was treated with methoxylamine hydrochloride to convert the glycosylulose residues into the corresponding *O*-methyloximes. The total yield of ketosylulose residues into the corresponding *O*-methyloximes. The total yield of keto groups was determined by elemental analysis of these derivatives, and the amount of carboxylic acid groups by titration (Table I).

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TABLE I

YIELDS OF GLYCOSYLULOSE AND DICARBOXYLIC ACID RESIDUES IN OXIDISED DEXTRAN

Mol of Br_2 per D-glucosyl residue	*Glycosylulose residues (%)*	*Dicarboxylic acid residues(%)*
0.81	54	2.9
0.97	61	2.7
1.13	73	3.5
1.30	76	4.0
1.46	78	4.9
1.94	84	7.0

When the oxidation was performed in the presence of borate, using 1 mol of bromine per glucosyl residue, the yield of glycosylulose residues was ~65% and that of dicarboxylic acid residues was less than 3%. The corresponding yields without borate were 43 and 11%, respectively. In the presence of borate, an increase in the relative amount of bromine raised the yield of glycosylulose residues and, to some extent, that of dicarboxylic acids also (Table I). The dicarboxylic acid to glycosylulose residue ratio increased somewhat with increasing, relative amounts of bromine, although not as drastically as when the reaction was performed without borate. The relative amounts of the various glycosylulose residues in the bromine–borate oxidised dextran were the same as those obtained by bromine oxidation without borate[7] (*i.e.*, equal amounts of 2- and 4-glycosylulose residues and traces of 3-glycosylulose residues), as determined by sugar analysis[10] and ^{13}C-n.m.r. spectroscopy. No units containing more than one keto group could be detected. The bromine oxidation of polysaccharides and of glycosides of low molecular weight in the presence of borate is being further investigated.

EXPERIMENTAL

General methods. — Solutions were concentrated at reduced pressure below 40°. Optical rotations were measured with a Perkin–Elmer 141 polarimeter. G.l.c. was performed with a Packard 427 instrument, fitted with a flame-ionisation detector. Separations were performed on a glass column (240 × 0.15 cm) containing 3% of OV-225 on Gas Chrom Q (100–120 mesh). ^{13}C-N.m.r. spectra were recorded with a Jeol FX 90 Q Fourier-transform spectrometer.

Bromine oxidations. — Solutions of dextran (T40; elaborated by *Leuconostoc mesenteroides* NRRL B-512; 1.0 g, 6.2 mmol of D-glucosyl residue) with sodium metaborate (10 g, 72 mmol) in water (40 mL) were prepared, aqueous bromine (0.2M; 25–60 mL, 5–12 mmol) was added, and the pH was adjusted to 7.0, using 4M hydrochloric acid. The mixtures were kept at room temperature, and the pH was kept constant by addition of M sodium hydroxide, using a Methrom E 300B pH-meter. After 24 h, the reaction mixtures were dialysed against distilled water (4 L),

0.5% acetic acid (3 × 4 L), and distilled water (2 × 4 L), and then freeze-dried, to yield ~70% of oxidised dextran from each reaction mixture. Part (300 mg) of each oxidised dextran was dissolved in water (30 mL), methoxylamine hydrochloride (450 mg) was added, and the pH was adjusted to 4.0. The solution was stirred at 50° for 3 h, adjusted to pH 7.0, dialysed against distilled water, and freeze-dried to yield the methoximated dextran. The results are given in Table I. Another part (250 mg) of the oxidised dextran was reduced with sodium borohydride (250 mg), acidified (acetic acid), dialysed against distilled water, and freeze-dried. Sugar analysis[10] revealed the presence of allose, galactose, glucose, and mannose. A sample of the reduced dextran was treated with Dowex 50W (H^+) resin and titrated with 5mM sodium hydroxide. The results are given in Table I.

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