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COMMUNICATIONS FROM RESEARCH GROUPS: STRUCTURE AND CONFORMATION OF POLYALCOHOLS AND POLYACIDS OBTAINED FROM PERIODATE OXYAMYLOSE AND OXYCELLULOSE

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Glycol-splitting reactions are widely used in the structural analysis of polysaccharides for determining the number of vicinal diol groups (through their conversion to dialdehydes) and the position of glycosidic linkages through analysis of fragments obtained by acid cleavage of reduced polydialdehydes (Perlin, 1981). However, little is known on the conformational and macromolecular properties of glycol-split polysaccharides themselves, in spite of the potential practical uses of these polymers. Dialdehyde starch (Sloan *et al.*, 1956) is being used as an additive for paper (Tegge, 1960). The corresponding product of further oxidation, dicarboxyl starch, DCS, is being considered as a substitute for polyphosphates as builder in detergents (Wilham *et al.*, 1970). DCS, and similar polycarboxylic derivatives of polysaccharides, were also reported to have antiviral properties (Claes *et al.*, 1970), probably associated with the binding of calcium and magnesium ions (G. Beaven, personal communication). Preliminary electrochemical, optical and NMR studies on dicarboxyl amylose (DCA) have shown that this stereoregular polyelectrolyte binds calcium, magnesium and other divalent cations (Casu *et al.*, 1979).

Glycol-split polysaccharides are an especially attractive class of polymers for the following reasons:

1. The glycol-splitting reaction can usually be controlled, in order to oxidise either a few, or all, the anhydropyranose residues of a polysaccharide chain, thus permitting the preparation of modified polysaccharides which vary systematic-

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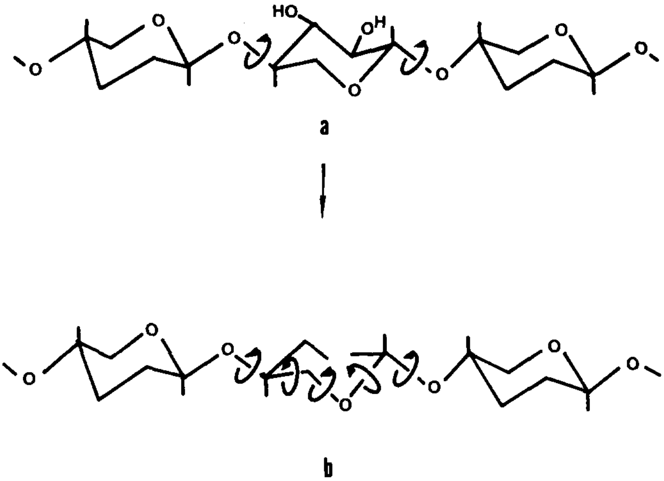

Fig. 1. 1,4-linked β-D-glucopyranose chain, (a) before and (b) after splitting of the C(2)—C(3) bond of one residue, showing an increase in number of rotatable bonds upon splitting.

ally in their physico-chemical and rheological properties. It is especially worthwhile noting that, as suggested for alginic acid (Smidsrød & Painter, 1973), the splitting reaction instigates extra degrees of rotational freedom along a polysaccharide chain. In fact, as illustrated in Fig. 1 for a β-1,4-linked polyglucose, three more rotatable bonds per monomeric residue become available upon splitting of the C(2)—C(3) bond. Each split residue can accordingly be regarded as a flexible joint, with associated increased segmental motion and decreased viscosity of the polymer.

2. The dialdehyde groups produced by the glycol splitting reaction can be easily derivatised to obtain a variety of new polymers. In particular, reduction of dialdehydes leads to polyalcohols that can be further etherified or esterified, and further oxidation of dialdehydes leads to polydicarboxylic acids.
3. Glycol-split polysaccharides are expected to be stereoregular, i.e. to retain the configuration of the original polysaccharide at carbons not belonging to the split bond. This permits a most interesting comparison of the conformational, physico-chemical and technological properties of modified polysaccharides differing from each other only by the configuration at one carbon atom.

As part of a collaborative investigation on the influence of splitting reactions on the physico-chemical and rheological properties of polysaccharides, polyalcohols ('reduced dialdehydes', RDAs) and polyacids ('dicarboxyl derivatives' DCs) were prepared by exhaustive periodate oxidation of the anhydroglucose residues of amylose and cellulose, followed by borohydride reduction or chlorite oxidation of the resulting 'dialdehydes, DAs, as shown in Fig. 2. The polyalcohols were also converted to the

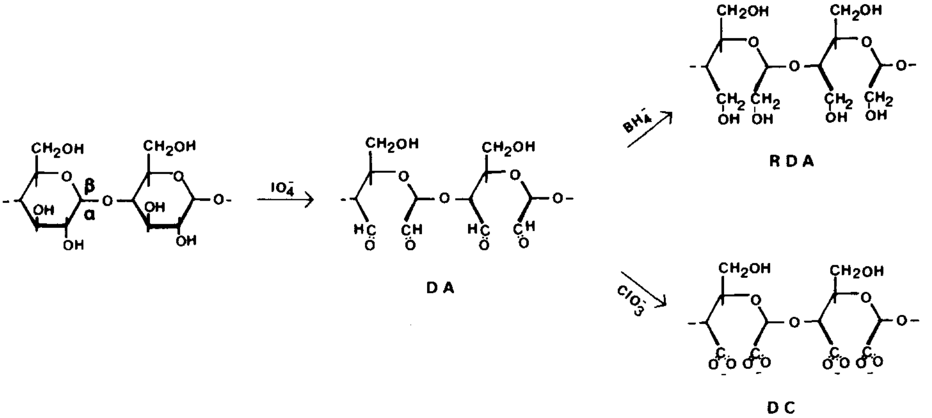

Fig. 2. Periodate oxidation of cellulose (β) and amylose (α), to give dialdehydes (DA). Reduction of dialdehydes gives reduced dialdehydes (RDA); oxidation gives dicarboxyl derivatives (DC).

corresponding triacetates; conversely, they were also prepared by deacetylation of their triacetates.

The products were characterised by chemical, electrochemical and spectroscopic methods. Also monomeric, dimeric and oligomeric model compounds were prepared and characterised. The present communication describes preliminary NMR studies.

A typical ^{13}C NMR spectrum of dicarboxyl cellulose, DCC, shown in Fig. 3, indicates a relatively high degree of homogeneity of the preparation. ^{13}C chemical shifts and C_1-H_1 coupling constants are reported in Tables 1 and 2 for the reduced dialdehyde of amylose (A-RDA), its triacetate, the triacetate of the reduced dialdehyde of β-cyclodextrin (RD-CD), and the dicarboxyl derivatives of cellulose and amylose (DCC and DCA). Data for cellulose, amylose and their triacetates are also included for comparison purposes.

The C_1-H_1 coupling constants of DCC and DCA are intermediate between those of the triacetates of amylose and cellulose, with values for the RD derivatives close to that of cellulose acetate. These values, as well as those of the interproton coupling constants, are being worked out for evaluating values (in combination with conformational analysis) for the average torsional angles across the 'glycosidic' bridges.

^{13}C NMR spectra were also obtained for solid samples, by the MAS/CP technique. In the MAS/CP ^{13}C NMR spectrum of A-RDA, the chemical shift of the C-4 signal is significantly different from that of the C-5 signal, suggesting a solid-state conformation substantially different from that in solution. In the solid-state spectrum of DCC, the composite nature of the C-1 signal suggests coexistence of different conformational rotamers.

The ^1H NMR spectra of DCA and DCC are strongly pH dependent. Signal shifts on repressing ionisation of the carboxyl groups are paralleled by evident changes in the coupling pattern, suggesting a rearrangement of the polyelectrolyte chain at least at

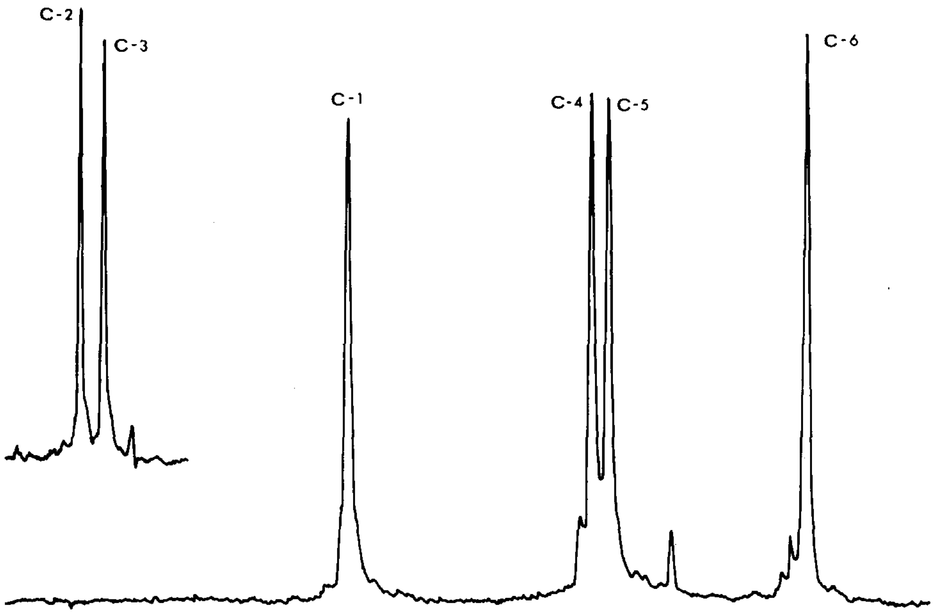

Fig. 3. ^{13}C NMR spectrum of dicarboxyl cellulose (DCC, Na salt). (20 MHz, D_2O solution.)

TABLE 1
^{13}C Chemical Shifts (ppm)

	A-RDA (D_2O)	*A-RDA triacetate ($CDCl_3$)*	*RD-CD triacetate ($CDCl_3$)*	*Amylose triacetate ($CDCl_3$)*	*Cellulose triacetate ($CDCl_3$)*	*DCC (D_2O)*	*DCA (D_2O)*	*Cellulose (DMSO)*	*Amylose (D_2O)*
C-1	104·1	100·4	99·2	95·8	100·7	101·9	101·2	103·2	100·9
C-2	64·1	63·4	63·3	70·6	72·3	177·0	177·1	73·7	72·7
C-3	61·8	62·4	62·4	71·9	72·8	174·9	175·4	75·3	74·5
C-4	79·3	75·0	74·6	73·7	76·2	80·8	80·9	80·5	78·4
C-5	79·3	75·0	74·6	69·2	73·1	79·4	78·8	75·5	72·4
C-6	61·8	62·4	62·4	62·8	62·2	62·1	62·1	61·0	61·8

TABLE 2
C_1–H_1 Coupling Constants (Hz)

Amylose triacetate	176
DCC	169·7
DCA	166·4
RDβCD triacetate	164·5
RDA triacetate	164
Cellulose triacetate	163

the level of the C_4H/C_5H dihedral angle. The ^1H signals of DCC are also temperature dependent, indicating a conformational transition at about 60°C.

The ^1H NMR titration curve of DCC (Na salt) with Ca^{2+} ions shows an inflexion corresponding to about 1 Ca^{2+} per dicarboxylic monomeric residue. Similar results were obtained in a microcalorimetric and circular dichroism study (Crescenzi *et al.*, 1982).

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