Linear Polyaldehydes and Polyalkenes Derived from Starch

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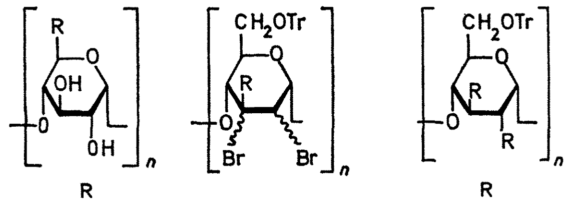
Summary Amylose (I) has been converted by photolysis of its 6-azido-6-deoxy-derivative (III) into a 6-aldehydo-analogue (IV) of amylose, and the 2,3-di-*O*-*p*-tolylsulphonly-6-*O*-trityl derivative (VII) of (I) has been converted into a 2,3-unsaturated polymer (VIII); the products (IV) and (VIII) may be useful for enzymic studies and as precursors for novel polyfunctional and crosslinked polymers.

AMYLOSE (I), the linear (1 → 4)-α-D-glucan component of starches, was converted[1,2] into the 6-*O*-*p*-tolylsulphonyl derivative (II) (77%) of degree of substitution (d.s.) 0·89. The latter underwent complete exchange of the *p*-tolylsulphonyl group by iodide ion (sodium iodide in hexane-2,5-dione), indicating exclusive 6-substitution. Treatment of (II) with sodium azide in dimethyl sulphoxide for 68 hr. at 80° gave, after dialysis, the 6-azido-6-deoxy-analogue (III) (73%) of d.s. 0·66; λ_{max} (KBr) 4·73 μm. (N_3). Photolysis of (III) 0·20 g. under nitrogen for 5 hr. at 20° in 3 : 1 2-methoxyethanol–benzene with unfiltered light from a mercury arc,[3] followed by evaporation and addition of methanol gave 0·19 g. of product having no azide absorption in the i.r. spectrum but showing carbonyl absorption at 6·0 μm. This product was formulated as the polyaldehyde (IV) of d.s. *ca.* 0·5 (probably containing hemiacetal forms); it was almost nitrogen-free, Schiff-positive, and it readily reacted with carbonyl-seeking reagents. With *p*-nitrophenylhydrazine hydrochloride in 1 : 1 pyridine–water a suspension of (IV) in dimethyl sulphoxide reacted to give a red product which, after removal of non-polymeric material, gave elemental analyses indicating it to be the *p*-nitrophenylhydrazone (V) of the aldehyde (IV), having a d.s. of 0·4.



R
(I) CH_2OH
(II) CH_2OTs
(III) CH_2N_3
(IV) CHO
(V) $HC{:}NNH{\cdot}C_6H_4{\cdot}p\text{-}NO_2$
(X) CO_2H

(IX)

R
(VI) OH
(VII) OTs
(VIII) Δ^2

Conversion of amylose into the 6-trityl ether[1,4] (VI) of d.s. 1·0 followed by *p*-toluenesulphonylation in pyridine for 3 hr. at 60° gave the 2,3-di-*O*-*p*-tolylsulphonyl-6-*O*-trityl derivative[5] (VII) in almost quantitative yield; the 2,3-di-*O*-(methylsulphonyl) analogue of (VII) was prepared similarly. Both products had a d.s. of 1·8—2·0 for the sulphonic ester group. The n.m.r. spectrum of (VII) in [$^2H_5$]pyridine showed signals for *ca.* 23 aryl protons, measured relative to signals of protons on the sugar residues and the aryl methyl groups.

Treatment of (VII) with an excess of sodium iodide and zinc dust[6] in boiling *NN*-dimethylformamide for 6 hr. gave a sulphur-free product formulated as the alkene (VIII) (80%). The n.m.r. spectrum of (VIII) in [$^2H_5$]pyridine showed a ratio of *ca.* 15 : 7 for aryl protons to protons on the sugar residues, and aryl *C*-methyl signals were absent. Further evidence for the structure 6-*O*-trityl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoglycan (VIII) was obtained by treating (VIII) with bromine in methanol in the presence of silver acetate, according to the procedure of Albano, Horton, and Lauterbach[7] for *trans*-addition of bromine to the 2,3-double bond in methyl 4,6-*O*-benzylidene-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside. The product obtained was formulated as the 2,3-dibromide (IX) of d.s.

ca. 2·0 probably having the D-*altro*-configuration, (43%). The n.m.r. spectrum of (IX) in [$^2H_5$]pyridine showed a 15-proton multiplet at τ 2·1—3·1 (trityl group) and a seven-proton multiplet from τ 5·0—6·8 (protons on the sugar chain). Aqueous acetic acid gave triphenylmethanol (bromine-free) from (IX).

The foregoing reactions provide routes for obtaining polymeric aldehydes and polymeric alkenes from natural polymers, both linear, such as amylose and cellulose, and also branched glycans such as amylopectin (and whole starch). The route to the aldehyde structure (IX) also provides simple and convenient access by mild oxidation to the glycuronan (X). These reactions, conducted to high or low d.s. levels, open up the possibility of increased use of starches and cellulosic materials as industrial polymers; the photochemical reaction (III)→(IV) further presents a potential method, by admixture of (III) with a suitable bifunctional, aldehyde-seeking group, for obtaining a linear polymer that can be crosslinked by exposure to light. The products are also of potential value for studies on the substrate specificity of glycan hydrolases.

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