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Amination of Amylose oxidized with Dimethyl Sulphoxide–Acetic Anhydride

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IN our programme for the increased utilization of starch, particularly amylose, a variety of aminated amylose derivatives has been prepared.[1,2] Degradation by acid hydrolyses showed that the amination procedures used effected complex modification of the original polysaccharide. Therefore, an aminated amylose containing a single amino-sugar component as the modified unit cannot be obtained by these methods.

A solution of dimethyl sulphoxide and acetic anhydride oxidizes hydroxyl groups to carbonyl functions in steroids,[3] alcohols,[4] and monosaccharide derivatives.[5,6] Reduction of the resulting hexosulose produces predominantly the hexose with inversion at the site of oxidation,[5] while oximation followed by reduction furnishes the hexosamine with a corresponding predominant inversion.[7]

6-*O*-Tritylamylose[8] was oxidized with a solution of dimethyl sulphoxide and acetic anhydride at 25° for 20 hr. Precipitation in methanol gave a cream-coloured, oxidized product (I) in high yield (90%). Controlled reduction[9] of (I) with sodium borohydride, in bis-(2-methoxyethyl) ether, followed by detritylation, acid hydrolysis, and paper chromatography (solvent B)† revealed the presence of much D-glucose, some D-mannose, and a small amount of a third component (R_G 0·77); analogous results have been reported by Bredereck[10] on tritylated cellulose. Oximation of (I) afforded a powder [(II), 90% yield; N, 2·7%; degree of substitution of 0·8; $[\alpha]_{21}^{D}$ + 50°, *c* 0·3 in dioxan]. Since repeated treatment of the exhaustively dried compound (I) with dimethyl sulphoxide and acetic anhydride, followed by oximation, failed to raise the nitrogen content, the maximum limit of oxidation therefore corresponds to a degree of substitution of 0·8 for this tritylated (1→4)-linked polysaccharide. Reduction of (II) with excess lithium aluminium hydride in tetrahydrofuran solution at reflux produced a white material [(III), 90% yield; N, 2·1%; sulphur-free; $[\alpha]_{21}^{D}$ + 45°, *c* 1·0 in dioxan] on precipitation from dilute hydrochloric acid. Detritylation of (III) in methanolic hydrogen chloride and subsequent precipitation in ether gave a pale yellow product which was dissolved in water, dialysed, and freeze-dried (60% yield). The aminated amylose (IV), whose elemental analyses corresponded to the formula $C_6H_7O_2(OH)_{2\cdot4}(NH_3Cl)_{0\cdot6}$ (Found: C, 39·17; H, 5·79; N, 4·51%; $[\alpha]_{21}^{D}$ + 156°, *c* 0·5 in water), gave a positive ninhydrin test, and formed a water-insoluble Schiff base with anisaldehyde.[11]

Acid hydrolysis of (IV) followed by paper chromatography (solvent C) revealed the presence of two major components with R_{Glu} 1·00 and 0·74 (ninhydrin positive). The acid hydrolysate was then percolated through a column of anion exchange resin. Paper chromatography (Solvent B) of the desorbed amino-sugar components

† Paper chromatography was effected by descending techniques with the upper layer of a 4 : 1 : 5 butan-1-ol–ethanol–water system (Solvent A), 5 : 5 : 3 : 1 pyridine–ethyl acetate–water–acetic acid (Solvent B), and 9 : 2 : 2 ethyl acetate–acetic acid–water (Solvent C). Zones were located by alkali–silver nitrate or with 0·2% alcoholic ninhydrin. R_{Gl} and R_{GlN} are mobilities relative to D-glucose and 2-amino-2-deoxy-D-glucose hydrochloride, respectively.

showed several ninhydrin-positive zones: R_{GlN} 1·00 (major component), 0·35, 0·66, and 1·21 (all traces). The component with R_{GlN} 1·00 was then isolated by preparative paper chromatography (Solvent A) and crystallized from acidified acetone.[12] This crystalline compound (72% yield) showed optical rotation, infrared spectrum, and *X*-ray powder diffraction pattern identical with an authentic 2-amino-2-deoxy-D-glucose hydrochloride. The product was homogeneous when rechromatographed on paper in three systems (Solvents A, B, and C).

The isolation of 2-amino-2-deoxy-D-glucose as the principal amino-sugar from the hydrolysate of (IV) demonstrated that the oxidation of a C-6-tritylated, (1→4)-linked polysaccharide occurred predominantly at C-2. Retention of configuration in the reduction of oxime (II) was achieved by the use of excess of lithium aluminium hydride and immediate reflux, while controlled reduction had been shown to favour inversion.[5] The present method produces an aminated amylose containing almost entirely 2-amino-2-deoxy-D-glucose as the modified unit and is also superior to our previous procedures[1,2] for the amination of secondary hydroxyl groups which require prolonged exposure of the polysaccharide to high temperature necessary in replacing the less active secondary toluene-*p*-sulphonyl ester groups with nitrogeneous bases.

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[1] M. L. Wolfrom, M. I. Taha, and D. Horton, *J. Org. Chem.*, 1963, **28**, 3553; M. L. Wolfrom, P. Chakravarty, and D. Horton, *ibid.*, 1965, **30**, 2728.
[2] M. L. Wolfrom, H. Kato, M. I. Taha, A. Sato, G. U. Yuen, T. Kinoshita, and E. J. Soltes, *J. Org. Chem.*, 1967, **32**, in the press.
[3] J. D. Albright and L. Goldman, *J. Amer. Chem. Soc.*, 1967, **89**, 2416.
[4] J. D. Albright and L. Goldman, *J. Amer. Chem. Soc.*, 1965, **87**, 4214.
[5] W. Sowa and G. H. S. Thomas, *Canad. J. Chem.*, 1966, **44**, 836; B. Lindberg and K. N. Slessor, *Carbohydrate Res.*, 1966, **1**, 492.
[6] D. Horton and J. S. Jewell, *Carbohydrate Res.*, 1966, **2**, 251.
[7] K. Onodera, S. Hirano, and N. Kashimura, *J. Amer. Chem. Soc.*, 1965, **87**, 4651.
[8] R. L. Whistler and S. Hirase, *J. Org. Chem.*, 1961, **26**, 4600; B. J. Bines and W. J. Whelan, *Chem. and Ind.*, 1960, 997.
[9] D. T. Williams and J. K. N. Jones, *Canad. J. Chem.*, 1967, **45**, 7.
[10] K. Bredereck, *Tetrahedron Letters*, 1967, **8**, 695.
[11] M. Bergmann and L. Zervas, *Ber.*, 1931, **64**, 975.
[12] M. L. Wolfrom, D. I. Weisblat, J. V. Karabinos, W. H. McNeely, and J. McLean, *J. Amer. Chem. Soc.*, 1943, **65**, 2077.