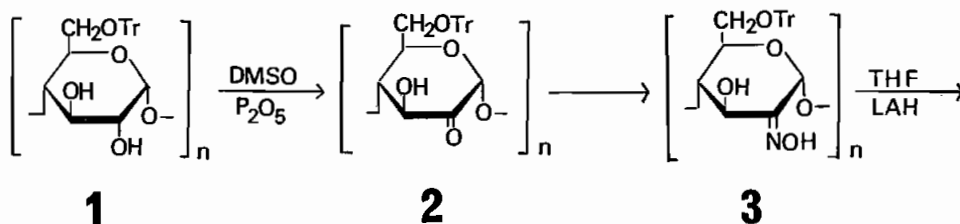


Partial Oxidation of Vicinal Hydroxyl Groups of 6-*O*-Tritylamylose with Dimethyl Sulfoxide and Phosphorus Pentoxide*

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Hydroxyl groups of mono- and polysaccharides can be effectively oxidized with dimethyl sulfoxide (DMSO)-acid anhydride system (1-3) and the resulting keto sugars are important in the synthesis of amino, branched-chain and rare sugars (4,5). The author previously reported partial oxidation of vicinal hydroxyl groups of methyl 4,6-*O*-benzylidene- α - and β -D-glucopyranosides with DMSO and phosphorus pentoxide (P_2O_5) (6). It would be worth to compare selectivity of the oxidation of hydroxyl groups in mono- and polysaccharides. This communication describes partial oxidation of vicinal hydroxyl groups of 6-*O*-tritylamylose with DMSO and P_2O_5 and preparation of aminated amylose.

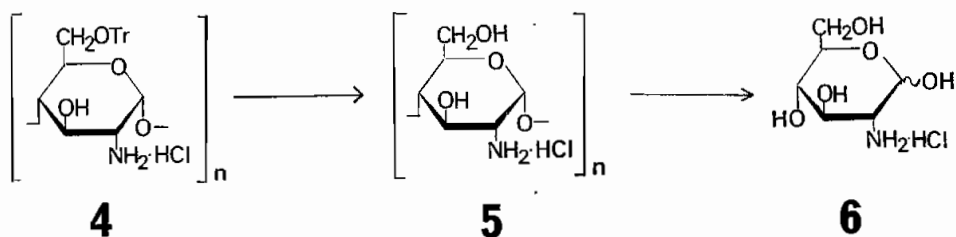


6-*O*-Tritylamylose (1, D.S. 0.95, trityl) was oxidized with DMSO and P_2O_5 for 20 hr at 40°C. The oxidized 6-*O*-tritylamylose (2, D.S. 0.63, C=O) was refluxed in a solution of pyridine and ethanol containing hydroxylamine hydrochloride to yield 6-*O*-tritylamylose oxime (3, D.S. 0.63, N=OH). Reduction of the oxime with lithium aluminum hydride in tetrahydrofuran at room temperature gave aminated 6-*O*-tritylamylose (4, D.S. 0.63, NH_2). Sequential detritylation in methanolic hydrochloric acid followed by dialysis and lyophilization yielded aminated amylose (5, D.S. 0.63, NH_2) as a white flocculent material. The aminated amylose was hydrolyzed with 1 N hydrochloric acid, and paper chromatographic examination of the hydrolyzate showed two components which were identified as D-glucose and 2-amino-2-deoxy-D-glucose hydrochloride (6). This result is in good agreement with that obtained with DMSO and acetic anhydride oxidation (3).

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The presence of 2-amino-2-deoxy-D-glucose as the amino sugar component in the hydrolyzate suggests that oxidation of 6-O-tritylamylose with DMSO and P_2O_5 occurs selectively at C-2 hydroxyl group. This result is of interest in view of the fact methyl 4,6-O-benzylidene- α -D-glucopyranoside is selectively oxidized at C-3 hydroxyl group (6). It further suggests that the stereoselectivity of the hydride reduction of the oxime at C-2 is due to the attack by the hydride ion from axial, where the approach of the hydride ion must be less hindered.



Experimental

Paper chromatography was carried out by the descending method on Toyo Roshi No. 51 filter paper in the following solvent systems; (a) pyridine / ethyl acetate / water / acetic acid (5:5:3:1, v/v), (b) *n*-butanol / pyridine / water (6:4:3, v/v) and (c) the upper layer of *n*-butanol / benzene / pyridine / water (5:1:3:3, v/v).

Oxidation of 6-O-Tritylamylose (1)

6-O-Tritylamylose (7) (1, 19.0 g) was stirred for 20 hr at 40°C in a mixture of DMSO (128 ml) and *N,N*-dimethyl-formamide (382 ml) containing P_2O_5 (24.8 g). The resulting dark-brown solution was poured into ice (500 g) -methanol (1500 ml). The precipitate formed was collected by centrifugation and washed with methanol and then with ether to yield a yellow powder 2 (18.5 g); IR: ν_{max}^{KBr} 690, 750, 1450, 1490 (aryl), 1760 (C=O), 3500cm^{-1} (OH), $[\alpha]_D^{15} + 221^\circ$ (*c*, 0.3, dioxane).

Anal. Calcd. for $[C_6H_8.24O_{4.37}(C_{19}H_{15})_{0.5}(C=O_{0.63})_n]$: C, 66.88; H, 5.49, Found: C, 66.85; H, 5.76.

Oximation of the Oxidized 6-O-Tritylamylose (2)

To a solution of the above ketoamylose 2 (18.0 g) in dry pyridine (120 ml) and abs. ethanol (120 ml) was added hydroxylamine hydrochloride (18.0 g). The solution was refluxed for 2 hr and then poured into water. The precipitate was collected and washed with ether to give a pink powder 3 (14.8 g) which was soluble in methanol but insoluble in ether and did not show any absorption of the carbonyl group in IR spectroscopy; $[\alpha]_D^{15} + 52.7^\circ$ (*c*, 0.52, dioxane).

Anal. Calcd. for $[C_6H_8.29O_{4.37}(C_{19}H_{15})_{0.45}(N=OH)_{0.63}]_n$: C, 62.57; H, 5.67; N, 3.15. Found: C, 62.17; H, 5.73; N, 2.91.

Reduction of the 6-O-Tritylamylose Oxime (3)

To a solution of the oxime **3** (14.5 g) in dry tetrahydrofuran (1800 ml) was added a suspension of lithium aluminum hydride (4.5 g) in tetrahydrofuran (180 ml). The mixture was stirred for 20 hr at room temperature and then heated at reflux temperature for 6 hr. The excess lithium aluminum hydride was destroyed by careful addition of water (500 ml) and the solution was neutralized with dil. hydrochloric acid (2000 ml). The resulting precipitate was washed with water until neutral and then with ether to yield a nearly colorless solid **4** (10.0 g), which was soluble in methanol but insoluble in dioxane and showed a positive ninhydrin test; IR: ν_{max}^{KBr} 1600 cm^{-1} (NH_2), $[\alpha]_D^{15} +285.4^\circ$ (c , 0.2, DMSO).

Anal. Calcd. for $[\text{C}_6\text{H}_9\cdot 0.7\text{O}_4\cdot 37(\text{C}_{19}\text{H}_{15})_{0.30}(\text{NH}_2\text{HCl})_{0.63}]_n$: C, 54.63; H, 6.07; N, 3.43. Found: C, 54.40; H, 5.81; N, 3.27.

Detritylation of the Aminated 6-O-Tritylamylose (4)

The above reduced product **4** (9.5 g) in methanol and conc. hydrochloric acid (2 ml) was stirred for 20 hr at room temperature. After dilution with ether (1000 ml) the precipitate formed was centrifuged and washed with ether to give a white powder (2.6 g). Repeated treatment for another 6 hr yielded a white solid (2.5 g). It showed the absence of the trityl group in IR spectroscopy and gave a positive ninhydrin test.

The detritylated amylose (1.0 g) was dissolved in saturated sodium bicarbonate solution (200 ml) to neutralize the residual acid and dialyzed against distilled water. After filtration, the clear filtrate was treated with activated carbon and then lyophilized to yield a white flocculent hygroscopic powder **5** (0.5 g); $[\alpha]_D^{15} +166.7^\circ$ (c , 0.11, water).

Anal. Calcd. for $[\text{C}_6\text{H}_9\cdot 37\text{O}_4\cdot 37(\text{NH}_2\text{HCl})_{0.63}]_n$: C, 39.06; H, 6.12; N, 4.78; Found: C, 38.81; H, 5.74; N, 4.65.

Acid Hydrolysis of the Aminated Amylose (5)

A solution of the aminated amylose **5** (1.2 g) in 1 N hydrochloric acid (70 ml) was heated on a boiling water bath. After hydrolysis for 5 hr the solution was treated with activated charcoal and filtered. The filtrate was neutralized with Amberite IRA-410 (carbonate form). The paper chromatography of the hydrolyzate showed the presence of two major components: R_{gl}^* 1.00 and 0.88 (ninhydrin positive) in solvent a; R_{glN}^* 1.75 and 1.00 (ninhydrin positive) in solvent b; R_{glN} 1.21 and 1.00 (ninhydrin positive) in solvent c. On the basis of the R_f data, the faster moving component was identified as D-glucose and the slower moving component as 2-amino-2-deoxy-D-glucose hydrochloride.

* R_{gl} and R_{glN} represent rate of movement on chromatogram relative to D-glucose and 2-amino-2-deoxy-D-glucose hydrochloride, respectively.

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