Carbohydrate Research, 52 (1976) 232–234

Note

Chemical transformation of cycloheptaamylose and amylose into compounds containing D-allose and D-glucose residues*

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(Received April 16th, 1976; accepted for publication in revised form, July 19th, 1976)

The sequential oxidation and reduction of a suitably protected sugar derivative is a useful procedure for the inversion of configuration of secondary hydroxyl groups[1–3]. The present paper describes the application of the oxidation–reduction sequence to selectively benzoylated derivatives of cycloheptaamylose (**1**) and 6-*O*-tritylamylose[4] (**5**) to obtain a cyclic oligosaccharide (**4**) and a polysaccharide (**9**), in both of which a proportion of the constituent D-glucose residues was converted into D-allose residues.

Treatment of **1** with 2.2 molar equivalents of benzoyl chloride at −40° gave an *O*-benzoyl-cycloheptaamylose (**2**) that was composed mainly of 2,6-di-*O*-benzoyl-D-glucose residues with a degree of substitution by benzoyl groups of 52%, as shown by g.l.c. after methylation[5], followed by debenzoylation and methanolysis. Oxidation of **2** with dimethyl sulfoxide and phosphorus pentoxide[3] gave the oxidized *O*-benzoyl derivative **3** having a degree of substitution by carbonyl groups of 0.72 (as estimated by the nitrogen content of the oxime). Reduction of **3** with sodium borohydride[2,3] in methanol with concomitant cleavage of the benzoyl groups, and subsequent isolation of the product by successive acetylation and deacetylation gave a cyclic oligomer **4** that was shown by g.l.c. analysis of the methanolyzate, to consist of D-allose (57%), D-glucose (41%), and D-mannose (2%) residues.

Similarly, treatment of **5** with 1.1 molar equivalents of benzoyl chloride in pyridine at −40° gave an *O*-benzoyl-*O*-tritylamylose (**6**) that was oxidized to afford the oxidized derivative **7**, which on borohydride reduction gave the reduced compound **8**. Detritylation of **8** gave a polymer **9** composed of D-glucose (73%), D-allose (26%), and D-mannose (2%) residues.

*Presented at the Annual Meeting of the Agricultural Chemical Society of Japan, April 3, 1976, Kyoto, Japan.

It is noteworthy that **4** produced no insoluble inclusion complexes in aqueous solution with the solvents that had previously been shown to precipitate **1**, and that **9** showed no blue coloration, characteristic of the amylose–iodine–iodide complex.

EXPERIMENTAL

General methods. — G.l.c. was performed with a Hitachi gas chromatograph 063 equipped with a column (3 × 200 mm) of 5% Silicone SE-30 on Chromosorb W (80–100 mesh) and a flame-ionization detector, under isothermal conditions at 190°, with N_2 as carrier gas at a flow rate of 80 ml/min. Percentages of component monosaccharides were expressed on a relative molar basis.

Selective O-benzoylation of cycloheptaamylose into **2**. — Benzoyl chloride (15.8 ml, 2.2 mol. equiv.) was added dropwise over a period of 20 min to a stirred solution of cycloheptaamylose (10 g) in anhydrous pyridine (300 ml) at −40°. The bath temperature was kept at −40° for 1 h, at −30° for 2 h, at 0° overnight, and at room temperature for 24 h. The mixture was poured into ice–water and the precipitate formed was collected by filtration, washed extensively with water, and dried. The product was purified by precipitation from ethanol to give **2** (19.2 g).

Location of the O-benzoyl groups in **2**. — Compound **2** (1 g) was methylated three times with diazomethane (prepared each time from 10 g of 1-methyl-1-nitrosourea) and BF_3 etherate in dichloromethane to give a fully methylated product (775 mg). A portion (100 mg) was debenzoylated with M sodium methoxide (0.2 ml) in methanol (2 ml). After 2 h at room temperature, the solution was neutralized with Amberlite IR-120 (H^+) cation-exchange resin and evaporated to dryness. The residual syrup was heated overnight under reflux in 1% methanolic HCl (10 ml) and the resulting methyl D-glucosides were converted into trimethylsilyl ethers. G.l.c. showed the presence of methyl di-*O*-methyl- (9%), methyl 3-*O*-methyl- (72%), and methyl 2-*O*-methyl-glucosides (2%), and methyl D-glucosides (17%).

Oxidized O-benzoylcycloheptaamylose (**3**). — A solution of **2** (6 g) in dimethyl sulfoxide (40 ml) and *N*,*N*-dimethylformamide (120 ml) was stirred with P_2O_5 (7.5 g) for 22 h at 40°. The mixture was poured into ice–water and the precipitated solid was filtered off, washed with water, and dried to afford **3** (5.7 g).

Compound **3** (1 g) was heated with pyridine (6 ml), ethanol (6 ml), and hydroxylamine hydrochloride (1 g) for 2 h at 100°, and isolation in the usual way gave the oxime derivative (1.2 g) of **3**.

Anal. Calc. for 0.72 oxime group per repeating unit: N, 2.66. Found: N, 2.53.

Reduction of oxidized O-benzoylcycloheptaamylose (**3**) *into* **4**. — To a solution of **3** (2 g) in abs. methanol (100 ml) and *N*,*N*-dimethylformamide (20 ml) was added $NaBH_4$ (4 g) in small portions. The mixture was stirred for 45 min at room temperature and heated for 20 min at 100°, and then evaporated. The residual syrup was dissolved in methanol and the solution neutralized with glacial acetic acid. Desalting of the solution with Amberlite IR-120 (H^+) cation-exchange resin, followed by evaporation gave a white solid that was acetylated with acetic anhydride (20 ml) and

pyridine (20 ml) overnight at room temperature. Isolation of the product in the usual way afforded a white powder (1.5 g). A portion of it (500 mg) was treated with M sodium methoxide (1 ml) in methanol (10 ml) and kept for 2 h at room temperature. The solution was neutralized with Amberlite IR-120 (H^+) cation-exchange resin and evaporated to give **4** (245 mg).

Conversion of 6-O-tritylamylose (**5**) *into a polymer* (**9**) *containing* D-*glucose and* D-*allose residues.* — Compound **5** (10 g) in pyridine (200 ml) was treated with benzoyl chloride (3.3 ml, 1.1 mol. equiv.) as described for **1**. The mixture was poured into methanol and the precipitate formed was filtered off, washed extensively with methanol, and dried to give **6** (12.2 g). A solution of **6** (6 g) in dimethyl sulfoxide (40 ml) and *N*,*N*-dimethylformamide (120 ml) containing P_2O_5 (5 g) was stirred for 23 h at 40° and then poured into methanol. The resulting precipitate was collected by filtration, washed with methanol and with ether, and dried to yield **7** (4 g). Compound **7** (4 g) was treated with $NaBH_4$ (3 g) in a solution of methanol (50 ml), tetrahydrofuran (20 ml), and *N*,*N*-dimethylformamide (50 ml) as described for **3**. The precipitate obtained by pouring the mixture into methanol was filtered off, washed with methanol, and dried to afford **8** (3.1 g). A solution of **8** (2 g) in methanol (30 ml) containing conc. HCl (0.4 ml) was stirred for 16 h at room temperature. After dilution with ether, the precipitate formed was filtered off and washed with ether to yield a white powder. The same treatment was repeated once more to give **9** (600 mg).

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