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SELECTIVE ACETYLATION OF BENZYL α-D-MANNOPYRANOSIDE, BENZYL β-D-GLUCOPYRANOSIDE, AND BENZYL β-D-GALACTOPYRANOSIDE*†

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ABSTRACT

Acetylation of benzyl α-D-mannopyranoside with acetic anhydride–sodium acetate at room temperature gave crystalline benzyl 2,3,6-tri-*O*-acetyl-α-D-mannopyranoside (25%) and benzyl 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranoside (~65%). Similar esterification of benzyl β-D-glucopyranoside yielded the crystalline benzyl 2,4,6-triacetate (66%), whereas the corresponding galactopyranoside gave the crystalline 3,4,6-, 2,3,6-, and 2,4,6-triacetates (3, 25, and 9%, respectively). The structures of these compounds were established by methylation with diazomethane–boron trifluoride etherate and were confirmed by n.m.r. studies.

INTRODUCTION

Systematic studies of the selective esterification of carbohydrates have been reported, and differences in the reactivities of the secondary hydroxyl groups of carbohydrates towards acylating reagents are now well recognised[1–5]. As we were interested in obtaining partially acetylated glycopyranoside derivatives for use as starting materials in syntheses, we have investigated and now report on the selective acetylation of some benzyl hexopyranosides.

RESULTS AND DISCUSSION

Reaction of benzyl α-D-mannopyranoside with 8.5 molar equivalents of acetic anhydride in the presence of anhydrous sodium acetate at room temperature gave a mixture of products, from which a syrupy tetra-acetate (65%) and a crystalline triacetate **1** (25%) were isolated by column chromatography on silica gel. The tetra-acetate was identical with benzyl tetra-*O*-acetyl-α-D-mannopyranoside (**2**) synthesized from benzyl α-D-mannopyranoside by using an excess of acetic anhydride. The triacetate was shown to be benzyl 2,3,6-tri-*O*-acetyl-α-D-mannopyranoside (**1**) in the following way. Methylation of **1** with diazomethane–boron trifluoride etherate[6] gave crystalline

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2,3,6-tri-*O*-acetyl-4-*O*-methyl-α-D-mannopyranoside (**3**). Deacetylation of **3** afforded syrupy benzyl 4-*O*-methyl-α-D-mannopyranoside (**4**) {$[\alpha]_D$ +75° (*c* 0.85, ethanol)} and acid hydrolysis gave 4-*O*-methyl-D-mannose.

Selective acetylation of benzyl β-D-glucopyranoside with 8.5 molar equivalents of acetic anhydride at room temperature gave a product mixture from which the crystalline tetra-acetate (32%) and a crystalline triacetate **5** (66%) were isolated, after column chromatography on silica gel. The physical constants of the tetra-acetate were in agreement with literature data for benzyl tetra-*O*-acetyl-β-D-glucopyranoside[7]. Compound **5**, the n.m.r. spectrum of which indicated HO-3 to be unsubstituted, was shown to be benzyl 2,4,6-tri-*O*-acetyl-β-D-glucopyranoside in the following way. Methylation[6] of **5**, under conditions where acetyl migration does not occur, gave crystalline benzyl 2,4,6-tri-*O*-acetyl-3-*O*-methyl-β-D-glucopyranoside (**6**). Deacetylation of **6** followed by acid hydrolysis gave 3-*O*-methyl-D-glucose.

Similar esterification of benzyl β-D-galactopyranoside with 5.7 equivalents of acetic anhydride gave a complex reaction mixture. Fractionation on a column of silica gel afforded benzyl tetra-*O*-acetyl-β-D-galactopyranoside (38%) and three crystalline triacetates which were characterised by methylation[6] as the 3,4,6- (**8**, 3%), 2,3,6- (**9**, 25%), and 2,4,6- (**10**, 9%) isomers.

In partial esterifications of pyranosides, secondary *eq* hydroxyl groups are esterified at a higher rate than are *ax* groups[8]. It is also evident from the results so far reported that the relative reactivities of free hydroxyl groups vary with the acylation conditions. Tribenzoylation of the methyl α-D-glycopyranosides of D-mannose, D-glucose, and D-galactose gave preferentially the 2,3,6-tribenzoates[3]. In addition, the glucoside gave the 2,4,6-tribenzoate in useful yield. Selective benzoylation of benzyl α-D-xylopyranoside gave a preponderance of the 2,4-dibenzoate over the 2,3-isomer[4].

Relatively little systematic work has been carried out to date on the partial acetylation of pyranosides. The preferential acetylation of HO-3 of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside by acetic anhydride in pyridine has been reported[1]. In partial acetylation studies of benzyl 4-*O*-methyl-β-D-xylopyranoside, it was found[2] that acetic anhydride in pyridine and, also, acetic anhydride–sodium acetate gave preferential substitution of HO-2. It is evident that the selective acetylation of benzyl glycopyranosides of D-mannose, D-glucose, and D-galactose, with acetic anhydride–sodium acetate, yields products which are closely paralleled by the products of selective benzoylation of the corresponding methyl glycosides. From our results, the order of reactivity of the secondary hydroxyl groups of the benzyl hexopyranosides may be described as HO-2 and HO-4>HO-3 for the glucoside, HO-2 and HO-3> HO-4 for the mannoside, and HO-2>HO-3>HO-4 for the galactoside.

EXPERIMENTAL

Melting points were determined on a Kofler hot-stage and are uncorrected. Solutions were evaporated under diminished pressure below 50°. Ascending t.l.c. was

performed on Silica Gel F-254 (Merck), using benzene–methanol (96:4). Column chromatography was carried out on silica gel (Grace, mesh 50–100). Paper electrophoresis was carried out in borate buffer (pH 10); differences in the applied voltage or paper had no significant influence on M_G values. Sugar acetates were deacetylated with sodium methoxide in methanol. Free sugars were detected with aniline hydrogen phthalate[9], and sugar acetates with the ferric hydroxamate reagent[10]. N.m.r. spectra were recorded on HA-100 and HR-220 spectrometers at normal operating temperatures, using the solvent stated. Optical rotations were determined with a Bellingham and Stanley Polarimeter Model B.

*Benzyl 2,3,4,6-tetra-*O*-acetyl-α-*D*-mannopyranoside* (**2**) *and benzyl 2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranoside* (**12**). — Benzyl α-D-mannopyranoside[16] (1 g) was treated with acetic anhydride (10 ml) and anhydrous sodium acetate (0.5 g). The mixture was heated under reflux for 30 min and then poured into ice–water, and **2** was isolated in the usual way as a syrup (1.6 g), $[\alpha]_D$ +53° (*c* 1.42, chloroform).

Anal. Calc. for $C_{21}H_{26}O_{10}$: C, 57.53; H, 5.93. Found: C, 57.14; H, 6.16.

Benzyl β-D-galactopyranoside (1 g), when acetylated under similar conditions, gave **12** as a syrup (1.1 g), $[\alpha]_D$ −34° (*c* 1.12, chloroform).

Anal. Calc. for $C_{21}H_{26}O_{10}$: C, 57.53; H, 5.93. Found: C, 57.21; H, 6.02.

Partial acetylation of benzyl α-D-mannopyranoside. — A mixture of benzyl α-D-mannopyranoside[16] (5 g), anhydrous sodium acetate (1.5 g), and acetic anhydride (15 ml) was stirred for 6 days at room temperature. The slurry was filtered, concentrated to a small volume, and diluted with a small volume of water, and the solvents were evaporated. The syrupy reaction product (9.5 g) was partitioned between chloroform and water. The aqueous extract (0.98 g) contained benzyl α-D-mannopyranoside and sodium acetate. T.l.c. of the chloroform-soluble material (8.4 g) revealed two major products which were separated on a column (44 × 4 cm) of silica gel. Fractions (125 ml) were collected and concentrated, and the residues were examined by t.l.c.

Elution with ether–benzene (1:9) (fractions 1–24), followed by ether–benzene (15:85) (fractions 25–33), gave homogeneous, syrupy benzyl 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranoside (**2**, 5.8 g), $[\alpha]_D$ +46° (*c* 1.2, chloroform).

Continued elution with ether–benzene (15:85) gave fractions 34–41 (a mixture of **2** and triacetate **1**), and fractions 42–64 which contained chromatographically homogeneous 2,3,6-triacetate **1** (1.98 g). Crystallisation from di-isopropyl ether gave **1**, m.p. 108°, $[\alpha]_D$ +48° (*c* 0.98, chloroform). N.m.r. data ($CDCl_3$): τ 5.15 (*d*, $J_{1,2}$ 2.0 Hz, H-1), 4.68–4.84 [broad *m*, H-2,3 (or 4)], 6.13 [broad *m*, H-3 (or 4), 5] 5.54–5.8 (*m*, H-6), 5.22–5.52 (PhCH_2, $J_{A,B}$ 12 Hz), 2.68 (*s*, Ph), 7.12 (broad, HO-4), 7.90 (overlapping signals, 3AcO).

Anal. Calc. for $C_{19}H_{24}O_9$: C, 57.57; H, 6.06. Found: C, 57.89; H, 6.13.

Fractions 65–70, eluted with ether–benzene (15:85), contained triacetate and, presumably, benzyl di-*O*-acetyl-α-D-mannopyranoside.

Fractions 71–75, eluted with ether–benzene (1:4), contained a trace of the diacetate.

Benzyl 2,3,6-tri-O-acetyl-4-O-methyl-α-D-mannopyranoside (3). — A solution of **1** (200 mg) in dichloromethane (5 ml) was cooled to −5°. Boron trifluoride etherate (0.01 ml) was added and the solution was kept at −5° during the addition of excess of diazomethane in dichloromethane. The mixture was then kept for 1 h to allow all colour to discharge. T.l.c. then showed ~90% conversion into a faster-moving product. Polymethylene was removed, and the filtrate was concentrated to a syrup which was dissolved in di-isopropyl ether. Starting material was recovered by fractional crystallisation, followed by **3** (162 mg), m.p. 79–81°, $[\alpha]_D$ +66° (*c* 0.66, chloroform).

Anal. Calc. for $C_{20}H_{26}O_9$: C, 58.53; H, 6.34. Found: C, 58.62; H, 6.42.

Benzyl 4-O-methyl-α-D-mannopyranoside (**4**) *and its hydrolysis.* — A solution of **3** (150 mg) in methanol (3 ml) was treated with 0.1M methanolic sodium methoxide (1 ml) for 4 h at room temperature. Cations were removed from the solution with Amberlite IR-120 (H^+) resin, which was then concentrated to give **4** as a chromatographically homogeneous syrup, $[\alpha]_D$ +75° (*c* 0.85, ethanol).

Anal. Calc. for $C_{14}H_{20}O_6$: C, 59.15; H, 7.04. Found: C, 57.75; H, 6.84.

The glycoside **4** (40 mg) was hydrolysed with 0.5M sulphuric acid (1 ml) for 4 h at ~95°. The hydrolysate was neutralised (barium carbonate) and centrifuged, and the supernatant was concentrated to dryness. Paper chromatography (1-butanol–ethanol–water, 5:1:4) of the residue revealed 4-*O*-methylmannose which co-chromatographed[11] with 3,4-di-*O*-methyl-D-galactose and methyl β-L-arabinoside. The methyl sugar had[12] M_G 0.52.

Partial acetylation of benzyl β-D-glucopyranoside. — When benzyl β-D-glucopyranoside[17] (2.57 g) was acetylated under conditions similar to those used for benzyl α-D-mannopyranoside, with acetic anhydride (7.7 ml) and sodium acetate (770 mg), and the resultant, syrupy reaction product (5.5 g) was partitioned between chloroform and water, a chloroform-soluble fraction (3.5 g) and a residue (1.2 g) of benzyl β-D-glucopyranoside and sodium acetate were obtained.

T.l.c. of the chloroform-soluble material showed two main products which were separated by fractionation on a column (42 × 4 cm) of silica gel. Fractions (125 ml) were collected and concentrated, and the residues were examined by t.l.c.

Elution with ether–benzene (5:95) (fractions 3–23), followed by ether–benzene (1:9) (fractions 24–26), gave the 2,3,4,6-tetra-acetate (1.1 g), contaminated with a trace amount of the triacetate **5**. Crystallisation from ethanol gave benzyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside, m.p. 100°, $[\alpha]_D$ −51° (*c* 0.77, ethanol); lit.[7] m.p. 96–101°, $[\alpha]_D$ −44° (ethanol).

Continued elution with ether–benzene (1:9) gave fractions 27–30 (triacetate **5** contaminated with a trace of the tetra-acetate).

Fractions 31–99, eluted with ether–benzene (1:4), contained chromatographically homogeneous 2,4,6-triacetate **5** (2.3 g), which crystallised readily from di-isopropyl ether and had m.p. 138–140°, $[\alpha]_D$ −64.5° (*c* 0.85, chloroform). N.m.r. data ($CDCl_3$): τ 5.50 (*d*, $J_{1,2}$ 8 Hz, H-1), 4.90–5.15 (*m*, H-2,4), 6.24–6.50 (*m*, H-3,5),

5.72–5.82 (*m*, H-6; at 220 MHz, two pairs of *d*, *J* 5 and 2.5 Hz), 5.06–5.48 (PhCH_2, $J_{A,B}$ 12 Hz), 2.70 (*s*, Ph), 7.90 (*s*, 3AcO).

Anal. Calc. for $C_{19}H_{24}O_9$: C, 57.57; H, 6.06. Found: C, 57.76; H, 6.10.

Fractions 100–104, eluted with ethanol, contained a trace of the triacetate and, presumably, benzyl di-*O*-acetyl-β-D-glucopyranoside.

Benzyl 2,4,6-tri-O-acetyl-3-O-methyl-β-D-glucopyranoside (**6**). — A solution of the triacetate **5** (250 mg) in dichloromethane (5 ml) was treated with diazomethane–boron trifluoride etherate in the usual manner. Polymethylene was removed, and the filtrate was concentrated to a syrup (220 mg) which crystallised from di-isopropyl ether, giving **6** as platelets, m.p. 104–106°, $[\alpha]_D$ −69° (*c* 0.67, chloroform).

Anal. Calc. for $C_{20}H_{26}O_9$: C, 58.53; H, 6.34. Found: C, 58.69; H, 6.38.

Benzyl 3-O-methyl-β-D-glucopyranoside (**7**) *and its hydrolysis.* — A solution of **6** (195 mg) in dry methanol (3 ml) was deacetylated, as described above, to give amorphous **7** (120 mg), which showed only one component (t.l.c.) and had $[\alpha]_D$ −58° (*c* 0.32, ethanol).

Anal. Calc. for $C_{14}H_{20}O_6$: C, 59.15; H, 7.04. Found: C, 58.12; H, 6.87.

The glycoside **7** (20 mg) was hydrolysed with 0.5M sulphuric acid (2 ml) for 3 h at 100°. After neutralisation with barium carbonate, the product was examined by paper electrophoresis. The main component was 3-*O*-methyl-D-glucose, M_G 0.83[13] (identified by comparison with an authentic sample), together with a trace of D-glucose. Compound **5** was different from benzyl 2,3,4-tri-*O*-acetyl-β-D-glucopyranoside, m.p. 125°, $[\alpha]_D$ −35° (*c* 0.86, chloroform), which has been prepared in this laboratory and fully characterised.

Partial acetylation of benzyl β-D-galactopyranoside. — Treatment of benzyl β-D-galactopyranoside[18] (3 g) with acetic anhydride (6 ml, 5.7 equiv.) in the presence of anhydrous sodium acetate (400 mg) gave a chloroform-soluble reaction product (3.9 g) which on t.l.c. showed two major components, and a residue (0.6 g) of sodium acetate and unreacted glycoside.

However, fractionation of the reaction mixture on a column (39 × 4 cm) of silica gel yielded four compounds. Fractions (125 ml) were collected and concentrated, and the residues were examined by t.l.c.

The component (1.46 g) eluted first from the column with ether–benzene (5:95) (fractions 2–12), followed by ether–benzene (1:9) (fractions 13–25), and benzyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranoside (**12**) had identical i.r. spectra and similar optical rotations.

Fractions 26–31, eluted with ether–benzene (15:85), contained a mixture of the tetra-acetate and triacetate **8**.

Fractions 32–35, eluted with ether–benzene (1:4), contained triacetate **8** contaminated with a trace of triacetate **9**, and were concentrated to a syrup (0.12 g) which crystallised to give the 3,4,6-triacetate **8** as needles, m.p. 121°, $[\alpha]_D$ −29° (*c* 1.145, chloroform).

Anal. Calc. for $C_{19}H_{24}O_9$: C, 57.57; H, 6.06. Found: C, 57.86; H, 6.10.

Fractions 36–39, eluted with ether–benzene (1:4), contained a mixture of triacetates **8** and **9**.

Fractions 40–49, eluted with ether–benzene (1:3), contained the 2,3,6-triacetate **9** which crystallised from di-isopropyl ether as prisms, m.p. 94–95°, $[\alpha]_D$ −38° (*c* 0.86, chloroform). N.m.r. data ($CDCl_3$): τ 5.50 (*d*, $J_{1,2}$ 8 Hz, H-1), 4.60–4.78 (*m*, H-2), 5.92–6.02 (broad *m*, H-4), 6.29 (broad *t*, *J* 6 Hz, H-5), 5.66 (*d*, *J* 6 Hz, H-6), 7.44 (*d*, *J* 6 Hz, HO-4), 5.04–5.44 [PhCH_2 (*J* 12 Hz) overlapping H-3], 2.70 (*s*, Ph), 7.92–8.00 (3AcO).

Anal. Calc. for $C_{19}H_{24}O_9$: C, 57.57; H, 6.06. Found: C, 57.64; H, 6.11.

Fractions 50–76, eluted with ether–benzene (1:3 → 1:1), contained triacetates **9** and **10** and were concentrated to a syrup (1.075 g). By fractional crystallisation from di-isopropyl ether, the 2,4,6-triacetate **10** was isolated as needles, m.p. 133°, $[\alpha]_D$ −40° (*c* 0.82, chloroform), and the 2,3,6-triacetate **9** as platelets, m.p. 94°, $[\alpha]_D$ −37° (*c* 1.0, chloroform). N.m.r. data for **10** ($CDCl_3$): τ 5.52 (*d*, $J_{1,2}$ 8 Hz, H-1), 4.86–5.04 [pair (?) of *d*, H-2], 6.10–6.32 (broad triplet of *d*, *J* 6 Hz, H-3,5), 4.18 (*d*, *J* 3 Hz, H-4), 5.82 (*d*, *J* 6 Hz, H-6), 7.22 (broad *d*, *J* 6 Hz, HO-3), 5.04–5.46 (PhCH_2, J_{AB} 12 Hz), 2.70 (*s*, Ph), 7.88 (overlapping signals, 3AcO).

Anal. Calc. for $C_{19}H_{24}O_9$: C, 57.57; H, 6.06. Found: C, 57.65; H, 6.16).

The triacetates **8**, **9**, and **10** were isolated in the ratios 1:8:3.

Methylations with diazomethane–boron trifluoride etherate. — To a solution of the substrate (**8**, **9**, or **10**, 60–70 mg) in dichloromethane (5 ml) at −5°, boron trifluoride etherate (0.01 ml) was added. The solution was maintained at the same temperature during the addition of excess of diazomethane in the usual manner. The mixture was then kept for 1 h to allow the discharge of all residual colour. T.l.c. then showed an almost complete conversion of each starting compound into material of higher R_F value. Polymethylene was removed, and the filtrate was washed with water to remove any trace of acid, and dried. Concentration left a syrupy residue (~60 mg) in each case. The following compounds were thus prepared.

Benzyl 3,4,6-tri-*O*-acetyl-2-*O*-methyl-β-D-galactopyranoside (**11**, 60 mg), m.p. 102–106° (from chloroform), $[\alpha]_D$ −10.5° (*c* 0.68 ethanol).

Anal. Calc. for $C_{20}H_{26}O_9$: C, 58.53; H, 6.34. Found: C, 58.64; H, 6.40.

Benzyl 2,3,6-tri-*O*-acetyl-4-*O*-methyl-β-D-galactopyranoside (**12**), m.p. 94–96° (from di-isopropyl ether), $[\alpha]_D$ −30° (*c* 0.32, chloroform).

Anal. Found: C, 58.62; H, 6.46.

Benzyl 2,4,6-tri-*O*-acetyl-3-*O*-methyl-β-D-galactopyranoside (**13**), m.p. 88–89° (from di-isopropyl ether), $[\alpha]_D$ −38° (*c* 0.63, chloroform).

Anal. Found: C, 58.62; H, 6.48.

Deacetylation and hydrolysis of the benzyl tri-O-acetyl-O-methylgalactopyranosides. — The triacetate **11** (50 mg) was conventionally deacetylated with sodium methoxide in methanol. The syrupy product (~30 mg), which showed only one component (t.l.c.) and had $[\alpha]_D$ −15° (*c* 0.42, ethanol), was hydrolysed with 0.5M sulphuric acid (1 ml) for 6 h at 100°. After neutralisation with barium carbonate and concentration of the solution, the sugar residue was dissolved in water and examined

by paper electrophoresis. The main product was 2-*O*-methyl-D-galactose, M_G 0.44[14], identified by comparison with 2-*O*-methyl-D-galactose, prepared from 1,3,4,6-tetra-*O*-acetyl-α-D-galactopyranose[15].

Compound **12** was deacetylated as described above, and the syrupy product, $[\alpha]_D$ −28° (*c* 0.42, ethanol), was hydrolysed with acid. On paper electrophoresis, the product had M_G 0.30, identical with that of 4-*O*-methyl-D-galactose provided by Professor E. G. Gros.

Deacetylation of **13** yielded a syrup, $[\alpha]_D$ −33° (*c* 0.57, ethanol), which was hydrolysed with acid and then examined by paper electrophoresis. The main product was 3-*O*-methyl-D-galactose, M_G 0.60 (lit.[14] 0.63), together with a trace amount of galactose.

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