

## Preparation of 2-Deoxy-sugars by Hydrogenolysis of Benzoylated Glycopyranosyl Bromides. Part II\*

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Hydrogenolysis of benzoylated glycopyranosyl bromides, having the substituents at C1 and C2 *cis*-oriented, gives 30–50 % yields of benzoylated 2-deoxy-pyranoses in addition to the expected 1,5-anhydro-alditol derivatives. The reaction has been used to prepare benzoylated 2-deoxy-D-*threo*-pentose, 2-deoxy-D-*lyxo*-hexose, 2,6-dideoxy-L-*arabino*-hexose and 2-deoxy-D-lactose.

In a preceding paper it was shown that benzoylated 2-deoxy-pyranoses can be prepared by hydrogenolysis of benzoylated glycopyranosyl bromides, provided the latter have the benzyloxy-group at C2 *cis* to the bromine atom at C1.<sup>1</sup> Thus hydrogenolysis of tri-*O*-benzoyl- $\beta$ -D-arabinopyranosyl bromide gave tri-*O*-benzoyl-2-deoxy- $\beta$ -D-*erythro*-pentopyranose in addition to the expected 1,5-anhydro-tri-*O*-benzoyl-D-arabinitol. Similarly, tetra-*O*-benzoyl- $\alpha$ -D-glucopyranosyl bromide gave substantial amounts of tetra-*O*-benzoyl-2-deoxy- $\alpha$ -D-*arabino*-hexopyranose. Benzoylated  $\beta$ -D-ribopyranosyl bromide or  $\alpha$ -D-mannopyranosyl bromide, both of which have the substituents at C1 and C2 *trans* oriented, did not give 2-deoxy-sugars on hydrogenolysis.

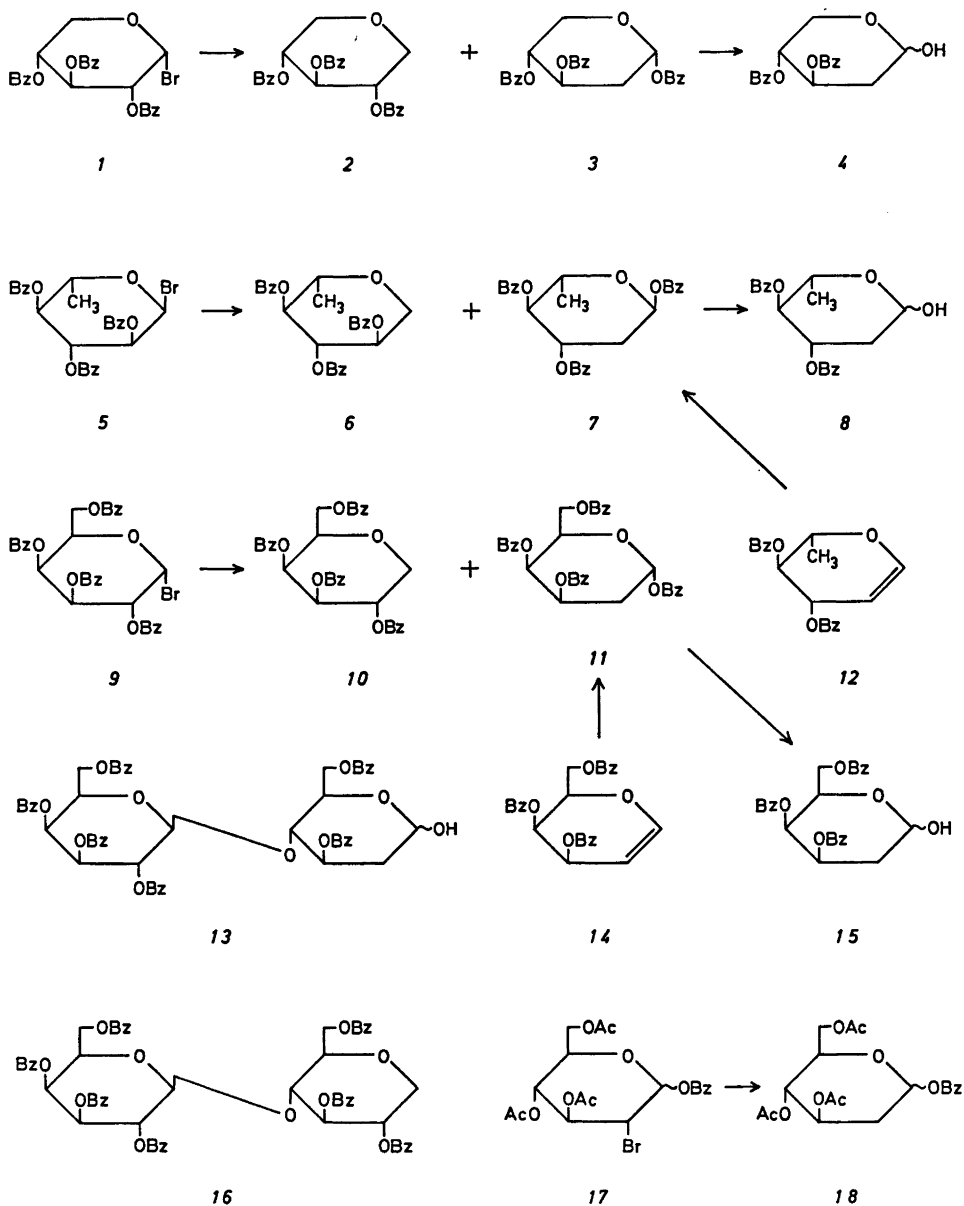
The optimum yield of benzoylated 2-deoxy-D-ribose was obtained when the hydrogenolysis of tri-*O*-benzoyl- $\beta$ -D-arabinopyranosyl bromide was carried out in ethyl acetate with palladium on carbon in the presence of 2 molar equivalents of triethylamine.<sup>1</sup> Other catalysts gave lower yields of benzoylated 2-deoxy-D-ribose. We have now studied the hydrogenolysis of tri-*O*-benzoyl- $\beta$ -D-arabinopyranosyl bromide in the presence of a number of different amines, but

otherwise under the conditions described previously.<sup>1</sup> With diisopropylamine or with diethylamine tri-*O*-benzoyl-2-deoxy- $\beta$ -D-*erythro*-pentopyranose was obtained in 40–46 % yield, as determined from NMR spectra of the crude reaction products. Piperidine or propylamine gave *ca.* 25 % of the 2-deoxy-ribose derivative whereas tributylamine or pyridine only yielded traces. Thus hydrogenolysis under the conditions described previously with triethylamine as the base seems to give the best yield of 2-deoxy sugars. Under these conditions the hydrogenolyses of a number of benzoylated glycopyranosyl bromides have now been studied.

Hydrogenolysis of tri-*O*-benzoyl- $\alpha$ -D-xylopyranosyl bromide (*1*) under these conditions gave a crude product which, as seen from a <sup>1</sup>H NMR spectrum, contained *ca.* 40 % tri-*O*-benzoyl-2-deoxy- $\alpha$ -D-*threo*-pentopyranose (*3*) and 1,5-anhydro-tri-*O*-benzoyl-xylitol (*2*). Some *2* could be crystallized from the mixture, but pure *3* could not be obtained. In a separate experiment the crude reaction mixture was treated with hydrogen bromide and the resulting product was hydrolysed. This converted *3* into the corresponding 1-hydroxy-compound (*4*) whereas *2* was unchanged. Chromatography then gave 30 % crystalline *4* which on benzylation yielded *3* and its  $\beta$ -anomer, both of which are known.<sup>2</sup>

Hydrogenolysis of 2,3,4-tri-*O*-benzoyl- $\alpha$ -L-quinovosyl bromide (*5*) under the same conditions gave a mixture which contained tri-*O*-benzoyl-2,6-dideoxy- $\alpha$ -L-*arabino*-hexopyranose (*7*) and the 1,5-anhydroalditol derivative (*6*). In this case *7* could be crystallized from the mixture in 40 % yield. Alternatively, treatment

\* For Part I see Ref. 1.



of the reaction mixture with hydrogen bromide followed by hydrolysis gave the 1-hydroxy-compound (8), which on benzylation yielded 7. In order to confirm the structure of 7 it was prepared from 3,4-di-*O*-benzoyl-1,2,3-trideoxy-*L*-arabino-hex-1-enopyranose (12) which on treatment with hydrogen bromide yielded di-*O*-benzoyl-2,6-dideoxy- $\alpha$ -*L*-arabino-hexopyran-

osyl bromide. Treatment of the latter with silver benzoate gave 7 and its  $\beta$ -anomer.

Tetra-*O*-benzoyl- $\alpha$ -*D*-galactopyranosyl bromide (9) on hydrogenation gave a mixture which contained tetra-*O*-benzoyl-2-deoxy- $\alpha$ -*D*-lyxo-hexopyranose (11) (ca. 60% as seen from an NMR spectrum) and 1,5-anhydro-tetra-*O*-benzoyl-*D*-galactitol (10). The products could

not be separated and the mixture was therefore treated with hydrogen bromide and hydrolysed as described above. Subsequent chromatography gave 39 % of the 1-hydroxy-compound (15). Benzoylation of the latter yielded (11) and its  $\beta$ -anomer. The structure of 11 was confirmed through its preparation from the unsaturated compound (14).

As a final example hepta-*O*-benzoyl- $\alpha$ -D-lactopyranosyl bromide was subjected to hydrogenolysis. The crude product contained ca. 40 % 2-deoxy-D-lactose heptabenzate as seen from an NMR spectrum. Treatment with hydrogen bromide, hydrolysis, and chromatography gave the 1-hydroxy-2-deoxy-derivative (13) and the 1,5-anhydride (16).

Thus hydrogenolysis of benzoylated pyranosyl bromides with a 1,2-*cis* configuration seems to provide a convenient method for the preparation of benzoylated 2-deoxy-sugars. Benzoylated bromides with a 1,2-*trans* structure do not give 2-deoxy compounds.<sup>1</sup> Previous results have shown that acetylated pyranosyl bromides do not form 2-deoxy-sugars on hydrogenolysis.<sup>1</sup> We have now carried out a hydrogenolysis of tri-*O*-(*p*-methoxybenzoyl)- $\beta$ -D-arabinopyranosyl bromide under the conditions described above and found that results similar to those of the benzoate were obtained.

The formation of benzoylated 2-deoxy-pyranoses must involve an acyl-migration from C2 to C1, probably *via* a cyclic intermediate. It was of interest to see whether acyl-migration from C1 to C2 could take place and to study this the two anomeric tri-*O*-acetyl-1-*O*-benzoyl-2-bromo-2-deoxy-D-glucopyranoses ( $\alpha$ - and  $\beta$ -17) were hydrogenolysed. However, only the two 2-deoxy-D-glucose derivatives ( $\alpha$ - and  $\beta$ -18) were obtained and no products resulting from acyl-migration were observed.

## EXPERIMENTAL

Melting points are uncorrected. NMR spectra were measured on a Bruker HX-90E instrument using deuteriochloroform as solvent. Thin layer chromatography (TLC) was performed on silica gel PF<sub>254</sub> ("Merck"); for preparative work 1 mm layers on 20 x 40 cm plates were used.

**Hydrogenolysis of tri-*O*-benzoyl- $\alpha$ -D-xylopyranosyl bromide (1).** A solution of 1 (5.0 g) in ethyl acetate (35 ml) and triethylamine (2.65 ml) was hydrogenated at 1 atm. pressure for ca.

18 h in the presence of 1.0 g of 5 % palladium on carbon. The mixture was then filtered through carbon and the carbon was washed with dichloromethane. The filtrate was washed twice with water, dried and evaporated to a syrup (4.8 g). An NMR spectrum showed the presence of ca. 40 % of the 2-deoxy-compound (3). Crystallization from ether gave 1.05 g (25 %) of 2,3,4-tri-*O*-benzoyl-1,5-anhydro-xylytol (2), m.p. 145–148 °C (reported<sup>3</sup> m.p. 146–147 °C). An NMR spectrum further proved the structure. The products in the mother liquor could not be separated.

In a separate experiment the product from the hydrogenation of 5.0 g of 1 was dissolved in benzene (50 ml) saturated with hydrogen bromide and kept for 1.25 h. The benzene was then evaporated, tetrachloromethane was added twice and evaporated. The resulting syrup was dissolved in acetone (50 ml) and water (5 ml) and stirred overnight with silver carbonate (15 g). The silver salts were filtered off, the filtrate was diluted with dichloromethane and washed twice with water, dried and evaporated to a syrup (3.45 g). Crystallization from methanol (10 ml) gave 1.12 g (26 %) of 2, m.p. 141–144 °C. Preparative TLC of the material in the mother liquor using ether-pentane (1:1) as eluent gave a further 560 mg (13 %) of 2. A slower running fraction yielded 1.0 g (31 %) of 3,4-di-*O*-benzoyl-2-deoxy-D-*threo*-pentopyranose (4), m.p. 108–113 °C. Recrystallization from ether gave the pure product, m.p. 110–112 °C,  $[\alpha]_D^{25} - 76.8^\circ$  (5 min)  $\rightarrow -87.2^\circ$  (42 h) (c 2.3, CHCl<sub>3</sub>). Anal. C<sub>19</sub>H<sub>18</sub>O<sub>6</sub>: C, H.

**Benzoylation of 4.** A solution of 4 (400 mg) in dichloromethane was added to a mixture of benzoyl chloride (0.5 ml) and pyridine (5 ml) at 0 °C. The mixture was kept over-night at room temperature and worked up in the usual way. The product was purified by preparative TLC (ether-pentane 1:2). The main fraction (361 mg) was crystallized from ether-pentane to give 62 mg of tri-*O*-benzoyl-2-deoxy- $\beta$ -D-*threo*-pentopyranose, m.p. 162–166 °C. Recrystallization gave a product with m.p. 164.5–165.5 °C,  $[\alpha]_D^{25} - 104.8^\circ$  (c 1.2, CHCl<sub>3</sub>) (recorded<sup>2</sup> m.p. 160–162 °C,  $[\alpha]_D - 104^\circ$ ). Preparative TLC of the material in the mother liquor using benzene as eluent gave pure tri-*O*-benzoyl-2-deoxy- $\alpha$ -D-*threo*-pentopyranose (3) as a syrup,  $[\alpha]_D^{25} + 13.2^\circ$  (c 0.9, CHCl<sub>3</sub>) (reported<sup>3</sup>  $[\alpha]_D + 12.2^\circ$ ). NMR spectra of both anomers were identical with those of previously described products.<sup>3</sup>

**Tri-*O*-benzoyl- $\alpha$ -L-quinovosyl bromide (5).** Benzoylation of L-quinovose<sup>4</sup> in the usual way with benzoyl chloride in pyridine gave a crude tetra-*O*-benzoyl- $\alpha$ -L-quinovopyranose, m.p. 120–121 °C. A <sup>1</sup>H NMR spectrum was in agreement with the structure. To the tetrabenzate (5.0 g) in dichloromethane (5 ml) was added 30 % hydrogen bromide in glacial acetic acid (20 ml) and the mixture was kept for 2 h at room temperature. It was then diluted with

dichloromethane, washed with water and with aqueous sodium hydrogen carbonate, dried and evaporated. The residue was recrystallized from ether-pentane to give 3.53 g (76 %) of **5**, m.p. 158–160 °C. Recrystallization from ether gave a product with m.p. 158–160 °C,  $[\alpha]_{\text{D}}^{20} = -108^\circ$  (*c* 3.3, CHCl<sub>3</sub>). Anal. C<sub>27</sub>H<sub>33</sub>BrO<sub>7</sub>: C, H.

<sup>1</sup>H NMR:  $\delta$  7.00 (H1), 5.45 (H2), 6.37 (H3), 5.60 (H4), 4.65 (H5), 1.41 (H6);  $J_{12} = 4.0$  Hz,  $J_{23} = J_{34} = J_{45} = 9.8$ ,  $J_{56} = 6.2$ .

**Hydrogenolysis of tri-O-benzoyl- $\alpha$ -L-quinovosyl bromide (5).** Hydrogenolysis of **5** (5.0 g) as described above gave 4.5 g of a crude product which was crystallized from methanol (15 ml) to give 1.8 g (41 %) of tri-O-benzoyl-2,6-dideoxy- $\alpha$ -L-arabino-hexopyranose (**7**), m.p. 108–118 °C. Recrystallization from methanol gave 1.4 g (30 %) with m.p. 122–124 °C and an additional recrystallization gave the pure product, m.p. 125–126 °C,  $[\alpha]_{\text{D}}^{25} = -38.5^\circ$  (*c* 1.1, CHCl<sub>3</sub>). Anal. C<sub>27</sub>H<sub>34</sub>O<sub>7</sub>: C, H. <sup>1</sup>H NMR:  $\delta$  6.59 (H1), 2.47 (H2e), 2.27 (H2a), 5.82 (H3), 5.62 (H4), 4.30 (H5), 1.33 (H6);  $J_{12e} = 1.6$  Hz,  $J_{12a} = 3.4$ ,  $J_{2e3a} = 13.6$ ,  $J_{2e3} = 5.2$ ,  $J_{2a3} = 11.2$ ,  $J_{34} = 9.8$ ,  $J_{45} = 9.8$ ,  $J_{56} = 6.4$ .

In a separate experiment the crude product (4.4 g) from the hydrogenolysis was treated with hydrogen bromide and then hydrolysed with aqueous acetone as described above. The product thus obtained (4.4 g) was chromatographed on a column of silica gel (400 g) eluting with ether-pentane (1:1). The first fraction to come off the column gave 1.77 g (42 %) of 1,5-anhydro-tri-O-benzoyl-6-deoxy-L-glucitol (**6**), m.p. 89–93 °C. Recrystallization from ethanol gave the pure product, m.p. 94–96 °C,  $[\alpha]_{\text{D}}^{20} \sim 0^\circ$  (*c* 9, CHCl<sub>3</sub>). Anal. C<sub>29</sub>H<sub>24</sub>O<sub>7</sub>: C, H. An NMR spectrum confirmed the structure.

The next fraction gave 1.02 g (31 %) of 3,4-di-O-benzoyl-2,6-dideoxy-L-arabino-hexopyranose (**8**), m.p. 94–97 °C,  $[\alpha]_{\text{D}}^{25} = +53.0^\circ$  (*c* 4.2, CHCl<sub>3</sub>); unchanged after 24 h. An NMR spectrum was in agreement with the structure and showed that a mixture of the two anomers was present.

**Benzoylation of 8.** To a mixture of pyridine (5 ml) and benzoyl chloride (0.2 ml) was added **8** (204 mg) in the course of 5 min at 0 °C. The mixture was kept for 1 h at 0 °C and for 2 h at room temperature. Work up in the usual way gave 265 mg (100 %) of almost pure **7**. Crystallization from ether-pentane gave 143 mg of a product with m.p. 124–125 °C, identical with that described above as seen from an NMR spectrum.

**Preparation of 7 from di-O-benzoyl-1,2,6-trideoxy-L-arabino-hex-1-enopyranose (12).** Hydrogen bromide was passed through a solution of **12**<sup>5</sup> (520 mg) in benzene (10 ml) for 15 min at 0 °C. The solvent was evaporated, carbon tetrachloride was added twice and again evaporated. An NMR spectrum of the syrupy residue (700 mg) showed that it was almost pure di-O-benzoyl-2,6-dideoxy- $\alpha$ -L-arabino-hexopyranosyl bromide. The product was stirred overnight

with silver benzoate (2.0 g) in acetonitrile (10 ml). The silver salts were filtered off and the solvent evaporated. The residue (680 mg) was separated into two fractions by preparative TLC eluting 3 times with benzene. The slow-moving fraction (159 mg) was rechromatographed under the same conditions to give 101 mg (14 %) of **7**, m.p. 124–125 °C after crystallization from methanol. An NMR spectrum proved its identity with the product described above.

The fast-moving fraction gave 299 mg (42 %) of tri-O-benzoyl-2,6-dideoxy- $\beta$ -L-arabino-hexopyranose as a syrup. <sup>1</sup>H NMR:  $\delta$  6.26 (H1), 2.78 (H2e), 2.29 (H2a), 5.68 (H3), 5.45 (H4), 3.98 (H5), 1.40 (H6);  $J_{12e} = 2.4$  Hz,  $J_{12a} = 9.6$ ,  $J_{2e3a} = 11.8$ ,  $J_{2e3} = 4.4$ ,  $J_{2a3} = J_{34} = J_{45} = 9.6$ ,  $J_{56} = 6.2$ .

**Hydrogenolysis of tetra-O-benzoyl- $\alpha$ -D-galactopyranosyl bromide (9).** Penta-O-benzoyl- $\alpha$ -D-galactopyranose<sup>6</sup> (5 g) was dissolved in dichloromethane (10 ml) and 30 % hydrogen bromide in glacial acetic acid (20 ml) was added. After 2 h at room temperature more dichloromethane was added and the solution was washed with ice-water and aqueous sodium hydrogen carbonate, dried and evaporated. The residue (*ca.* 5 g) consisted of syrupy tetra-O-benzoyl- $\alpha$ -D-galactopyranosyl bromide (**9**) as seen from an NMR spectrum. The anomeric proton gave a doublet at 7.0 ppm;  $J_{12} = 4$  Hz. The crude bromide was hydrogenolysed as described above to give 3.9 g of a syrupy product which, as seen from an NMR spectrum, contained *ca.* 60 % of the 2-deoxy-galactose derivative (**11**) in addition to the anhydro-galactitol (**10**). These compounds could not be separated and the mixture was therefore treated with hydrogen bromide and subsequently hydrolysed as described above. The product thus obtained was chromatographed on a column of silica gel (400 g) eluting with ether-pentane (1:1).

The fastest moving fraction gave 1.1 g (27 %) of 1,5-anhydro-tetra-O-benzoyl-D-galactitol (**10**) as a syrup,  $[\alpha]_{\text{D}}^{25} = +89.6^\circ$  (*c* 1.5, CHCl<sub>3</sub>). (Found: C 70.90; H 4.85. Calc. for C<sub>34</sub>H<sub>28</sub>O<sub>8</sub>: C 70.34; H 4.86). The structure was confirmed by NMR spectroscopy.

The next fraction gave 1.26 g (39 %) of syrupy 3,4,6-tri-O-benzoyl-2-deoxy-D-lyxo-hexopyranose (**15**),  $[\alpha]_{\text{D}}^{23} = +31.2^\circ$  (*c* 1.5, CHCl<sub>3</sub>). Anal. C<sub>27</sub>H<sub>24</sub>O<sub>8</sub>: C, H.

**Benzoylation of (15)** (200 mg) with benzoyl chloride in pyridine as described above gave a syrup which was separated into two fractions by preparative TLC using benzene as eluent. The first fraction gave 180 mg (74 %) of tetra-O-benzoyl-2-deoxy- $\alpha$ -D-lyxo-hexopyranose (**11**) as a syrup,  $[\alpha]_{\text{D}}^{20} = +51.8^\circ$  (*c* 3.9, CHCl<sub>3</sub>). (Found: C 69.93; H 5.28. Calc. for C<sub>33</sub>H<sub>28</sub>O<sub>9</sub>: C 70.34; H 4.86). <sup>1</sup>H NMR:  $\delta$  6.76 (H1), 2.65 (H2a), 2.38 (H2e), 5.82 (H3), 6.01 (H4), 4.3–4.9 (H5, H6);  $J_{12e} \simeq 1$  Hz,  $J_{12a} = 3.8$ ,  $J_{2e2a} = 13$ ,  $J_{2e3} = 5.5$ ,  $J_{2a3} = 12$ ,  $J_{34} = 2.5$ .

The next fraction consisted of tetra-*O*-benzoyl-2-deoxy- $\beta$ -D-lyxo-hexopyranose, syrup,  $[\alpha]_D^{25} + 14.1^\circ$  (*c* 6.3, CHCl<sub>3</sub>), (reported<sup>7</sup>  $[\alpha]_D + 14.8^\circ$ ). An NMR spectrum confirmed the structure.

*Preparation of 11 from tri-O-benzoyl-1,2-di-deoxy-D-lyxo-hex-1-enopyranose (14)*. A solution of 14 (396 mg) in benzene was treated with hydrogen bromide, as described above for 12, to give crude syrupy tri-*O*-benzoyl-2-deoxy- $\alpha$ -D-lyxo-hexopyranosyl bromide. An NMR spectrum was in agreement with the structure. The bromide was treated with silver benzoate in acetonitrile as described above to give 385 mg of a mixture of 11 and its  $\beta$ -anomer. Preparative TLC eluting 3 times with benzene gave 160 mg (32 %) of 11 and 128 mg (26 %) of tetra-*O*-benzoyl-2-deoxy- $\beta$ -D-lyxo-hexopyranose. NMR spectra showed that they were identical with the products described above.

*Hydrogenolysis of hepta-O-benzoyl- $\alpha$ -D-lactopyranosyl bromide*. Octa-*O*-benzoyl- $\alpha$ , $\beta$ -D-lactose<sup>8</sup> was treated with hydrogen bromide in glacial acetic acid for 2 h at room temperature. The mixture was then diluted with dichloromethane, washed with water and aqueous sodium hydrogen carbonate, dried and evaporated. This gave hepta-*O*-benzoyl- $\alpha$ -D-lactopyranosyl bromide as a syrup. An NMR spectrum showed H1 as a doublet at  $\delta$  6.8,  $J_{12} = 4.2$  Hz.

The bromide (1.0 g) was hydrogenated as described above to give a crude product (900 mg) which contained ca. 40 % hepta-*O*-benzoyl-2-deoxy- $\alpha$ -D-lactopyranose as seen from an NMR spectrum. The product was treated with hydrogen bromide and then hydrolyzed as described above. The material thus obtained was separated into two fractions by preparative TLC using ether-pentane (1:1) as eluent.

The fast-moving fraction gave 298 mg (32 %) of the 1,5-anhydro-hepta-*O*-benzoyl-D-lactitol (16) as a syrup,  $[\alpha]_D^{25} + 59.5^\circ$  (*c* 6.0, CHCl<sub>3</sub>). Anal. C<sub>61</sub>H<sub>50</sub>O<sub>17</sub>: C, H. Both <sup>1</sup>H and <sup>13</sup>C NMR spectra were in agreement with the structure.

The next fraction gave 245 mg (26 %) of hexa-*O*-benzoyl-2-deoxy-D-lactopyranose (13) as a syrup,  $[\alpha]_D^{20} + 64.6^\circ$  (*c* 2.8, CHCl<sub>3</sub>). Anal. C<sub>54</sub>H<sub>46</sub>O<sub>16</sub>: C, H. An NMR spectrum confirmed the structure.

*3,4,6-Tri-O-acetyl-1-O-benzoyl-2-bromo-2-deoxy- $\alpha$ -D-glucopyranose ( $\alpha$ -17)*. To tri-*O*-acetyl-1-*O*-benzoyl-2-bromo-2-deoxy- $\beta$ -D-glucopyranose<sup>9,10</sup> ( $\beta$ -17) (500 mg) in chloroform (5 ml) was added boron trifluoride etherate (1 ml) and the mixture was kept at room temperature for 24 h. It was then washed with aqueous sodium hydrogen carbonate, dried and evaporated. The residue (458 mg) was purified by preparative TLC using benzene-chloroform (1:1) as eluent. The first fraction gave 168 mg (34 %) of  $\alpha$ -17, which was crystallized from ethanol, m.p. 107–111 °C (reported<sup>9</sup> m.p. 112–113 °C). An NMR spectrum was identical with that described.<sup>9</sup> A second fraction gave 66 mg (13 %) of unchanged  $\beta$ -17.

*Hydrogenolysis of  $\beta$ -17* (500 mg) was performed as described above. The product (405 mg) was separated into two fractions by preparative TLC using 4 elutions with ethyl acetate-pentane (1:4). The fast-moving fraction gave 167 mg (40 %) of tri-*O*-acetyl-1-*O*-benzoyl-2-deoxy- $\beta$ -D-arabino-hexopyranose ( $\beta$ -18), m.p. 85–87 °C. Recrystallization from ether-pentane gave a product with m.p. 86–87 °C,  $[\alpha]_D^{20} - 7.04^\circ$  (*c* 3.4, CHCl<sub>3</sub>). Anal. C<sub>18</sub>H<sub>22</sub>O<sub>5</sub>: C, H. <sup>1</sup>H NMR:  $\delta$  6.52 (H1), 2.0–2.6 (H2), 5.0–5.4 (H3, H4), 3.89 (H5), 4.26 (H6), 4.16 (H6');  $J_{12e} = 2.5$  Hz,  $J_{12a} = 9.5$ ,  $J_{56} = 4.8$ ,  $J_{56'} = 2.5$ .

The next fraction gave 92 mg (31 %) of tri-*O*-acetyl-1,5-anhydro-2-deoxy-D-glucitol as seen from an NMR spectrum. It was not identified further.

*Hydrogenolysis of  $\alpha$ -17* (190 mg) gave 130 mg of crude product. Preparative TLC (ethyl acetate-pentane, 2:1) yielded 63 mg (40 %) of tri-*O*-acetyl-1-*O*-benzoyl-2-deoxy- $\alpha$ -D-arabino-hexopyranose ( $\alpha$ -18), crystallized from ether, m.p. 115.5–117 °C,  $[\alpha]_D^{20} + 92.3^\circ$  (*c* 1.2, CHCl<sub>3</sub>). Anal. C<sub>19</sub>H<sub>22</sub>O<sub>6</sub>: C, H. <sup>1</sup>H NMR:  $\delta$  6.52 (H1), 2.49 (H2e), 2.11 (H2a), 5.40 (H3), 5.16 (H4), 4.0–4.6 (H5, H6);  $J_{12e} = 1.4$  Hz,  $J_{12a} = 3.4$ ,  $J_{2e3} = 5.4$ ,  $J_{2a3} = 11.4$ ,  $J_{34} = J_{45} = 9.6$ .

Microanalyses were performed by Novo analytical laboratory.

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