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A NEW SYNTHETIC ROUTE TO 2-AMINO-2-DEOXY-D-MANNOSE DERIVATIVES FROM 3,4:5,6-DI-*O*-ISOPROPYLIDENE-*aldehydo*-D-GLUCOSE DIBENZYL ACETAL*

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ABSTRACT

When treated with 2,2-dibenzyloxypropane in 1,4-dioxane solution in the presence of *p*-toluenesulfonic acid, D-glucose gave a mixture of 3,4:5,6-di-*O*-isopropylidene-*aldehydo*-D-glucose dibenzyl acetal (**1**) and 2,3:5,6-di-*O*-isopropylidene-*aldehydo*-D-glucose dibenzyl acetal in good yield. The conversion of **1** into 2-amino-2-deoxy-D-mannose derivatives was accomplished, stepwise, *via* the nucleophilic displacement reaction of the trifluoromethanesulfonic ester of **1** with sodium azide.

INTRODUCTION

2,2-Dibenzyloxypropane[2] in *N,N*-dimethylformamide, as a reagent for acetal exchange, has been successfully introduced[3–5] into synthetic studies of biologically active carbohydrates. When this reagent was applied[6,7] to some aldohexoses, in the absence of *N,N*-dimethylformamide, or in 1,4-dioxane, acyclic 1,1-dibenzyl acetals were mainly formed, and it has been emphasized[7] that these acetal derivatives might be potentially useful as synthetic intermediates, especially for the extension of carbon chains.

We here describe the acetalation of D-glucose with 2,2-dibenzyloxypropane reagent, and indicate a new synthetic route to 2-amino-2-deoxy-D-mannose derivatives from the product obtained.

RESULTS AND DISCUSSION

Treatment of D-glucose with 2,2-dibenzyloxypropane in dry 1,4-dioxane in the presence of *p*-toluenesulfonic acid at 65°, gave, in good yield, a mixture of 3,4:5,6-di-*O*-isopropylidene-*aldehydo*-D-glucose dibenzyl acetal (**1**) and 2,3:5,6-di-*O*-isopropylidene-*aldehydo*-D-glucose dibenzyl acetal (**2**) that showed a single spot in t.l.c. In order to separate **1** from **2**, the crude mixture was acetylated, to give a

*The Behavior of Some Aldoses with Acetal-Exchange Reagents, Part XIII, For Part XII, see ref. 1.

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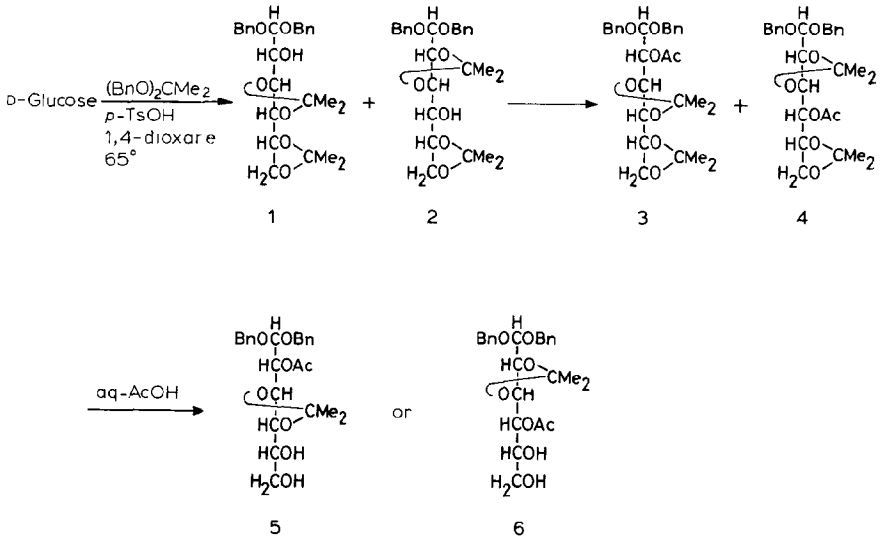
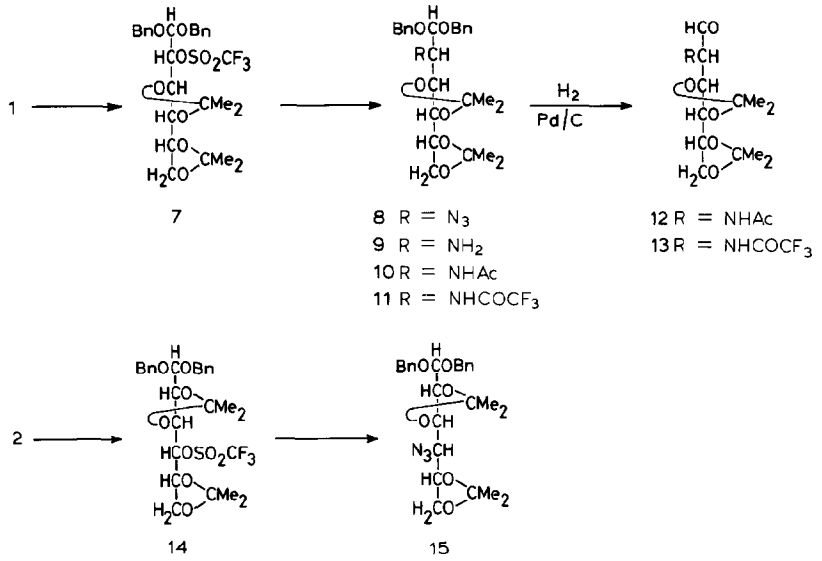


mixture of **3** and **4**, which was then treated with 70% aqueous acetic acid at 45°. T.l.c. showed the formation of partially *O*-deisopropylidenated derivatives **5** and **6** in the ratio of ~1:1, which were chromatographed on a column of silica gel: compound **6** was eluted slightly faster than **5**. The isolated yield from D-glucose was 32% for **5**, and 31% for **6**. These compounds were reconverted, by 5,6-*O*-isopropylidenation and deacetylation, into **1** and **2**, respectively, and then employed for the following reactions.

For the preparation of 2-amino-2-deoxy-D-mannose derivatives from compound **1**, the use of nucleophilic displacement of a sulfonyloxy group by an azide group appeared the most suitable. However, the conventional displacement reactions of secondary sulfonic esters often requires forcing and, sometimes destructive, conditions. This problem has been solved by the use of a trifluoromethylsulfonyloxy group as an exceedingly good leaving-group[8].

Thus, ester **7** was prepared by adding dropwise a solution of trifluoromethanesulfonic anhydride in dichloromethane to a cooled solution of **1** in pyridine. The nucleophilic displacement of the sulfonyloxy group in **7** by sodium azide[9,10] was conducted in *N*,*N*-dimethylformamide at room temperature, to give **8** in good yield. Raney nickel reduction of the azide group in **8** afforded quantitatively the amino derivative **9**, which was treated with acetic anhydride or trifluoroacetic anhydride. The structure of the resulting 2-amino-2-deoxy-D-mannose derivatives **10** and **11** was carefully characterized in comparison with those of the corresponding 2-amino-2-deoxy-D-glucose derivatives[7]. 2-Acetamido-2-deoxy-3,4:5,6-di-*O*-isopropylidene-*aldehydo*-D-mannose[11] (**12**) and 2-deoxy-3,4:5,6-di-*O*-isopropylidene-2-(trifluoroacetamido)-*aldehydo*-D-mannose (**13**) were readily prepared from **10** and **11**, respectively, by a procedure described[7].

The hydroxyl group in compound **2** was also trifluoromethylsulfonylated, to



give **14**, which was treated with sodium azide as just described, to give **15**. The nucleophilic displacement at C-4 was, unexpectedly, complete within 2 h at room temperature, in contrast to that at C-2, which required 36 h under the same conditions. This synthetic route may, therefore, also be useful for the preparation of a variety of 4-amino sugars.

EXPERIMENTAL

General methods. — See ref. 7.

Acetalation of D-*glucose with 2,2-dibenzyloxypropane.* — A suspension of D-glucose (1 g) in dry 1,4-dioxane (5 mL) and 2,2-dibenzyloxypropane (6 mL) was stirred at 65°, while *p*-toluenesulfonic acid (150 mg) was added; stirring was continued for 1.5 h at 65°. The mixture was cooled, and freed of the acid by adding an excess of sodium hydrogencarbonate; this deacidification must be complete, otherwise decomposition of the product occurs during subsequent evaporation. The suspension was filtered, and the solid washed with methanol. The filtrate and washings were combined, and evaporated at 45°. Most of the benzyl alcohol was removed by evaporation at 100°, to give a brown syrup which was, without purification, acetylated with acetic anhydride (3.5 mL) and pyridine (15 mL). Methanol was added to decompose the excess of acetic anhydride, and the mixture was evaporated to a syrup that contained 2-*O*-acetyl-3,4:5,6-di-*O*-isopropylidene-*aldehydo*-D-glucose dibenzyl acetal (**3**) and 4-*O*-acetyl-2,3:5,6-di-*O*-isopropylidene-*aldehydo*-D-glucose dibenzyl acetal (**4**) as the major products. The syrup was dissolved in 70% aqueous acetic acid (70 mL) and kept for 2–3 h at 45°, to hydrolyze the 5,6-*O*-isopropylidene group selectively. The mixture was evaporated at 45°, and the residue was

chromatographed on a column of silica gel with (*a*) chloroform, (*b*) 400:1, (*c*) 200:1, and (*d*) 100:1 chloroform–methanol. Eluants *b* and *c* gave 4-*O*-acetyl-2,3-*O*-isopropylidene-*aldehydo*-D-glucose dibenzyl acetal (**6**; 830 mg; 32% from D-glucose), and eluant *d* yielded 2-*O*-acetyl-3,4-*O*-isopropylidene-*aldehydo*-D-glucose dibenzyl acetal (**5**: 800 mg; 31% from D-glucose). Compounds **5** and **6** were each reconverted, by 5,6-*O*-isopropylidenation and deacetylation, into 3,4:5,6-di-*O*-isopropylidene-*aldehydo*-D-glucose dibenzyl acetal (**1**) and its 2,3:5,6-di-*O*-isopropylidene isomer (**2**), respectively.

3,4:5,6-Di-O-*isopropylidene*-aldehydo-D-*glucose dibenzyl acetal* (**1**). — To a solution of **5** (1.93 g) and 2,2-dimethoxypropane (2 mL) in dry 1,4-dioxane (20 mL) was added a trace of *p*-toluenesulfonic acid. The mixture was stirred for 2 h at room temperature, and treated with Amberlite IRA-410 (OH^-) ion-exchange resin to remove the acid. The resin was filtered off, and the filtrate evaporated to syrupy **3**, which was deacetylated with sodium methoxide in methanol. The desired product **1** (1.8 g, 93%), purified by chromatography on a column of silica gel, was a syrup; $[\alpha]_D$ +21.5° (*c* 1, chloroform); ν_{max}^{film} 3460 (OH), 3100–3000, 2000–1650, 730 and 690 (Ph), 1150–950 (ether), and 890 and 850 cm^{-1} (Me_2C); n.m.r. data: δ 1.31 and 1.36 (2 s, 6 H, Me_2C), 1.38 (s, 6 H, Me_2C), 2.23 (broad s, 1 H, OH), 3.7–4.3 (m, 6 H, H-2–6), 4.5–4.85 (m, 5 H, H-1 and 2 CH_2Ph), and 7.15–7.4 (m, 10 H, 2 Ph).

Anal. Calc. for $C_{26}H_{34}O_7$: C, 68.10; H, 7.47. Found: C, 68.26; H, 7.42.

2,3:5,6-Di-O-*isopropylidene*-aldehydo-D-*glucose dibenzyl acetal* (**2**). — The reconversion of **6** into **2** was performed as just described for the preparation of **1** from **5**. Compound **2** was a syrup, $[\alpha]_D$ +5.8° (*c* 1, chloroform); ν_{max}^{film} 3460 (OH), 3100–3000, 2000–1600, 730 and 690 (Ph), 1150–1000 (ether), and 880 and 850 cm^{-1} (Me_2C);,n.m.r. data: δ 1.31, 1.38 and 1.42 (3 s, 12 H, 2 Me_2C), 2.22 (broad s, 1 H, OH), and 7.15–7.4 (m, 10 H, 2 Ph).

Anal. Calc. for $C_{26}H_{34}O_7$: C, 68.10; H, 7.47. Found: C, 68.40; H, 7.53.

2-O-Acetyl-3,4:5,6-di-O-*isopropylidene*-aldehydo-D-*glucose dibenzyl acetal* (**3**). — Isopropylidenation of **5** and chromatographic purification gave compound **3** as a syrup, $[\alpha]_D$ +10.7° (*c* 1.4, chloroform); ν_{max}^{film} 3080–3000, 2000–1600, 730 and 690 (Ph), 1750 and 1220 (ester), 1150–1000 (ether), and 840 cm^{-1} (Me_2C); n.m.r. data: δ 1.3, 1.36 and 1.38 (3 s, 12 H, 2 Me_2C), 2.03 (s, 3 H, AcO), 4.35 (dd, $J_{2,3}$ 1.8, $J_{3,4}$ 7.5 Hz, H-3), 4.45–4.85 (m, 4 H, 2 $PhCH_2$), 4.93 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1), 5.34 (dd, 1 H, H-2), and 7.25 and 7.28 (2 s, 10 H, 2 Ph).

Anal. Calc for $C_{28}H_{36}O_8$: C, 67.18; H, 7.25. Found: C, 67.39; H, 7.12.

4-O-Acetyl-2,3:5,6-di-O-*isopropylidene*-aldehydo-D-*glucose dibenzyl acetal* (**4**). — Isopropylidenation of **6** as just described gave **4** as a syrup, $[\alpha]_D$ +5.1° (*c* 0.75, chloroform); ν_{max}^{film} 3100–3000, 730 and 690 (Ph), 1750 and 1230 (ester), 1150–1020 (ether), and 850 cm^{-1} (Me_2C); n.m.r. data: δ 1.3 and 1.38 (2 s, 12 H, 2 Me_2C), 2.1 (s, 3 H, AcO), 5.25 (dd, 1 H, *J* 2.2, 5.8 Hz, H-4), and 7.26 (s, 10 H, 2 Ph).

Anal. Calc. for $C_{28}H_{36}O_8$: C, 67.18; H, 7.25. Found: C, 67.36; H, 7.37.

2-O-Acetyl-3,4-O-*isopropylidene*-aldehydo-D-*glucose dibenzyl acetal* (**5**). —

The procedure for the preparation of **5** was described in the section on *acetalation of* D-*glucose with 2,2-dibenzyloxypropane.* Compound **5** was a syrup, $[\alpha]_D$ +21.2° (*c* 1, chloroform); ν_{max}^{film} 3400 (OH), 3060–3000, 2000–1600, 730 and 690 (Ph), 1740 and 1230 (ester), and 870 cm^{-1} (Me_2C); n.m.r. data: δ 1.36 (s, 6 H, 2 Me_2C), 2.03 (s, 3 H, AcO), 2.93 (broad s, 2 H, 2 OH), 3.5–3.9 (m, 4 H, H-4–6), 4.4 (m, 1 H, H-3), 4.93 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1), 5.29 (dd, 1 H, $J_{2,3}$ 2 Hz, H-2), and 7.23 and 7.26 (2 s, 10 H, 2 Ph).

Anal. Calc. for $C_{25}H_{32}O_8$: C, 65.20; H, 7.00. Found: C, 65.38; H, 6.92.

*4-*O*-Acetyl-2,3-*O*-isopropylidene-*aldehydo-D-*glucose dibenzyl acetal* (**6**). — Compound **6**, purified by column chromatography as described in a previous section, was a syrup, $[\alpha]_D$ +12.2° (*c* 1, chloroform); ν_{max}^{film} 3400 (OH), 3060–3000, 2000–1600, 730 and 690 (Ph), 1740 and 1230 (ester), and 860 cm^{-1} (Me_2C); n.m.r. data: δ 1.38 and 1.40 (2 s, 6 H, Me_2C), 2.1 (s, 3 H, AcO), 3.05 (broad s, 2 H, 2 OH), 4.97 (dd, 1 H, *J* 7.4, 2.0 Hz, H-4), and 7.25 and 7.26 (2 s, 10 H, 2 Ph).

Anal. Calc. for $C_{25}H_{32}O_8$: C, 65.20; H, 7.00. Found: C, 64.95; H, 6.88.

*3,4:5,6-Di-*O*-isopropylidene-2-*O*-(trifluoromethylsulfonyl)-*aldehydo-D-*glucose dibenzyl acetal* (**7**). — A solution of **1** (1 g) in dry pyridine (5 mL) was stirred at −15°, while trifluoromethanesulfonic anhydride (0.8 mL) in dichloromethane (2 mL) was added dropwise, and the mixture was stirred for 1.5 h at 0°. Ice and sodium hydrogencarbonate were added, the mixture was extracted with chloroform, and the extract washed successively with water, ice-cold M hydrochloric acid, M sodium carbonate, and water, dried, and evaporated, to give syrupy **7** (1.2 g, 93%) as a single, almost pure sample, $[\alpha]_D$ +19.7° (*c* 0.7, chloroform); ν_{max}^{film} 3060–3000, 2000–1700, 730 and 690 (Ph), 1400 (SO_3), and 880 and 840 cm^{-1} (Me_2C); n.m.r. data: δ 1.3 (s, 3 H, 0.5 Me_2C), 1.36 (s, 9 H, 1.5 Me_2C), 4.33 (dd, 1 H, $J_{2,3}$ 1.2, $J_{3,4}$ 7.2 Hz, H-3), 5.0 (d, 1 H, $J_{1,2}$ 7.3 Hz, H-1), 5.12 (dd, 1 H, H-2), and 7.26 and 7.3 (2 s, 10 H, 2 Ph). Compound **7** was employed, without further purification, for the next reaction.

*2-Azido-2-deoxy-3,4:5,6-di-*O*-isopropylidene-*aldehydo-D-*mannose dibenzyl acetal* (**8**). — To a solution of **7** (1.2 g) in dry *N,N*-dimethylformamide (5 mL) was added sodium azide (790 mg). The mixture was stirred for 36 h at room temperature, and then the solvent was evaporated at 60°. The syrupy residue was taken up in chloroform, and the solution was washed with water, dried, and evaporated. The syrup obtained was chromatographed on a column of silica gel with chloroform, to give **8** (600 mg, 61% from **1**) as a syrup, $[\alpha]_D$ +7.8° (*c* 1, chloroform); ν_{max}^{film} 3060–3000, 2000–1700, 730 and 690 (Ph), 2100 (N_3), and 870 and 840 cm^{-1} (Me_2C); n.m.r. data: δ 1.30, 1.33, and 1.38 (3 s, 12 H, 2 Me_2C), 3.85 (dd, 1 H, $J_{1,2}$ 6.4, $J_{2,3}$ 3.8 Hz, H-2), 4.45–4.8 (m, 4 H, 2 PhCH_2), 4.92 (d, 1 H, H-1), and 7.2–7.4 (m, 10 H, 2 Ph).

Anal. Calc. for $C_{26}H_{33}N_3O_6$: C, 64.58; H, 6.88; N, 8.69. Found: C, 64.46; H, 6.86; N, 8.58.

*2-Acetamido-2-deoxy-3,4:5,6-di-*O*-isopropylidene-*aldehydo-D-*mannose dibenzyl acetal* (**10**). — A solution of **8** (900 mg) in methanol was stirred with Raney-

Ni (4 mL in ethanol) for 15 h at room temperature. The catalyst was filtered off, and the filtrate evaporated, giving syrupy **9** which was acetylated with acetic anhydride (1 mL) and pyridine (2 mL). Methanol was added, and then the mixture was evaporated to a syrup that was chromatographed on a column of silica gel with (*a*) 400:1 and (*b*) 200:1 chloroform–methanol. Eluant *b* gave compound **10** as a syrup in almost quantitative yield; $[\alpha]_D$ +20.7° (*c* 1.2, chloroform); ν_{max}^{film} 3260 (NH), 3060–3000, 730 and 690 (Ph), 1650 and 1520 (amide), and 840 cm^{-1} (Me_2C); n.m.r. data: δ 1.3–1.4 (~s, 12 H, 2 Me_2C), 1.98 (s, 3 H, AcN), 3.75–4.2 (m, 5 H, H-3–6), 4.45 (m, 1 H, H-2), 4.48–4.88 (m, 4 H, 2 PhCH_2), 4.91 (d, 1 H, $J_{1,2}$ 2.1 Hz, H-1), 5.88 (d, 1 H, $J_{2,NH}$ 9.6 Hz, NH), and 7.25–7.4 (~s, 10 H, 2 Ph).

Anal. Calc. for $C_{28}H_{37}NO_7$: C, 67.31; H, 7.47; N, 2.80. Found: C, 67.19; H, 7.51; N, 2.65.

*2-Deoxy-3,4:5,6-di-*O*-isopropylidene-2-(trifluoroacetamido)-*aldehydo-D-*mannose dibenzyl acetal* (**11**). — A solution of **9** (780 mg) in dry pyridine (3 mL) was stirred at 0°, while trifluoroacetic anhydride (1.3 g) in dichloromethane (2 mL) was added, and stirring was continued overnight at 0°. Methanol was added, and then the mixture was evaporated to a syrup which was chromatographed on a column of silica gel with chloroform, to give compound **11** as a syrup, $[\alpha]_D$ +19.7° (*c* 0.7, chloroform); ν_{max}^{film} 3400 and 3280 (NH), 3060–3000, 2000–1600, 730 and 690 (Ph), 1720 and 1530 (amide), and 880 and 840 cm^{-1} (Me_2C); n.m.r. data: δ 1.3 and 1.32 (2 s, 12 H, 2 Me_2C), 3.6–4.23 (m, 5 H, H-3–6), 4.38 (~dd, 1 H, $J_{2,3}$ ~0, H-2), 4.5–4.9 (m, 4 H, 2 PhCH_2), 4.96 (d, 1 H, $J_{1,2}$ 2.2 Hz, H-1), 6.76 (d, 1 H, $J_{2,NH}$ 9 Hz, NH), and 7.32 and 7.33 (2 s, 10 H, 2 Ph).

Anal. Calc. for $C_{28}H_{34}F_3NO_7$: C, 60.75; H, 6.19; N, 2.53. Found: C, 60.51; H, 6.06; N, 2.51.

*2-Acetamido-2-deoxy-3,4:5,6-di-*O*-isopropylidene-*aldehydo-D-*mannose* (**12**). — Compound **10** (340 mg) in 2-propanol was hydrogenolyzed in the presence of 10% palladium–carbon catalyst (190 mg) to give **12** (quantitative) as a syrup, $[\alpha]_D$ +67° (*c* 0.6, chloroform) {lit.[11] $[\alpha]_D$ +39° (*c* 6.59, chloroform)}; ν_{max}^{film} 3320 (NH), 1740 (CHO), 1670 and 1530 (amide), and 850 cm^{-1} Me_2C); n.m.r. data: δ 1.2–1.5 (m, 12 H, 2 Me_2C), 2.2 (s, 3 H, AcN), 4.4 (dd, 1 H, $J_{2,3}$ 7, $J_{2,NH}$ 8 Hz, H-2), 6.3 (d, 1 H, NH), and 9.3 (s, 1 H, CHO).

Anal. Calc. for $C_{14}H_{23}NO_6$: C, 55.80; H, 7.69; N, 4.65. Found: C, 56.31; H, 7.48; N, 4.39.

*2-Deoxy-3,4:5,6-di-*O*-isopropylidene-2-(trifluoroacetamido)-*aldehydo-D-*mannose* (**13**). — Hydrogenolysis of **11** (200 mg) in 2-propanol as just described gave **13** (140 mg) as a syrup, $[\alpha]_D$ +12° (*c* 1, chloroform); ν_{max}^{film} 3380 and 3280 (NH), 1740 (CHO), 1720 and 1540 (amide), and 850 cm^{-1} Me_2C); n.m.r. data: δ 1.3–1.5 (m, 12 H, 2 Me_2C), 3.7–4.4 (m, 5 H, H-3–6), 4.7 (dd, 1 H, $J_{2,3}$ 6, $J_{2,NH}$ 6.4 Hz, H-2), 7.45 (broad d, 1 H, NH), and 9.69 (s, 1 H, CHO).

Anal. Calc. for $C_{14}H_{20}F_3NO_6$: C, 47.32; H, 5.67; N, 3.94. Found: C, 47.76; H, 5.36; N, 4.25.

*2,3:5,6-Di-*O*-isopropylidene-4-*O*-(trifluoromethylsulfonyl)-*aldehydo-D-*glu-*

cose dibenzyl acetal (**14**). — To a stirred solution of **2** (250 mg) in dry pyridine (2 mL) at −15° was added, dropwise, trifluoromethanesulfonic anhydride (0.2 mL) in dichloromethane (1 mL). The mixture was stirred for 1.5 h at 0°, and processed as described for **7**, to afford compound **14** as a syrup in almost quantitative yield; $[\alpha]_D$ +3.7° (*c* 0.9, chloroform); ν_{max}^{film} 1400 cm^{-1} (SO_3); n.m.r. data: δ 1.26 and 1.37 (2 s, 12 H, 2 Me_2C), 4.77 (d, 1 H, *J* 4 Hz, H-1), 5.2 (dd, 1 H, *J* 3.8 and 2.0 Hz, H-4), and 7.25 and 7.27 (2 s, 10 H, 2 Ph).

Anal. Calc. for $C_{27}H_{33}F_3O_9S$: C, 54.91; H, 5.63. Found: C, 55.32; H, 5.40.

*4-Azido-4-deoxy-2,3:5,6-di-*O*-isopropylidene*-aldehydo-D-*galactose dibenzyl acetal* (**15**). — To a solution of **14** (320 mg) in *N,N*-dimethylformamide (2 mL) was added sodium azide (260 mg). The mixture was stirred for 1 h at room temperature, and evaporated at 60°; the syrupy residue was taken up in chloroform, and the solution washed with water, dried, and evaporated. The product (170 mg; 65%), purified by chromatography, was a syrup; $[\alpha]_D$ −27.6° (*c* 0.51, chloroform); ν_{max}^{film} 3060–3000, 2000–1600, 730 and 690 (Ph), 2100 (N_3), and 850 cm^{-1} (Me_2C).

Anal. Calc. for $C_{26}H_{33}N_3O_6$: C, 64.58; H, 6.88; N, 8.69. Found: C, 64.25; H, 7.01; N, 8.63.

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