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SYNTHESES OF THE *p*-TRIFLUOROACETAMIDOPHENYL GLYCOSIDES OF 2-ACETAMIDO-2-DEOXY-4-*O*-α-D-GLUCOPYRANOSYL-β-D-GLUCOPYRANOSE AND 2-ACETAMIDO-2-DEOXY-6-*O*-α-D-GLUCOPYRANOSYL-β-D-GLUCOPYRANOSE*

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ABSTRACT

The *p*-trifluoroacetamidophenyl glycosides of 2-acetamido-2-deoxy-4-*O*-α-D-glucopyranosyl-β-D-glucopyranose and its (1→6)-α-linked isomer, both related to *Shigella flexneri* O-antigens, have been synthesised. The (1→4)-linked derivative was synthesised from maltose, the key step being azidonitration of maltal hexa-acetate. The (1→6)-linked derivative was synthesised from its component monosaccharides, using the halide-ion catalysed glycosidation procedure.

INTRODUCTION

2-Acetamido-2-deoxy-4-*O*-α-D-glucopyranosyl-β-D-glucopyranose and 2-acetamido-2-deoxy-6-*O*-α-D-glucopyranosyl-β-D-glucopyranose have been identified[1] as immunological determinants in *Shigella flexneri* O-antigens, responsible for O-factors I and IV, respectively. We now report syntheses of the *p*-trifluoroacetamidophenyl glycosides **8** and **13** of these disaccharides, which are suitable for attachment[2] to larger molecules, to form conjugates that can be used in immunological experiments.

RESULTS AND DISCUSSION

Treatment of maltal hexa-acetate[3] with ceric ammonium nitrate and sodium azide in acetonitrile[4] gave three 2-azido-1-nitrates, having the α-D-*gluco* (**1**, 22% yield), β-D-*gluco* (**2**, 25%), and α-D-*manno* (**3**, 26%) configurations. This result accords with the observation[4] that azidonitration of glycals tends to give mainly 1,2-*trans* addition products. The unwanted *manno* compound **3** could be removed from the crude reaction mixture by crystallisation, and the remaining mixture of **1** and **2** was treated with lithium bromide in acetonitrile to give the 2-azidobromide **4**.

*Disaccharides Related to *Shigella flexneri* O-Antigens, Part I.

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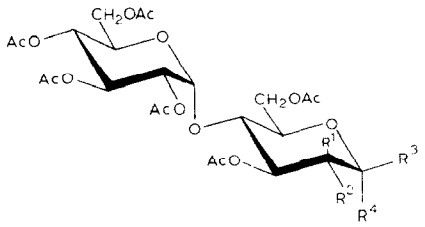
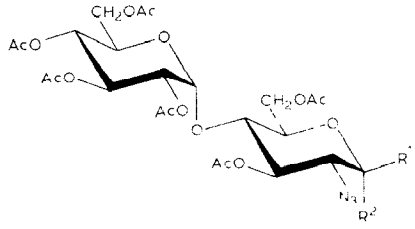
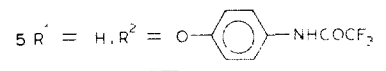
Treatment of **4** with sodium *p*-trifluoroacetamidophenolate in dimethyl sulfoxide caused dehydrobromination, and the reaction with *p*-trifluoroacetamidophenol and silver triflate in dichloromethane or nitromethane gave mainly the α-derivative **5**; however, with *p*-trifluoroacetamidophenol and silver silicate[5] in nitromethane, 36% of the desired *p*-trifluoroacetamidophenyl 3,6-di-*O*-acetyl-2-azido-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-β-D-glucopyranoside (**6**) was formed. These findings accord with the observation[6] that insoluble catalysts are to be preferred for inversion-type glycosidations with 2-azidobromides.



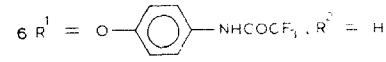
1 R^1 = H, R^2 = N_3, R^3 = H, R^4 = ONO_2
2 R^1 = H, R^2 = N_3, R^3 = ONO_2, R^4 = H
3 R^1 = N_3, R^2 = H, R^3 = H, R^4 = ONO_2



4 R^1 = H, R^2 = Br

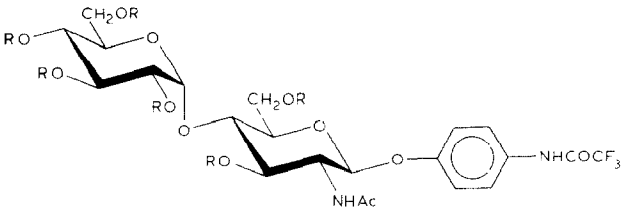


5 R^1 = H, R^2 = O—C$_6$H$_4$—NHCOCF$_3$



6 R^1 = O—C$_6$H$_4$—NHCOCF$_3$, R^2 = H

Catalytic hydrogenation of **6** followed by *N*-acetylation afforded 48% of compound **7**, Zemplén deacetylation of which gave 59% of the target molecule *p*-trifluoroacetamidophenyl 2-acetamido-2-deoxy-4-*O*-α-D-glucopyranosyl-β-D-glucopyranoside (**8**). Sugar analysis[7] of **8** revealed glucose and 2-acetamido-2-deoxyglucose, in a 1:1 ratio, as the only sugars.



7 R = Ac
8 R = H

For the synthesis of **13**, *p*-nitrophenyl 2-acetamido-2-deoxy-β-D-glucopyranoside[8] was tritylated and then benzoylated to give 78% of **9**. Catalytic hydrogenation of **9** followed by *N*-trifluoroacetylation gave 55% of **10**. Detritylation with aqueous (80%) acetic acid then gave 69% of *p*-trifluoroacetamidophenyl 2-acetamido-3,4-di-*O*-benzoyl-2-deoxy-β-D-glucopyranoside (**11**). The reaction of **11** with 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl bromide[9] under conditions of halide-ion catalysis[10], using 3A molecular sieves[11] as acid acceptor, gave 81% of

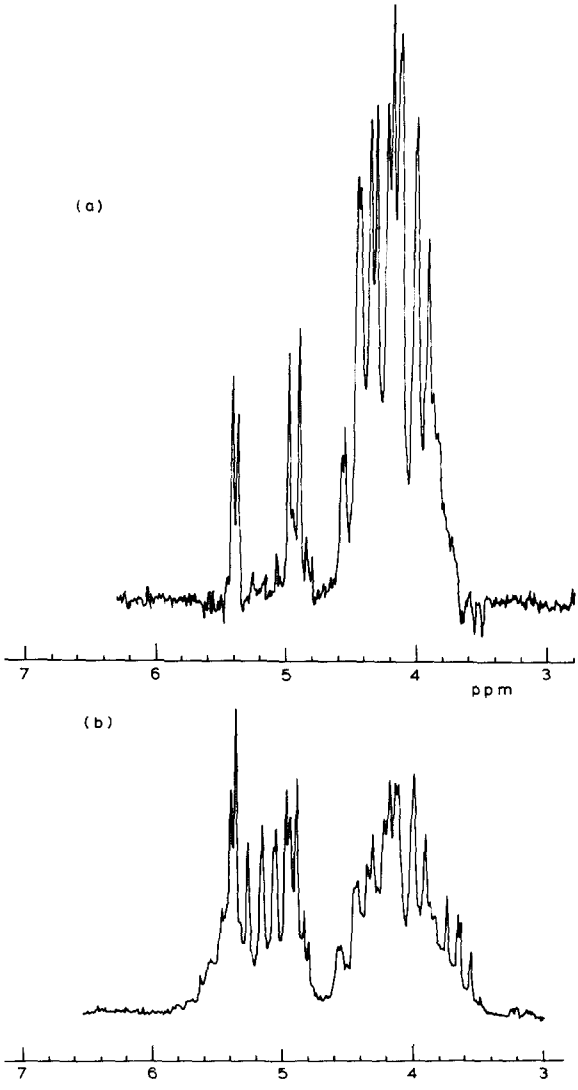
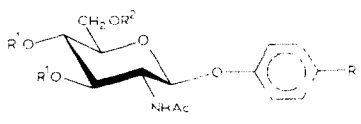
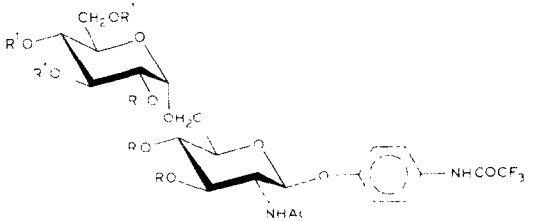


Fig. 1. ^{1}H-N.m.r. spectra ($CDCl_3$) of *p*-trifluoroacetamidophenyl 3,6-di-*O*-acetyl-2-azido-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-β-D-glucopyranoside (**6**): (*a*) normal spectrum; (*b*) partially relaxed spectrum obtained by applying the pulse sequence (180°-t-90°-delay), where the delay was 4.5 s and t was 0.3 s.

12, catalytic hydrogenation of which, followed by Zemplén deacetylation, gave 88% of the target molecule *p*-trifluoroacetamidophenyl 2-acetamido-2-deoxy-6-*O*-α-D-glucopyranosyl-β-D-glucopyranoside (**13**).



9 R = NO_2, R^1 = Bz, R^2 = Tr
10 R = $NHCOCF_3$, R^1 = Bz, R^2 = Tr
11 R = $NHCOCF_3$, R^1 = Bz, R^2 = H



12 R = Bz, R^1 = Bzl
13 R = R^1 = H

In the 100-MHz, ^{1}H-n.m.r. spectra of the protected intermediates in the above syntheses, signals from the anomeric protons were often difficult to assign because of overlapping signals from ring protons attached to acetoxylated carbons. However, such assignments were possible from partially relaxed spectra[12]. Fig. 1 shows the normal (*a*) and a partially relaxed (*b*) spectrum of **6**. The reason for the simplification achieved in (*b*) is that anomeric protons in acetylated di- and oligosaccharides have considerably shorter T_1 relaxation times than ring protons linked to acetoxylated carbons (see, for example, ref. 13).

EXPERIMENTAL

General methods. — Melting points are corrected. Concentrations were performed at reduced pressure (1–2 kPa) at <40° (bath). Optical rotations were recorded for solutions in chloroform, unless otherwise stated, at 22–24° with a Perkin–Elmer 241 polarimeter. N.m.r. spectra (100 MHz for ^{1}H, and 25 MHz for ^{13}C) were recorded in the Fourier-transform mode with a JEOL JNM FX-100 instrument. Chemical shifts are given in p.p.m. downfield from those of internal ($CDCl_3$ solutions) or external (D_2O solutions) Me_4Si. N.m.r. spectra for all new compounds accorded with the postulated structures, and only selected data are reported. T.l.c. was performed on silica gel F_{254} (Merck) with detection by u.v. light and/or charring with sulfuric acid. Column chromatography was performed on silica gel 60 (0.04–0.063 mm, Merck) in the flash mode[14]. The loading was in the range 1/25–1/100. Distilled solvents were used for elution. Organic solutions were dried over anhydrous magnesium sulfate. Molecular sieves (3A, Union Carbide) were desiccated *in vacuo* at 300° overnight and ground immediately before use.

3,6-Di-O-acetyl-2-azido-2-deoxy-4-O-(2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl)-α- and -β-D-glucopyranosyl nitrate (**1** *and* **2**) *and 3,6-di-O-acetyl-2-azido-2-deoxy-4-O-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-α-D-mannopyranosyl nitrate* (**3**). — A solution of 3,6-di-*O*-acetyl-1,5-anhydro-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-D-*arabino*-hex-1-enitol[3] (maltal hexa-acetate, 6.80 g) in dry acetonitrile (61 mL) was stirred with a mixture of ceric ammonium nitrate (18.6 g) and sodium azide (1.38 g) under nitrogen at −20° for 16 h. The mixture was then partitioned between ether and water (0°), and the or-

ganic layer was separated, dried, and concentrated. The syrupy residue was subjected to column chromatography. Elution with toluene–ethyl acetate (7:2) gave, first, a 1:1 mixture (^{13}C-n.m.r. data) of **2** and **3** (4.1 g, 51%). Crystallisation from ethyl acetate–hexane gave **3** (2.1 g, 26%), m.p. 155–158°, $[\alpha]_D$ +114° (*c* 0.5). N.m.r. data ($CDCl_3$, 25°): ^{13}C, δ 20.61 (acetyl Me), 58.24 (C-2), 61.60, 62.43 (C-6,6'), 68.08, 68.77, 69.45, 70.37, 70.38, 71.50, 73.06 (C-3,4,5 and C-2',3',4',5'), 96.11 (C-1', $J_{C-1',H-1'}$173 Hz), 97.33 (C-1, $J_{C-1,H-1}$ 182 Hz), and 169.41–170.29 (C=O); ^{1}H, δ 6.17 (d, $J_{1,2}$ 2.9 Hz, H-1). The J_{C-H} values are indicative[16] of α configurations.

Anal. Calc. for $C_{24}H_{32}N_4O_{18}$: C, 43.4; H, 4.85. Found: C, 43.4; H, 4.89.

Concentration of the mother liquor from the crystallisation of **3** gave **2** (2.0 g, 25%) as a syrup. The spectral data indicated a purity of at least 90%. N.m.r. data ($CDCl_3$, 25°): ^{13}C, δ 95.77 (C-1') and 97.65 (C-1); ^{1}H, δ 3.54 (q, $J_{1,2}$ 8.1, $J_{2,3}$ 9.5 Hz, H-2) and 5.66 (d, $J_{1,2}$ 8.1 Hz, H-1).

The second fraction eluted from the column contained reasonably pure (>90%) **1** (1.8 g, 22%) as a colorless syrup. ^{13}C-N.m.r. data ($CDCl_3$, 25°): δ 20.52–20.81 (acetyl Me), 61.36, 61.51, 62.14 (C-2,6,6'), 68.04, 68.81, 69.21, 70.08, 70.86, 72.03, 72.28 (C-3,4,5, and C-2',3',4',5'), 95.91 (C-1'), 96.64 (C-1), and 169.41–170.68 (C=O).

*3,6-Di-*O*-acetyl-2-azido-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-*D*-glucopyranosyl)-α-*D*-glucopyranosyl bromide* (**4**). — A crude mixture (290 mg) of **1**–**3**, prepared as described above, was freed from **3** by crystallisation from ethyl acetate–hexane. The residual, syrupy mixture (200 mg) of **1** and **2** was dissolved in acetonitrile (5 mL) containing molecular sieves, and lithium bromide (190 mg) was added. After stirring at room temperature for 2 h, the mixture was diluted with ether, washed twice with water (0°), dried, and concentrated. The residue (204 mg) contained **4** in a reasonably pure (90%) state, as indicated by its n.m.r. spectra. N.m.r. data ($CDCl_3$, 25°): ^{13}C, δ 20.49–20.78 (acetyl Me), 61.33, 61.87, 62.94 (C-2,6,6'), 67.91, 68.69, 69.13, 69.96, 72.00, 72.98, 73.00 (C-3,4,5 and C-2',3',4',5'), 87.36 (C-1), 95.88 (C-1'), and 169.33–170.60 (C=O); ^{1}H, δ 3.60 (q, $J_{1,2}$ 3.9, $J_{2,3}$ 10.3 Hz, H-2), 5.39 (d, $J_{1,2}$ 3.8 Hz, H-1'), and 6.40 (d, $J_{1,2}$ 3.9 Hz, H-1). The crude compound was used directly in the next step.

*p-Trifluoroacetamidophenyl 3,6-di-*O*-acetyl-2-azido-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-*D*-glucopyranosyl)-α-*D*-glucopyranoside* (**5**). — A stirred solution at −20° of *p*-trifluoroacetamidophenol (180 mg, 0.88 mmol, m.p. 177–179°) and **4** (400 mg, 0.59 mmol) in 1:1 nitromethane–toluene (2 mL) containing molecular sieves was treated with a solution of silver triflate (180 mg, 0.70 mmol) in 1:1 nitromethane–toluene (1 mL). After 10 min, the mixture was neutralised with pyridine, diluted with dichloromethane, filtered, washed successively with aqueous sodium thiosulfate, water, 2M sulfuric acid, 2M sodium hydroxide, and water, dried, and concentrated. The residue was subjected to column chromatography using 2:1 toluene–ethyl acetate. The main u.v.-absorbing component was **5** (118 mg, 25%), isolated as a colorless syrup, $[\alpha]_D$ +52° (*c* 0.5). ^{13}C-N.m.r. data ($CDCl_3$,

25°): δ 20.57–20.96 (acetyl Me), 96.01 (C-1′), 97.23 (C-1), 117.65, 122.38, 131.00, 153.91 (aromatic C), and 170.09–170.77 (C=O).

p-*Trifluoroacetamidophenyl 3,6-di-*O*-acetyl-2-azido-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-*D*-glucopyranosyl)-β-*D*-glucopyranoside* (**6**). — The bromide **4** (100 mg, 0.15 mmol) was stirred with a solution of *p*-trifluoroacetamidophenol (123 mg, 0.60 mmol) in dry nitromethane (1.5 mL) containing silver silicate[5] (200 mg) and molecular sieves for 4 h at room temperature. The mixture was then diluted with dichloromethane, filtered, washed with 2M sodium hydroxide and water, dried, and concentrated. The syrupy residue was subjected to column chromatography on silica gel. The main u.v.-absorbing compound eluted with 9:1 chloroform–acetone was syrupy **6** (44 mg, 38%), $[\alpha]_D$ +77° (*c* 0.5). N.m.r. data ($CDCl_3$, 25°): ^{13}C, δ 20.62–20.96 (acetyl Me), 61.70, 62.77 (C-6,6′), 64.09 (C-2), 68.13, 68.77, 69.25, 70.08, 72.61, 72.62, 73.98, (C-3,4,5 and C-2′,3′,4′,5′), 95.67 (C-1′), 100.30 (C-1), 117.80, 122.38, 131.39, 154.40 (aromatic C), and 169.50–170.63 (C=O); ^1H, δ 3.65 (q, $J_{1,2}$ 7.8, $J_{2,3}$ 10.2 Hz, H-2), 4.95 (d, $J_{1,2}$ 7.8 Hz, H-1), 5.38 (d, $J_{1,2}$ 3.9 Hz, H-1′), 7.05, 7.14, 7.51, and 7.60 (aromatic H).

p-*Trifluoroacetamidophenyl 2-acetamido-3,6-di-*O*-acetyl-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-*D*-glucopyranosyl)-β-*D*-glucopyranoside* (**7**). — A solution of **6** (345 mg) in ethanol (95%, 10 mL) was hydrogenated over 10% Pd/C (100 mg) at 400 kPa overnight, filtered, and concentrated. A solution of the residue in methanol (9 mL) containing acetic anhydride (1 mL) was stored overnight at room temperature and then concentrated, and the residue was subjected to column chromatography. Elution with chloroform–methanol (12:1) gave **7** (168 mg, 48%) as the main component. Recrystallisation from methanol–water gave material having m.p. 221–222°, $[\alpha]_D$ +47° (*c* 0.5). ^{13}C-N.m.r. data ($CDCl_3$, 25°): δ 20.59–20.93 (*O*-acetyl Me), 22.97 (*N*-acetyl Me), 54.17 (C-2), 61.72, 62.99 (C-6,6′), 68.25, 68.59, 69.32, 70.15, 72.44, 72.83, 74.34 (C-3,4,5 and C-2′,3′,4′,5′), 95.74 (C-1′), 98.76 (C-1), 117.48, 122.54, 130.98, 154.66 (aromatic C), and 169.52–170.94 (C=O).

Anal. Calc. for $C_{34}H_{41}F_3N_2O_{18}$: C, 49.6; H, 5.02; F, 6.93. Found: C, 49.5; H, 4.88; F, 7.10.

p-*Trifluoroacetamidophenyl 2-acetamido-2-deoxy-4-*O*-α-*D*-glucopyranosyl-β-*D*-glucopyranoside* (**8**). — Compound **7** (41.4 mg) was treated conventionally with methanolic 0.1M sodium methoxide. The mixture was neutralised with Dowex-50 (H^+) resin and then concentrated. The residue was eluted with water from a column of Sephadex G-15, to give **8** (17 mg, 59%), which, after crystallisation from water, had m.p. 200–203°, $[\alpha]_D$ +54° (*c* 0.5, water). N.m.r. data (D_2O, 85°): ^{13}C, δ 23.93 (acetyl Me), 57.36 (C-2), 62.63 (C-6,6′), 71.45, 73.59, 74.66, 74.86, 75.64, 76.91, 79.20 (C-3,4,5 and C-2′,3′,4′,5′), 101.42, 101.61 (C-1,1′), 119.40, 125.84, 131.83, 156.88 (aromatic C), and 176.42 (acetyl C=O); ^1H, δ 2.00 (s, acetyl Me), 5.16 (m, due to virtual coupling, $J_{1,2}$ ~8 Hz, H-1), 5.37 (d, $J_{1,2}$ 3.4 Hz, H-1′), 7.06, 7.15, 7.42, and 7.52 (aromatic H).

Anal. Calc. for $C_{22}H_{29}F_3N_2O_{12} \cdot 2H_2O$: C, 43.6; H, 5.48. Found: C, 43.4; H, 5.31.

p-*Nitrophenyl 2-acetamido-3,4-di-*O*-benzoyl-2-deoxy-6-*O*-trityl-β-*D*-glucopyranoside* (**9**). — A solution of *p*-nitrophenyl 2-acetamido-2-deoxy-β-D-glucopyranoside[8] (0.27 g) and trityl chloride (0.64 g) in dry pyridine (10 mL) was stirred overnight at room temperature, and then benzoyl chloride (0.38 mL) was added dropwise, with cooling in ice. After 2 h, water (0.1 mL) was added, and the mixture was stirred for an additional 30 min and then partitioned between dichloromethane and water. The organic layer was separated, washed with 2M sulfuric acid, aqueous sodium hydrogencarbonate, and water, dried, and concentrated. The residue was subjected to column chromatography, using 3:1 toluene–ethyl acetate. The main component crystallised from ethanol, to give **9** (0.49 g, 78%), m.p. 207–208°, $[\alpha]_D$ −16° (*c* 0.5). ^{13}C-N.m.r. data ($CDCl_3$, 25°): δ 22.88 (acetyl Me), 54.80 (C-2), 62.31 (C-6), 69.40, 72.54, 74.08 (C-3,4,5), 86.80 (Ph_3CO), 98.08 (C-1), 116.82, 125.52, 143.35, 161.85 (*p*-nitrophenyl C), 164.80, 166.16 (benzoyl C=O), and 170.89 (acetyl C=O).

Anal. Calc. for $C_{47}H_{40}N_2O_{10}$: C, 71.2; H, 5.09. Found: C, 71.3; H, 5.20.

p-*Trifluoroacetamidophenyl 2-acetamido-3,4-di-*O*-benzoyl-2-deoxy-6-*O*-trityl-β-*D*-glucopyranoside* (**10**). — A solution of **9** (4.30 g) in ethyl acetate (100 mL) was hydrogenated conventionally over Adams' catalyst (100 mg) at atmospheric pressure, filtered, and concentrated. To a solution of the residue in pyridine (20 mL) at −10° was added trifluoroacetic anhydride (0.73 mL) dropwise with stirring. After 30 min, water (0.2 mL) was added and stirring was continued for 30 min. The mixture was diluted with dichloromethane, washed with water, 2M sulfuric acid, and aqueous sodium hydrogencarbonate, dried, and concentrated. The residue was subjected to column chromatography, using 2:1 toluene–ethyl acetate. The main component was **10** (2.58 g, 55%), which, after crystallisation from ether, had m.p. 207–209°, $[\alpha]_D$ −24° (*c* 0.5). ^{13}C-N.m.r. data ($CDCl_3$, 25°): δ 23.17 (acetyl Me), 55.19 (C-2), 62.70 (C-6), 69.71, 73.08, 74.24 (C-3,4,5), 87.01 (Ph_3CO), 99.83 (C-1), 143.65 (Ph_3CO, substituted aromatic C), 118.16, 122.40, 133.46, 155.29 (*p*-trifluoroacetamidophenyl aromatic C), 165.09, 166.60 (benzoyl C=O), and 170.79 (acetyl C=O).

Anal. Calc. for $C_{49}H_{41}F_3N_2O_9$: C, 68.5; H, 4.81. Found: C, 68.4; H, 4.90.

p-*Trifluoroacetamidophenyl 2-acetamido-3,4-di-*O*-benzoyl-2-deoxy-β-*D*-glucopyranoside* (**11**). — A solution of **10** (2.24 g) in aqueous 80% acetic acid (50 mL) was kept at 80° until t.l.c. indicated complete detritylation (30 min). Water (10 mL) was added to precipitate the trityl alcohol, the mixture was filtered and concentrated, and the residue was subjected to column chromatography, using 2:1 toluene–ethyl acetate, to give **11** (1.10 g, 65%). Crystallisation from ethanol–water gave material having m.p. 227–229°, $[\alpha]_D$ −30° (c 0.5). N.m.r. data: ^{13}C (CD_3OD, 25°), δ 22.76 (acetyl Me), 55.75 (C-2), 61.99 (C-6), 71.11, 74.66, 76.13 (C-3,4,5), 100.49 (C-1), 118.43, 123.79, 134.46, 156.49 (*p*-trifluoroacetamidophenyl aromatic

C), 166.87, 167.46 (benzoyl C=O), and 173.50 (acetyl C=O); ^{1}H [$(CD_3)_2SO$, 25°], δ 4.97 (t, J 6 Hz, primary OH)[15].

Anal. Calc. for $C_{30}H_{27}F_3N_2O_9$: C, 58.4; H, 4.41. Found: C, 58.2; H, 4.49.

p-*Trifluoroacetamidophenyl 2-acetamido-3,4-di-*O*-benzoyl-2-deoxy-6-*O*-(2,3,4,6-tetra-*O*-benzyl-α-*D*-glucopyranosyl)-β-*D*-glucopyranoside* (**12**). — A solution of **11** (550 mg, 0.91 mmol) and 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl bromide (prepared[9] from 1.82 mmol of precursor 1-*p*-nitrobenzoate) in dichloromethane (4 mL) containing tetraethylammonium bromide (0.42 g, 2.0 mmol), *N*,*N*-dimethylformamide (0.4 mL), and molecular sieves was stirred at room temperature for 24 h, diluted with dichloromethane, filtered, washed with aqueous sodium hydrogencarbonate and water, dried, and concentrated. The residue was subjected to column chromatography. Elution with toluene–ethyl acetate (3:2) gave **12** (842 mg, 81%) as the main component. Crystallisation from ether–hexane gave material having m.p. 125–127°, $[\alpha]_D$ −3° (*c* 0.5). ^{13}C-N.m.r. data ($CDCl_3$, 25°): δ 23.12 (acetyl Me), 54.80 (C-2), 97.30, 99.83 (C-1,1'), 117.91, 122.69, 133.61, 155.34 (*p*-trifluoroacetamidophenyl aromatic C), 165.33, 166.60 (benzoyl C=O), and 170.79 (acetyl C=O).

Anal. Calc. for $C_{64}H_{61}F_3N_2O_{14}$: C, 67.5; H, 5.40. Found: C, 67.4; H, 5.44.

p-*Trifluoroacetamidophenyl 2-acetamido-2-deoxy-6-*O*-α-*D*-glucopyranosyl-β-*D*-glucopyranoside* (**13**). — A solution of **12** (447 mg) in 95% ethanol (20 mL) was hydrogenated over 10% Pd/C (200 mg) at 400 kPa for 16 h, filtered, and concentrated. The residue was dissolved in methanolic 0.1M sodium methoxide (10 mL). When t.l.c. indicated complete debenzoylation, the solution was neutralised with Dowex-50 (H^+) resin and concentrated, and the residue was partitioned between water and ether. The aqueous phase was lyophilised to give chromatographically homogeneous **13** (198 mg, 88%). Crystallisation from ethanol–ethyl acetate gave material having m.p. 239–241°, $[\alpha]_D$ +27° (*c* 0.4, water). N.m.r. data (D_2O, 85°): ^{13}C, δ 24.03 (acetyl Me), 57.56 (C-2), 62.58 (C-6), 68.13, 71.64, 71.98, 73.45, 73.74, 75.20, 75.69, 76.56 (C-3,4,5 and C-2',3',4',5',6'), 99.96, 101.42 (C-1,1'), 119.31, 125.64, 131.93, 156.78 (aromatic C), and 176.33 (C=O); ^{1}H, δ 2.01 (s, acetyl Me), 4.93 (d, $J_{1,2}$ 3.4 Hz, H-1'), 5.18 (d, $J_{1,2}$ 7.8 Hz, H-1), 7.07, 7.16, 7.43, and 7.53 (aromatic H).

Anal. Calc. for $C_{22}H_{29}F_3N_2O_{12}$: C, 46.3; H, 5.12; F, 9.99. Found: C, 46.5; H, 5.15; F, 9.99.

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