

Syntheses of the 2'-Acetate and Some Deoxy Analogues of *p*-Trifluoroacetamidophenyl 3-*O*-(3,6-Dideoxy- α -D-xylo-hexopyranosyl)- α -D-mannopyranoside

BJÖRN CLASSON, PER J. GAREGG and THOMAS NORBERG

Department of Organic Chemistry, Arrhenius Laboratory, University of Stockholm, S-106 91 Stockholm, Sweden

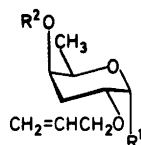
Syntheses are described of derivatives of *p*-trifluoroacetamidophenyl 3-*O*-(3,6-dideoxy- α -D-xylo-hexopyranosyl*)- α -D-mannopyranoside carrying an acetyl group in the 2-position of the abequosyl group, corresponding to the *Salmonella* O-antigen 5 and also of various deoxy derivatives of the parent compound.

In our continuing programme aimed at obtaining improved diagnostic methods for diseases caused by infections with *Salmonella* bacteria, several di- and oligosaccharide derivatives have been synthesized and evaluated in immunological systems.¹ In the present paper we present a facile synthesis of the title *O*-acetylated disaccharide fragment corresponding to the *Salmonella* O-antigen 5, linked to a moiety suitable for attachment to a protein.²

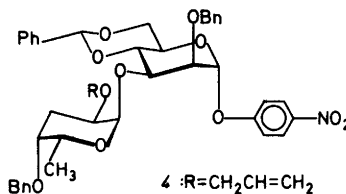
Hydrophobic interactions have been proposed to provide the main driving force for the binding between oligosaccharides and proteins.^{3,4} One way of examining this hypothesis is to remove hydroxyl groups from various positions of an oligosaccharide hapten and thus obtain a series of deoxy derivatives. The binding properties of the compounds obtained are tested and compared to those of the parent compound. This approach has yielded important information of the nature on the interactions of blood group antigens with antibodies and lectins.^{4,5} In the present work we describe syntheses of deoxy derivatives of *p*-

trifluoroacetamidophenyl 3-*O*- α -abequosyl- α -D-mannopyranoside destined for studies of binding with polyclonal and monoclonal antibody preparations. These will be published elsewhere.

Methyl α -abequoside⁶ was allylated⁷ with 1 molar equivalent of allyl bromide and sodium hydride in dimethyl formamide to yield the 2-*O*-allyl derivative **1**. The position of the allyl group was established by means of NMR studies of **1** and of the derived 4-acetate. Benzylation of **1** yielded **2**, carrying the required different



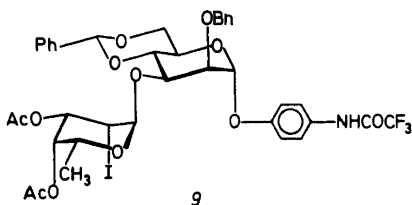
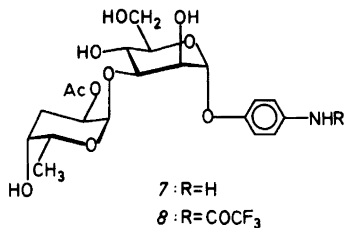
- 1: R¹ = OCH₃, R² = H
 2: R¹ = OCH₃, R² = Bn
 3: R¹ = Br, R² = Bn



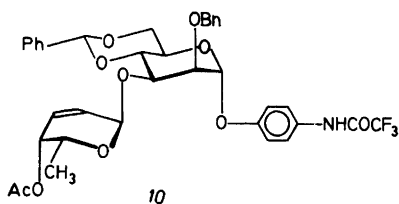
- 4: R = CH₂CH=CH₂
 5: R = H
 6: R = Ac

* 3,6-Dideoxy-D-xylo-hexose is henceforth termed abequose.

protecting groups, in 27 % yield from methyl α -abequoside. Compound 2 was converted into the glycosyl bromide 3 which was used immediately in a halide-assisted⁸ glycosylation with *p*-nitrophenyl 2-*O*-benzyl-4,6-*O*-benzylidene- α -D-mannopyranoside^{9,10} to give the disaccharide

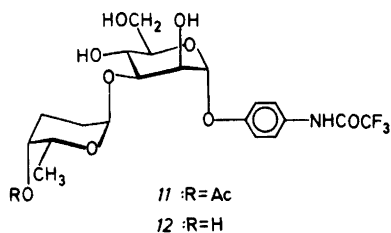


derivative 4 in 71 % yield. Isomerization and removal^{7,11} of the allyl group of 4 to give 5 was followed by acetylation to give 6 in 68 % yield from 4. The nitro group of 6 was reduced to an amino group and the benzyl and benzylidene protecting groups were removed from 6 by



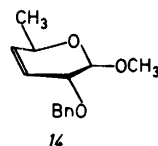
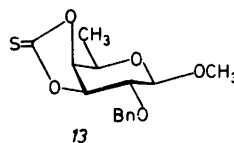
catalytic hydrogenation to give 7 which was converted into the more stable derivative 8 for storage.

3,4-Di-*O*-acetyl-1,2,6-trideoxy-D-*lyxo*-hex-1-enopyranose¹² was treated with iodine, mercury(II) chloride and silver imidazolite¹³ and then reacted with *p*-trifluoroacetamidophenyl 2-*O*-benzyl-4,6-*O*-benzylidene- α -D-mannopyranoside¹⁴ to yield the disaccharide derivative 9 in 49 % yield. Reductive elimination from 9 by treatment with zinc dust in ethanol containing acetic acid¹⁵ yielded 10. Catalytic hydrogenation of 10 gave



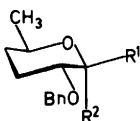
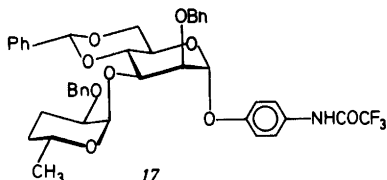
11. This was then deacetylated to yield the target compound 12 with a 2,3,6-trideoxy- α -D-*threo*-hexopyranosyl group instead of an abequosyl group attached to O-3 of the mannopyranosyl residue. Compound 12 was obtained in 52 % yield from 9.

The synthesis of the corresponding analogue with a 3,4,6-trideoxy- α -D-*erythro*-hexopyranosyl group attached to the mannopyranosyl residue started from methyl 2-*O*-benzyl- β -D-fucopyranoside.¹⁶ This was converted¹⁷ into the 3,4-thiocarbonate 13, which upon treatment with trimethyl phosphite¹⁸ yielded the olefinic compound 14. This,

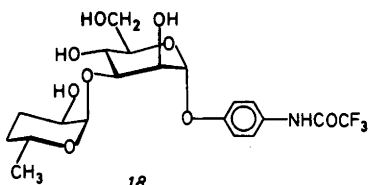


upon catalytic hydrogenation, gave 15 in a total yield of 67 %. Treatment of 15 with bromotrimethylsilane afforded the glycosyl bromide 16 which was used directly in a halide-assisted glycosylation⁸ with *p*-trifluoroacetamidophenyl 2-*O*-benzyl-4,6-*O*-benzylidene- α -D-mannopyranoside¹⁴ to yield the disaccharide derivative 17 in 50 % yield. Deprotection of 17 by means of catalytic hydrogenation afforded the target compound 18.

Finally, a deoxy function was introduced at C-6 of the parent molecule *p*-trifluoroacetamidophenyl 3-*O*-abequosyl- α -D-mannopyranoside. Thus the benzylidene group was removed by careful partial hydrolysis of *p*-trifluoroacetamidophenyl 2-*O*-benzyl-3-*O*-(2,4-di-*O*-benzyl-3,6-

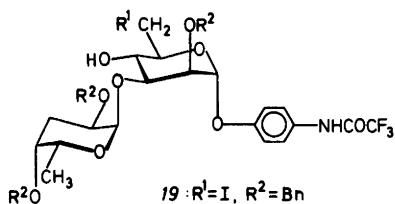
15: R¹ = OCH₃, R² = H16: R¹ = H, R² = Br

17



18

dideoxy- α -D-xylo-hexopyranosyl)-4,6-O-benzylidene- α -D-mannopyranoside.¹⁴ The product was then treated with triphenylphosphine, iodine and imidazole¹⁹ to give the 6-deoxy-6-iodo derivative 19. This upon hydrogenation yielded the target compound 20 in 68 % yield from the disaccharide starting material.

19: R¹ = I, R² = Bn20: R¹ = R² = H

EXPERIMENTAL

General methods. Melting points are corrected. Concentrations were performed at reduced pressure (1–2 kPa) at <40 °C (bath). Optical rotations were recorded for solutions in chloroform unless otherwise stated at 22–24 °C using a Perkin-Elmer 241 polarimeter. NMR spectra (100 or 400 MHz for ¹H and 25 MHz for ¹³C) were recorded at 25 °C unless otherwise stated, using a JEOL JNM FX-100 or a JEOL GX-400 instrument. Chemical shifts are given in ppm

downfield from those of internal (CDCl₃ or CD₃OD solutions) or external (D₂O solutions) Me₄Si. NMR spectra for all new compounds were in accordance with the postulated structures and only selected data are reported. TLC was performed on silica gel F₂₅₄ (Merck) with detection by UV light and/or charring with sulfuric acid. Column chromatography was performed on silica gel 60 (0.04–0.063 mm, Merck) in the flash mode²⁰ using, unless otherwise stated, a suitable toluene–ethyl acetate mixture for elution. The loading was in the range 1/25–1/100. Organic solutions were dried over anhydrous magnesium sulfate. Molecular sieves (4Å, Union Carbide) were desiccated *in vacuo* at 300 °C overnight and ground immediately before use.

Methyl 2-O-allyl-3,6-dideoxy- α -D-xylo-hexopyranoside (1). Sodium hydride (630 mg, 26.3 mmol) was added to a stirred and cooled (ice bath) solution of methyl 3,6-dideoxy- α -D-xylo-hexopyranoside⁶ (4.0 g, 24.7 mmol) in *N,N*-dimethylformamide (80 ml). After 30 min, allyl bromide (3.0 g, 24.7 mmol) was added. After 6 h at 0 °C, ethanol (2 ml) was added and the mixture was filtered and concentrated (100 Pa). TLC of the residual syrup showed three minor spots tentatively assigned to starting material, the 2,4-diallyl and the 4-allyl derivative and a main spot corresponding to compound 1. Purification by column chromatography, using 1:4 ethanol-hexane for elution gave pure, syrupy 1 (1.75 g, 35 %), [α]_D +109° (c 1.0). ¹³C NMR (CDCl₃): δ 16.3 (C-6), 32.2 (C-3), 55.2 (OCH₃), 65.7, 69.3, 70.1, 70.6 (C-2,4,5 and allyl CH₂–CH=CH₂), 98.0 (C-1), 117.3, 134.9 (allyl olefinic C). Acetylation of 1 with acetic anhydride in pyridine produced a single compound, whose ¹H NMR spectrum showed, *inter alia*, a multiplet, not present in the spectrum of 1 at δ 4.98, assigned by spin decoupling to H-4. The position of acetylation and allylation is therefore proved.

Methyl 2-O-allyl-4-O-benzyl-3,6-dideoxy- α -D-xylo-hexopyranoside (2). Compound 1 (1.48 g) was treated with benzyl bromide (1.17 ml) and sodium hydride (180 mg) in *N,N*-dimethyl formamide (30 ml) essentially as described above for the analogous allylation. Pure, syrupy 2 (1.61 g, 75 %) was obtained after column chromatography, [α]_D +35° (c 1.0). ¹³C NMR (CDCl₃): δ 16.4 (C-6), 27.7 (C-3), 54.9 (OCH₃), 97.8 (C-1), 117.3, 134.9 (allyl olefinic C).

2-O-Allyl-4-O-benzyl-3,6-dideoxy- α -D-xylo-hexopyranosyl bromide (3). Compound 2 (560 mg) was dissolved in bromotrimethylsilane (5.0 ml) at room temperature. After 3 h, the solution was concentrated and subsequently co-concentrated twice with dry dichloromethane. The unstable syrup obtained (650 mg) was used directly in the

next step. ^1H NMR (CDCl_3): δ 6.69 (d, $J_{1,2}$ 2 Hz, H-1).

p-Nitrophenyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-allyl-4-*O*-benzyl-3,6-dideoxy- α -D-xylohexopyranosyl)- α -D-mannopyranoside (4). A solution of freshly prepared 3 (650 mg) in 9:1 dichloromethane-*N,N*-dimethylformamide (4 ml) was added to a stirred and cooled (-25°C) solution of *p*-nitrophenyl 2-*O*-benzyl-4,6-*O*-benzylidene- α -D-mannopyranoside^{9,10} (984 mg) and tetraethylammonium bromide (420 mg) in the same solvent (5 ml) containing molecular sieves. The mixture was allowed to attain room temperature and was then stirred overnight, filtered, diluted with dichloromethane, washed with aqueous sodium hydrogencarbonate and concentrated. Purification by column chromatography gave pure, syrupy 4 (1.0 g, 71%), $[\alpha]_{\text{D}} +112^\circ$ (*c* 0.7). ^{13}C NMR (CDCl_3): δ 16.8 (C-6'), 28.1 (C-3'), 97.2, 97.5 (C-1, 1'), 102.3 (benzylidene acetal C).

p-Nitrophenyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-*O*-((4-*O*-benzyl-3,6-dideoxy- α -D-xylohexopyranosyl)- α -D-mannopyranoside) (5). A solution of 4 (1.66 g) in 8:3:1 ethanol-benzene-water (83 ml) containing tris-(triphenylphosphine)-rhodium(I) chloride (325 mg) was boiled under reflux for 24 h. The concentrated mixture was dissolved in 10:1 acetone-water (60 ml). Mercury(II) oxide (832 mg) and mercury(II) chloride were added with stirring at room temperature. After 16 h, the mixture was concentrated. The residue was dissolved in chloroform, washed with 5% aqueous EDTA solution and water, concentrated, and purified by column chromatography. Pure 5 (1.23 g, 78%) was obtained. Crystallized from chloroform-diethyl ether-hexane it had m.p. 121°C , $[\alpha]_{\text{D}} +114^\circ$ (*c* 1.0). ^{13}C NMR (CDCl_3): δ 16.8 (C-6'), 30.8 (C-3'), 96.9 (C-1), 101.1 (C-1'), 101.9 (benzylidene acetal C). Anal: $\text{C}_{39}\text{H}_{41}\text{NO}_{11}$: C, H, N.

p-Nitrophenyl 3-*O*-(2-*O*-acetyl-4-*O*-benzyl-3,6-dideoxy- α -D-xylohexopyranosyl)-2-*O*-benzyl-4,6-*O*-benzylidene- α -D-mannopyranoside (6). Compound 5 (1.10 g) was dissolved in 2:1 pyridine-acetic anhydride. After 16 h at room temperature, the mixture was poured into ice-water and the crude product was filtered off. Purification by column chromatography gave pure, syrupy 6 (1.02 g, 87%), $[\alpha]_{\text{D}} +102^\circ$ (*c* 1.0). ^{13}C NMR (CDCl_3): δ 16.7 (C-6'), 20.7 (acetyl Me), 26.8 (C-3'), 96.7 (C-1), 97.7 (C-1'), 102.0 (benzylidene acetal C).

p-Aminophenyl 3-*O*-(2-*O*-acetyl-3,6-dideoxy- α -D-xylohexopyranosyl)- α -D-mannopyranoside (7). A solution of 6 (250 mg) in absolute ethanol (5 ml) was added to a suspension of 10% Pd/C (150 mg) in absolute ethanol (10 ml) containing

concentrated hydrochloric acid (0.05 ml). The mixture was hydrogenated at 400 kPa for 16 h. Chromatographic purification (solvent system: ethyl acetate-methanol-water, 85:10:5) of the filtered and concentrated material gave fractions containing 7. These were pooled and concentrated to about 5 ml then diluted with 10 ml of water and lyophilized to give pure 7 (130 mg, 87%), $[\alpha]_{\text{D}} +150^\circ$ (*c* 0.5, water). NMR (D_2O , 50°C): ^{13}C , δ 16.8 (C-6'), 21.9 (acetyl Me), 31.6 (C-3'), 99.4, 100.8 (C-1, C-1'), 119.4, 120.3, 142.1, 150.6 (*p*-aminophenyl C), 174.8 (acetyl C=O); ^1H NMR (CDCl_3), δ 1.03 (d, $J_{5',6'}$ 6.9 Hz, H-6'), 1.96 (s, acetyl Me), 4.88 (m, H-2'), 5.09 (d, $J_{1',2'}$ 3.4 Hz, H-1'), 5.24 (d, $J_{1,2}$ 1.4 Hz, H-1).

p-Trifluoroacetamidophenyl 3-*O*-(2-*O*-acetyl-3,6-dideoxy- α -D-xylohexopyranosyl)- α -D-mannopyranoside (8). Trifluoroacetic anhydride (0.07 ml) was added in portions to a solution of 7 (44 mg) in pyridine (1 ml) while stirring and cooling in ice. After 1 h, water (0.1 ml) was added and the mixture was stirred at room temperature for 16 h. The residue after concentration was subjected to column chromatography (solvent system: ethyl acetate-methanol, 95:5), yielding pure 8 (30 mg, 56%), $[\alpha]_{\text{D}} +128^\circ$ (*c* 0.5, water). ^{13}C NMR (D_2O): δ 16.6 (C-6'), 21.6 (acetyl Me), 31.3 (C-3'), 61.7 (C-6), 66.8, 68.1, 68.3, 69.3, 71.2, 75.2, 80.0 (C-2,3,4,5, C-2', 4', 5'), 99.3, 99.4 (C-1, 1'), 118.7, 125.1, 130.7, 154.9 (*p*-trifluoroacetamidophenyl aromatic C), 174.5 (acetyl C=O). ^1H NMR (D_2O , 85°C): δ 1.15 (d, $J_{5',6'}$ 6.8 Hz, H-6'), 1.87-2.34 (m, H-3'_{ax}, H-3'_{eq}), 2.09 (s, acetyl Me), 4.96-5.17 (m, H-2'), 5.26 (d, $J_{1',2'}$ 3.9 Hz, H-1'), 5.56 (d, $J_{1,2}$ 1.9 Hz H-1), 7.14, 7.23, 7.43, 7.52 (aromatic H).

p-Trifluoroacetamidophenyl 3-*O*-(3,4-di-*O*-acetyl-2-deoxy-2-iodo- α -D-talo-hexopyranosyl)-2-*O*-benzyl-4,6-*O*-benzylidene- α -D-mannopyranoside (9). A mixture of silver imidazolite¹³ (1.09 g), mercury(II) chloride (2.54 g) and molecular sieves was stirred in acetonitrile (38 ml) for 1 h, then 3,4-di-*O*-acetyl-1,2,6-trideoxy-D-lyxo-hex-1-enopyranose¹² (1.00 g) was added, followed by iodine (1.59 g). After 1 h, *p*-trifluoroacetamidophenyl 2-*O*-benzyl-4,6-*O*-benzylidene- α -D-mannopyranoside¹⁴ (2.55 g) was added and stirring was continued at room temperature for 4 h, then more iodine (0.40 g) and silver imidazolite (0.27 g) were added. After another 4 h, triethylamine (9 ml) was added and the mixture was diluted with toluene-ethyl acetate (1:1) and filtered. The filtrate was washed with 5% aqueous EDTA solution, aqueous sodium hydrogencarbonate and brine. The residue after drying and concentrating was purified by column chromatography to give pure, syrupy 9 (2.02 g,

49 %), $[\alpha]_D +46^\circ$ (c 0.5). ^{13}C NMR (CDCl_3): δ 16.0 (C-6'), 20.7, 20.8, 20.9 (C-2', acetyl Me), 96.6 (C-1), 101.2 (benzylidene acetal C), 103.8 (C-1'), 116.9, 122.2, 137.1, 153.5 (*p*-trifluoroacetamidophenyl aromatic C) 163.5, 170.5 (acetyl C=O).

p-Trifluoroacetamidophenyl 3-O-(4-O-acetyl-2,3,6-trideoxy- α -D-threo-hex-2-enopyranosyl)-2-O-benzyl-4,6-O-benzylidene- α -D-mannopyranoside (10). Acetic acid (130 mg) was added to a stirred mixture of 9 (1.8 g) and zinc dust (1.46 g) in ethanol (54 ml). After 20 min, pyridine (2 ml) was added and the mixture was filtered and concentrated. The residue was dissolved in dichloromethane, washed with water, dried and concentrated. Purification by column chromatography gave pure, syrupy 10 (1.01 g, 71 %), $[\alpha]_D -117^\circ$ (c 0.4). ^{13}C NMR (CDCl_3): δ 16.1 (C-6'), 20.8 (acetyl Me), 95.4 (C-1), 97.1 (C-1'), 101.6 (benzylidene acetal C), 117.0, 122.3, 137.3, 153.7 (*p*-trifluoroacetamidophenyl aromatic C), 170.8 (acetyl C=O).

p-Trifluoroacetamidophenyl 3-O-(4-O-acetyl-2,3,6-trideoxy- α -D-threo-hexopyranosyl)- α -D-mannopyranoside (11). A solution of 10 (1.0 g) in ethanol (40 ml) was added to a suspension of 10 % Pd/C (0.50 g) in absolute ethanol (10 ml) containing concentrated hydrochloric acid (0.05 ml). The mixture was hydrogenated at 400 kPa for 16 h. Chromatographic purification (solvent system: ethyl acetate-methanol-water, 85:10:5) of the filtered and concentrated material gave pure 11 (0.56 g, 74 %) as a glass, $[\alpha]_D +136^\circ$ (c 0.5, methanol). ^{13}C NMR ($\text{Me}_2\text{SO}-d_6$, 50 °C): δ 16.6 (C-6'), 20.4 (acetyl Me), 22.1, 23.6 (C-2', 3'), 98.2, 99.1 (C-1,1'), 169.7 (acetyl C=O).

p-Trifluoroacetamidophenyl 3-O-(2,3,6-trideoxy- α -D-threo-hexopyranosyl)- α -D-mannopyranoside (12). Compound 11 (50 mg) was dissolved in 0.5 M methanolic sodium methoxide (0.5 ml) at room temperature. After 30 min, the solution was neutralized with Dowex-50 (H^+) resin. Saturated methanolic ammonia (0.05 ml) was added, and the solution was concentrated. The residue was purified by chromatography on a small silica gel column, using methanol as eluant. Pure 12 (46 mg, 99 %) was obtained, $[\alpha]_D +170^\circ$ (c 1.0, methanol). NMR (CD_3OD): ^{13}C , δ 17.6 (C-6'), 24.5, 26.6 (C-2',3'), 62.6, 67.4, 67.9, 68.0, 71.8, 75.7, 79.3 (C-2,3,4,5,6, C-4',6') 100.3 (C-1), 101.2 (C-1'), 118.1, 123.8, 132.3, 155.5 (aromatic C); ^1H δ 1.17 (d, $J_{5,6}$ 6.6 Hz, H-6'), 5.13 (broad s, H-1'), 5.47 (d, $J_{1,2}$ 1.7 Hz, H-1).

Methyl 2-O-benzyl-3,4-O-thiocarbonyl-6-deoxy- β -D-galactopyranoside (13). A solution of methyl 2-O-benzyl-6-deoxy- β -D-galactopyranoside¹⁶ (3.43 g, 12.8 mmol) and 4-dimethylaminopyridine (3.75 g, 30.7 mmol) in dichloro-

methane (50 ml) was stirred and cooled in an ice bath while thiophosgene (1.18 ml, 15.4 mmol) was added dropwise. After 30 min, 15 g of silica gel was added and the mixture was concentrated. The residue was slurried in 7:3 toluene-ethyl acetate and applied to a column of silica gel. Elution with the same solvent mixture gave pure 16 (3.8 g, 95 %). Crystallized from diethyl ether-hexane it had m.p. 91-92 °C, $[\alpha]_D +48^\circ$ (c 0.6). Anal: $\text{C}_{15}\text{H}_{18}\text{O}_5\text{S}$: C, H, S.

Methyl 2-O-benzyl-3,4,6-trideoxy- β -D-erythro-hex-3-enopyranoside (14). A solution of 13 (3.6 g) in trimethylphosphite (10 ml) was kept at 110 °C for 40 h, and then concentrated. The residue was purified by column chromatography to give an oil (3.8 g) which, according to TLC, still contained non-carbohydrate impurities. It was used directly in the next step. ^{13}C NMR (CDCl_3): δ 21.0 (C-6), 56.0 (OCH_3), 70.2, 72.3, 73.9 (C-2,5 and benzyl CH_2), 103.4 (C-1), 125.1, 132.7 (C-3,4).

Methyl 2-O-benzyl-3,4,6-trideoxy- β -D-erythro-hexopyranoside (15). Crude 14 (3.6 g) was hydrogenated over platinum oxide (900 mg) in ethyl acetate solution and atmospheric pressure for 5 h. The filtered and concentrated material was purified by column chromatography to give pure, oily 15 (1.9 g, 71 %, calculated from 13), $[\alpha]_D -34^\circ$ (c 0.4). NMR (CDCl_3): ^{13}C , δ 21.1 (C-6), 29.4, 32.5 (C-3,4), 56.5 (OCH_3), 71.7, 72.6, 76.5 (C-2,5 and benzyl CH_2), 106.5 (C-1); ^1H , δ 1.16 (d, $J_{5,6}$ 6.5 Hz, H-6), 3.44 (s, OCH_3), 4.12 (d, $J_{1,2}$ 7.9 Hz, H-1), 4.61 (AB q, benzyl CH_2).

2-O-Benzyl-3,4,6-trideoxy- α -D-erythro-hexopyranosyl bromide (16). Compound 15 (200 mg) was dissolved in bromotrimethylsilane (1.5 ml) at room temperature. After 10 min, 20 ml of dry toluene was added and the solution was concentrated. After two more concentrations with toluene, the unstable oil obtained (210 mg) was taken up in dichloromethane and used directly in the next step. NMR (CDCl_3): ^{13}C , δ 20.5 (C-6), 25.1, 31.1 (C-3,4), 69.5, 70.3, 74.7 (C-2,5 and benzyl CH_2), 95.8 (C-1); ^1H , δ 6.55 (d, $J_{1,2}$ 3.4 Hz, H-1).

p-Trifluoroacetamidophenyl 2-O-benzyl-4,6-O-benzylidene-3-O-(2-O-benzyl-3,4,6-trideoxy- α -D-erythro-hexopyranosyl)- α -D-mannopyranoside (17). A solution of 16 (freshly prepared from 830 mg, 3.5 mmol of 15) in dichloromethane (2 ml) was added, at room temperature, to a stirred solution of *p*-trifluoroacetamidophenyl 2-O-benzyl-4,6-O-benzylidene- α -D-mannopyranoside¹⁴ (700 mg, 1.3 mmol) and tetraethylammonium bromide (500 mg) in 9:1 dichloromethane-*N,N*-dimethylformamide (5.5 ml) containing molecular sieves. After 6 h, triethylamine (0.5 ml) was

added, and the mixture was diluted with dichloromethane and filtered. After concentration of the filtrate to a fourth of the original volume, diethyl ether was added and the solution was washed with water, 2M sulfuric acid, and aqueous sodium hydrogencarbonate. The residue after concentration was purified twice by column chromatography to give pure, syrupy 17 (480 mg, 50%), $[\alpha]_D +129^\circ$ (*c* 0.4). NMR data (CDCl₃): ¹³C, δ 21.2 (C-6'), 24.6, 32.6 (C-3', 4'), 64.9, 65.1, 68.7, 69.4, 72.2, 73.9, 74.1, 77.8, 79.5, (C-2, 3, 4, 5, 6, C-2', 5', and benzyl CH₂), 97.2, 97.7 (C-1, C-1'), 102.5 (benzylidene O-C-O); ¹H, δ 1.14 (d, *J*_{5',6'} 6.5 Hz, H-6'), 5.42 (d, *J*_{1',2'} 3.2 Hz, H-1'), 5.48 (s, benzylidene acetal H), 5.59 (d, *J*_{1,2} 1.4 Hz, H-1).

p-Trifluoroacetamidophenyl 3-O-(3,4,6-trideoxy- α -D-erythro-hexopyranosyl)- α -D-mannopyranoside (18). A solution of 17 (240 mg) in 5:1 ethanol-ethyl acetate (24 ml) was hydrogenated over Pd/C (10%, 150 mg) at 400 kPa for 20 h. The residue after filtration and concentration was partitioned between diethyl ether and water. The aqueous phase was extracted twice with diethyl ether, and the combined ethereal extracts were concentrated. The residue was partitioned between hexane and water. The aqueous phase was lyophilized to give pure 18 (120 mg, 78%) as an amorphous powder, $[\alpha]_D +145^\circ$ (*c* 0.3, water). ¹³C NMR (CD₃OD): δ 21.3 (C-6'), 27.8 (C-4'), 33.4 (C-3'), 62.5, 66.1, 67.3, 70.0, 71.8, 75.4, 80.7 (C-2, 3, 4, 5, 6 and C-2', 5'), 100.3 (C-1), 102.5 (C-1'), 118.2, 123.7, 132.0, 155.5 (*p*-trifluoroacetamidophenyl aromatic C). ¹H NMR (D₂O, 85 °C): δ 1.11 (d, *J*_{5',6'} 6.4 Hz, H-6'), 5.10 (d, *J*_{1',2'} 3.4 Hz, H-1'), 5.57 (d, *J*_{1,2} 2.0 Hz, H-1).

p-Trifluoroacetamidophenyl 2-O-benzyl-3-O-(2,4-di-O-benzyl-3,6-dideoxy- α -D-xylo-hexopyranosyl)-6-deoxy-6-iodo- α -D-mannopyranoside (19). A solution of *p*-trifluoroacetamidophenyl 2-O-benzyl-3-O-(2,4-di-O-benzyl-3,6-dideoxy- α -D-xylo-hexopyranosyl)-4,6-O-benzylidene- α -D-mannopyranoside¹⁴ (260 mg) in 80% aqueous acetic acid (2 ml) was kept at 80 °C for 2 h and was then evaporated. The residue was taken up in 2:1 toluene-acetonitrile (3 ml) and added, at 70 °C, to a mixture of triphenylphosphine (120 mg), iodine (120 mg) and imidazole (60 mg) in 2:1 toluene-acetonitrile (7 ml). After 1 h at 70 °C, the mixture was washed with water, dried and evaporated. The residue was purified by column chromatography to give compound 19 (250 mg, 92%) as a syrup, which, crystallized from dichloromethane-hexane, had m.p. 170–173 °C, $[\alpha]_D +60^\circ$ (*c* 0.5). Anal: C₄₁H₄₃F₃INO₉; C, H, I. NMR (CDCl₃): ¹³C, δ 6.36 (C-6), 16.7 (C-6'), 27.0 (C-3'), 67.3, 70.9, 71.2, 71.5, 71.9, 72.9, 73.4, 75.6, 77.9, 81.9

(C-2, 3, 4, 5, C-2', 4', 5', and benzyl CH₂), 96.9, 101.1 (C-1, C-1').

p-Trifluoroacetamidophenyl 3-O-(3,6-dideoxy- α -D-xylo-hexopyranosyl)-6-deoxy- α -D-mannopyranoside (20). A solution of 19 (134 mg) in 3:1 ethanol-ethyl acetate (12 ml) was hydrogenated at 400 kPa for 20 h in the presence of 10% Pd/C (200 mg) and powdered 4Å molecular sieves (750 mg). The residue after filtration and evaporation was purified by column chromatography. The main band eluted was, according to ¹³C NMR data, the tribenzyl ether of 20. Hydrogenation as above over fresh Pd/C (100 mg) but without molecular sieves gave, after purification by gel filtration on a column of Bio-gel P-2, compound 20 (53 mg, 74%). Crystallized from water it had m.p. 228–231 °C, $[\alpha]_D +137^\circ$ (*c* 0.2, water).

Anal: C₂₀H₂₆F₃NO₉; C, H, N. ¹H NMR (D₂O, 85 °C): δ 1.15 (d, *J*_{5',6'} 6.6 Hz, H-6'), 1.24 (d, *J*_{5,6} 6.1 Hz, H-6), 1.98 (m, H-3'_{eq}), 2.04 (m, H-3'_{ax}), 3.70 (t, *J*_{3,4}, *J*_{4,5} 9.8 Hz, H-4), 3.83 (q, *J*_{5,6} 6.1 Hz, H-5), 3.85 (m, H-4'), 4.02 (m, H-2'), 4.04 (dd, *J*_{2,3} 3.4, *J*_{3,4} 9.8 Hz, H-3), 4.11 (dq, *J*_{5',6'} 6.6, *J*_{4',5'} 1.5 Hz, H-5'), 4.24 (dd, *J*_{1,2} 2.0, *J*_{2,3} 3.4 Hz, H-2), 5.15 (d, *J*_{1',2'} 3.9 Hz, H-1'), 5.53 (d, *J*_{1,2} 2.0 Hz, H-1), 7.18, 7.20, 7.49, 7.51 (aromatic H).

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