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Synthetic Mucin Fragments: 2-(*p*-Trifluoroacetamidophenyl)ethyl 2-Acetamido-6-*O*-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-2-deoxy-3-*O*-(β-D-galactopyranosyl)-α-D-galactopyranoside and 2-(*p*-Trifluoroacetamidophenyl)ethyl 2-Acetamido-6-*O*-[2-acetamido-2-deoxy-4-*O*-(β-D-galactopyranosyl)-β-D-glucopyranosyl]-2-deoxy-3-*O*-(β-D-galactopyranosyl)-α-D-galactopyranoside

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The title compounds were synthesized from methyl 2-azido-3-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-2-deoxy-1-thio-β-D-galactopyranoside, which was β-glycosylated in the 6-position with glucosamine or lactosamine derivatives.

The tri- and tetrasaccharide thioglycosides obtained were then converted to the 2-(*p*-trifluoroacetamidophenyl)ethyl α-glycosides and deprotected.

In glycoproteins such as the mucins, the majority of the oligosaccharide chains are *O*-glycosidically linked through a 2-acetamido-2-deoxy-galactosyl residue to serine or threonine in the peptide backbone. The structures of the carbohydrate moieties of various glycoproteins have been well documented [1, 2]. In mucins the *O*-linked oligosaccharides are derived by galactose, *N*-acetylglucosamine, *N*-acetylneuraminic acid or larger oligosaccharide substitution of a basic β-D-Gal*p*-(1-3)-α-D-GalNAc*p*- unit. This gives a series of structures, a number of these having the core elements depicted in Fig. 1.

In a research programme aimed at developing monoclonal antibodies which recognize mucin structures, representative synthetic oligosaccharides were needed. We now report syntheses of the trisaccharide **5** and the tetrasaccharide **10** in a form suitable for

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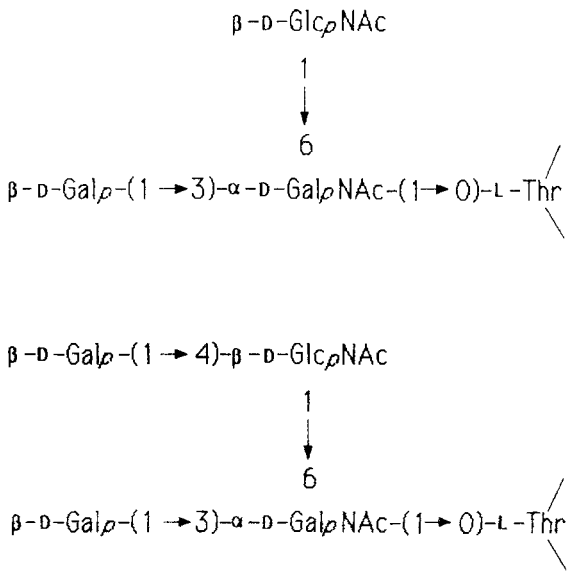


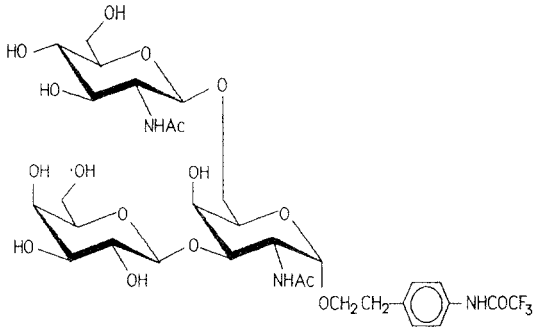
Figure 1. Oligosaccharide core structures in mucins.

attachment to proteins to form artificial antigens. The 2-(*p*-trifluoroacetamidophenyl)-ethyl linking arm is analogous to the 2-(*p*-nitrophenyl)ethyl group previously used by Schuerch *et al.* [3]. The synthesis, by a different route to ours, of the benzyl α-glycoside analogue of **5** has previously been reported [4]. In the present work, the strategy outlined [5-7] for block synthesis using thioglycoside intermediates was followed. Starting from the disaccharide thioglycoside **1**, tri- (**2**) and tetrasaccharide (**6**) thioglycosides were assembled. These were then converted into glycosides of 2-(*p*-trifluoroacetamidophenyl)ethanol and deprotected.

Results and Discussion

Treatment of methyl 2-azido-3-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-4,6-*O*-benzylidene-2-deoxy-1-thio-β-D-galactopyranoside [8] with aqueous acetic acid gave the diol **1** in 91% yield. This compound was treated with 2-methyl-(3,4,6-tri-*O*-acetyl-1,2-dideoxy-α-D-glucopyrano)-[2,1*d*]-2-oxazoline [9] and anhydrous *p*-toluenesulfonic acid at 75°C to give the trisaccharide **2** in 70% yield. That glycosylation had occurred at the 6-position of the $GalN_3$ residue was indicated by the ^{13}C-NMR spectrum of **2**. Only two methylene signals (for Gal-6 and GlcNAc-6) were found below 65 p.p.m., *i.e.* $GalN_3$-6 had been shifted downfield from its position in **1**, indicative [10] of alkyl or glycosyl substitution.

The trisaccharide **2** was treated with bromine in dichloromethane to give the corresponding bromide, which was directly used in a halide ion-promoted glycosidation of 2-(*p*-trifluoroacetamidophenyl)ethanol to give **3** in 82% yield. Treatment with hydrogen sulfide in pyridine/triethylamine converted the azido group of **3** to an amino group, and subsequent acetylation with acetic anhydride gave compound **4** (80% yield),



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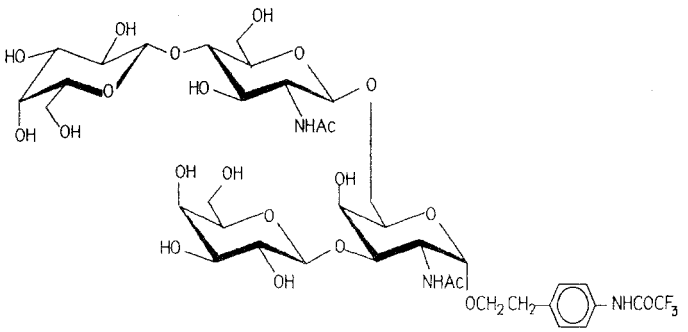

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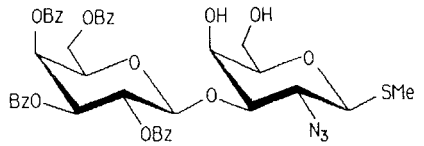
O-deacetylation then gave the target compound **5** (83% yield). The ^{13}C-NMR spectrum of **5** agreed reasonably well with that reported [4] for the corresponding benzyl glycoside. The structure of **5** was also confirmed by ^{1}H-NMR, methylation analysis, and FAB-MS.

Silver triflate-promoted glycosidation of the diol **1** with 3,6-di-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-2-deoxy-2-phthalimido-β-D-glucopyranosyl bromide [11] gave the tetrasaccharide **6** in 74% yield. The position of glycosidation in **6** was verified as for **2** by the ^{13}C-NMR spectrum. Also, in the ^{1}H-NMR spectrum of **6**, the only OH signal (at 2.74 p.p.m.) showed scalar coupling to H-4, indicating that this position was not glycosylated. Treatment of **6** with hydrazine acetate [12] followed by deacylation (methanolic sodium methoxide) and acetylation (pyridine/acetic anhydride) gave **7** in 89% yield. Treatment of **7** with bromine in dichloromethane gave the corresponding bromide, which was directly used in a halide ion-promoted glycosidation of 2-(*p*-trifluoroacetamidophenyl)ethanol to give **8** (81% yield). Conversion of the azido group to an amino group followed by acetylation (as for preparation of **4**) gave **9** in 80% yield, deprotection of which, with methanolic sodium methoxide gave the target compound **10** (82% yield). The structure was verified by the NMR and FAB-MS spectra and by methylation analysis.



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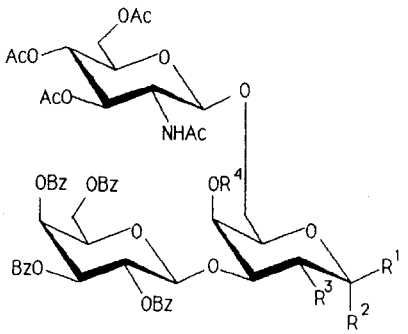


2: R^1 = SMe , R^2 = H , R^3 = N_3 , R^4 = H

3: R^1 = H , R^2 = $O(CH_2)_2$ (C_6H_4) $NHCOCF_3$, R^3 = N_3 , R^4 = H

4: R^1 = H , R^2 = $O(CH_2)_2$ (C_6H_4) $NHCOCF_3$, R^3 = NHAc , R^4 = Ac

Experimental

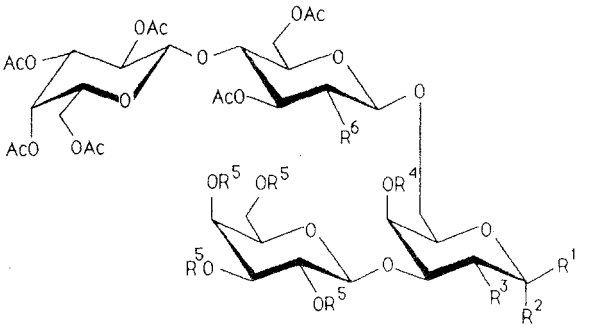
General Methods

These methods were the same as previously reported [8] except that TMS = δ 0.00 was used as reference signal for ^{13}C-NMR spectra in C^2HCl_3 solution. In the NMR spectral assignments below, atoms of galactosamine carry no superscript, atoms of 3-linked galactose, glucosamine and 6-linked galactose carry the (′), (″) and (‴) superscripts, respectively. The FAB-MS spectra was recorded with a VG ZAB-SE mass spectrometer. The primary beam consisted of xenon atoms with a maximum energy of 8 keV. The samples were dissolved in thioglycerol and the positive ions were extracted and accelerated over a potential of 10 kV.

2-(*p*-Trifluoroacetamidophenyl)ethanol was prepared in 69% yield from 2-(*p*-aminophenyl)ethanol (Aldrich, Milwaukee, WI, USA) by treatment with an excess of trifluoroacetic anhydride in pyridine (0°C) followed by mild hydrolysis in pyridine/water. Crystallisation from ethyl acetate/hexane gave material with m.p. 131-132°C.

*Methyl 2-Azido-3-O-(2,3,4,6-tetra-O-benzoyl-β-D-galactopyranosyl)-2-deoxy-1-thio-β-D-galactopyranoside (**1**)*

A solution of methyl 2-azido-4,6-*O*-benzylidene-3-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-2-deoxy-1-thio-β-D-galactopyranoside [8] (2.8 g) in 90% aqueous acetic acid



6: R^1 = SMe , R^2 = H , R^3 = N_3 , R^4 = H , R^5 = Bz , R^6 = NPhth

7: R^1 = SMe , R^2 = H , R^3 = N_3 , R^4 = R^5 = Ac , R^6 = NHAc

8: R^1 = H , R^2 = $O(CH_2)_2(C_6H_4)NHCOCF_3$, R^3 = N_3 , R^4 = R^5 = Ac , R^6 = NHAc

9: R^1 = H , R^2 = $O(CH_2)_2(C_6H_4)NHCOCF_3$, R^3 = R^6 = NHAc , R^4 = R^5 = Ac

(30 ml) was heated to 100°C for 1 h and then concentrated. The residue was purified by column chromatography to give amorphous **1** (2.5 g, 91%), $[\alpha]_D$ +58°. NMR data: ^{13}C, δ 11.7 (SCH_3), 61.0, 62.2, 62.3 (C-2, 6, C-6'), 68.0, 68.2, 69.4, 71.4, 72.2, 78.0, 83.4, 84.7 (C-1, 3, 4, 5, C-2', 3', 4', 5'), 102.3 (C-1').

Analytical data. Calculated for $C_{41}H_{39}N_3O_{13}S$: C, 60.5; H, 4.8; N 5.2; S, 4.0. Found: C, 60.5; H, 4.9; N, 5.0; S, 3.6.

*Methyl 6-O-(2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-glucopyranosyl)-2-azido-3-O-(2,3,4,6-tetra-O-benzoyl-β-D-galactopyranosyl)-2-deoxy-1-thio-β-D-galactopyranoside (**2**)*

A solution of **1** (425 mg), 2-methyl-3,4,6-tri-*O*-acetyl-1,2-dideoxy-α-D-glucopyrano)-[2,1-*d*]-2-oxazoline [9] (265 mg and anhydrous *p*-toluenesulfonic acid (20 mg) in toluene (40 ml) was heated, in a nitrogen atmosphere, to 75°C for 16 h. Triethylamine (0.1 ml) was added, and the mixture was concentrated. The residue was purified by column chromatography to give **2** (416 mg, 70%). Crystals were obtained from ethanol, m.p. 127-128°C, $[\alpha]_D$ +43°. NMR data: ^{13}C, δ 11.2 (SCH_3), 20.7, 20.8 ($\mathbf{C}H_3COO$), 23.2 ($\mathbf{C}H_3CONH$), 54.1 (C-2''), 60.8, 62.2, 62.3 (C-2, C-6', C-6''), 67.7, 68.2, 68.6, 69.5, 71.4, 72.0, 72.2, 73.0, 77.7, 83.0, 84.1 (C-1, 3, 4, 5, C-2',3',4',5', C-3'',4'',5''), 102.0, 102.3 (C-1', C-1''); ^1H, δ 4.00 (d, *J* 9.9 Hz, H-1), 4.54 (d, *J* 8.4 Hz, H-1''), 5.04 (d, *J* 8.2 Hz, H-1').

Analytical data. Calculated for $C_{55}H_{58}N_4O_{21}S$: C, 57.8; H, 5.0; N, 4.9; S, 2.8. Found: C, 57.4; H, 5.2; N, 5.0; S, 2.6.

*2-(p-Trifluoroacetamidophenyl)ethyl 6-O-(2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-glucopyranosyl)-2-azido-3-O-(2,3,4,6-tetra-O-benzoyl-β-D-galactopyranosyl)-2-deoxy-α-D-galactopyranoside (**3**)*

Bromine (25 μl) was added, in a nitrogen atmosphere, to a stirred mixture of **2** (375 mg), dichloromethane (10 ml) and molecular sieves. After 30 min, 1-hexene (0.05 ml) was added, followed by a mixture of tetraethylammonium bromide (650 mg), 2-(*p*-trifluoroaceta-

midophenyl)ethanol (225 mg), *N,N*-dimethyl formamide (0.5 ml), dichloromethane (20 ml) and molecular sieves. After stirring overnight, pyridine (1 ml) was added and the mixture was filtered, washed with water, dried, and concentrated. The residue was purified by column chromatography to give **3** (351 mg, 82%). Crystals were obtained from diethyl ether, m.p. 128-129°C, $[\alpha]_D$ +72°. NMR data: ^{13}C, δ 97.3 (C-1), 101.4, 102.4 (C-1′, C-1″); ^1H, δ 4.48 (d, *J* 8.3 Hz, H-1″), 4.81 (d, *J* 3.6 Hz, H-1), 5.09 (d, *J* 8.1 Hz, H-1′).

Analytical data: Calculated for $C_{64}H_{64}F_3N_5O_{23}.H_2O$: C, 57.1; H, 4.9; N, 5.2. Found: C, 56.9; H, 4.8; N, 5.2.

*2-(p-Trifluoroacetamidophenyl)ethyl 2-Acetamido-6-O-(2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-glucopyranosyl)-4-O-acetyl-3-O-(2,3,4,6-tetra-O-benzoyl-β-D-galactopyranosyl)-2-deoxy-α-D-galactopyranoside (**4**)*

Hydrogen sulfide was bubbled through a solution of **3** (255 mg) in pyridine/triethylamine (2/1 by vol, 15 ml) for 1 h. After another 2 h, acetic anhydride (10 ml) was added and the solution was left overnight at room temperature. Concentration and purification of the residue by column chromatography (chloroform/methanol, 20/1 by vol, as eluant) gave amorphous **4** (206 mg, 80%), $[\alpha]_D$ +77°. NMR data: ^{13}C, δ 22.1, 22.9 (**C**H_3CONH), 96.7 (C-1), 102.0, 102.2 (C-1′, C-1″).

*2-(p-Trifluoroacetamidophenyl)ethyl 2-Acetamido-6-O-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-2-deoxy-3-O-(β-D-galactopyranosyl)-α-D-galactopyranoside (**5**)*

A solution of **4** (95 mg) in methanolic sodium methoxide (0.1 M, 10 ml) was kept at room temperature for 1 h, then neutralized with Dowex-50 and concentrated. The residue was purified by gel filtration on a Bio-Gel P-2 column. Elution with water gave amorphous **5** (48 mg, 83%), $[\alpha]_D$ +24° (*c* 0.2, water). NMR data: ^{13}C (DMSO-d_6, Me_2SO = δ 39.6), 22.5, 22.8 (**C**H_3CONH), 34.4 (Ph**C**$H_2$$CH_2O$), 48.5 (C-2), 55.4 (C-2″), 60.5, 61.1 (C-6′, C-6″), 67.2, 67.5, 68.2, 68.6, 69.3, 70.8, 73.3, 74.2, 75.3, 75.4, 75.8, 76.7 (C-3, 4, 5, 6, C-2′, 3′,4′,5′, C-3″,4″,5″, PhCH_2**C**H_2O), 96.7 (C-1), 101.6 (C-1″), 103.5 (C-1′), 121.0, 129.2, 134.6, 136.4 (aromatic C), 169.2, 169.6 (CH_3**C**ONH); ^1H (^2H_2O), δ 4.41 (d, $J_{1,2}$ 7.9 Hz, H-1′), 4.49 (d, $J_{1,2}$ 8.4 Hz, H-1″), 4.81 (d $J_{1,2}$ 3.6 Hz, H-1).

The FAB-MS of **5** showed an $(M+H)^+$ ion m/z = 802.

Analytical data: Calculated for $C_{32}H_{46}F_3N_3O_{17}.3H_2O$: C, 44.4; H, 6.0; N, 4.9. Found: C, 44.8; H, 6.1; N, 4.5.

Methylation analysis showed the presence of unsubstituted 2-acetamido-2-deoxy-hexopyranoside, unsubstituted hexopyranoside, and 3,6-disubstituted 2-acetamido-2-deoxy-hexopyranoside.

*Methyl 6-O-[3,6-Di-O-acetyl-4-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-2-deoxy-2-phthalimido-β-D-glucopyranosyl]-2-azido-3-O-(2,3,4,6-tetra-O-benzoyl-β-D-galactopyranosyl)-2-deoxy-1-thio-β-D-galactopyranoside (**6**)*

A solution of silver triflate (0.21 g) and 2,4,6-trimethylpyridine (0.11 ml) in dichloromethane (10 ml) was added dropwise, in a nitrogen atmosphere, to a stirred and cooled

(-20°C) mixture of **1** (0.67 g), 3,6-di-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-2-deoxy-2-phthalimido-β-D-glucopyranosyl bromide [11] (0.67 g), dichloromethane (10 ml) and molecular sieves. After 30 min, the mixture was diluted with dichloromethane, filtered through Celite, and washed with 10% aqueous sodium thiosulfate, and water. The organic layer was dried and concentrated, and the residue was taken up in methanol. Crystalline **6** (0.82 g, 66%) was obtained. Purification of the mother liquor by column chromatography gave more **6** (0.11 g, 8%). The crystalline material had m.p. 225-226°C, $[\alpha]_D$ +57°. NMR data: ^{13}C, δ 11.4 (SCH_3), 20.6, 20.9 ($\mathbf{C}H_3COO$), 54.9, C-2''), 60.7, 61.0, 62.1, 62.2 (C-2, C-6', C-6'', C-6'''), 66.6, 67.4, 68.0, 69.1, 69.2, 69.4, 70.6, 71.0, 71.2, 71.4, 71.9, 72.7, 77.0, 83.2, 84.0 (C-1,3,4,5,6, C-2',3',4',5', C-3'',4'',5'', C-2''',3''',4''',5'''), 98.2 (C-1''), 101.1, 102,2 (C-1', C-1'''); ^1H, δ 1.89, 1.90, 1.97, 2.02, 2.07, 2.14, 2.15 ($C\mathbf{H}^3COO$), 2.74 (m, OH-4), 3.93 (d, *J* 10.0 Hz, H-1), 4.56 (d, *J* 8.0 Hz, H-1'''), 4.93 (d, *J* 8.1 Hz, H-1'), 5.34 (d, *J* 8.4 Hz, H-1'').

Analytical data: Calculated for $C_{73}H_{74}N_4O_{30}S.2H_2O$: C, 56.4; H, 5.0; N, 3.6; S, 2.0. Found: C, 56.4; H, 4.7; N, 3.6; S, 1.9.

Methyl 6-O-[2-Acetamido-3,6-di-O-acetyl-4-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-2-deoxy-β-D-glucopyranosyl]-4-O-acetyl-3-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-2-azido-2-deoxy-1-thio-β-D-galactopyranoside (7)

A solution of acetic acid (1.2 ml), hydrazine hydrate (1.0 ml), and **6** (0.35 g) in ethanol/toluene (40/1 by vol, 41 ml) was refluxed overnight and then concentrated. The residue was dissolved in methanolic sodium methoxide (0.1 M, 10 ml). After 1 h, the mixture was neutralized with Dowex-50 and concentrated. The residue was dissolved in acetic anhydride/pyridine (1/1 by vol, 20 ml) and heated to 100°C for 30 min, then concentrated. The residue was purified by column chromatography to give amorphous **7** (0.24 g, 89%), $[\alpha]_D$ -4°. NMR data: ^{13}C, δ 20.5-20.8 (CH_3COO), 23.2 (CH_3CONH), 53.2 (C-2''), 60.9, 61.1, 62.1, 62.4 (C-2, C-6', C-6'', C-6'''), 66.8, 66.9, 68.4, 68.9, 69.0, 69.2, 70.8 (two signals), 70.9 (two signals), 72.6, 72.7, 75.8, 77.2, 79.2, 84.6 (C-1,3,4,5,6, C-2',3',4',5', C-3'',4'',5'', C-2''',3''',4''',5''') 101.0, 101.2, 101.3 (C-1', C-1'', C-1''').

*2-(p-Trifluoroacetamidophenyl)ethyl 6-O-[2-Acetamido-3,6-di-O-acetyl-4-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-2-deoxy-β-D-glucopyranosyl]-4-O-acetyl-3-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-2-azido-2-deoxy-α-D-galactopyranoside (**8**)*

Compound **7** (142 mg) was converted into the corresponding bromide and then immediately reacted with 2-(*p*-trifluoroacetamidophenyl)ethanol (200 mg) and tetraethylammonium bromide (200 mg), essentially as described for the preparation of **3**. Purification of the crude product by column chromatography gave amorphous **8** (130 mg, 81%), $[\alpha]_D$ +29°. NMR data: ^{13}C, δ 97.0 (C-1), 101.0, 101.1, 101.4 (C-1', C-1'', C-1'''), 120.6, 130.1, 134.3, 137.0 (aromatic C).

*2-(p-Trifluoroacetamidophenyl)ethyl 2-Acetamido-6-O-[acetamido-3,6-di-O-acetyl-4-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-2-deoxy-β-D-glucopyranosyl]-4-O-acetyl-3-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-2-deoxy-α-D-galactopyranoside (**9**)*

Compound **8** (225 mg) was treated as described under the preparation of **4** to give, after chromatographic purification, amorphous **9** (182 mg, 80%), $[\alpha]_D$ +19°. NMR data: ^{13}C, δ 20.4-20.7 ($\mathbf{C}H_3COO$), 23.1, 23.3 ($\mathbf{C}H_3CONH$), 35.0 ($Ph\mathbf{C}H_2CH_2O$), 49.1 (C-2), 53.1 (C-2''), 96.5 (C-1), 100.1, 101.0, 101.1 (C-1', C-1'', C-1'''), 121.0, 129.8, 134.4, 136.9 (aromatic C).

*2-(p-Trifluoroacetamidophenyl)ethyl 2-Acetamido-6-O-[2-acetamido-2-deoxy-4-O-(β-D-galactopyranosyl)-β-D-glucopyranosyl]-2-deoxy-3-O-(β-D-galactopyranosyl)-α-D-galactopyranoside (**10**)*

Treatment of **9** (150 mg) essentially as described under the preparation of **5** gave, after purification by gel filtration, amorphous 10 (88 mg, 82%), $[\alpha]_D$ +46° (*c* 1.0, water). NMR data: ^{13}C, (^2H_2O), δ 23.0, 23.1 (**C**H_3CONH), 35.1 (Ph**C**H_2CH_2O), 49.5 (C-2), 56.1 (C-2″), 61.4, 61.8 (two signals) (C-6′, C-6″, C-6‴), 68.3, 69.6 (three signals), 70.1, 70.3, 71.7, 71.9, 73.5, 73.6 (two signals), 75.7, 75.8, 76.2, 78.0, 80.1 (C-3, 4, 5, 6, C-2′, 3′, 4′, 5′, C-3″, 4″, 5″, C-2‴, 3‴, 4‴, 5‴, and PhCH_2**C**H_2O), 97.6 (C-1), 102.2, 103.8, 105.1 (C-1′, C-1″, C-1‴), 123.1, 130.6, 133.9, 139.0 (aromatic C), 174.9 (CH_3**C**ONH); ^1H (^2H_2O), δ 1.91, ,1.99 (C**H**$_3$CONH), 3.86 (dd, $J_{3,4}$ 3.5, $J_{2,3}$ 10.9 Hz, H-3), 4.09 (m, H-4) , 4.21 (dd, $J_{1,2}$ 3.7 Hz, H-2), 4.41 (d, *J* 7.9 Hz, H-1′), 4.47 (d, *J* 7.3 Hz, H-1‴), 4.52 (d, *J* 8.3 Hz, H-1″), 4.81 (d, *J* 3.7 Hz, H-1).

The FAB-MS of **10** showed an $(M+H)^+$ ion m/z = 964.

Analytical data: Calculated for $C_{38}H_{56}F_3N_3O_{22}.4H_2O$: C, 44.0; H, 6.2; N, 4.0. Found: C, 43.9; H, 6.0; N, 3.7.

Methylation analysis showed the presence of 4-substituted 2-acetamido-2-deoxy-hexopyranoside, unsubstituted hexopyranoside, and 3,6-disubstituted 2-acetamido-2-deoxy-hexopyranoside.

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