Glycoconjugate J (1989) 6:21-34

Synthesis of an H Type 2 and a Y (Le^y) Glycoside from Thioglycoside Intermediates

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Received January 10, 1989.

Key words: synthesis, thioglycoside, H type 2 trisaccharide, Y (Le^y) tetrasaccharide

The trisaccharide 2-(*p*-trifluoroacetamidophenyl)ethyl 2-acetamido-2-deoxy- 4-*O*-[2-*O*-(α-L-fucopyranosyl)-β-D-galactopyranosyl]-β-D-glucopyranoside 1 and the tetrasaccharide 2-(*p*-trifluoroacetamidophenyl)ethyl 2-acetamido-2-deoxy-3-*O*-(α-L-fucopyranosyl)-4-*O*-[2-*O*-(α-L-fucopyranosyl)-β-D-galactopyranosyl]-β-D-glucopyranoside 2 were synthesized. Thioglycosides, suitably protected, activated directly with methyl trifluoromethanesulfonate or dimethyl(methylthio)sulfonium tetrafluoroborate or activated after bromine treatment with halophilic reagents, were used as glycosyl donors in the construction of the glycosidic linkages.

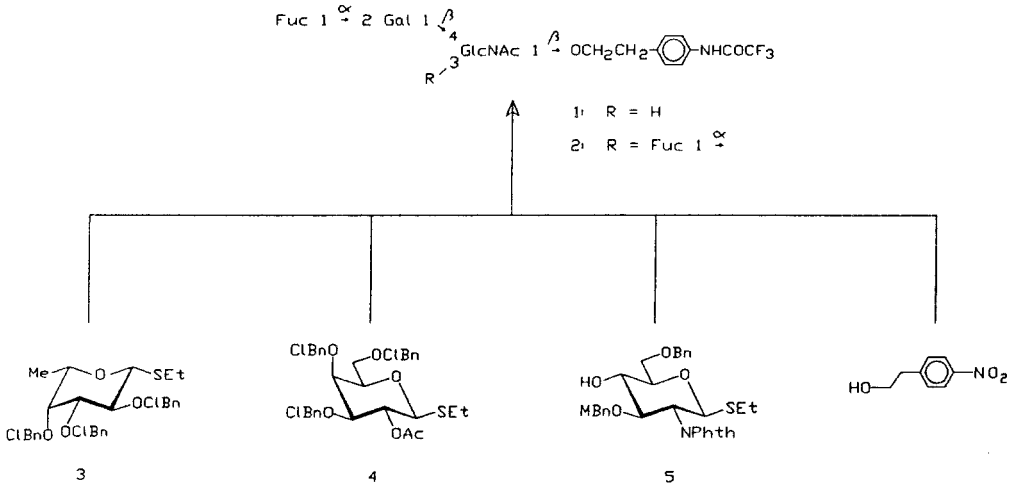
The fucosylated glycosides, H type 2 trisaccharide and Y (Le^y) tetrasaccharide, are parts of structures found in human glycosphingolipids, and also parts of glycosphingolipids associated with oncogenic transformation [1]. Synthesis of the H type 2 and Y (Le^y) determinants as the free saccharides or as glycosides of 8-carboxymethyloctanol and methanol have been described previously [2-8].

The H type 2 and Y (Le^y) spacer glycosides reported here can be coupled to proteins or to solid supports to be useful tools in various studies of biological phenomena where carbohydrates are involved. Hydrophobic spacer glycosides of this type are also useful in glycosyltransferase assays [9]. Saccharide **1** was found to be an acceptor for α(1-3)fucosyltransferase from human colon carcinoma cell lines [10].

The chemical synthesis of oligosaccharides is more complex than the synthesis of other natural biopolymers, such as peptides or proteins and ribo- or deoxyribonucleotides, due to the greater possibility of combining the monosaccharides into oligosaccharides. However, several reasonable strategies can be used for oligosaccharide synthesis.

The use of suitably protected thioglycosides as synthons for the monosaccharide units in oligo- and polysaccharide synthesis has been proved to be successful [11]. The thioalkyl group protects the anomeric centre during the *O*-protection reactions and effectively reacts

Abbreviations: DMTSB, dimethyl(methylthio)sulfonium tetrafluoroborate; Phth, phthaloyl; MBn, *p*-methoxybenzyl; ClBn, *p*-chlorobenzyl.

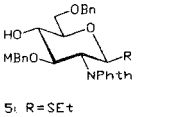


with various agents to form an active glycosyl donor. In this paper we present further examples of the use of thioglycosides in oligosaccharide synthesis.

Results

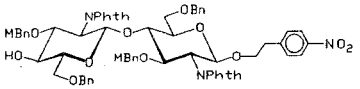
From the retrosynthesis of the oligosaccharides 1 and 2 we designed the monosaccharide synthons to be, for the α-fucosyl group ethyl 2,3,4-tri-*O*-*p*-chlorobenzyl-1-thio-β-L-fucopyranoside **3**, for the 2-substituted-β-galactosyl group ethyl 2-*O*-acetyl-3,4,6-tri-*O*-*p*-chlorobenzyl-1-thio-β-D-galactopyranoside **4**, and for the 3,4-substituted-β-*N*-acetylglucosaminyl group ethyl 6-*O*-benzyl-2-deoxy-3-*O*-*p*-methoxybenzyl-2-phthalimido-1-thio-β-D-glucopyranoside **5**. The *p*-chlorobenzyl protective group for thioglycosides **3** and **4** was chosen because of its better crystallization properties [12]. As the starting material for the spacer arm 2-(*p*-nitrophenyl)ethanol was chosen.

The synthesis of the monosaccharide building blocks was as follows: α-L-fucose was treated, successively, with acetic anhydride/pyridine, ethanethiol/boron trifluoride etherate, sodium methoxide/methanol, and *p*-chlorobenzylchloride/sodium hydride to give thiofucoside **3** in 39% yield. Acetobromogalactose was reacted, successively, with ethanethiol/tetraethylammonium bromide/2,6-lutidine in nitromethane [13], sodium methoxide/methanol, *p*-chlorobenzyl chloride/sodium hydride, and trimethylsilyl triflate yielding thiogalactoside **4** in 59% yield. The thioglucosimide **5** was prepared as described [14].



5: R=SEt

6: R=OCH$_2$CH$_2$-C$_6$H$_4$-NO$_2$



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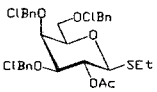

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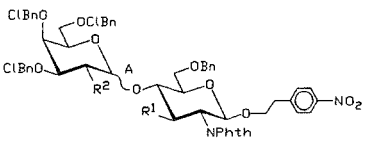
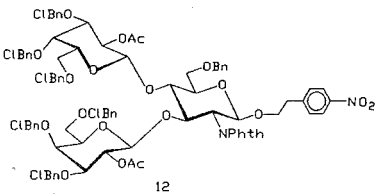


	A	R^1	R^2
8:	β	OMBn	OAc
9:	α	OMBn	OAc
10:	β	OMBn	OH
11:	β	OH	OH



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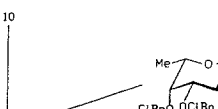

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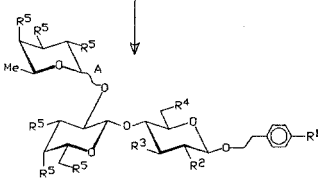
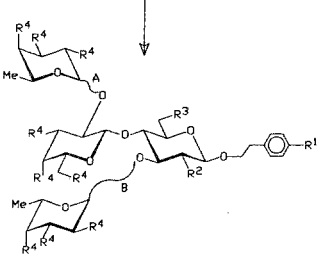


	A	R^1	R^2	R^3	R^4	R^5
13:	α	NO_2	NPhth	OMBn	OBn	OClBn
14:	β	NO_2	NPhth	OMBn	OBn	OClBn
1:	α	$NHCOCF_3$	NHAc	OH	OH	OH



	A	B	R^1	R^2	R^3	R^4
15:	α	α	NO_2	NPhth	OBn	OClBn
16:	β	α	NO_2	NPhth	OBn	OClBn
17:	α	β	NO_2	NPhth	OBn	OClBn
2:	α	α	$NHCOCF_3$	NHAc	OH	OH

Dimethyl(methylthio)sulfonium tetrafluoroborate (DMTSB) [15] or methyl trifluoromethanesulfonate (methyl triflate) [16] promoted condensation of thioglucosimide **5** with 2-(*p*-nitrophenyl)ethanol gave **6** in 83 or 70% yield, respectively. With methyl triflate the corresponding β(1-4)-linked dimer **7** could also be isolated in 8% yield.

Glycosylation of **6** with thiogalactoside **4** promoted by DMTSB gave disaccharide **8** in 91% yield. With methyl triflate promotion the yield of **8** was 79%. The lower yield was due to the formation of the corresponding α-isomer (8%) **9** and the trisaccharide **12** (8%).

Disaccharide **8** was de-*O*-acetylated with sodium methoxide in dichloromethane-methanol in 80% yield to give disaccharide derivative **10**. DMTSB promoted α-fucosylation of **10** with thiofucoside **3** gave the trisaccharide derivative **13** in 65% yield. The major by-product was the β-fucosyl isomer **14** (19%). If instead the thiofucoside **3** was converted into the corresponding glycosyl bromide with bromine and then condensed with **10** under halide ion promotion the isolated yield of trisaccharide **13** was raised to 90%. Deblocking of the trisaccharide derivative was performed by the following sequence. Compound **13** was treated with hydrazine acetate followed by acetylation and purification. The nitro group was reduced with hydrogen over platinum oxide and the obtained arylamine derivative was *N*-trifluoroacetylated with trifluoroacetic anhydride. The *O*-benzyl protective groups were removed by hydrogenolysis over Pd/C and the trisaccharide glycoside **1** could be isolated after chromatographic purification in 74% overall yield.

For the synthesis of tetrasaccharide derivative **15** the crystalline diol **11**, obtained from **10** in 89% yield by de-*O*-*p*-methoxybenzylation using ceric ammonium nitrate in aqueous acetonitrile [17], was used as glycosyl acceptor. The diol **11** was glycosylated with the glycosyl bromide derived from thiofucoside **3** using mercury(II) cyanide/mercury(II) bromide, bromide ion or silver triflate promotion. The isolated yields of **15** were 82%, 86% or 59% respectively. The lower yield with silver triflate was due to the formation of the 2'-β-fucosyl isomer **16**. The mercury(II) cyanide/mercury(II) bromide promotion gave a minor amount of the 3-β-fucosyl isomer **17**. With direct condensation of diol **11** with thiofucoside **3** under DMTSB promotion the isolated yield of **15** was 57%. The lower yield was due to formation of the β-fucosyl isomers **16** and **17**. Thus, as was the case with the trisaccharide derivative **13**, the halide ion promoted fucosylation gave the best yield and stereoselectivity. The tetrasaccharide glycoside **2** was finally obtained from **15** in 56% overall yield, using the same deblocking sequence as for **1**.

Experimental

General Methods

Melting points are corrected. Concentrations were performed under reduced pressure at <40°C bath temperature. Optical rotations were measured at 23°C (c=0.5, chloroform) unless otherwise stated, using a Perkin-Elmer 241 polarimeter. NMR spectra were recorded at 300 K with a Bruker AM 500 instrument. The following reference signals were used: Me_4Si, δ 0.0 (^1H in C^2HCl_3); $CHCl_3$ δ 77.0 (^{13}C in C^2HCl_3); Me_2CO, δ 2.225 (^1H in ^2H_2O); and external dioxan, δ 67.4 (^{13}C in ^2H_2O). Only selected NMR data are reported. In the assignments below atoms of glucosamine carry no superscript, while atoms of galactose, 2-linked fucose and

3-linked fucose carry the ', '' and ''' superscripts, respectively. Assignments were based on 2 D COSY and *J* resolved experiments, decoupling techniques, DEPT and proton-carbon correlation experiments (CHORTLE) [18]. In the case of compound **17** the two fucose residues were differentiated with a NOE experiment. The fucose protons in compound **15** and **16** were assigned by analogy to **17**. The FAB-MS spectra were recorded with a VG ZAB-SE mass spectrometer. TLC was performed on Silica Gel F_{254} (Merck, Darmstadt, W. Germany) with detection by u.v. light and/or by charring with sulfuric acid. Column chromatography was performed on silica gel (Matrex, 60 Å, 20-45 μm or 35-70 μm; Grace, Worms, W. Germany). Organic solutions were dried over sodium sulfate. Powdered molecular sieves (4Å; Fluka, Buchs, Switzerland) were heated to 300°C under vacuum overnight. DMF, pyridine and dichloromethane were distilled from P_2O_5 and acetonitrile from CaH_2. Toluene and diethyl ether were dried over sodium wire. THF was dried by passage through a column of activated alumina. DMTSB was prepared as described [19].

*Ethyl 2,3,4-Tri-O-p-chlorobenzyl-1-thio-β-L-fucopyranoside (**3**)*

α-L-Fucose (20 g, 0.122 mol) was acetylated with 450 ml acetic anhydride/pyridine, 2/1 by vol, at 100°C for 2 h. The solution was concentrated and co-evaporated with xylene (3 x 75 ml). To a solution of the residue and ethanethiol (13.5 ml, 0.183 mol) in chloroform (80 ml) was added boron trifluoride etherate (18.4 ml, 0.146 mol) at 4°C. The solution was stirred at 4°C for 24 h, diluted with dichloromethane, washed with saturated sodium hydrogencarbonate and water, dried and concentrated. The residue was treated with sodium methoxide in methanol overnight, neutralized with Dowex 50 (H^+) resin, filtered, concentrated and co-evaporated with toluene.

The residue was dissolved together with *p*-chlorobenzyl chloride (58.9 g, 0.366 mol) in *N,N*-dimethylformamide (300 ml) and added to sodium hydride (17.6 g, 0.732 mol) at 0°C under nitrogen. The mixture was allowed to attain room temperature overnight. Methanol (40 ml) was then added and the mixture was partitioned between toluene and water. The organic layer was washed with water, dried and concentrated. Crystallization from iso-octane, treatment with activated carbon and recrystallization from methanol gave **3** (18 g, 25%). The mother liquors were purified by column chromatography (light petroleum/ethyl acetate, 10/3 by vol) and crystallization from methanol to give more of compound **3** (10 g, 14%). M.p. 80-81°C, $[\alpha]_D$ -34°.

NMR data (C^2HCl_3): ^{13}C; δ 15.0, 24.8 (SEt), 17.2 (C-6), 72.0, 74.0, 74.8 (O**C**H_2Ph), 74.4 (C-5), 77.0 (C-4), 78.3 (C-2), 84.2 (C-3), 84.9 (C-1), 128.3-137.0 (aromatic C). ^1H; δ 1.24 (d, $J_{5,6}$ 6.4 Hz, H-6), 3.50 (dq, $J_{4,5}$ 1.0 Hz, H-5), 3.51 (dd, $J_{2,3}$ 9.5 Hz, $J_{3,4}$ 3.0 Hz, H-3), 3.59 (dd, H-4), 3.75 (t, $J_{1,2}$ 9.5 Hz, H-2), 4.37 (d, H-1).

Analytical data. Calculated for $C_{29}H_{31}Cl_3O_4S$: C, 59.9; H, 5.4; S, 5.5. Found: C, 60.0; H, 5.4; S, 5.5.

*Ethyl 2-O-Acetyl-3,4,6-tri-O-p-chlorobenzyl-1-thio-β-D-galactopyranoside (**4**)*

A solution of 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide (9.80 g, 24 mmol), tetraethylammonium bromide (0.50 g, 2.4 mmol), 2,6-lutidine (4.1 ml, 35 mmol) and ethanethiol (7.1 ml, 96 mmol) in nitromethane (20 ml) was stirred at room temperature for

24 h. (The starting material and the product were difficult to separate on TLC. The reaction was followed by taking out aliquots of the reaction solution, adding a drop of piperidine and stirring at room temperature for 0.5 h. Any remaining bromo sugar gave rise to a slower moving TLC spot.) Ethyl acetate and water were then added. The organic layer was washed with water, dried and concentrated. The residue was treated with sodium methoxide in methanol for 3 h, concentrated and co-evaporated with toluene without previous neutralization. A solution of the residue and *p*-chlorobenzyl chloride (12.7 g, 79 mmol) in *N,N*-dimethylformamide (25 ml) was added to sodium hydride (3.4 g, 142 mmol) at 0°C under nitrogen. The mixture was allowed to attain room temperature overnight. Methanol (2 ml) was added dropwise at 0°C and the mixture was partitioned between toluene and water. The organic layer was washed with water, dried and concentrated.

Trimethylsilyl triflate (488 µl, 2.5 mmol) was added at 0°C to a solution of the residue in acetonitrile (40 ml). The cooling bath was removed and the mixture was stirred for 25 min. Saturated sodium hydrogencarbonate and ethyl acetate was added. The organic layer was washed with water, dried and concentrated. Crystallization from ethyl acetate-light petroleum and recrystallization from diethyl ether-light petroleum gave **4** (4.98 g, 33%). The mother liquors were purified by column chromatography (toluene/ethyl acetate, 15/1 by vol) and crystallization from diethyl ether-light petroleum to give more of compound **4** (4.01 g, 26%). M.p. 93-95°C, $[\alpha]_D$ -6°.

NMR data (C^2HCl_3): ^{13}C; δ 14.8, 23.6 (SEt), 21.0 (**C**H_3CO), 69.5, 73.3, 77.2, 81.6, 83.7 (C-1,2,3,4,5), 68.3, 71.4, 72.7, 73.7 (C-6, O**C**H_2Ph), 128.3-136.9 (aromatic C), 169.6 (CH_3**C**O). ^1H; δ 3.52 (dd, $J_{2,3}$ 9.8 Hz, $J_{3,4}$ 3.1 Hz, H-3), 3.94 (dd, $J_{4,5}$ 0.6 Hz, H-4), 4.34 (d, $J_{1,2}$ 9.8 Hz, H-1), 5.39 (t, H-2).

Analytical data. Calculated for $C_{31}H_{33}Cl_3O_6S$: C, 58.2; H, 5.2; S, 5.0. Found: C, 58.3; H, 5.2; S, 4.9.

*2-(p-Nitrophenyl)ethyl 6-O-Benzyl-2-deoxy-3-O-p-methoxybenzyl-2- phthalimido-β-D-glucopyranoside (**6**)*

Method A. DMTSB (7.10 g, 36.2 mmol) was added to a stirred mixture of **5** [14] (10.1 g, 17.9 mmol), 2-(*p*-nitrophenyl)ethanol (6.00 g, 35.9 mmol), 2,4,6-collidine (1.90 ml, 14.3 mmol) and 4 Å molecular sieves (36 g) in dichloromethane (220 ml) at -15°C. The temperature was raised to 15°C during 3 h, then saturated sodium hydrogen carbonate and ethyl acetate was added. The mixture was filtered through a layer of Celite and the organic layer was washed with water, dried and concentrated. The product was purified by column chromatography (light petroleum/ethyl acetate, 1/1 by vol) followed by crystallization from ethyl acetate-light petroleum to give **6** (9.93 g, 83%). M.p. 94-95°C, $[\alpha]_D$ -2°.

NMR data (C^2HCl_3): ^{13}C; δ 35.4 (OCH_2**C**H_2), 54.8, 55.1 (OMe, C-2), 68.8, 70.5, 73.7, 74.0 (C-6, O**C**H_2CH_2, O**C**H_2Ph), 73.7, 74.2, 78.2 (C-3,4,5), 98.1 (C-1), 113.4, 158.8 (aromatic C MBn), 122.6-146.7 (aromatic C), 167.5, 167.8 (C=O NPhth). ^1H; δ 3.62 (m, $J_{4,5}$ 9.4 Hz, $J_{5,6a}$ 4.9 Hz, $J_{5,6b}$ 4.9 Hz, H-5), 3.76 (broad t, $J_{3,4}$ 8.2 Hz, H-4), 3.80 (m, $J_{6a,6b}$ 10.2 Hz, H-6a, H-6b), 4.03 (dd, $J_{1,2}$ 8.2 Hz, $J_{2,3}$ 10.7 Hz, H-2), 4.09 (dd, H-3), 5.06 (d, H-1).

Analytical data. Calculated for $C_{37}H_{36}N_2O_{10}$: C, 66.5; H, 5.4; N, 4.2. Found: C, 66.0; H, 5.4; N, 4.1.

Method B. Methyl triflate (3.1 ml, 28.4 mmol) was added to a stirred mixture of 5 [14] (3.72 g, 6.60 mmol), 2-(*p*-nitrophenyl)ethanol (2.40 g, 14.4 mmol) and 4 Å molecular sieves (25 g) in diethyl ether (250 ml) at room temperature. After 25 h the solution was diluted with dichloromethane and piperidine (6 ml) was added. The mixture was stirred for 20 min, filtered through a layer of Celite, concentrated and co-evaporated with toluene. The residue was purified by column chromatography (light petroleum/ethyl acetate, 1/1 by vol) followed by crystallization from ethyl acetate-light petroleum to give 6 (3.11 g, 70%) (R_F 0.31).

The column chromatography yielded also 2-(*p*-nitrophenyl)ethyl 6-*O*-benzyl-4-*O*-(6-*O*-benzyl-2-deoxy-3-*O*-*p*-methoxybenzyl-2-phthalimido-β-D-glucopyranosyl)-2-deoxy-3-*O*-*p*-methoxybenzyl-2-phthalimido-β-D-glucopyranoside (7) as an amorphous material (0.32 g, 8%) (R_F 0.25). $[\alpha]_D$ -14°. NMR data (C^2HCl_3): ^{13}C; δ 35.3 ($OCH_2\mathbf{C}H_2$), 54.7, 54.8 (OMe), 55.3, 56.1 (C-2,2´), 96.9, 97.9 (C-1,1´), 113.1, 113.4, 158.4, 158.7 (aromatic C MBn). ^1H; δ 4.85 (m, $J_{1,2}$ 8.5 Hz, H-1), 5.27 (d, $J_{1',2'}$ 8.5 Hz, H-1´).

*2-(p-Nitrophenyl)ethyl 4-O-(2-O-Acetyl-3,4,6-tri-O-p-chlorobenzyl-β-D-galactopyranosyl)-6-O-benzyl-2-deoxy-3-O-p-methoxybenzyl-2-phthalimido-β-D-glucopyranoside (**8**)*

Method A. DMTSB (3.00 g, 15.3 mmol) was added to a stirred mixture of **4** (6.00 g, 9.37 mmol), **6** (5.00 g, 7.48 mmol), 2,6-di-*tert*-butyl-4-methylpyridine (1.25 g, 6.08 mmol) and 4 Å molecular sieves (20 g) in dichloromethane (100 ml) at -10°C. The mixture was allowed to attain room temperature overnight. Saturated sodium hydrogen carbonate and ethyl acetate was added and the mixture was filtered through a layer of Celite. The organic layer was washed with water, dried and concentrated. Column chromatography (toluene/ethyl acetate, 4/1 by vol) yielded amorphous **8** (8.48 g, 91%). $[\alpha]_D$ +13°.

NMR data (C^2HCl_3): ^{13}C; δ 21.0 ($\mathbf{C}H_3CO$), 35.4 ($OCH_2\mathbf{C}H_2$), 54.8, 55.4 (C-2, OMe), 67,8-74.2 (C-6,6´, $O\mathbf{C}H_2CH_2$, $O\mathbf{C}H_2Ph$), 71.8-80.5 (C-3,4,5,2´,3´,4´,5´), 98.2, 100.6 (C-1,1´), 113.0, 158.4 (aromatic C MBn), 122.6-146.7 (aromatic C), 167.2, 167.6 (C=O NPhth), 169.1 ($CH_3\mathbf{C}O$). ^1H; δ 3.30 (dd, $J_{2',3'}$ 10.4 Hz, $J_{3',4'}$ 3.0 Hz, H-3´), 3.84 (dd, $J_{4',5'}$ 0.9 Hz, H-4´), 3.95 (dd, $J_{3,4}$ 8.6 Hz, $J_{4,5}$ 9.8 Hz, H-4), 4.01 (dd, $J_{1,2}$ 8.5 Hz, $J_{2,3}$ 11.0 Hz, H-2), 4.09 (dd, H-3), 4.46 (d, $J_{1',2'}$ 7.9 Hz, H-1´), 5.00 (d, H-1), 5.29 (dd, H-2´).

Method B. Methyl triflate (1.15 ml, 10.4 mmol) was added to a stirred mixture of **4** (2.39 g, 3.73 mmol), **6** (2.00 g, 2.99 mmol), 2,4,6-collidine (395 µl, 2.99 mmol) and 4Å molecular sieves (10 g) in diethyl ether (25 ml) at room temperature. After 18 h piperidine (4 ml) was added. The mixture was stirred for 20 min, filtered through a layer of Celite and concentrated. The residue was partitioned between toluene and water. The organic layer was dried and concentrated. Column chromatography (toluene/ethyl acetate, 45/10 by vol) gave **8** as a syrup (2.94 g, 79%) (R_F 0.17).

The column chromatography yielded also the corresponding α-isomer **9** as a syrup (298 mg, 8%) (R_F 0.26), $[\alpha]_D$ +43°, NMR-data (C^2HCl_3): ^{13}C; δ 21.0 ($\mathbf{C}H_3CO$), 35.3 ($OCH_2\mathbf{C}H_2$), 54.6, 55.3 (C-2, OMe), 96.8, 97.8 (C-1,1´), 170.0 ($CH_3\mathbf{C}O$). ^1H; δ 4.99 (d, $J_{1,2}$ 8.5 Hz, H-1), 5.44

(dd, $J_{1',2'}$ 3.8 Hz, $J_{2',3'}$ 10.5 Hz, H-2′), 5.56 (d, H-1′) and 2-(*p*-nitrophenyl)ethyl 3,4-di-*O*-(2-*O*-acetyl-3,4,6-tri-*O*-*p*-chlorobenzyl-β-D-galactopyranosyl)-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (**12**) as a syrup (415 mg, 8%) (R_F 0.21). $[\alpha]_D$ -16°. NMR data (C^2HCl_3) (The ′ and ″ designations are arbitrary): ^{13}C; δ 20.8, 21.0 ($\mathbf{C}H_3CO$), 35.3 ($OCH_2\mathbf{C}H_2$), 55.5 (C-2), 97.7, 99.3, 99.5 (C-1,1′,1″), 169.3, 169.5 ($CH_3\mathbf{C}O$). ^1H; δ 4.88 (d, $J_{1,2}$ 8.5 Hz, H-1), 5.11 (dd, $J_{1',2'}$ 7.9 Hz, $J_{2',3'}$ 10.1 Hz, H-2′), 5.25 (dd, $J_{1'',2''}$ 7.8 Hz, $J_{2'',3''}$ 9.9 Hz, H-2″).

*2-(p-Nitrophenyl)ethyl 6-O-Benzyl-2-deoxy-3-O-p-methoxybenzyl-2-phthalimido-4-O-(3,4,6-tri-O-p-chlorobenzyl-β-D-galactopyranosyl)-β-D-glucopyranoside (**10**)*

Sodium methoxide in methanol (6 ml, 0.2 M) was added to a solution of **8** (2.80 g, 2.25 mmol) in 10 ml dichloromethane/methanol, 3/2 by vol, at room temperature. After two days the solution was neutralized with Dowex 50 (H^+) resin, filtered and concentrated. Column chromatography (toluene/ethyl acetate, 45/10 by vol) gave **10** as a syrup (2.17 g, 80%). $[\alpha]_D$ +24°.

NMR data (C^2HCl_3): ^{13}C; δ 35.4 ($OCH_2\mathbf{C}H_2$), 54.7, 55.5 (C-2, OMe), 68.3-74.4 (C-6,6′, $O\mathbf{C}H_2CH_2$, $O\mathbf{C}H_2Ph$), 72.5-81.7 (C-3,4,5,2′,3′,4′,5′), 98.3, 103.6 (C-1,1′), 113.1, 158.4 (aromatic C MBn), 122.7-146.7 (aromatic C), 167.6 (C=O NPhth). ^1H; δ 3.28 (dd, $J_{2',3'}$ 9.8 Hz, $J_{3',4'}$ 3.1 Hz, H-3′), 3.78 (dd, $J_{4',5'}$ 0.9 Hz, H-4′), 3.87 (dd, $J_{1',2'}$ 7.9 Hz, H-2′), 4.02 (dd, $J_{1,2}$ 8.5 Hz, $J_{2,3}$ 11.0 Hz, H-2), 4.06 (dd, $J_{3,4}$ 8.6 Hz, $J_{4,5}$ 9.8 Hz, H-4), 4.22 (dd, H-3), 4.54 (d, H-1′), 5.00 (d, H-1).

*2-(p-Nitrophenyl)ethyl 6-O-Benzyl-2-deoxy-2-phthalimido-4-O-(3,4,6-tri-O-p-chlorobenzyl-β-D-galactopyranosyl)-β-D-glucopyranoside (**11**)*

A solution of **10** (3.38 g, 2.81 mmol) and ceric ammonium nitrate (4.24 g, 7.73 mmol) in 70 ml acetonitrile/water, 9/1 by vol, was stirred at room temperature for 2 h. The formed precipitate was filtered off, washed with water and ether. The precipitate was taken up in dichloromethane and a small amount of undissolved material was filtered off. The filtrate was concentrated and recrystallized from warm ethyl acetate to yield **11** (2.55 g, 84%). The filtrate from the reaction mixture was concentrated and partitioned between dichloromethane and water. The organic layer was washed with saturated sodium hydrogencarbonate, dried and concentrated. Crystallization from ethyl acetate gave more of compound **11** (0.16 g, 5%). M.p. 179-180°C, $[\alpha]_D$ -10°.

NMR data (C^2HCl_3): ^{13}C; δ 35.4 ($OCH_2\mathbf{C}H_2$), 55.5 (C-2), 68.7-73.5 (C-6,6′, $OCH_2\mathbf{C}H_2$), 69.7-84.5 (C-3,4,5,2′,3′,4′,5′), 98.2, 104.5 (C-1,1′), 122.7-146.7 (aromatic C), 167.5, 167.9 (C=O NPhth). ^1H; δ 3.33 (dd, $J_{2',3'}$ 9.2 Hz, $J_{3',4'}$ 3.1 Hz, H-3′), 3.59 (t, $J_{3,4}$ 9.8 Hz, $J_{4,5}$ 9.8 Hz, H-4), 3.74 (d, H-4′), 3.86 (dd, $J_{1',2'}$ 7.9 Hz, H-2′), 4.09 (dd, $J_{1,2}$ 8.5 Hz, $J_{2,3}$ 11.0 Hz, H-2), 4.27 (d, H-1′), 4.33 (m, H-3), 5.12 (d, H-1).

Analytical data. Calculated for $C_{56}H_{53}Cl_3N_2O_{14}$: C, 62.0; H, 4.9; N, 2.6. Found: C, 61.8; H, 4.8; N, 2.7.

*2-(p-Nitrophenyl)ethyl 6-O-Benzyl-2-deoxy-3-O-p-methoxybenzyl-2-phthalimido-4-O-[3,4,6-tri-O-p-chlorobenzyl-2-O-(2,3,4-tri-O-p-chlorobenzyl-α-L-fucopyranosyl)-β-D-galactopyranosyl]-β-D-glucopyranoside (**13**)*

Method A. Bromine (90 µl, 1.91 mmol) in dichloromethane (2.0 ml) was added to a stirred solution of **3** (0.97 g, 1.66 mmol) in dichloromethane (8 ml) at 0°C. After 15 min cyclohexene was added dropwise until the yellow colour of bromine disappeared. The solution was added to a stirred mixture of **10** (1.00 g, 0.83 mmol), tetraethylammonium bromide (0.35 g, 1.66 mmol) and 4Å molecular sieves (6 g) in 8 ml dichloromethane/*N,N*-dimethylformamide, 5/3 by vol, at room temperature. The mixture was stirred for 24 h, pyridine (1.5 ml) was then added, and after 3 h the mixture was filtered through a layer of Celite. The solution was concentrated and the residue was partitioned between toluene and saturated sodium hydrogencarbonate. The organic layer was washed with water, dried and concentrated. Column chromatography (toluene/ethyl acetate, 4/1 by vol) gave amorphous **13** (1.29 g, 90%). $[\alpha]_D$ -25°.

NMR data (C^2HCl_3): ^{13}C; δ 16.7 (C-6´´), 35.4 ($OCH_2\mathbf{C}H_2$), 54,8, 55.4 (C-2, OMe), 66.4-83.7 (C-3,4,5,2',3',4',5',2'',3'',4'',5''), 68.4-74.2 (C-6,6', $O\mathbf{C}H_2CH_2$, $O\mathbf{C}H_2Ph$), 97.5, 98.4, 100.6 (C-1,1',1''), 113.1, 158.6 (aromatic C MBn), 122.6-146.7 (aromatic C), 167.2, 167.8 (C=O NPhth): ^1H; δ 1.32 (d, $J_{5'',6''}$ 6.5 Hz, H-6''), 3.68 (d, $J_{3'',4''}$ 2.8 Hz, H-4''), 3.80 (dd, $J_{2'',3''}$ 10.3 Hz, H-3''), 3.86 (d, $J_{3',4'}$ 3.0 Hz, H-4'), 3.95 (dd, $J_{1'',2''}$ 3.8 Hz, H-2''), 4.00 (broad m, H-4), 4.05 (m, H-2,3), 4.13 (dd, $J_{1',2'}$ 7.6 Hz, $J_{2',3'}$ 9.8 Hz, H-2'), 4.48 (d, H-1'), 5.00 (m, $J_{1,2}$ 8.2 Hz, H-1), 5.57 (d, H-1'').

Method B. DMTSB (130 mg, 0.664 mmol) was added to a stirred mixture of **3** (387 mg, 0.664 mmol), **10** (400 mg, 0.332 mmol) and 4Å molecular sieves (3.2 g) in THF (15 ml) at -10°C. The mixture was allowed to attain room temperature. After 16 h saturated sodium hydrogencarbonate and ethyl acetate was added, and the mixture was filtered through a layer of Celite. The organic layer was washed with water, dried and concentrated. Column chromatography (toluene/ethyl acetate, 4/1 by vol) yielded **13** as a syrup (370 mg, 65%) (R_F 0.22).

The column chromatography yielded also the corresponding β-isomer **14** as a syrup (111 mg, 19%) (R_F 0.37). $[\alpha]_D$ -21°. NMR data (C^2HCl_3): ^{13}C; δ 16.9 (C-6´´), 35.4 ($OCH_2\mathbf{C}H_2$), 54.9, 55.3 (C-2, OMe), 98.2 (C-1), 101.5 (C-1'), 101.8 (C-1''):. ^1H; δ 4.53 (d, $J_{1',2'}$ 7.9 Hz, H-1'), 4.74 (d, $J_{1'',2''}$ 8.0 Hz, H-1''), 4.93 (d, $J_{1,2}$ 8.5 Hz, H-1).

*2-(p-Trifluoroacetamidophenyl)ethyl 2-Acetamido-2-deoxy-4-O-[2-O-(α-L-fucopyranosyl)-β-D-galactopyranosyl]-β-D-glucopyranoside (**1**)*

Hydrazine hydrate (1.42 ml, 29 mmol) and acetic acid (1.25 ml, 22 mmol) were added to a mixture of **13** (2.40 g, 1.39 mmol) in 70 ml toluene/95% ethanol,1/18 by vol. The mixture was refluxed overnight, cooled, concentrated and co-evaporated with toluene-ethanol. The residue was acetylated with 30 ml acetic anhydride/pyridine, 1/1 by vol, at room temperature. After 3 h the reaction mixture was concentrated, co-evaporated with xylene and partitioned between toluene and water. The organic layer was dried and concentrated. Chromatography (toluene/ethyl acetate, 2/1 by vol) gave amorphous material (2.13 g). NMR data (C^2HCl_3): ^{13}C; δ 23.5 ($\mathbf{C}H_3CONH$), 97.4, 99.8, 101.1 (C-1,1´,1´´), 170.1 ($CH_3\mathbf{C}ONH$).

Table 1. NMR data for compound **1**.

^{1}H-NMR	H-1	H-2	H-3	H-4	H-5	H-6a	H-6b
GlcNAc	4.43 8.3_{12}	3.65 10.6_{23}	3.58 8.9_{34}	3.74 10.0_{45}	3.43 5.9_{56a} 2.0_{56b}	3.79 11.8_{6a6b}	3.97
Gal	4.52 7.7_{12}	3.65 9.6_{23}	3.86 3.6_{34}	3.88 1.2_{45}	3.68 N.D.[a]	3.73 N.D.	3.77
Fuc(1-2)	5.30 2.7_{12}	3.81 N.D.	3.79 N.D	3.82 N.D.	4.23 6.6_{56}	1.22	

^{13}C-NMR	C-1	C-2	C-3	C-4	C-5	C-6
GlcNAc	101.8	55.9	73.1	76.9	76.1	61.0
Gal	101.1	77.3	74.4	69.9	76.1	61.9
Fuc(1-2)	100.2	69.0[b]	70.5[b]	72.5[b]	67.7	16.2
CH_3CONH	22.8					
OCH_2**C**H_2	35.2					
O**C**H_2CH_2	71.1					
CF_3CO	116.7 (*J* 286 Hz)					
Ar	123.1-138.7					
CF_3**C**O	157.8 (*J* 36.2 Hz)					
CH_3**C**ONH	175.0					

[a] N.D. = not determined.
[b] Assigned through comparison with NMR data in [6].

A solution of the material (2.05 g, 1.25 mmol) in ethyl acetate (40 ml) was hydrogenated over platinum oxide (100 mg) at atmospheric pressure. After 6 h the mixture was filtered and concentrated. The residue was dissolved in 30 ml pyridine/THF, 1/1 by vol, cooled to -25°C under nitrogen and trifluoroacetic anhydride (355 µl, 2.50 mmol) was added. The solution was allowed to attain room temperature. Water (0.15 ml) was added at 0°C and after 1 h at room temperature the solution was concentrated and partitioned between water and toluene. The organic layer was washed with cold 1 M sulfuric acid, saturated sodium hydrogencarbonate and water, dried and concentrated. Column chromatography (toluene/ethyl acetate, 15/10 by vol) yielded amorphous material (1.88 g). NMR data (C^2HCl_3): ^{13}C; δ 97.4, 99.8, 101.0 (C-1,1´,1´´), 115.7 (q, *J* 288 Hz, **C**F_3CO), 154.7 (q, *J* 35 Hz, CF_3**C**O).

A solution of the material (900 mg, 0.53 mmol) in 95% ethanol (30 ml) was hydrogenated over Pd/C (10%, 250 mg) at atmospheric pressure for 3 h. The mixture was neutralized with pyridine, filtered and partitioned between water and dichloromethane. The water phase was concentrated and purified on a Bio-Gel P-2 column, using water as eluent. After freeze-drying **1** was obtained as an amorphous powder (359 mg, 74 % yield calculated from **13**). $[\alpha]_D$ -62° (c=0.5, H_2O). NMR data (^2H_2O) are shown in Table 1.

FAB-MS of **1** showed an M+1 ion of m/z 745. (The nuclide mass sum of **1** is 744.26.)

*2-(p-Nitrophenyl)ethyl 6-O-Benzyl-2-deoxy-2-phthalimido-3-O-(2,3,4-tri-O-p-chlorobenzyl-α-L-fucopyranosyl)-4-O-[3,4,6-tri-O-p-chlorobenzyl- 2-O-(2,3,4-tri-O-p-chlorobenzyl-α-L-fucopyranosyl)-β-D-galactopyranosyl]-β-D-glucopyranoside (**15**)*

Method A. Bromine (149 µl, 2.88 mmol) in dichloromethane (3 ml) was added to a solution of **3** (1.52 g, 2.62 mmol) in dichloromethane (8 ml) at room temperature. After 15 min the excess of bromine was destroyed through addition of cyclohexene. The solution was added under nitrogen to a mixture of **11** (710 mg, 0.655 mmol), mercury(II) cyanide (455 mg, 1.80 mmol), mercury(II) bromide (390 mg, 1.08 mmol) and 4Å molecular sieves (7 g) in dichloromethane (10 ml) during 1.5 h at -10°C. The mixture was allowed to attain room temperature and after 8 h pyridine (3 ml) was added. The mixture was stirred for 3 h, filtered and concentrated. The residue was taken up in toluene, washed with 0.5 M sodium iodide (3 x 25 ml), 1 M sulfuric acid and saturated sodium hydrogencarbonate, dried and concentrated. Column chromatography (toluene/dichloromethane/ethyl acetate, 16/8/3 by vol) afforded amorphous **15** (1.14 g, 82%). $[\alpha]_D$ -48°.

NMR data (C^2HCl_3): ^{13}C; δ 16.2, 16.3 (C-6'', 6'''), 35.3 ($OCH_2\mathbf{C}H_2$), 56.1 (C-2), 66.6-83.7 (ring C), 67.8-74.7 (C-6,6', $O\mathbf{C}H_2CH_2$, $O\mathbf{C}H_2Ph$), 97.7 (C-1'''), 98.0 (C-1''), 98.4 (C-1), 100.0 (C-1'), 122.9-146.6 (aromatic C), 166.6, 168.3 (C=O NPhth). ^1H; δ 1.04 (d, $J_{5''',6'''}$ 6.4 Hz, H-6'''), 1.35 (d, $J_{5'',6''}$ 6.4 Hz, H-6''), 2.93 (broad s, H-4'''), 3.50 (dd, $J_{2',3'}$ 9.5 Hz, $J_{3',4'}$ 2.8 Hz, H-3'), 3.52 (dd, $J_{1''',2'''}$ 3.7 Hz, $J_{2''',3'''}$ 10.1 Hz, H-2'''), 3.66 (d, $J_{3'',4''}$ 2.7 Hz, H-4''), 3.69 (dd, $J_{3''',4'''}$ 2.4 Hz, H-3'''), 3.75 (dd, $J_{2'',3''}$ 10.3 Hz, H-3''), 3.88 (d, H-4'), 3.96 (dd, $J_{1',2'}$ 8.2 Hz, H-2'), 4.00 (dd, $J_{1'',2''}$ 4.0 Hz, H-2''), 4.11 (t, $J_{3,4}$ 9.4 Hz, $J_{4,5}$ 9.4 Hz, H-4), 4.31 (dd, $J_{1,2}$ 8.5 Hz, $J_{2,3}$ 10.5 Hz, H-2), 4.49 (dd, H-3), 4.52 (d, H-1'), 4.55 (d, H-1'''), 4.93 (d, H-1), 5.56 (d, H-1'').

The pre-fraction was concentrated and chromatographed once more (toluene/ethyl acetate, 7/1 by vol) to give the 2'-O-α-fucosyl, 3-O-β-fucosyl isomer **17** as a syrup (70 mg, 4%). $[\alpha]_D$ -41°. NMR data (C^2HCl_3): ^{13}C; δ 16.0, 16.4 (C-6'',6'''), 35.6 ($OCH_2\mathbf{C}H_2$), 55.5 (C-2), 97.4 (C-1''), 98.8 (C-1), 99.5 (C-1'), 100.5 (C-1'''). ^1H; δ 4.50 (d, $J_{1',2'}$ 7.8 Hz, H-1'), 4.74 (d, $J_{1''',2'''}$ 7.8 Hz, H-1'''), 5.17 (d, $J_{1,2}$ 8.5 Hz, H-1), 5.54 (d, $J_{1'',2''}$ 3.8 Hz, H-1'').

Method B. Bromine (16 µl, 0.316 mmol) was added to a solution of **3** (161 mg, 0.276 mmol) in dichloromethane (1 ml). After 10 min the excess of bromine was destroyed with cyclohexene. DMF (1.2 ml) was added and dichloromethane evaporated. The solution was added to a stirred mixture of **11** (60 mg, 0.055 mmol), tetraethylammonium bromide (58 mg, 0.276 mmol) and 4Å molecular sieves (0.5 g) in DMF (800 µl). After three days at room temperature no **11** or intermediate product remained according to TLC, and pyridine (100 µl) was added. After stirring for 0.5 h the mixture was filtered through a layer of Celite. The solution was concentrated and the residue was partitioned between toluene and 1 M sulfuric acid. The organic layer was washed with saturated sodium hydrogencarbonate, dried and concentrated. Column chromatography (toluene/dichloromethane/ethyl acetate, 8/4/1 by vol) yielded **15** (101 mg, 86%).

Method C. Bromine (16 µl, 0.316 mmol) was added to a mixture of **3** (161 mg, 0.276 mmol) and 4 Å molecular sieves (0.5 g) in dichloromethane (1.5 ml) at room temperature. After 10 min the excess of bromine was destroyed with the addition of cyclohexene. After addition

Table 2.. NMR data for compound **2**..

^{1}H-NMR	H-1	H-2	H-3	H-4	H-5	H-6a	H-6b
GlcNAc	4.45 8.0_{12}	3.76 N.D.[a]	3.76 N.D.	3.89 10.0_{45}	3.42 5.6_{56a} 1.8_{56b}	3.83 11.8_{6a6b}	4.01
Gal	4.49 7.8_{12}	3.63 9.1_{23}	3.85 3.6_{34}	3.86 N.D.	3.58 4.6_{56a} 7.8_{56b}	3.69 11.3_{6a6b}	3.73
Fuc(1-2)[b]	5.27 3.4_{12}	3.79 N.D.	3.78 N.D.	3.82 N.D.	4.24 6.7_{56}	1.26	-
Fuc(1-3)[b]	5.01 4.0_{12}	3.65 10.4_{23}	3.89 3.2_{34}	3.79 N.D.	4.85 6.7_{56}	1.22	-

^{13}C-NMR	C-1	C-2	C-3	C-4	C-5	C-6
GlcNAc	101.6	56.5	75.7	74.2	76.4	60.7
Gal	101.0	77.2	74.3	69.5	75.6	62.2
Fuc(1-2)	100.2	69.1	70.5	72.5	67.7	16.2
Fuc(1-3)	99.3	68.4	69.9	72.7	67.6	16.2
CH_3CO	22.8					
OCH_2**C**H_2	35.2					
O**C**$H_2$$CH_2$	71.1					
CF_3CO	116.7 (*J* 288 Hz)					
Ar	123.0-138.7					
CF_3**C**O	157.8 (*J* 34.3 Hz)					
CH_3**C**O	174.7					

[a] N.D. = not determined.
[b] The NMR signals for 2-linked and 3-linked fucose were assigned by comparison with trisaccharide **1**.

of **11** (60 mg, 0.055 mmol) the mixture was cooled to -70°C under nitrogen. silver triflate (56 mg, 0.22 mmol) in toluene (1 ml) was added and the cooling bath was removed. At 10°C pyridine (200 µl) was added and then 0.5 M sodium thiosulfate. The mixture was filtered and the organic layer was washed with water, 2 M sulfuric acid and saturated sodium hydrogencarbonate, dried and concentrated. Chromatography (toluene/dichloromethane/ethyl acetate, 8/4/1 by vol) gave **15** (70 mg, 59%) (R_F 0.14). The major by-product of the reaction was the 2'-O-β-fucosyl, 3-O-α-fucosyl isomer **16** obtained in an impure state from the chromatography (R_F 0.37).

Method D. DMTSB (260 mg, 1.33 mmol) was added to a stirred mixture of **3** (773 mg, 1.33 mmol), **11** (360 mg, 0.332 mmol) and 4Å molecular sieves (3.2 g) in THF (15 ml) at -15°C. The mixture was allowed to attain room temperature. After 23 h only minor amounts of unreacted **11** and intermediate product remained according to TLC. Saturated sodium hydrogencarbonate and ethyl acetate were added and the mixture was filtered through a layer of Celite. The organic layer was washed with water, dried and concentrated. Column chromatography (toluene/dichloromethane/ethyl acetate, 16/8/3 by vol) yielded **15** as a syrup (405 mg, 57%).

The pre-fraction was concentrated and chromatographed once more (light petroleum/ethyl acetate, 2/1 by vol) to give the 2'-O-β-fucosyl, 3-O-α-fucosyl isomer **16** as a syrup (61 mg, 9%)(R_F 0.30). $[\alpha]_D$ -40°. NMR data (C^2HCl_3): ^{13}C; δ 16.0, 16.9 (C-6'',6'''), 35.3 ($OCH_2\mathbf{C}H_2$), 56.0 (C-2), 96.8 (C-1'''), 97.8 (C-1), 101.1 (C-1''), 101.3 (C-1'). ^1H, δ 4.50 (d, $J_{1',2'}$ 8.2 Hz, H-1'), 4.55 (d, $J_{1''',2'''}$ 4.0 Hz, H-1'''), 4.71 (d, $J_{1'',2''}$ 7.4 Hz, H-1''), 4.87 (d, $J_{1,2}$ 8.5 Hz, H-1) and the 2'-O-α-fucosyl, 3-O-β-fucosyl isomer **17** as a syrup (24 mg, 3%) (R_F 0.16).

*2-(p-Trifluoroacetamidophenyl)ethyl 2-Acetamido-2-deoxy-3-O-(α-L-fucopyranosyl)-4-O-[2-O-(α-L-fucopyranosyl)-β-D-galactopyranosyl]-β-D-glucopyranoside (**2**)*

Compound **15** (2.64 g, 1.24 mmol) was treated with hydrazine hydrate (2.27 ml, 46.8 mmol) and acetic acid (1.98 ml, 34.6 mmol) in 70 ml toluene/95% ethanol, 7/30 by vol, followed by 30 ml acetic anhydride/pyridine, 1/1 by vol, as described for **1**. Purification by column chromatography (toluene/ethyl acetate, 2/1 by vol) yielded the *N*-acetylated product (2.35 g). NMR data (C^2HCl_3): ^{13}C; δ 23.2 ($\mathbf{C}H_3CONH$), 97.8, 97.8, 99.1, 100.1 (C-1,1',1'',1'''), 170.2 ($CH_3\mathbf{C}ONH$).

This material (2.20 g, 1.08 mmol) was hydrogenated in ethyl acetate (35 ml) over platinum oxide (90 mg), followed by treatment with trifluoroacetic anhydride (305 µl, 2.16 mmol) in 30 ml pyridine/THF, 1/1 by vol, as described for **1**. Column chromatography (toluene/ethyl acetate, 2/1 by vol) gave amorphous material (1.87 g). NMR data (C^2HCl_3): ^{13}C; δ 97.8, 97.8, 99.0, 100.1 (C-1,1',1'',1'''), 115.7 (q, *J* 288 Hz, $\mathbf{C}F_3CO$), 154.6 (q, *J* 36 Hz, $CF_3\mathbf{C}O$).

A solution of this material (800 mg, 0.381 mmol) in 40 ml acetic acid/ethyl acetate/water, 12/5/3 by vol, containing sodium acetate (565 mg), was hydrogenated over Pd/C (10%, 300 mg) at atmospheric pressure overnight. The mixture was filtered, concentrated and purified by column chromatography (ethyl acetate/acetic acid/methanol/water, 8/3/3/2 by vol). The purified product was taken up in water and applied to a C-18 column (8 g, 40 µm, Sepralyte; Analytichem International, Harbor City, CA, USA) in water. Soluble salts were washed out with water, and the product was then eluted with 30% aqueous methanol. Concentration and freeze-drying gave amorphous **2** (251 mg, 56% yield calculated from **15**). $[\alpha]_D$ -95° (c=0.5, H_2O). NMR data (^2H_2O) are shown in Table 2.

FAB-MS of **2** showed an M+1 ion of m/z 891. (The nuclide mass sum of **2** is 890.31.)

Acknowledgements

We are grateful to Mr Gunnar Grönberg and Mr Bo Nylander for recording and assigning the NMR spectra and to Mr Stefan Strömberg for recording the FAB mass spectra.

References

1 Hakomori S (1986) Chem Phys Lipids 42:209-233.
2 Jacquinet JC, Sinaÿ P (1976) Tetrahedron 32:1693-1697.
3 Jacquinet JC, Sinaÿ P (1977) J Org Chem 42:720-724.
4 Milat ML, Sinaÿ P (1979) Angew Chem 91:501-502.
5 Paulsen H, Kolár C (1979) Tetrahedron Lett 31:2881-2884.
6 Hindsgaul O, Norberg T, Le Pendu J, Lemieux RU (1982) Carbohydr Res109:109-142.
7 Rana SS, Vig R, Matta KL (1983) J Carbohydr Chem 1:261-276.
8 Spohr U, Lemieux RU (1988) Carbohydr Res 174:211-237.
9 Palcic MM, Heerze LD, Pierce M, Hindsgaul O (1988) Glycoconjugate J 5:49-63.
10 Bailey D, Kline T, Greig R, Chester MA, Nilsson S (1988) Abstr 14th Int Carbohydr Symp, Stockholm, p 322.
11 Fügedi P, Garegg PJ, Lönn H, Norberg T (1987) Glycoconjugate J 4:97-108.
12 Koto S, Inada S, Morishima N, Zen S (1980) Carbohydr Res 87:294-296.
13 Magnusson G (1976) J Org Chem 41:4110-4112.
14 Nilsson M, Norberg T (1988) Carbohydr Res 183:71-82.
15 Fügedi P, Garegg PJ (1986) Carbohydr Res 149:C9-C12.
16 Lönn H (1985) Carbohydr Res 139:105-113.
17 Classon B, Garegg PJ, Samuelsson B (1984) Acta Chem Scand B 38:419-422.
18 Pearson GA (1985) J Magn Reson 64:487-500.
19 Meerwein H, Zenner KF, Gipp R (1965) Justus Liebigs Ann Chem 688:67-77.