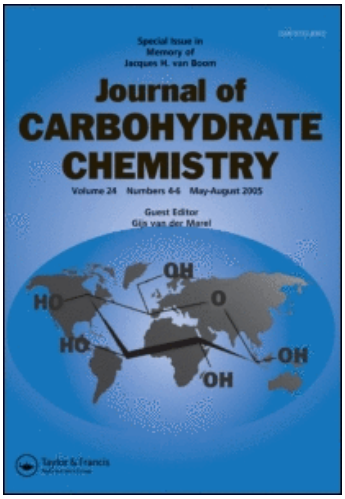

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Synthesis of Two Isomeric Tetrasaccharides *O*-α-L-Fucopyranosyl-(1→3) and (1→4)-*O*-(2-Acetamido-2-Deoxy-β-D-Glucopyranosyl)-(1→3)-*O*-(β-D-Galactopyranosyl)-(1→4)-D-Glucopyranose and a Related Tetrasaccharide *O*-α-L-Fucopyranosyl-(1→3)-*O*-(2-Acetamido-2-Deoxy-β-D-Glucopyranosyl-(1→6)-*O*-(β-D-Galactopyranosyl)-(1→4)-D-Glucopyranose

Arun K. Sarkar; Sushama M. Pawar; Khushi L. Matta

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SYNTHESIS OF TWO ISOMERIC TETRASACCHARIDES *0*-α-L-FUCOPYRANOSYL-(1→3) AND (1→4)-*0*-(2-ACETAMIDO-2-DEOXY-β-D-GLUCOPYRANOSYL)-(1→3)-*0*-(β-D-GALACTOPYRANOSYL)-(1→4)-D-GLUCOPYRANOSE AND A RELATED TETRASACCHARIDE *0*-α-L-FUCOPYRANOSYL-(1→3)-*0*-(2-ACETAMIDO-2-DEOXY-β-D-GLUCOPYRANOSYL-(1→6)-*0*-(β-D-GALACTOPYRANOSYL)-(1→4)-D-GLUCOPYRANOSE[1]

Arun K. Sarkar, Sushama M. Pawar, and Khushi L. Matta*

Department of Gynecologic Oncology, Roswell Park Cancer Institute, Elm & Carlton Streets, Buffalo, NY 14263 (U.S.A.)

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ABSTRACT

Synthesis of three tetrasaccharides, namely, *0*-α-L-fucopyranosyl-(1→3)-*0*-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→3)-*0*-(β-D-galactopyranosyl)-(1→4)-β-D-glucopyranose (7), *0*-α-L-fucopyranosyl-(1→4)-*0*-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→3)-*0*-(β-D-galactopyranosyl)-(1→4)-D-glucopyranose (9), and *0*-α-L-fucopyranosyl-(1→3)-*0*-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→6)-*0*-(β-D-galactopyranosyl)-(1→4)-D-glucopyranose (15) has been described. Their structures have been established by ^{13}C NMR spectroscopy.

INTRODUCTION

A series of glycolipids having an L-fucopyranosyl group α-(1→3)-linked to a 2-acetamido-2-deoxy-D-glucopyranosyl residue have been isolated[2-6] from tumor tissues and characterized. Our continued interest in the study of human L-fucosyltransferase derivatives as reference compounds and low molecular weight oligosaccharides as acceptor substrate warranted the synthesis of several

fucose containing oligosaccharides. In continuation of this effort,[7] we describe herein the synthesis of title tetrasaccharides.

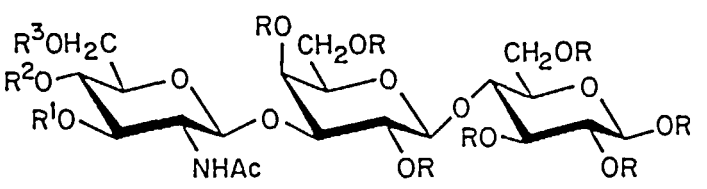
RESULTS AND DISCUSSION

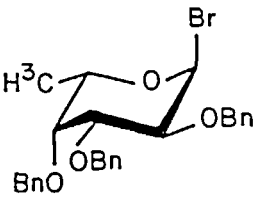
Treatment of benzyl 2,3,6-tri-*O*-benzyl-4-*O*-[2,4,6-tri-*O*-benzyl-3-*O*-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-β-D-galactopyranosyl]-β-D-glucopyranoside[8] (**2**) with α, α-dimethoxy toluene in the presence of 4-toluenesulfonic acid afforded the benzylidene acetal **3**. Benzylation of **3** using benzyl bromide and sodium hydride in DMF[9] gave **4** in 75% yield. Reductive ring opening[10] of compound **4** in presence of sodium cyanoborohydride afforded compound **5**.

Halide ion catalyzed[11,12] glycosylation of compound **3** with 2,3,4-tri-*O*-benzyl-α-L-fucosyl bromide (**1**) gave the tetrasaccharide derivative **6** (scheme 1). Hydrogenolysis of the benzyl and benzylidene groups of **6** in the presence of 10% palladium-on-carbon then furnished the tetrasaccharide *O*-α-L-fucopyranosyl-(1→3)-*O*-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→3)-*O*-(β-D-galactopyranosyl)-(1→4)-D-glucopyranose (**7**) in 76% yield. A similar condensation of compound **5** with **1** gave tetrasaccharide derivative **8** in 55% yield. Conventional removal of the benzyl groups from compound **8** furnished the tetrasaccharide *O*-α-L-fucopyranosyl-(1→4)-*O*-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→3)-*O*-(β-D-galactopyranosyl)-(1→4)-β-D-glucopyranose (**9**) in 74% yield.

Benzyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,3,4-tri-*O*-benzyl-β-D-galactopyranosyl)-β-D-glucopyranoside[13] (**10**) was treated with 2-methyl-(3,4,6-tri-*O*-acetyl-1,2-dideoxy-α-D-glucopyrano)-[2,1-d]-2-oxazoline[14] in 1,2-dichloroethane in the presence of 4-toluenesulfonic acid, to afford trisaccharide **11**. Compound **11** was not isolated but directly *O*-deacetylated to give (scheme 2) compound **12** in 72% overall yield. Benzylidenation of the trisaccharide derivative **12** afforded 4,6-*O*-benzylidene acetal **13**. Condensation of compound **13** with bromide **1** afforded the fully protected tetrasaccharide derivative **14**. Removal of the benzyl and benzylidene groups by hydrogenolysis gave the tetrasaccharide *O*-α-L-fucopyranosyl-(1→3)-*O*-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→6)-*O*-(β-D-galactopyranosyl-(1→4)-D-glucopyranose (**15**).

In the ^{13}C NMR spectra of the three tetrasaccharides **7**, **9**, and **15**, the resonances for C-1 observed at δ 98.5 (C-1β) and 94.6 (C-1α) clearly indicate the pre-





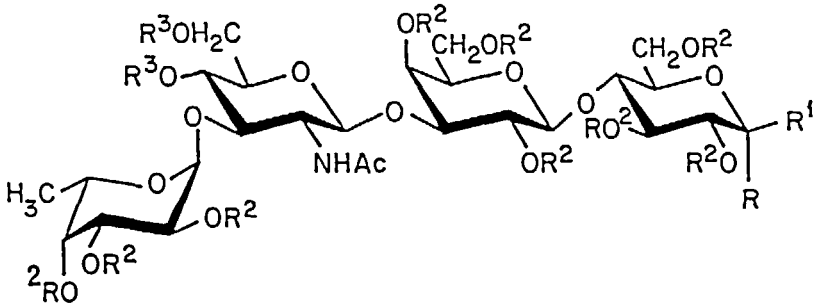
1

2 R = Bn, $R^1 = R^2 = R^3 = H$

3 R = Bn, $R^1 = H$, $R^2 R^3 = -CHC_6H_5$

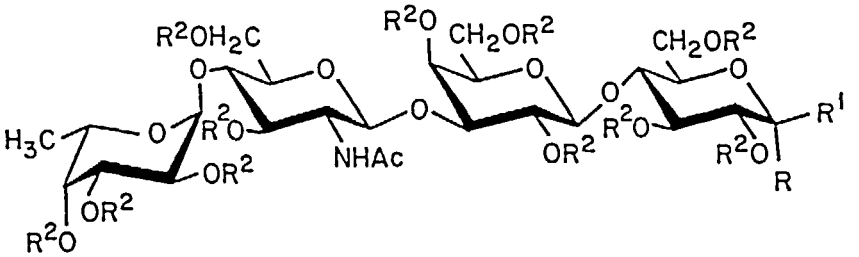
4 $R = R^1 = Bn$, $R^2 R^3 = -CHC_6H_5$

5 $R = R^1 = R^3 = Bn$, $R^2 = H$



6 R = H, R^1 = OBn, R^2 = Bn, $R^3 = -CHC_6H_5$

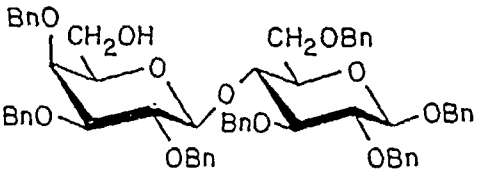
7 R, R^1 = H, OH, $R^2 = R^3 = H$



8 R = H, R^1 = OBn, R^2 = Bn

9 R, R^1 = H, OH, R^2 = H

Scheme 1



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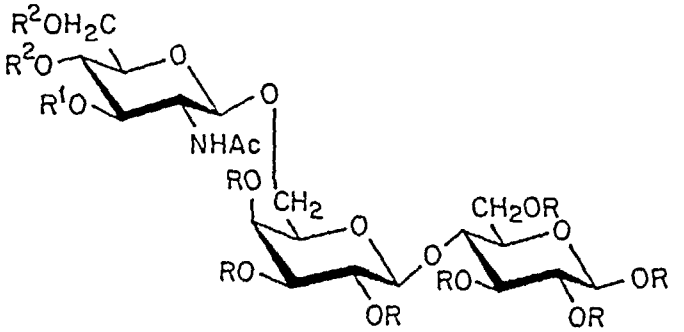
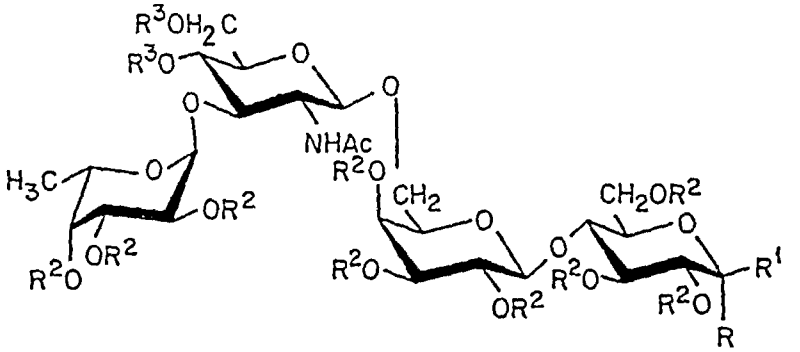


11 R = Bn, $R^1 = R^2 = Ac$

12 R = Bn, $R^1 = R^2 = H$

13 R = Bn, $R^1 = H$, $R^2 = -CHC_6H_5$



14 R = H, R^1 = OBn, R^2 = Bn, R^3 R^3 = $-CHC_6H_5$

15 R, R^1 = H, OH, $R^2 = R^3 = H$

Scheme 2

TABLE I. ^{13}C NMR CHEMICAL SHIFTS[a,b] FOR COMPOUND 7, 9, and 15

Residue	Compound	C-1	C-2	C-3	C-4	C-5	C-6	$CH_3C=O$	C=O
α-D-Glc		94.59	74.15	73.91	81.22	72.87	62.75	–	–
β-D-Glc		98.52	76.57	77.12	81.12	77.64	62.87	–	–
β-D-Gal (1→4)	7	105.71	71.12	84.72	72.29	77.55	63.70	–	–
β-D-GlcNAc (1→3)		105.30	58.16	82.91	71.12	78.45	63.32	24.96	177.76
α-L-Fuc (1→3)		102.61	70.75	72.79	74.60	69.65	17.92	–	–
α-D-Glc		94.62	74.15	73.91	81.24	72.76	62.50	–	–
β-D-Glc		98.53	76.58	77.12	81.17	77.80	62.61	–	–
β-D-Gal (1→4)	9	105.70	71.10	84.74	72.17	77.65	63.70	–	–
β-D-GlcNAc (1→3)		105.44	58.89	75.09	79.91	77.80	63.98	24.89	177.25
α-L-Fuc (1→4)		102.34	70.82	72.76	74.65	69.76	17.92	–	–
α-D-Glc		94.56	74.15	73.72	81.76	72.81	62.67	–	–
β-D-Glc		98.49	76.29	77.12	81.64	77.45	62.81	–	–
β-D-Gal (1→4)	15	105.79	71.05	75.12	71.19	77.45	71.36	–	–
β-D-GlcNAc (1→6)		103.58	57.96	83.14	71.36	78.59	63.46	25.12	177.42
α-L-Fuc (1→3)		102.68	70.71	72.74	74.57	69.67	17.89	–	–

a. For solutions in D_2O with Me_4Si as external standard.
b. The assignments of ^{13}C resonances for tetrasaccharides **7**, **9**, and **15** were made by comparing their spectra with those of (not shown in Table I) α-L-Fuc-1→OMe[7], β-D-Gal-(1→4)-D-Glc[15], β-D-GlcNAc-(1→3)-β-D-Gal-(1→4)-D-Glc[16], and β-D-GlcNA(1→6)-β-D-Gal-(1→4)-D-Glc[16].

sence of a free reducing sugar (glucose). On the other hand the resonances for C-1' (105.70-105.79 ppm), C-1" (103.6-105.44 ppm) were all in the region indicative of β-glycosidic linkages. Resonances for C-1" ' for all three compounds were observed at δ 102.30-102.68, a clear indication of α-L-configurations for the newly introduced L-fucosyl groups in compounds **7**, **9** and **15**. In the ^{13}C spectrum of **7** and **15** the resonances for C-3 of the GlcNAc residue suffered a downfield shift of 7.82 and 8.05 ppm, respectively, indicating that the *0*-3" was the site of fucosylation. However, for compound **9** an analogous downfield shift of 8.79 ppm was observed for the C-4 resonance of the corresponding GlcNAc residue confirming that fucosylation had occurred at *0*-4". Downfield shifts of 9.60 and 9.62 ppm, for the C-3 of galactose residue in compound **7** and **9**, respectively, clearly indicate the substitution at *0*-3 of the galactose residue in those two compounds. A similar downfield shift of 7.66 ppm for C-6' of compound **15** confirms that *0*-6' is engaged in another glycosidic linkage.

EXPERIMENTAL

General methods. Optical rotations were measured at 25 °C with a Perkin-Elmer 241 polarimeter. All NMR spectra were recorded at 25 °C; ^1H NMR with a

Varian EM-390 instrument operating at 90 MHz. Chemical shifts are reported downfield from the Me_4Si signal. ^{13}C NMR spectra were recorded with a Varian XL-100 instrument at 25.2 MHz. TLC was performed using aluminum sheets, precoated with 0.2 mm layers on silica gel 60F-254 (E. Merck, Darmstadt, Germany); the components were located by exposure to UV light, and/or by spraying the plates with 5% H_2S0_4 in ethanol and heating. Silica gel used for column chromatography was Baker Analyzed (60-200 mesh). Solvents used for column chromatography (v/v) were: *A*, ethyl acetate-hexane (2:1); *B*, ethyl acetate-hexane (1:1); and *C*, chloroform-methanol-water (5:4:1), unless otherwise stated. Generally solutions in organic solvents were dried with anhydrous Na_2S0_4. Elemental analyses were performed by Robertson Laboratory, 29 Samson Ave., Madison, New Jersey 07940, U.S.A.

Benzyl 2,3,6-Tri-*O*-benzyl-4-*O*-[2,4,6-tri-*O*-benzyl-3-*O*-(2-acetamido-2-deoxy-4,6-*O*-benzylidene-β-D-glucopyranosyl)-β-D-galactopyranosyl]-β-D-glucopyranoside (3). To a solution of 2 (5.5 g, 4.7 mmol) in *N,N*-dimethylformamide (25 mL) was added α, α-dimethoxy toluene (1.5 mL) and 4-toluenesulfonic acid (0.2 g) and the mixture was stirred for 1.5 h at 65 °C under vacuum (150 mm of Hg). Triethylamine (0.5 mL) was added and the solution was concentrated. A solution of the syrupy residue in chloroform was washed successively with water, saturated sodium bicarbonate solution and water, dried, and concentrated to dryness. The residue was chromatographed (solvent *B*) to give 3 (5 g, 85%); $[\alpha]_D$ -32.3° (*c* 1; chloroform). ^1H NMR data ($CDCl_3$) δ 7.50-7.00 (m, 40 H, arom), 5.40 (s, 1 H, PhCH), 1.60 (s, 3 H, NAc).

Anal. Calcd for $C_{76}H_{81}NO_{16}$: C, 72.19; H, 6.46; N, 1.11. Found: C, 72.40; H, 6.61; N, 1.01.

Benzyl 2,3,6-Tri-*O*-benzyl-4-*O*-[2,4,6-tri-*O*-benzyl-3-*O*-(2-acetamido-2-deoxy-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-β-D-galactopyranosyl]-β-D-glucopyranoside (4). To a cold (0 °C), vigorously stirred mixture of compound 3 (3 g, 2.4 mmol) and sodium hydride (0.12 g, 3 mmol, 40% oil coated) in dry *N,N*-dimethylformamide (25 mL) was added benzyl bromide (0.37 mL, 3 mmol), and the reaction mixture was stirred for 5 h at room temperature. Methanol (2 mL) was added with cooling, the reaction mixture was partitioned between chloroform and water, dried (Na_2S0_4) and concentrated to a syrup.

Purification of the product by column chromatography using solvent *A* afforded pure **4** (2.4 g, 75%) $[\alpha]_D$ -17° (*c* 1.5; chloroform). ^{1}H NMR ($CDCl_3$) δ 7.60-7.00 (m, 45 H, arom), 5.40 (s, 1 H, PhCH), and 1.50 (a, 3 H, NAc).

Anal. Calcd for $C_{83}H_{87}NO_{16}$: C, 73.59; H, 6.47; N, 1.03. Found: C, 73.80; H, 6.40; N, 1.00.

Benzyl 2,3,6-Tri-*O*-benzyl-4-*O*-[2,4,6-tri-*O*-benzyl-3-*O*-(2-acetamido-2-deoxy-3,6-di-*O*-benzyl-β-D-glucopyranosyl)-β-D-galactopyranosyl]-β-D-glucopyranoside (5). A cooled (0 °C) mixture of **4** (1.6 g, 1.2 mmol), sodium cyanoborohydride (1 g), and powdered molecular sieves (4A°, 4 g) in dry tetrahydrofuran (25 mL) was stirred vigorously, and a saturated solution of hydrogen chloride in ether (12 mL) was added dropwise during 10 min. After 15 min, the reaction mixture was filtered through a Celite bed, the filtrate was concentrated to dryness, and the residue was dissolved in chloroform. The chloroform layer was washed successively with water, a saturated solution of sodium hydrogen carbonate and water, dried, filtered, and concentrated. The crude **5** was purified by column chromatography (solvent *A*). Yield 1.25 g (78%), $[\alpha]_D$ -19° (*c* 1.1; chloroform). ^{1}H NMR ($CDCl_3$) δ 7.60-7.00 (m, 45 H, arom), 1.50 (s, 3 H, NAc).

Anal. Calcd for $C_{83}H_{89}NO_{16}$: C, 73.48; H, 6.61; N, 1.03. Found: C, 73.75; H, 6.81; N, 0.90.

Benzyl 2,3,6-Tri-*O*-benzyl-4-*O*-[2,3,4-tri-*O*-benzyl-6-*O*-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-β-D-galactopyranosyl]-β-D-glucopyranoside (12). A solution of benzyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,3,4-tri-*O*-benzyl-β-D-galactopyranosyl)-β-D-glucopyranoside[13] (**10**) (2 g, 2.1 mmol) and 2-methyl-(3,4,6-tri-*O*-acetyl-1,2-dideoxy-α-D-glucopyrano)-[2,1-d]-2-oxazoline[14] (1.05 g, 3.15 mmol) in dry 1,2-dichloroethane (10 mL) was stirred at 70 °C. To this solution was added a hot (70 °C) solution of 4-toluenesulfonic acid (0.04 g, 10 mL) in 1,2-dichloroethane. Heating and stirring was continued for 24 h under nitrogen. After cooling, pyridine (0.1 mL) was added, and the dark solution containing crude **11** was concentrated to a syrup which was de-*O*-acetylated with 0.1 M sodium methoxide (20 mL). The crude product was chromatographed (10% methanol in ethyl acetate) to give **12** (1.75 g, 72%, overall), $[\alpha]_D$ -23.4° (*c* 1; chloroform). ^{1}H NMR ($CDCl_3$) δ 7.70-7.10 (m, 35 H, arom), 1.60 (s, 3 H, NAc).

Anal. Calcd for $C_{69}H_{77}NO_{16}$: C, 70.45; H, 6.60; N, 1.19. Found: C, 70.20; H, 6.62; N, 1.24.

Benzyl 2,3,6-Tri-*O*-benzyl-4-*O*-[2,3,4-tri-*O*-benzyl-6-*O*-(2-acetamido-2-deoxy-4,6-*O*-benzylidene-β-D-glucopyranosyl)-β-D-galactopyranosyl]-β-D-glucopyranoside (13). Compound **12** (1 g, 0.9 mmol) was treated with α, α-dimethoxy toluene and 4-toluenesulfonic acid in *N,N*-dimethylformamide as described before. Purification of the product by column chromatography (solvent *B*) gave pure **13** (0.8 g, 74%). $[\alpha]_D$ -28.4° (*c* 1.1; chloroform). ^1H NMR ($CDCl_3$) δ 7.70-7.10 (m, 40 H, arom), 5.50 (s, 1 H, PhCH); 1.50 (s, 3 H, NAc).

Anal. Calcd for $C_{76}H_{81}NO_{16}$: C, 72.19; H, 6.46; N, 1.11. Found: C, 72.28; H, 6.54; N, 1.12.

Benzyl *O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(1→3)-*O*-(2-acetamido-2-deoxy-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (6). A mixture of 2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl bromide[11,12] (1) [0.4 g, 0.82 mmol; freshly prepared from the 1-(*p*-nitrobenzoate)[12]], tetraethylammonium bromide (0.17 g, 0.8 mmol),and 4A molecular sieves (0.5g) in dry dichloromethane (5 mL) was stirred for 0.5 h with protection from light and moisture. A solution of **3** (0.5 g, 0.4 mmol) in dichloromethane (2.5 mL) was added followed by ethyldiisopropylamine (0.14 mL, 0.8 mmol), and the mixture was stirred for two days at room temperature. Further amounts of **1** (0.08 g) and tetraethylammonium bromide (0.04 g), and ethyldiisopropylamine (0.03 mL) were added, and the stirring was continued for two more days. The mixture was filtered through Celite, the solids were washed with dichloromethane, and the combined filtrate and washings were washed successively with water, saturated aqueous $NaHCO_3$ and water, dried (Na_2SO_4), filtered and the filtrate concentrated. The syrupy residue was chromatographed (solvent *A*) to give compound **6** (0.4 g, 60%), $[\alpha]_D$ -50° (*c* 1; chloroform). ^1H NMR ($CDCl_3$) δ 7.60-7.15 (m, 55 H, arom), 5.40 (s, 1 H, PhCH), 1.50 (s, 3 H, NAc), 0.90 (d, 3 H, J 6 Hz, CMe).

Anal. Calcd for $C_{103}H_{109}NO_{20}$: C, 73.59; H, 6.54; N, 0.83. Found: C, 73.40; H, 6.68; N, 1.04.

***O*-(α-L-Fucopyranosyl)-(1→3)-*O*-(2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-*O*-(β-D-galactopyranosyl)-(1→4)-D-glucopyranose (7).** A mixture of **6** (0.32 g, 0.19 mmol) and 10% Pd-C (0.3 g) in glacial acetic acid (5 mL) was shaken at room temperature under hydrogen at 345 kPa for 24 h, filtered and the

solids were washed thoroughly with acetic acid-methanol (1:1). The combined filtrates were concentrated and the residue was chromatographed (solvent *C*) to afford compound **7** (0.1 g, 76%) as white solid. $[\alpha]_D$ -26° (10 min.) to -28° (24 h) (*c* 1.1, water). ^{13}C NMR spectra, see Table I.

Anal. Calcd for $C_{26}H_{45}NO_{20}$: C, 45.15; H, 6.56; N, 2.02. Found: C, 45.23; H, 6.17; N, 1.85.

Benzyl *0*-(2,3,4-tri-*0*-benzyl-α-L-fucopyranosyl)-(1→4)-*0*-(2-acetamido-2-deoxy-3,6-di-*0*-benzyl-β-D-glucopyranosyl)-(1→3)-*0*-(2,4,6-tri-*0*-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*0*-benzyl-β-D-glucopyranoside (8). Compound **5** (0.5 g, 0.37 mmol) was treated with bromide **1** (0.46 g) as described for the preparation of **6** from **3**. The crude **8** was purified by column chromatography (solvent *A*) to give amorphous **8** (0.36 g, 55%). $[\alpha]_D$ -35° (*c* 1.2, chloroform). ^1H NMR data ($CDCl_3$) δ 7.75-7.10 (m, 60 H, arom), 1.55 (s, 3 H, NAc), 1.00 (d, 3 H, J 6 Hz, CMe).

Anal. Calcd for $C_{110}H_{117}N0_{20}$: C, 74.51; H, 6.65; N, 0.79. Found: C, 74.80; H, 6.40; N, 1.05.

***0*-(α-L-Fucopyranosyl)-(1→4)-*0*-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→3)-*0*-(β-D-galactopyranosyl)-(1→4)-β-D-glucopyranose (9).** Hydrogenolysis of compound **8** (0.28 g, 0.16 mmol) in glacial acetic acid (5 mL), in the presence of 10% Pd-C (0.28 g) at 345 kPa, gave compound **9** (0.08 g, 73%) as a white solid after column chromatography (solvent *C*) $[\alpha]_D$ -21° (10 min.) to -24° (24 h) (*c* 1, water) ^{13}C NMR spectra see Table I.

Anal. Calcd for $C_{26}H_{45}NO_{20}.2.5\ H_2O$: C, 42.39; H, 6.84; N, 1.90. Found: C, 42.46; H, 6.49; N, 1.83.

Benzyl *0*-(2,3,4-tri-*0*-benzyl-α-L-fucopyranosyl)-(1→3)-*0*-(2-acetamido-2-deoxy-4,6-*0*-benzylidene-β-D-glucopyranosyl)-(1→6)-*0*-(2,3,4-tri-*0*-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*0*-benzyl-β-D-glucopyranoside (14). Compound **13** (0.5 g) in di-chloromethane (10 mL) was treated with bromide **1** (0.5 g) in the presence of tetraethylammonium bromide (0.21 g), ethyldiisopropylamine (0.17 mL) and 4A molecular sieves (0.5 g) for 48 h at room temperature. After the usual processing, the crude product was chromatographed (solvent *A*) to give **14** (0.42 g, 63%). $[\alpha]_D$ -42 ° (*c* l, chloroform). ^1H NMR ($CDCl_3$) δ 7.70-7.20 (m, 55 H, arom), 5.45 (s, 1 H, PhCH), 1.50 (s, 3 H, NAc), 1.00 (d, 3 H, J 6 Hz, CMe).

Anal. Calcd for $C_{103}H_{109}NO_{20}$: C, 73.59; H, 6.54; N, 0.83. Found: C, 73.45; H, 6.70; N, 0.80.

***O*-(α-L-Fucopyranosyl)-(1→3)-*O*-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→6)-*O*-β-D-galactopyranosyl)-(1→4)-D-glucopyranose (15).** Compound **14** (0.34 g, 0.2 mmol) was hydrogenated as described before and the crude product mixture was chromatographed (solvent C) to give pure **15** (0.11 g, 79%); $[\alpha]_D$ -43.6° (10 min.) to -46° (24 h) (*c* 1.1, water) ^{13}C NMR spectra see Table I.

Anal. Calcd for $C_{26}H_{45}NO_{20}.2\ H_2O$: C, 42.91; H, 6.78; N, 1.92. Found: C, 42.82; H, 6.40; N, 1.75.

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