Synthetic Studies on Glycosphingolipids from Protostomia Phyla: Synthesis of a Glycosphingolipid Analogue from the Parasite *Spirometra erinacei*

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Received March 3, 2000; accepted April 27, 2000

Novel neutral glycosphingolipids isolated from the plerocercoids of a tapeworm, *Spirometra erinacei*, may be expected to be involved in host-parasite interactions. We have synthesized this glycosphingolipid analogue containing 2-branched fatty alkyl residue in place of ceramide. Glycosylation of nonreducing-end trisaccharide derivative 15 with the reducing-end disaccharide derivative 17 in the presence of trimethylsilyl triflate (TMSOTf) gave the desired oligosaccharide derivative in good yield. The fully per-*O*-acylated 2-(trimethylsilyl)ethyl glycoside 19 was converted to glycosylimidate 20, which was condensed with 2-(tetradecyl)hexadecanol and subsequently deacylated to give the target glycosphingolipid analogue 22.

Key words glycosphingolipid; *Spirometra erinacei*; chemical synthesis; glycosylation

Glycosphingolipids are components of cell membranes and are thought to play important roles in a variety of biological events, including extracellular recognition and cell–cell interaction.[1] Similarly, parasite glycosphingolipids are expected to be involved in host-parasite interactions such as species-related infestation and stage development or the choice of target organs that parasites preferentially invade, however, few structural analyses of such molecules in platyhelminth parasites have been performed. In our previous paper, we reported the synthesis of four glycosphingolipid analogues from *Echinococcus multilocularis* in the neogala series, the structures which have a β-D-Gal*p*-(1→6)-β-D-Gal*p*-core and a fucose residue, suggesting the functional importance of glycolipids in parasitism.[2] Recently, Kawakami *et al.*[3] found and characterized a novel glycosphingolipid from the parasite *Spirometra erinacei*, the carbohydrate structure of which has a penultimate glucose residue attached to the reducing end galactose through a β1-3 linkage and a fucose attached to a glucose through an α1→3 linkage, Galβ(1→4)[Fucα(1→3)]Glcβ(1→3)[Galβ(1→6)]Galβ(1→1)Cer (Fig. 1). Glycosphingolipids found in nature are classified into many types according to basic carbohydrate structure *e.g.*, globo-, lacto-, ganglio-, mollu-, and gala series, and so on,[4] however this new carbohydrate structure, Galβ(1→4)Glcβ(1→3)Gal, may represent a new type of glycolipid core series. Furthermore, fucose-containing glycolipids derived from a number of tumor tissues have been shown to be highly immunogenic in mammalian systems.[5] For these reasons, the oligosaccharide of this glycolipid was the target of the synthetic studies described herein as part of our investigation into oligosaccharides of structural and biological interest.

Results and Discussion

For analogue synthesis of the target compound, nonreducing-end trisaccharide derivative **15** and reducing-end disaccharide derivative **17** were selected as glycosyl donor and acceptor, respectively.

Synthesis of Monosaccharide Derivatives Synthesis of the glucopyranosyl building block **3**, which is a component of the nonreducing-end trisaccharide, was carried out as depicted in Chart 1. 2-(Trimethylsilyl)ethyl 2-*O*-benzoyl-3,6-di-*O*-benzyl-β-D-glucopyranoside (**3**) was prepared from known 2-(trimethylsilyl)ethyl 4,6-*O*-benzylidene-3-*O*-benzyl-β-D-glucopyranoside (**1**)[6] by the following two-step procedure. Compound **1** was benzoylated to give **2** and reductive ring-opening of the benzylidene acetal in **2** with sodium cyanoborohydride-hydrogen chloride in dry diethylether afforded compound **3**. On the other hand, galactopyranoside derivative **6**, which is a component of the reducing-end disaccharide, was obtained from 2-(trimethylsilyl)ethyl β-D-galactopyranoside (**4**)[6] by regioselective *p*-methoxybenzylation[7] of the *in situ* prepared stannylidene derivative of **4**, with *p*-methoxybenzyl chloride and subsequent regioselective silylation with *tert*-butyldimethylsilyl chloride (TBDMS-Cl), followed by benzylation. Removal of the TBDMS group from **5** by Bu_4NF gave the galactose acceptor **6**.

Synthesis of Target glycolipid Analogues The glycosylation of **3** with known phenyl 2,3,4,6-tetra-*O*-benzoyl-1-thio-β-D-galactopyranoside **8**[8] in the presence of *N*-iodosuccinimide (NIS) and trifluoromethanesulfonic acid (TfOH) (cat)[9] and 4 Å MS in dichloromethane for 30 min at 0 °C gave the desired disaccharide **10** (52%), as evidenced by ^{1}H-NMR spectroscopy (H-1′, 4.45 ppm, J=7.9 Hz). Compound **10** was converted by *O*-debenzylation to **11**, and subsequent regioselective pivaloylation afforded the 3-OH compound **12**. Glycosylation of **12** with phenyl 2,3,4-tri-*O*-benzyl-1-thio-β-L-fucopyranoside **9**[10] in the presence of NIS/TfOH, as described for compound **10**, gave the desired α-glycoside **13** in 64% yield. The anomeric hydrogen atom of the fucose unit showed a signal at δ 4.96 (d, J=3.7 Hz). The α-L configuration of the newly formed glycosidic bond was also indicated by the $J_{C,H}$ value of 169.7 Hz in the ^{13}C-NMR spectrum.[11] Catalytic hydrogenolysis (10%, Pd–C) of the benzyl groups in **13** in methanol–AcOH and subsequent *O*-acetylation gave the trisaccharide **14**. For selective removal of the 2-

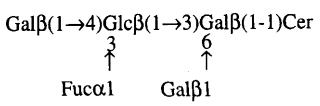

Fig. 1

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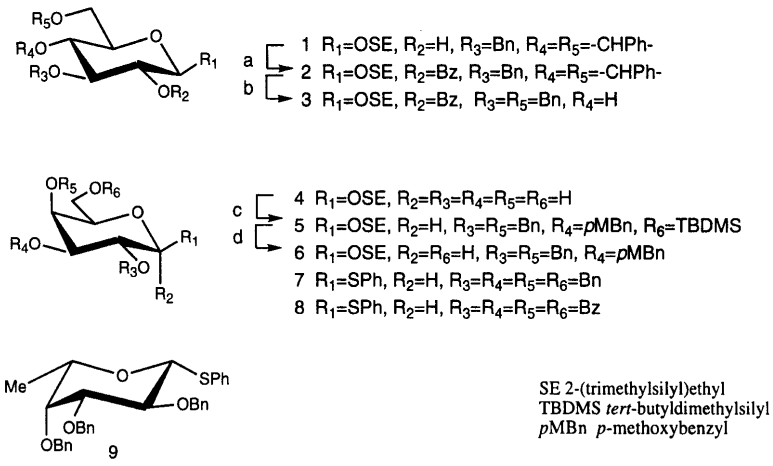
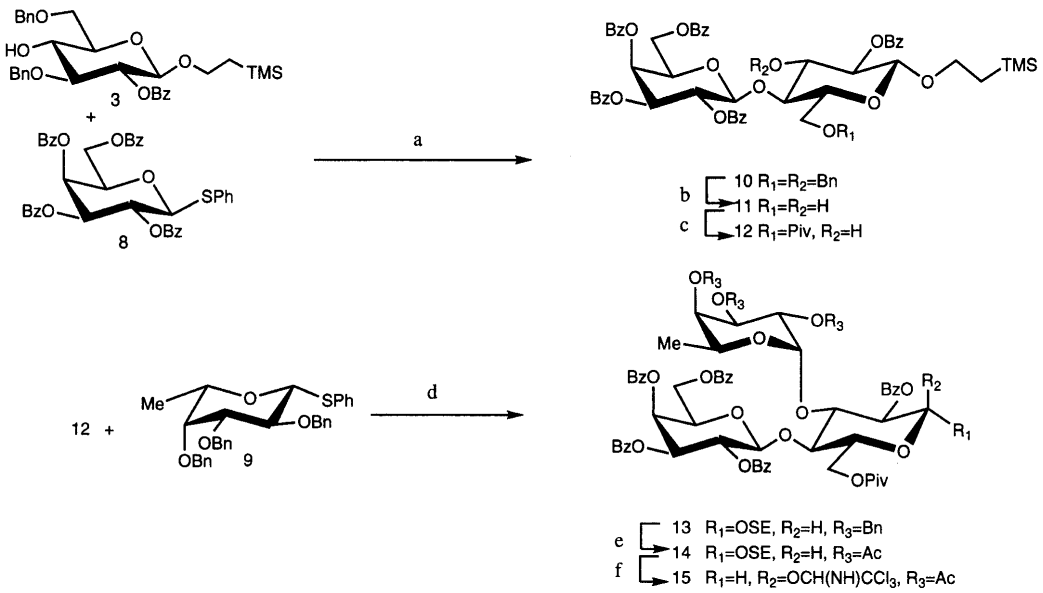


Reagents: a: BzCl / Pyr., 94 %; b: $NaBH_3CN$, HCl-Et_2O / THF, 76 %; c: 1 Bu_2SnO, MeOH, reflux; *p*MBnCl, CsF / DMF, 67 %; 2 TBDMSCl, imidazole / DMF; 3 BnBr, NaH / DMF, 60 % (2 steps); d: TBAF / THF, 82 %

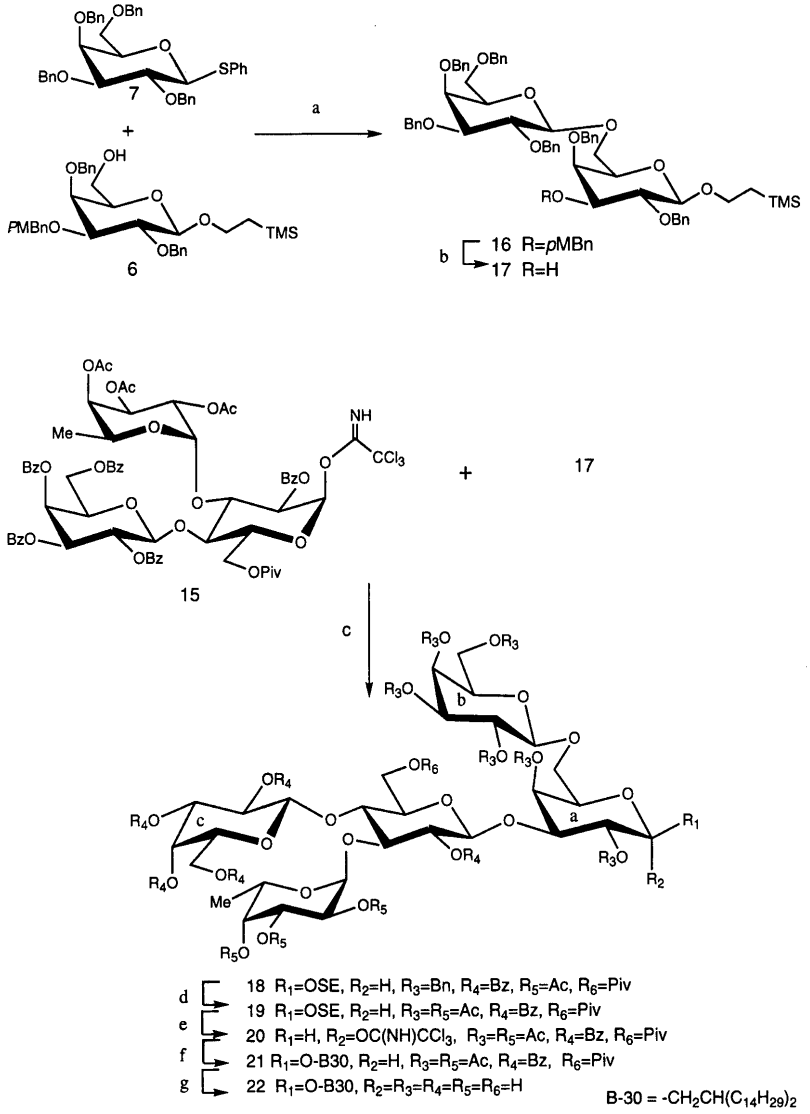
Chart 1



Reagents: a: NIS-TfOH, 4 Å MS / CH_2Cl_2, 52 %; b: Pd-C, H_2 / MeOH-AcOH, 98 %; c: PivCl / Pyr., 79 %; d: NIS-TfOH, 4 Å MS / CH_2Cl_2, 64 %; e: 1 Pd-C, H_2 / MeOH-AcOH; 2 Ac_2O / Pyr. 47 % (2 steps); f: 1 CF_3COOH / CH_2Cl_2; 2 CCl_3CN, DBU / CH_2Cl_2 86 %

Chart 2

(trimethylsilyl)ethyl group, the fully acylated oligosaccharide **14** was treated[6] with trifluoroacetic acid in dichloromethane for 30 min at 0 °C to give the 1-hydroxy compound, which on further treatment[12] with trichloroacetonitrile in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in dichloromethane for 2 h at 0 °C, gave the corresponding reducing-end trisaccharide donor **15** (Chart 2). On the other hand, for synthesis of the reducing-end disaccharide derivative as the glycosyl acceptor, we chose a 2-(trimethylsilyl)ethyl 2,3,4,6-tetra-*O*-benzoyl-*β*-D-galactopyranosyl-(1→6)-2,4-di-*O*-benzoyl-*β*-D-galactopyranoside. However, coupling of this acceptor with the donor **15** in the presence of trimethylsilyl triflate (TMSOTf) was not successful. (date was not shown) Therefore, the more reactive compound 2-(trimethylsilyl)-ethyl 2,3,4,6-tetra-*O*-benzyl-*β*-D-galactopyranosyl-(1→6)-2,4-di-*O*-benzyl-*β*-D-galactopyranoside **17**, was selected as the acceptor. Glycosylation of the former acceptor **6** with known donor **7**[12] in the presence of NIS/TfOH gave the desired *β*-glycoside **16** in 98% yield making use of the solvent effect of acetonitrile. The anomeric hydrogen atom of the nonreducing-end galactose unit appeared as a signal at δ 4.45 (d, J=7.9 Hz). The *β*-D configuration of the newly formed glycosidic bond was also indicated by the $J_{C,H}$ value of 159.7 Hz in the ^{13}C-NMR spectrum.[11] Selective removal of the *p*-methoxybenzyl group in **16** with ceric ammonium nitrate (CAN) gave 3-OH compound **17**. Glycosylation of **17**



Reagents: a: NIS-TfOH, 4 Å MS / CH_2Cl_2-CH_3CN, 98 %; b: CAN / CH_3CN-H_2O, 62 %; c: TMSOTf, 4 Å MS / CH_2Cl_2, 85 %; d: 1 Pd-C, H_2 / MeOH-AcOH, 98 %; 2 Ac_2O / Pyr. 65 % (2 steps); e: 1 CF_3COOH / CH_2Cl_2; 2 CCl_3CN, DBU / CH_2Cl_2 65 %; f: HO-B30, TMSOTf, 4 Å MS / CH_2Cl_2, 31 %; g: NaOMe / 1,4-dioxane-MeOH 85 %

Chart 3

with the glycosyl donor **15** in the presense of TMSOTf and 4 Å MS for 5 h at 0 °C afforded the desired β-glycoside **18** in high yield (85%). The ^{13}C-NMR spectrum showed five anomeric carbon atom signals at δ 103.9 (J=159.3 Hz, Gal b), 103.0 (J=157.1 Hz, Gal a), 101.3 (J=160.4 Hz, Gal c), 100.7 (J=161.5 Hz, C-1 of Glc) and 96.4 (J=177.9 Hz, C-1 of Fuc). The ^{1}H-NMR spectrum of **18** showed an anomeric proton doublet for a β-D-glucose unit at δ 5.04 (d, J=8.5 Hz, H-1) indicating the newly formed glycosidic linkage to be β-D configuration. Removal of the benzyl groups from **18** by catalytic hydrogenolysis over 10% Pd–C, and subsequent acetylation gave the per-*O*-acylated pentasaccharide **19**. For selective removal of the 2-(trimethylsilyl)ethyl group, fully acylated oligosaccharide **19** was treated[12] with trifluoroacetic acid in dichloromethane for 1 h at 0 °C to give the 1-hydroxy compound, which, on further treatment with trichloroacetonitrile in the presence of DBU in dichloromethane for 2 h at 0 °C, gave the corresponding receptor carbohydrate **20**. Glycosylation[14] of 2-(tetradecyl)hexadecanol[15] with the glycosyl donor was carried out in the presence of TMSOTf and 4 Å MS for 2 h at 0 °C and afforded the desired β-glycoside **21** (31%). Finally, removal of all acyl groups with sodium methoxide in 1 : 1 methanol/1,4-dioxane for 5 h at room temperature afforded the desired glycolipid analogue **22**. The anomeric configuration of compound **22** was confirmed by ^{1}H-NMR spectroscopy. Signals were observed at δ: 6.10 (d, J=3.7 Hz, H-1 of Fuc), 5.19 (d, J=7.9 Hz, H-1of Glc), 5.15 (d, J=7.9 Hz, H-1 of Gal c), 4.82 (d, J=7.3 Hz, H-1 of Gal b) and 4.63 (d, J=7.9 Hz, H-1of Gal a). Compound **22** revealed an $[M+H]^+$ ion peak at m/z 1233.7571 in the HR-FAB-MS spectrum (Chart 3).

Experimental

Optical rotations were determined with a JASCO digital polarimeter. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a JNM A 500 FT NMR spectrometer in $CDCl_3$ with Me_4Si as the internal standard. MALDI-TOFMS was recorded on a Perceptive Voyager RP mass spectrometer. High-resolution mass spectra were recorded on a JEOL JMS-SX102 under FAB conditions. TLC was performed on Silica gel 60 F_{254} (E. Merck) with detection by quenching of UV fluorescence and by spraying with 10% H_2SO_4. Column chromatography was carried out on Silica gel 60 (E. Merck). 2-(Trimethylsilyl)ethyl 4,6-*O*-benzylidene-3-*O*-benzyl-β-D-glucopyranoside (**1**), phenyl

2,3,4,6-tetra-*O*-benzyl-1-thio-β-D-galactopyranoside (**7**) and phenyl 2,3,4,6-tetra-*O*-benzoyl-1-thio-β-D-galactopyranoside (**8**) were prepared by literature methods.[6,8,12]

2-(Trimethylsilyl)ethyl 2-*O*-Benzoyl-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranoside (2) To a solution of compound **1** (1.57 g, 3.42 mmol) in pyridine (10 ml) was added benzoyl chloride (150 μl), and the mixture was stirred for 4 h at 0 °C. The reaction mixture was poured into ice-water and extracted with $CHCl_3$. The extract was washed sequentially with 5% HCl, aq. $NaHCO_3$ and water, dried (Na_2SO_4), and concentrated. The product was purified by silica gel column chromatography using 8 : 1 hexane–ethyl acetate as eluent to give **2** (1.81 g, 94.2%). $[\alpha]_D^{24}$ +14.6° (c=1.9, $CHCl_3$). ^{1}H-NMR δ: 7.66—7.16 (15H, m, 3×Ph), 5.70 (1H, s, benzylidene methine), 5.40 (1H, t, $J_{1,2}=J_{2,3}$=8.0 Hz, H-2), 4.92 and 4.79 (2H, each d, benzyl methylene), 4.72 (1H, d, H-1), 4.49 (1H, dd, H-6a), 4.05 (1H, ddd, $OC\underline{H}_2CH_2$–), 3.98—3.93 (3H, m, H-3, 5, 6b), 3.63—3.61 (2H, m, H-4, $OC\underline{H}_2CH_2$–), 0.94 (2H, m, $OCH_2C\underline{H}_2$–), −0.09 (9H, s, $Si(CH_3)_3$). MALDI-TOFMS: Calcd for $C_{32}H_{38}O_7Si$ *m/z*: 562. Found *m/z*: 585 $(M+Na)^+$.

2-(Trimethylsilyl)ethyl 2-*O*-Benzoyl-3,6-di-*O*-benzyl-β-D-glucopyranoside (3) To a solution of compound **2** (1.81 g, 3.22 mmol) and sodium cyanoborohydride (2.10 g, 33.49 mmol) in dry tetrahydrofuran (THF, 30 ml) was added powdered 3 Å MS (3 g). and the mixture was stirred for 2 h at room temperature, followed by cooling to 0 °C. Hydrogen chloride in diethyl ether was added until the solution was acidic (pH paper, gas evolution). After 10 min., the reaction mixture was poured into ice-water and extracted with $CHCl_3$. The extract was successively washed with aq. $NaHCO_3$ and water, dried (Na_2SO_4), and concentrated. The product was purified by silica gel column chromatography using 4 : 1 hexane–ethyl acetate as eluent to give **3** (1.37 g, 75.5%). $[\alpha]_D^{24}$ −0.5° (c=1.6, $CHCl_3$). ^{1}H-NMR δ: 8.14—7.22 (15H, m, 3×Ph), 5.40 (1H, t, $J_{1,2}=J_{2,3}$=8.0 Hz, H-2), 4.81 and 4.78, 4.75 and 4.64 (4H, each d, 2×benzyl methylene), 4.70 (1H, d, H-1), 4.07 (1H, ddd, $OC\underline{H}_2CH_2$–), 3.91—3.86 (3H, m, H-4, 6a, 6b), 3.77 (1H, t, H-3), 3.65 (1H, m, $OC\underline{H}_2CH_2$–), 3.60 (1H, brt, H-5), 3.01 (1H, brs, OH), 0.99 (2H, m, $OCH_2C\underline{H}_2$–), −0.09 (9H, s, $Si(CH_3)_3$). MALDI-TOFMS: Calcd for $C_{32}H_{40}O_7Si$ *m/z*: 564. Found *m/z*: 587 $(M+Na)^+$.

2-(Trimethylsilyl)ethyl 2,4-Di-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl-3-*O*-*p*-methoxybenzyl-β-D-galactopyranoside (5) A mixture of phenyl 2-(trimethylsilyl)ethyl β-D-galactopyranoside (900 mg, 3.21 mmol), dibutyltin oxide (875 mg, 3.53 mmol) and 20 ml of dry MeOH was stirred under reflux for 2 h. The solvent was evaporated and the residue was dried. The stannylidene derivative was redissolved in DMF (10 ml) and cesium fluoride (488 mg, 3.21 mmol) and *p*-methoxybenzyl chloride (0.48 ml, 3.53 mmol) were added. After the reaction mixture was stirred for 5 h, the solution was concentrated. Purification of the residue by column chromatography (20 : 1 $CHCl_3$–MeOH) on silica gel gave 2-(trimethylsilyl) 3-*O*-*p*-methoxybenzyl-β-D-galactopyranoside (860 mg, 66.9%). To a solution of this compound (586 mg, 1.47 mmol) in DMF (4 ml) were added imidazole (200 mg, 2.94 mmol) and *tert*-butyldimethylsilyl chloride (266 mg, 1.76 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 3 h, and then diluted with $CHCl_3$ and washed with 5% HCl, aq. $NaHCO_3$ and water, dried (Na_2SO_4), and concentrated. The product was chromatographed on silica gel using 2 : 1 hexane–ethyl acetate as eluent to provide 2-(trimethylsilyl) 6-*O*-*tert*-butyldimethylsilyl-3-*O*-*p*-methoxybenzyl-β-D-galactopyranoside. To a solution of this compound in DMF (5 ml) was added NaH in oil (162 mg) and benzyl bromide (0.6 ml). The mixture was stirred for 4 h at 0 °C and then methanol was added to destroy excess NaH. The reaction mixture was poured into ice-water and extracted with EtOAc. The extract was successively washed with aq. $NaHCO_3$ and water, dried (Na_2SO_4), and concentrated. The product was purified by silica gel column chromatography using 4 : 1 hexane–ethyl acetate as eluent to give **5** (605 mg, 59.3%, 2 steps). ^{1}H-NMR δ: 7.36—6.80 (14H, m, 3×Ph), 4.93—4.57 (6H, m, 3×benzyl methylene), 4.30 (1H, d, $J_{1,2}$=7.9 Hz, H-1), 3.95 (1H, ddd, $OC\underline{H}_2CH_2$–), 3.77—3.73 (5H, m, H-2, 4, OCH_3), 3.67 (1H, dd, $J_{5,6a}$=6.1 Hz, $J_{5,6b}$=9.8 Hz, H-6a), 3.61 (1H, dd, $J_{5,6b}$=6.7 Hz, H-6b), 3.50 (1H, ddd, $OC\underline{H}_2CH_2$–), 3.44 (1H, dd, $J_{2,3}$=3.1 Hz, $J_{3,4}$=9.8 Hz, H-3), 3.32 (1H, brt, H-5), 0.98 (2H, m, $OCH_2C\underline{H}_2$–), 0.84 (9H, s, $C(CH_3)_3$), −0.02 (9H, s, $-Si(CH_3)_3$), −0.03 (9H, s, $-Si(CH_3)_2$–). MALDI-TOFMS: Calcd for $C_{39}H_{58}O_7Si_2$ *m/z*: 695. Found *m/z*: 718 $(M+Na)^+$.

2-(Trimethylsilyl)ethyl 2,4-Di-*O*-benzyl-3-*O*-*p*-methoxybenzyl-β-D-galactopyranoside (6) A solution of compound **5** (600 mg, 0.96 mmol) in 10 ml of THF was treated with 1 M TBAF (1 ml) in THF solution at 0 °C. The reaction mixture was stirred at room temperature for 3 h, and then diluted with $CHCl_3$ and washed with water, dried (Na_2SO_4), and concentrated. The product was chromatographed on silica gel using 2 : 1 hexane–ethyl acetate as eluent to give compound **6** (455 mg, 81.7%). ^{1}H-NMR δ: 7.38—6.85 (14H, m, 3×Ph), 4.95—4.63 (6H, m, 3×benzyl methylene), 4.35 (1H, d, $J_{1,2}$=7.9 Hz, H-1), 3.99 (1H, ddd, $OC\underline{H}_2CH_2$–), 3.80 (3H, s, OCH_3), 3.80 (1H, dd, $J_{2,3}$=11.5 Hz, H-2), 3.77 (1H, brd, H-6a), 3.73 (1H, d, $J_{3,4}$=3.7 Hz, H-4), 3.55 (1H, ddd, $OC\underline{H}_2CH_2$–), 3.49 (1H, dd, H-3), 3.48 (1H, brd, H-6b), 3.35 (1H, brt, H-5), 1.66 (1H, brs, OH), 1.00 (2H, m, $OCH_2C\underline{H}_2$–), −0.07 (9H, s, $-Si(CH_3)_3$). MALDI-TOFMS: Calcd for $C_{33}H_{44}O_7Si$ *m/z*: 580. Found *m/z*: 603 $(M+Na)^+$.

2-(Trimethylsilyl)ethyl 2,3,4,6-Tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→4)-2-*O*-benzoyl-3,6-di-*O*-benzyl-β-D-glucopyranoside (10) To a solution of **3** (1.34 g, 1.95 mmol) and compound **8** (1.18 g, 2.09 mmol) in dry CH_2Cl_2 (5 ml) was added powdered 4 Å MS (3 g) and the mixture was stirred for 2 h at room temperature, then cooled to 0 °C. NIS (796 mg, 3.54 mmol) and TfOH (42 μl, 0.47 mmol) were added to the mixture, which was stirred for 3 h at 0 °C, then neutralized with Et_3N. The solids were filtered off and washed with $CHCl_3$. The combined filtrate and washings were successively washed with aq. $Na_2S_2O_3$ and water, dried (Na_2SO_4), and concentrated. The product was chromatographed on silica gel using 15 : 1 benzene–acetone as eluent to give **10** (1.24 g, 51.7%). $[\alpha]_D^{24}$ +21.0° (c=0.6 $CHCl_3$), ^{1}H-NMR δ: 8.02—6.99 (35H, m, 7×Ph), 5.87 (1H, d, $J_{3',4'}$=3.1 Hz, H-4′), 5.77 (1H, dd, $J_{1',2'}$=7.9 Hz, $J_{2',3'}$=10.4 Hz, H-2′), 5.41 (1H, dd, H-3′), 5.25 (1H, dd, $J_{1,2}$=7.9 Hz, $J_{2,3}$=9.2 Hz, H-2), 5.03 and 4.82, 4.73 and 4.39 (4H, each d, 2×benzyl methylene), 4.95 (1H, d, H-1′), 4.45 (1H, d, H-1), 4.31—4.22 (3H, m, H-4, H-6′a and H-6′b), 3.98 (1H, t, $J_{5',6a'}=J_{5',6b'}$=6.7 Hz, H-5′), 3.83 (1H, t, $J_{3,4}$=9.2 Hz,H-3), 3.98—3.88 (1H, m, $-C\underline{H}_2CH_2$–Si), 3.71 (1H, d, $J_{5,6a}=J_{6a,6b}$=11.0 Hz, H-6a), 3.60 (1H, t, $J_{5,6b}$=1.8 Hz, H-6b), 3.43 (1H, dt, $-C\underline{H}_2CH_2$–), 3.34 (1H, d, H-5), 0.80—0.65 (2H, m, $-CH_2C\underline{H}_2$–Si), −0.12 (9H, s, $Si(CH_3)_3$). MALDI-TOFMS: Calcd for $C_{66}H_{66}O_{16}Si$ *m/z*: 1142. Found *m/z*: 1165 $(M+Na)^+$.

2-(Trimethylsilyl)ethyl 2,3,4,6-Tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→4)-2-*O*-benzoyl-β-D-glucopyranoside (11) A solution of **10** (1.24 g, 1.08 mmol) in MeOH (8 ml) and AcOH (2 ml) was hydrogenated over 10% Pd–C (400 mg) for 5 h at room temperature, then filtered through Celite and the residue was washed with methanol and concentrated. The product was chromatographed on silica gel using 10 : 1 benzene–acetone as eluent to give **11** (1.03 g, 98.1%). $[\alpha]_D^{24}$ +66.3° (c=1.0, $CHCl_3$). ^{1}H-NMR δ: 8.05—7.12 (25H, m, 5×Ph), 5.98 (1H, d, $J_{3',4'}$=3.7 Hz, H-4′), 5.92 (1H, dd, $J_{1',2'}$=7.9 Hz, $J_{2',3'}$=10.4 Hz, H-2′), 5.62 (1H, dd, H-3′), 5.20 (1H, dd, $J_{1,2}$=8.5 Hz, $J_{2,3}$=9.8 Hz, H-2) 5.01 (1H, d, H-1′), 4.68 (1H, dd, $J_{5',6a'}$= 3.7 Hz, $J_{6a',6b'}$=11.6 Hz, H-6′a), 4.58 (1H, d, H-1), 4.45 (1H, dd, $J_{5',6b'}$= 8.5 Hz, H-5′), 4.38 (1H, dd, H-6′b), 4.05 (1H, t, $J_{3,4}$=9.2 Hz, H-3), 3.98—3.88 (2H, m, H-4, $-C\underline{H}_2CH_2$–Si), 3.61 (1H, d, $J_{5,6a}=J_{6a,6b}$=11.6 Hz, H-6a), 3.53—3.47 (2H, H-5, H-6b), 3.43 (1H, dt, $-C\underline{H}_2CH_2$–), 1.80 (2H, d, OH), 0.80—0.65 (2H, m, $-CH_2C\underline{H}_2$–Si), −0.12 (9H, s, $Si(CH_3)_3$). MALDI-TOFMS: Calcd for $C_{52}H_{54}O_{16}Si$ *m/z*: 962. Found *m/z*: 985 $(M+Na)^+$.

2-(Trimethylsilyl)ethyl 2,3,4,6-Tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→4)-2-*O*-benzoyl-6-*O*-pivaloyl-β-D-glucopyranoside (12) To a solution of compound **11** (1.03 g, 1.07 mmol) in pyridine (12 ml) was added dropwise pivaloyl chloride (0.67 ml, 5.41 mmol) for 30 min at 0 °C, and the mixture was allowed to warm to room temperature and stirred for 2 h. After general work up, the residue was chromatographed (benzene–acetone, 15 : 1) to give **12** (874 mg, 78.5%). $[\alpha]_D^{24}$ +69.3° (c=1.6, $CHCl_3$). ^{1}H-NMR δ: 8.07—7.22 (25H, m, 5×Ph), 5.98 (1H, d, $J_{3',4'}$=3.7 Hz, H-4′), 5.90 (1H, dd, $J_{1',2'}$=7.9 Hz, $J_{2',3'}$=10.4 Hz, H-2′), 5.60 (1H, dd, H-3′), 5.19 (1H, dd, $J_{1,2}$=8.5 Hz, $J_{2,3}$=9.8 Hz, H-2) 4.96 (1H, d, H-1′), 4.70 (1H, dd, $J_{5',6a'}$= 3.1 Hz, $J_{6a',6b'}$=11.0 Hz, H-6′a), 4.54 (1H, d, H-1), 4.47—4.42 (1H, m, H-5′), 4.37 (1H, dd, H-6′b), 4.24 (1H, d, $J_{5,6a}$=1.8 Hz, $J_{6a,6b}$=12.2 Hz, H-6a), 4.03 (1H, t, $J_{3,4}$=8.9 Hz, H-3), 3.98—3.88 (2H, m, H-6b, $-C\underline{H}_2CH_2$–Si), 3.86—3.47 (2H, H-4, 5), 3.43 (1H, dt, $-C\underline{H}_2CH_2$–), 2.04 (1H, d, OH), 1.07 (9H, s, Piv), 0.80—0.65 (2H, m, $-CH_2C\underline{H}_2$–Si), −0.12 (9H, s, $Si(CH_3)_3$). MALDI-TOFMS: Calcd for $C_{57}H_{62}O_{17}Si$ *m/z*: 1047. Found *m/z*: 1070 $(M+Na)^+$.

2-(Trimethylsilyl)ethyl 2,3,4,6-Tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→4)-[(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(1→3)]-2-*O*-benzoyl-6-*O*-pivaloyl-β-D-glucopyranoside (13) To a solution of **12** (698 mg, 0.67 mmol) and compound **9** (528 mg, 1.00 mmol) in dry CH_2Cl_2 (8 ml) was added powdered 4 Å MS (3 g) and the mixture stirred for 3 h at room temperature, then cooled to 0 °C. NIS (334 mg, 1.48 mmol) and TfOH (18 μl, 0.20 mmol) were then added to the mixture, which was stirred for 3 h at 0 °C, then neutralized with Et_3N. The solids were filtered off and washed with $CHCl_3$. The combined filtrate and washings were successively washed with aq. $Na_2S_2O_3$ and water, dried (Na_2SO_4), and concentrated. The product was chromatographed on silica gel using 15 : 1 benzene–acetone as eluent to give **13** (744.0 mg, 63.9%). ^{1}H-NMR δ: 8.16—6.91 (40H, m, 8×Ph), 5.90 (1H, d, $J_{3',4'}$=2.4 Hz, H-4′), 5.88 (1H, dd, $J_{1',2'}$=8.5 Hz, $J_{2',3'}$=10.3 Hz, H-

2′), 5.53 (1H, dd, H-3′), 5.44 (1H, $J_{1,2}$=4.3 Hz, H-1 of Fuc), 5.32 (1H, t, $J_{1,2}$=$J_{2,3}$=8.5 Hz, H-2), 5.03—4.39 (6H, m, 3×benzyl methylene), 4.84 (1H, d, H-1′), 4.39 (1H, d, H-1), 4.29 (1H, t, $J_{3,4}$=8.5 Hz, H-3), 3.97 (1H, t, H-4), 3.88 (1H, dd, H-4 of Fuc), 3.76—3.73 (1H, m, –C<u>H</u>$_2$CH$_2$–Si), 3.71 (1H, d, $J_{5,6a}$=$J_{6a,6b}$=11.0 Hz, H-6a), 3.57 (1H, t, $J_{5,6b}$=1.8 Hz, H-6b), 3.43 (1H, dt, –C<u>H</u>$_2$CH$_2$–), 3.34 (1H, d, H-5), 1.10 (9H, s, Piv), 0.80—0.65 (2H, m, –CH$_2$C<u>H</u>$_2$–Si), −0.12 (9H, s, Si(CH$_3$)$_3$). MALDI-TOFMS: Calcd for $C_{84}H_{90}O_{21}Si$ *m/z*: 1463. Found *m/z*: 1486 $(M+Na)^+$.

2-(Trimethylsilyl)ethyl 2,3,4,6-Tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→4)-[(2,3,4-tri-*O*-acetyl-α-L-fucopyranosyl)-(1→3)]-2-*O*-benzoyl-6-*O*-pivaloyl-β-D-glucopyranoside (14) A solution of **13** (744 mg, 0.51 mmol) in MeOH (8 ml) and AcOH (2 ml) was hydrogenated over 10% Pd–C (400 mg) for 3 h at room temperature, then filtered through Celite and the residue was washed with methanol and concentrated. The residue was acetylated with Ac_2O (4 ml) in pyridine (6 ml) for 10 h at room temperature. Work-up was as described for **2** and the crude product was purified by silica gel column chromatography using 2 : 1 hexane–ethyl acetate as an eluent to give **14** (317 mg, 47.1%). $[\alpha]_D^{24}$ −16.5° (*c*=0.5, $CHCl_3$). ^{1}H-NMR δ: 8.17—7.23 (25H, m, 5×Ph), 5.97 (1H, d, $J_{3',4'}$=3.7 Hz, H-4′), 5.74 (1H, dd, $J_{1',2'}$=7.9 Hz, $J_{2',3'}$=9.7 Hz, H-2′), 5.56 (1H, dd, H-3′), 5.44 (1H, d, $J_{3,4}$=2.4 Hz, H-4 of Fuc), 5.39 (1H, d, $J_{2,3}$=11.0 Hz, H-3 of Fuc), 5.36 (1H, d, $J_{1,2}$=4.3 Hz, H-1 of Fuc), 5.27 (1H, t, $J_{1,2}$=$J_{2,3}$=8.5 Hz, H-2), 5.20 (1H, dt, H-5 of Fuc), 5.11 (1H, dd, H-2 of Fuc), 4.93—4.90 (2H, m, H-6′a, 6′b), 4.83 (1H, d, H-1′), 4.56 (1H, dd, $J_{5,6a}$=1.8 Hz, $J_{5,6b}$=12.2 Hz, H-6a), 4.38 (1H, d, H-1), 4.23 (1H, dt, H-5′), 4.20—4.14 (2H, m, H-3, 6b), 3.96 (1H, t, H-4), 3.78—3.73 (1H, m, –C<u>H</u>$_2$CH$_2$–Si), 3.41-3.36 (2H, dt, H-5, –C<u>H</u>$_2$CH$_2$–), 2.14, 1.93 and 1.81(9H, s, 3Ac), 1.39 (3H, d, H-6 of Fuc), 1.09 (9H, s, Piv), 0.80—0.65 (2H, m, –CH$_2$C<u>H</u>$_2$–Si), −0.12 (9H, s, Si(CH$_3$)$_3$). ^{13}C-NMR ($CDCl_3$) δ: 101.0 (159.3 Hz, C-1′), 100.3 (161.3 Hz, C-1), 97.1 (169.7 Hz, C-1 of Fuc). MALDI-TOFMS: Calcd for $C_{69}H_{78}O_{24}Si$ *m/z*: 1319. Found *m/z*: 1342 $(M+Na)^+$.

***O*-2,3,4,6-Tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→4)-[(2,3,4-tri-*O*-acetyl-α-L-fucopyranosyl)-(1→3)]-2-*O*-benzoyl-6-*O*-pivaloyl-β-D-glucopyranosyl Trichloroacetimidate (15)** A solution of **14** (100 mg, 0.08 mmol) in CH_2Cl_2 (2 ml) was cooled to 0 °C and treated with CF_3COOH (2 ml), and the mixture stirred for 30 min at room temperature and concentrated. Ethyl acetate and toluene (1 : 2) were added and then removed by evaporation to give the 1-hydroxy compound. To a solution of the residue in CH_2Cl_2 (1 ml) at 0 °C, were added trichloroacetonitrile (228 μl, 2.28 mmol) and DBU (11 μl, 0.08 mmol). The mixture was stirred for 2 h at 0 °C. After completion of the reaction, the mixture was concentrated. Column chromatography (20 : 1 benzene–acetone) of the residue on silica gel gave **15** (89 mg, 86.2%) as an amorphous mass. $[\alpha]_D^{24}$ +28.1° (*c*=0.2, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): δ: 8.61 (s, 1H, NH), 6.82 (d, 1H, *J*=3.7 Hz, H-1), 5.35 (d, 1H, *J*=3.7 Hz, H-1 of Fuc), 4.80 (d, 1H, *J*=7.9 Hz, H-1′); MALDI-TOFMS: Calcd for $C_{66}H_{66}Cl_3NO_{24}$: *m/z* 1363. Found: *m/z* 1386 $(M+Na)^+$.

2-(Trimethylsilyl)ethyl 2,3,4,6-Tetra-*O*-benzyl-β-D-galactopyranosyl-(1→6)-2,4-di-*O*-benzyl-3-*O*-*p*-methoxybenzyl-β-D-galactopyranoside (16) To a solution of **7** (711 mg, 1.13 mmol) and compound **6** (435 mg, 0.75 mmol) in dry CH_2Cl_2–CH_3CN (1 : 3, 4 ml) was added powdered 4 Å MS (1 g), and the mixture stirred for 2 h at room temperature, then cooled to 0 °C. NIS (253 mg, 1.69 mmol) and TfOH (15 μl, 0.17 mmol) were added to the mixture, which was stirred for 30 min at −40 °C, then neutralized with Et_3N. The solids were filtered off and washed with $CHCl_3$. The combined filtrate and washings were successively washed with aq. $Na_2S_2O_3$ and water, dried (Na_2SO_4), and concentrated. The product was chromatographed on silica gel using 4 : 1 hexane–ethyl acetate as eluent to give **16** (809 mg, 97.9%). $[\alpha]_D^{24}$ −0.5° (*c*=2.5, $CHCl_3$). ^{1}H-NMR δ: 7.39—6.81 (34H, m, 5×Ph, MeO<u>Ph</u>), 4.94—4.37 (14H, m, benzyl methylene), 4.41 (1H, d, *J*=7.9 Hz, H-1′), 4.31 (1H, d, *J*=7.4 Hz, H-1), 3.98—3.75 (10H, m, H-2, 2′, 4, 4′, 6a, 6b, –OC<u>H</u>$_2$CH$_2$–, OMe), 3.58—3.42 (7H, m, H-3, 3′, 5, 5′, 6′a, 6′b, –OC<u>H</u>$_2$CH$_2$–), 0.97—0.94 (2H, m, –CH$_2$C<u>H</u>$_2$–Si), −0.08 (9H, s, Si(CH$_3$)$_3$). ^{13}C-NMR ($CDCl_3$) δ: 103.7 (157.2 Hz, C-1′), 103.4 (159.3 Hz, C-1), 82.1 (C-3′), 81.8 (C-3), 79.5 (C-2), 79.4 (C-2′), 73.8 (C-5), 73.4 (C-4), 73.3 (C-4′), 72.9 (C-5′), 68.3 (C-6), 68.1 (C-6′) 75.0, 74.8, 74.9, 74.1, 73.4, 72.9 and 72.6 (benzyl methylene), 67.2 (–O<u>C</u>H$_2$CH$_2$–), 55.1 (OCH$_3$), 18.3 (–OCH$_2$<u>C</u>H$_2$–), −1.6 (SiMe$_3$). MALDI-TOFMS: Calcd for $C_{67}H_{78}O_{12}Si$ *m/z*: 1103. Found *m/z*: 1126 $(M+Na)^+$.

2-(Trimethylsilyl)ethyl 2,3,4,6-Tetra-*O*-benzyl-β-D-galactopyranosyl-(1→6)-2,4-di-*O*-benzyl-β-D-galactopyranoside (17) To a solution of **16** (367 mg, 0.33 mmol) in CH_3CN (4.5 ml) and water (0.5 ml) was added ceric ammonium nitrate (CAN, 365 mg, 0.66 mmol), and the mixture was stirred for 3 h at room temperature and extracted with $CHCl_3$. The extract was successively washed with aq. $NaHCO_3$ and water, dried (Na_2SO_4) and concentrated. The product was chromatographed on silica gel using 3 : 1 hexane–ethyl acetate as eluent to give **17** (207 mg, 62.4%). $[\alpha]_D^{24}$ −10.5° (*c*=2.5, $CHCl_3$). ^{1}H-NMR δ: 7.39—7.10 (30H, m, 5×Ph), 4.98—4.40 (12H, m, benzyl methylene), 4.39 (1H, d, *J*=7.9 Hz, H-1′), 4.29 (1H, d, *J*=7.4 Hz, H-1), 3.98—3.75 (6H, m, H-2, 2′, 4, 4′, 6a, –OC<u>H</u>$_2$CH$_2$–), 3.59—3.44 (8H, m, H-3, 3′, 5, 5′, 6b, 6′a, 6′b, –OC<u>H</u>$_2$CH$_2$–), 2.20 (1H, d, OH) 0.97—0.94 (2H, m, –CH$_2$C<u>H</u>$_2$–Si), −0.08 (9H, s, Si(CH$_3$)$_3$). MALDI-TOFMS: Calcd for $C_{59}H_{70}O_{11}Si$ *m/z*: 983. Found *m/z*: 1006 $(M+Na)^+$.

2-(Trimethylsilyl)ethyl 2,3,4,6-Tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→4)-[(2,3,4-tri-*O*-acetyl-α-L-fucopyranosyl)-(1→3)]-2-*O*-benzoyl-6-*O*-pivaloyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranosyl-(1→6)]-2,4-di-*O*-benzyl-β-D-galactopyranoside (18) To a solution of the trichloroacetimidate **15** (176 mg, 0.13 mmol) and **17** (100 mg, 0.10 mmol) in CH_2Cl_2 (1 ml) were added molecular sieves 4 Å (300 mg) and the mixture was stirred for 3 h at room temperature, then cooled to −20 °C. TMSOTf (6.7 μl, 37 μmol) was added and the mixture was stirred for 1 h at −20 °C then neutralized with Et_3N. The solids were filtered off and washed with $CHCl_3$. The combined filtrate and washings were successively washed with water, dried (Na_2SO_4), and concentrated. The product was purified by silica gel column chromatography using 10 : 1 benzene–ethyl acetate as eluent to give **18** (185 mg, 84.7%). $[\alpha]_D^{24}$ −0.4° (*c*=3.7, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 5.54 (1H, d, *J*=3.7 Hz, H-1 of Fuc), 5.04 (1H, d, *J*=8.5 Hz, H-1 of Glc), 4.97 (1H, d, *J*=8.5 Hz, H-1 of Gal c), 4.52 (1H, d, *J*=8.0 Hz, H-1 of Gal b), 4.26 (1H, d, *J*=7.4 Hz, H-1 of Gal a). ^{13}C-NMR ($CDCl_3$) δ: 103.9 (159.3 Hz, C-1 of Gal b), 103.0 (157.1 Hz, C-1 of Gal a), 101.3 (160.4 Hz, C-1 of Gal c), 100.7 (161.5 Hz, C-1 of Glc), 96.4 (177.9 Hz, C-1 of Fuc). MALDI-TOFMS: Calcd for $C_{123}H_{134}O_{34}Si$ *m/z*: 2183. Found *m/z*: 2206 $(M+Na)^+$.

2-(Trimethylsilyl)ethyl 2,3,4,6-Tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→4)-[(2,3,4-tri-*O*-acetyl-α-L-fucopyranosyl)-(1→3)]-2-*O*-benzoyl-6-*O*-pivaloyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→6)]- 2,4-di-*O*-acetyl-β-D-galactopyranoside (19) A solution of **18** (150 mg, 68.7 μmol) in MeOH (5 ml) and AcOH (0.1 ml) was hydrogenated over 10% Pd–C (100 mg) for 3 h at room temperature, then filtered through Celite and the residue was washed with methanol and concentrated. The residue was acetylated with Ac_2O (2 ml) in pyridine (3 ml) for 10 h at room temperature. Work-up as described for **2** gave a product which was purified by silica gel column chromatography using 2 : 1 hexane–ethyl acetate as an eluent to give **18** (85 mg, 65.3%). $[\alpha]_D^{24}$ +1.5° (*c*=1.9, $CHCl_3$); ^{1}H-NMR ($CDCl_3$) δ: 5.33 (1H, d, *J*=4.0 Hz, H-1 of Fuc), 4.89 (1H, d, *J*=8.5 Hz, H-1 of Gal c), 4.48 (1H, d, *J*=7.9 Hz, H-1 of Glc), 4.45 (1H, d, *J*=7.9 Hz, H-1 of Gal b), 4.18 (1H, d, *J*=7.9 Hz, H-1 of Gal a). MALDI-TOFMS: Calcd for $C_{93}H_{110}O_{40}Si$ *m/z*: 1895. Found *m/z*: 1918 $(M+Na)^+$.

***O*-2,3,4,6-Tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→4)-[(2,3,4-tri-*O*-acetyl-α-L-fucopyranosyl)-(1→3)]-2-*O*-benzoyl-6-*O*-pivaloyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→6)]-2,4-di-*O*-acetyl-β-D-galactopyranosyl Trichloroacetimidate (20)** To a solution of **19** (75 mg, 39.6 μmol) in CH_2Cl_2 (1 ml) cooled to 0 °C was added CF_3COOH (1 ml), and the mixture was stirred for 1 h at room temperature and concentrated. Ethyl acetate and toluene (1 : 2) were added and the solvent evaporated to give the 1-hydroxy compound. To a solution of the residue in CH_2Cl_2 (1 ml), cooled at 0 °C were added trichloroacetonitrile (120 μl, 1.29 mmol) and DBU (6 μl, 0.04 mmol). The mixture was stirred for 2 h at 0 °C. After completion of the reaction, the mixture was concentrated. Column chromatography (10 : 1 benzene–acetone) of the residue on silica gel gave **20** (50 mg, 65.1%) as an amorphous mass. $[\alpha]_D^{24}$ +19.0° (*c*=1.2, $CHCl_3$); ^{1}H-NMR ($CDCl_3$): δ: 8.53 (s, 1H, NH), 6.40 (d, 1H, *J*=3.7 Hz, H-1), 5.34 (1H, d, *J*=3.7 Hz, H-1 of Fuc), 4.90 (1H, d, *J*=8.5 Hz, H-1 of Gal c), 4.59 (1H, d, *J*=7.9 Hz, H-1 of Glc), 4.43 (1H, d, *J*=7.9 Hz, H-1 of Gal b).

2-(Tetradecyl)hexadecyl 2,3,4,6-Tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→4)-[(2,3,4-tri-*O*-acetyl-α-L-fucopyranosyl)-(1→3)]-2-*O*-benzoyl-6-*O*-pivaloyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→6)]-2,4-di-*O*-acetyl-β-D-galactopyranoside (21) To a solution of trichloroacetimidate **20** (46 mg, 24 μmol) and 2-(tetradecyl)hexadecanol (21 mg, 48 μmol) in CH_2Cl_2 (1 ml) were added molecular sieves 4 Å (200 mg) and the mixture was stirred for 3 h at room temperature, then cooled to 0 °C. TMSOTf (2.2 μl, 12 μmol) was added and the mixture was stirred for 2 h at 0 °C then neutralized with Et_3N. The solids were filtered off and washed with $CHCl_3$. The combined filtrate and washings were successively washed with water, dried (Na_2SO_4), and concentrated. The product was purified by silica gel column chromatography using 15 : 1 benzene–acetone as eluent to give **21** (14 mg, 30.7%). $[\alpha]_D^{24}$ +3.2° (*c*=0.4, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 5.30 (1H, d, *J*=4.0 Hz, H-1 of Fuc), 4.89 (1H,

d, J=8.5 Hz, H-1 of Gal c), 4.47 (1H, d, J=7.9 Hz, H-1 of Glc), 4.46 (1H, d, J=7.9 Hz, H-1 of Gal b), 4.10 (1H, d, J=7.9 Hz, H-1 of Gal a), 3.92 (1H, dd, $-OCH_2-$), 3.33 (1H, dd, $-OCH_2-$), 1.34 (52H, br s, $2\times CH_2$), 0.96 (6H, t, $2\times-CH_2\underline{CH_3}$). MALDI-TOFMS: Calcd for $C_{118}H_{158}O_{40}$ *m/z*: 2215. Found *m/z*: 2238 $(M+Na)^+$.

2-(Tetradecyl)hexadecyl β-D-Galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)]-β-D-glucopyranosyl-(1→3)-[β-D-galactopyranosyl-(1→6)]-β-D-galactopyranoside (22) To a solution of **21** (14 mg, 6.3 μmol) in 1 : 1 MeOH/1,4-dioxane (2 ml) was added NaOMe (20 mg) and the mixture was stirred for 3 h at room temperature, then neutralized with Amberlite IR-120 (H^+) resin. The resin was filtered off and washed with 1 : 1 $CHCl_3$–MeOH. The filtrate and washings were combined and concentrated. Column chromatography (1 : 1 $CHCl_3$–MeOH) of the residue on Sephadex LH-20 gave **22** (6.6 mg, 84.9%). $[\alpha]_D^{24}$ −14.4° (c=0.1, 1 : 1 $CHCl_3$–MeOH). ^{1}H-NMR (C_5D_5N) δ: 6.10 (1H, d, J=3.7 Hz, H-1 of Fuc), 5.19 (1H, d, J=7.9 Hz, H-1 of Glc), 5.15 (1H, d, J=7.9 Hz, H-1 of Gal c), 4.82 (1H, d, J=7.3 Hz, H-1 of Gal b), 4.63 (1H, d, J=7.9 Hz, H-1 of Gal a). HR-FAB-MS: Calcd for $C_{60}H_{113}O_{25}$ $[M+H]^+$: 1233.7571. Found 1233.7600.

Acknowledgement This work was supported by the Sasagawa Scientific Research Grant from The Japan Science Society and also supported by a Grant-in-Aid for Encouragement of Young Scientists, No. 70296531 from the Ministry of Education, Science, Sports and Culture of Japan.

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