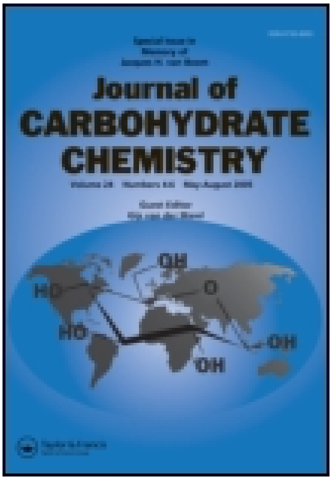

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Synthesis of a Di-And a Trisaccharide Related to the Repeating Unit of E.Coli O128 Lipopolysaccharide

Prabal Sengupta , Sumanta Basu & Bishnu P. Chatterjee
[a] Department of Biological Chemistry , Indian Association for the Cultivation of Science Jadavpur , Calcutta 700 032, India
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SYNTHESIS OF A DI- AND A TRISACCHARIDE RELATED TO THE REPEATING UNIT OF *E.coli* O128 LIPOPOLYSACCHARIDE

Prabal Sengupta, Sumanta Basu and Bishnu P. Chatterjee*

Department of Biological Chemistry
Indian Association for the Cultivation of Science
Jadavpur, Calcutta 700 032, India.

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ABSTRACT

Starting from L-fucose, D-galactose and 2-amino-2-deoxy-D-galactose, methyl 2-acetamido-2-deoxy-β-D-galactopyranosyl-(1→4)-α-D-galactopyranoside and methyl 2-acetamido-2-deoxy-β-D-galactopyranosyl-(1→6)-[α-L-fucopyranosyl-(1→2)]-β-D-galactopyranoside, which are related to the repeating unit of *E.coli* O128, have been synthesized using NIS and TfOH as promoter.

INTRODUCTION

The structure of the repeating unit of the O-antigenic polysaccharide from *E.coli* O128 has been reported[1] as:

→3)-β-D-Gal*p*NAc-(1→4)-α-D-Gal*p*-(1→3)-β-D-Gal*p*NAc-(1→6)-β-D-Gal*p*-(1→
2
↑
1
α-L-Fuc*p*

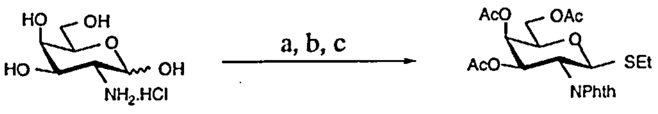
In continuation of our previous efforts to understand the relationship between structure and immunological specificity of the antigen, it is necessary to study the inhibitory effect of the related sugar groupings in the corresponding polysaccharide. As a part of our program to undertake the immunochemical study of the polysaccharide, which will help us to understand the nature of the biological repeating units, and also the chemical basis of their serological specificities, we recently reported[2] the synthesis of some branched disaccharides related to this antigen. The purpose of this program was to provide a variety of oligosaccharides and their corresponding synthetic glycoconjugates which could be used in inhibition studies to determine the immunodominant sugar of the repeating unit of *E.coli* O128 lipopolysaccharide by enzyme-linked immunosorbent assay (ELISA). As a further extension of our synthetic program, we now report a route to the synthesis of a di- and a trisaccharide related to the repeating unit of this O-antigenic polysaccharide. The synthesis of the methyl glycosides of these oligosaccharides, β-D-Gal*p*NAc-(1→4)-α-D-Gal*p* and β-D-Gal*p*NAc-(1→6)-[α-L-Fuc*p*-(1→2)]-β-D-Gal*p* have not yet been previously reported, as far as we are aware.

The immunological work was described separately (Communicated in *FEMS Immunol. Med. Microbiol.*). Briefly, the antiserum against *E.coli* O128 was raised in rabbits and ELISA was performed with the purified LPS as well as the inhibitors (oligosaccharides) prepared synthetically with the antibody raised to get an antigen-antibody reaction in microtiter plates which can be monitored by HRP-conjugated goat anti-rabbit IgG. The inhibitory effect of the sugars was calculated by comparing the absorbance values of the LPS and the 50% inhibition value (IC_{50}) of each sugar, which was obtained from the semilogarithmic curves.

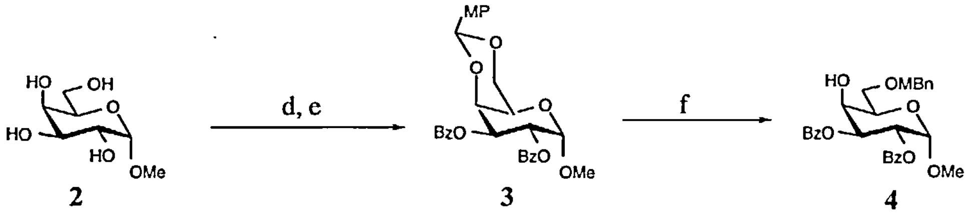
As mentioned previously,[2] the de-blocked di- and trisaccharides were characterized by considering the glycosidation effects for the anomeric residues as well as by comparison of their ^{1}H and ^{13}C NMR spectra.[3,4]

RESULTS AND DISCUSSION

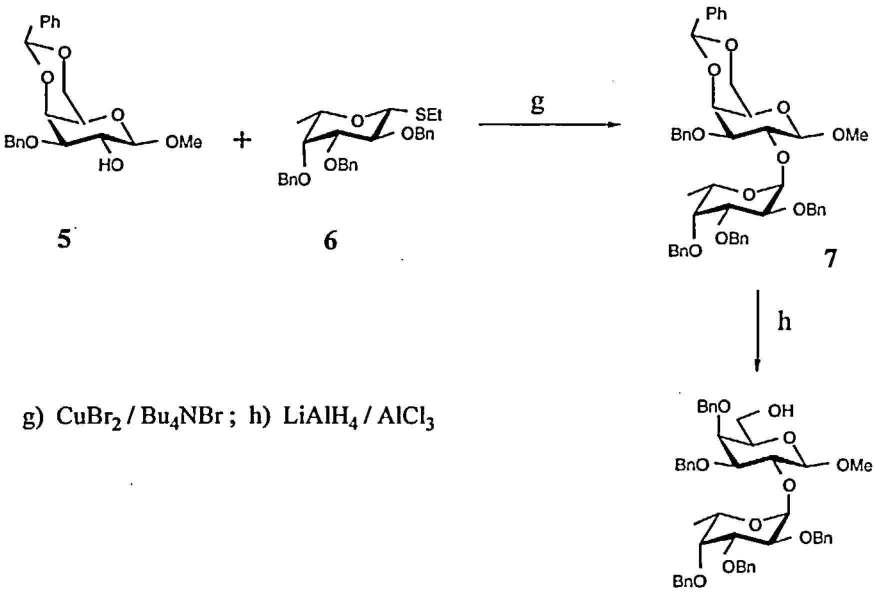
Ethyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-1-thio-β-D-galactopyranoside **1** was prepared as described before.[5] In a set of experiments, methyl α-D-galactopyranoside **2** was first treated with 4-methoxybenzaldehyde dimethyl acetal to give the corresponding 4,6-*O*-(4-methoxybenzylidene) derivative which was then benzoylated to afford methyl 2,3-di-*O*-benzoyl-4,6-*O*-(4-methoxybenzylidene)-α-D-galactopyranoside **3**. Regioselective opening of the 4-methoxybenzylidene ring with $NaCNBH_3$ and trifluoroacetic acid gave methyl 2,3-di-*O*-benzoyl-6-*O*-(4-methoxybenzyl)-α-D-galactopyranoside 4.[6] In a separate experiment, disaccharide methyl 2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-galactopyranoside 7,[2] prepared by condensation of methyl 3-*O*-benzyl-4,6-*O*-benzylidene-β-D-galactopyranoside 5[7] and ethyl 2,3,4-tri-*O*-benzyl-1-thio-β-L-fucopyranoside 6[8] with $CuBr_2$ and Bu_4NBr,[9] was treated with $LiAlH_4$ and $AlCl_3$[10] to give methyl 2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl-(1→2)-3,4-di-*O*-benzyl-β-D-galactopyranoside 8 (Scheme 1).



a) Phthalic Anhydride, NaOH ; b) Acetic Anhydride / Pyridine ; c) Ethanethiol



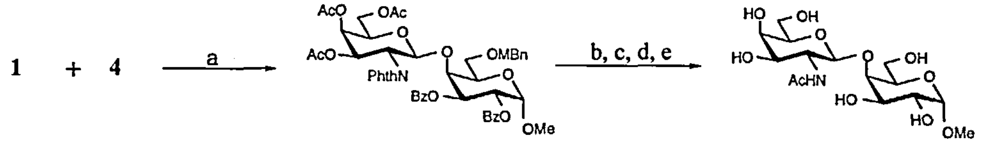
d) *p*-Methoxybenzaldehyde dimethyl acetal / *p*-Toluenesulfonic Acid ;
e) Benzoyl chloride / Pyridine ; f) Sodium cyanoborohydride / Trifluoroacetic acid / DMF



g) $CuBr_2$ / Bu_4NBr ; h) $LiAlH_4$ / $AlCl_3$

Scheme 1

The donor **1** and acceptor **4** were then allowed to condense in the presence of *N*-iodosuccinimide (NIS) and trifluoromethanesulfonic acid (TfOH)[11] as promoter to yield methyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzoyl-6-*O*-(4-methoxybenzyl)-α-D-galactopyranoside **9** in 67% yield. Dephthaloylation of **9** with hydrazine hydrate,[12] followed by *N*-acetylation and Zemplén deacetylation[13] and finally oxidative removal of the 4-methoxybenzyl group with ceric ammonium nitrate (CAN) gave methyl 2-acetamido-2-deoxy-β-D-galactopyranosyl-(1→4)-α-D-galactopyranoside **10** in 85% yield (Scheme 2).

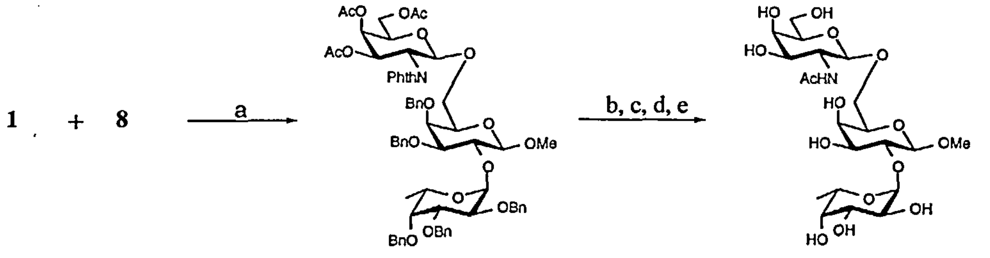


9 **10**

a) NIS-TfOH ; b) $N_2H_4.H_2O$, EtOH ; c) Ac_2O / Py ; d) NaOMe / MeOH ; e) CAN

Scheme 2

The donor **1** was also condensed with acceptor **8** using the same promoter to yield the trisaccharide derivative methyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-galactopyranosyl-(1→6)-[2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl-(1→2)]-3,4-di-*O*-benzyl-β-D-galactopyranoside **11** in 61% yield. Removal of the phthalimido group and subsequent *N*-acetylation of the compound, followed by Zemplén deacetylation and hydrogenolysis with 10% Pd-C afforded the de-blocked trisaccharide methyl 2-acetamido-2-deoxy-β-D-



11 **12**

a) NIS-TfOH ; b) $N_2H_4.H_2O$, EtOH ; c) Ac_2O / Py ; d) NaOMe / MeOH ; e) H_2 / Pd-C

Scheme 3

galactopyranosyl-(1→6)-[α-L-fucopyranosyl-(1→2)]-β-D-galactopyranoside **12** in 74% yield (Scheme 3).

EXPERIMENTAL

General. All reactions were monitored by TLC on Silica Gel G (E. Merck, India). Column chromatography was performed using 100 - 200 mesh silica gel (SRL, India). All solvents were dried and/or distilled before use and all evaporations were conducted below 50 °C under reduced pressure, unless stated otherwise. Optical rotations were measured at 24 °C with a Perkin-Elmer 241 MC polarimeter. The ^{1}H and ^{13}C NMR spectra were recorded with a Bruker DPX-300 spectrometer using $CDCl_3$ as the solvent (internal standard TMS) unless otherwise stated. The organic extracts were dried over anhydrous Na_2SO_4.

Ethyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-1-thio-β-D-galactopyranoside (1). 1,3,4,6-Tetra-*O*-acetyl-2-deoxy-2-phthalimido-β-D-galactopyranose[14] (2.00 g, 4.18 mmol) was treated as mentioned[5] to give **1** (1.6 g, 82%); $[\alpha]_D$ +20.4° (*c* 0.1, $CHCl_3$); ^{1}H NMR δ 1.15 (t, 3H, SCH_2CH_3), 1.78, 1.91, 2.10 (3s, 3H each, 3xAc), 2.60-2.65 (m, 2H, SCH_2CH_3), 4.02-4.18 (m, 2H, H-5, H-6), 4.54 (t, 1H, J = 10.7 Hz, H-2), 5.40 (d, 1H, J = 10.5 Hz, H-1), 5.45 (bd, 1H, J = 3 Hz, H-4), 5.78 (dd, 1H, J = 3.3 Hz, 10.8 Hz, H-3), 7.66-7.79 (m, 4H, NPhth).

Anal. Calcd for $C_{22}H_{25}O_9NS$: C, 55.10; H, 5.25. Found: C, 54.89, H, 5.67.

Methyl 2,3-Di-*O*-benzoyl-6-*O*-(4-methoxybenzyl)-α-D-galactopyranoside (4). To a stirred mixture containing methyl 2,3-di-*O*-benzoyl-4,6-*O*-(4-methoxybenzylidene)-α-D-galactopyranoside (1.17 g, 2.24 mmol) and $NaCNBH_3$ (0.7 g, 11.2 mmol) was added dropwise a chilled soln (0 °C) of TFA (1.72 mL, 22.4 mmol) in DMF (14 mL). After 7 h, the mixture was filtered through celite and poured into ice-cold saturated aq $NaHCO_3$. The aq phase was repeatedly extracted with CH_2Cl_2. The combined extracts were washed with saturated aq $NaHCO_3$, dried, filtered and concentrated to give **4** as syrup (0.88 g, 75%); $[\alpha]_D$ +29.7° (*c* 0.8, $CHCl_3$); ^{1}H NMR δ 3.39 (s, 3H, OCH_3), 3.76 (s, 3H, $CH_2C_6H_4OCH_3$), 5.67 (d, 1H, J = 3.3 Hz, H-1), 7.23-7.98 (m, 14H, aromatic protons).

Anal. Calcd for $C_{29}H_{32}O_9$: C, 66.40; H, 6.14. Found: C, 65.76; H, 6.82.

Methyl 2,3,4-Tri-*O*-benzyl-α-L-fucopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-galactopyranoside (7). To a stirred mixture of $CuBr_2$ (0.76 g, 3.43 mmol), Bu_4NBr[9] (0.11 g, 0.34 mmol) and molecular sieves 4Å was added a soln of **6**[8] (1.1 g, 2.29 mmol) and **5**[7] (0.7 g, 1.87 mmol) in 1,2-dichloroethane-DMF (5:1) at 20 °C. After stirring for 48 h at 20 °C, the mixture was diluted with 1,2-dichloroethane and filtered through celite. The organic layer was washed successively with water, aq $NaHCO_3$ and water, dried (Na_2SO_4) and concentrated. The residue was chromatographed with 9:1 toluene-EtOAc giving **7** as syrup (1.08 g, 72%); $[\alpha]_D$ -68.7° (*c* 0.9, $CHCl_3$); ^{1}H NMR δ 1.21 (d, 3H, J = 6.6 Hz, CH_3), 3.48 (s, 3H, OCH_3), 3.76-3.81 (m, 2H, H-3, H-5), 3.96 (dd, 1H, $J_{1,2}$ = 8 Hz, $J_{2,3}$ = 7.8 Hz, H-2), 4.00-4.05 (m, 2H, H-2', H-4'), 4.12 (dd, 1H, $J_{2,3}$ = 9.6 Hz, $J_{3,4}$ = 2.7 Hz, H-3'), 4.15 (dd, 1H, J = 11 Hz & 1.8 Hz, H-6), 4.39 (d, 1H, J = 7.8 Hz, H-1), 4.53 (dd, 1H, J = 10.7 Hz & 2 Hz, H-6'), 4.62-4.95 (m, 8H, 4PhCH_2), 5.40 (s, 1H, PhC*H*), 5.65 (d, 1H, J = 3.6 Hz, H-1'), 7.17-7.39 (m, 25H, aromatic protons); ^{13}C NMR δ 17.1 (CH_3), 56.75 (OCH_3), 66.79 (C-6), 69.75, 71.11, 72.93, 73.19, 73.48, 75.19, 76.48, 77.84, 78.41, 80.03, 81.69, 97.99 (C-1'), 101.39 (C-1), 103.14 (PhC*H*), 126.88-139.60 (aromatic carbons).

Anal. Calcd for $C_{48}H_{52}O_{10}$: C, 73.07,; H, 6.64. Found: C, 72.76; H, 6.86.

Methyl 2,3,4-Tri-*O*-benzyl-α-L-fucopyranosyl-(1→2)-3,4-di-*O*-benzyl-β-D-galactopyranoside (8). Compound **7** (0.5 g, 0.63 mmol) was dissolved in 1:1 ether-CH_2Cl_2 (20 mL) and to it $LiAlH_4$ (0.2 g) was added in 3-4 portions at 0 °C. The mixture was heated to reflux temp following addition of $AlCl_3$ (0.5 g) in ether (10 mL) to the hot soln for 1 h and refluxing was continued for another 45 min. The mixture was cooled and excess $LiAlH_4$ was decomposed with EtOAc (5 mL). The $Al(OH)_3$ was precipitated by the addition of water (15 mL) and filtered off. The filtrate was diluted with ether (50 mL) and the organic phase was separated, washed with water (3x20 mL) and dried. The solution was concentrated to dryness to give pure syrup **8** (0.35 g, 70%); $[\alpha]_D$ -41.5° (*c* 0.65, $CHCl_3$); ^{1}H NMR δ 1.04 (d, 1H, J = 6.3 Hz, CH_3), 3.40 (s, 3H, OCH_3), 3.62-3.69 (m, 2H, H-3, H-5), 3.89 (dd, 1H, $J_{1,2}$ = 8.4 Hz, $J_{2,3}$ = 6 Hz, H-2), 3.94-3.97 (m, 2H, H-2', H-4'), 4.04 (dd, 1H, $J_{2,3}$ = 7.8 Hz, $J_{3,4}$ = 3.9 Hz, H-3'), 4.32 (d, 1H, $J_{1,2}$ = 7.8 Hz, H-1), 5.48 (d, 1H, $J_{1',2'}$ = 3.6 Hz, H-1'), 7.08-7.29 (m, 30H, aromatic protons); ^{13}C NMR δ 16.90 (CH_3), 56.98 (OCH_3), 66.83 (C-6), 71.88, 73.27, 73.37, 73.52, 74.35, 74.84, 75.08, 76.18, 78.23, 80.16, 84.49, 98.01 (C-1'), 103.52 (C-1), 126.86-138.52 (aromatic carbons).

Anal. Calcd for $C_{48}H_{54}O_{10}$: C, 72.89; H, 6.88. Found: C, 72.42; H, 7.02.

Methyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzoyl-6-*O*-(4-methoxybenzyl)-α-D-galactopyranoside (9). To a solution of **1** (201 mg, 0.419 mmol), **4** (132 mg, 0.251 mmol) and molecular sieves 4Å (1 g) in CH_2Cl_2 (15 mL) were added NIS (122 mg, 0.544 mmol) and TfOH[11] (11 μL, 0.125 mmol). The mixture was then stirred for 3 h at 0 °C, filtered and the filtrate diluted with aq 5% $Na_2S_2O_3$ soln, $NaHCO_3$, water and then dried (Na_2SO_4). Column chromatographic purification (19:1 toluene-EtOAc) gave **9** as syrup (160 mg, 67%); $[\alpha]_D$ +23.7° (*c* 0.9, $CHCl_3$); ^{1}H NMR δ 1.83, 2.03 and 2.18 (3s, 9H, 3 OAc), 3.38 (s, 3H, OC*H*$_3$), 3.83 (s, 3H, $CH_2C_6H_4OCH_3$), 3.95-4.01 (m, 1H, H-5), 4.09-4.19 (m, 2H, H-5', H-6'), 4.52-4.64 (m, 4H, H-2, H-3, H-4, H-6), 4.96 (dd, 1H, $J_{1',2'}$ = 7.6 Hz, $J_{2',3'}$ = 9.2 Hz, H-2'), 5.45 (d, 1H, $J_{1',2'}$ = 8.4 Hz, H-1'), 5.48 (dd, 1H, $J_{3',4'}$ = 2.4 Hz, $J_{4',5'}$ = 1.6 Hz, H-4'), 5.51 (d, 1H, $J_{1,2}$ = 2.4 Hz, H-1), 5.80 (dd, 1H, $J_{2',3'}$ = 8.1 Hz, $J_{3',4'}$ = 3.3 Hz, H-3'), 7.20-7.77 (m, 20H, aromatic protons); ^{13}C NMR δ 20.17, 20.33 and 20.39 (3xCO*C*H$_3$), 51.32 (C-2'), 54.95 (O*C*H$_3$), 55.04 ($CH_2C_6H_4OCH_3$), 66.18, 67.15, 68.13, 68.98, 69.07, 70.33, 71.58, 72.87, 73.09, 76.31, 76.74, 77.16, 97.09 (C-1), 102.69 (C-1'), 113.51 (*C*H$_2$C$_6$H$_4$OCH$_3$), 128.07-134.09 (aromatic carbons), 164.88-166.27 (3x*C*OCH$_3$), 169.37 and 169.97 (2x*C*OPh).

Anal. Calcd for $C_{49}H_{51}O_8N$: C, 62.48; H, 5.45. Found: C, 62.16; H, 5.69.

Methyl 2-Acetamido-2-deoxy-β-D-galactopyranosyl-(1→2)-α-D-galactopyranoside (10). To a soln of **9** (100 mg, 0.106 mmol) in 95% aq ethanol (10 mL) was added hydrazine hydrate (1 mL). The mixture was heated at 85 °C for 2 h and then concentrated. The residue was treated with pyridine (5 mL) and Ac_2O (5 mL) at rt for 3 h and concentrated. The residue was purified by column chromatography using 3:1 toluene-EtOAc. This material was deacetylated[13] and purified by column chromatography (4:1 toluene-EtOAc) and then to the product in acetonitrile-water (9:1) was added ceric ammonium nitrate (50 mg) and the mixture was stirred for 2 h at rt. Usual workup and column chromatographic separation with 4:1 toluene-EtOAc gave **10** as syrup (34 mg, 85%); $[\alpha]_D$ +9.4° (*c* 0.6, H_2O); ^{1}H NMR (D_2O) δ 3.45 (s, 3H, OC*H*$_3$), 3.97-4.02 (m, 1H, H-5), 4.07-4.15 (m, 2H, H-5', H-6'), 4.51 (dd, 1H, $J_{1,2}$ = 3.6 Hz, $J_{2,3}$ = 8.3 Hz, H-2), 4.54-4.62 (m, 2H, H-3, H-4), 4.97 (dd, 1H, $J_{1',2'}$ = 6.9 Hz, $J_{2',3'}$ = 8.1 Hz, H-2'), 5.26 (d, 1H, $J_{1',2'}$ = 8.2 Hz, H-1'), 5.39 (dd, 1H, $J_{3',4'}$ = 2.6 Hz, $J_{4',5'}$ = 2.1 Hz, H-4'), 5.48 (d, 1H, $J_{1,2}$ = 2.4 Hz, H-1), 5.69 (dd, 1H, $J_{2',3'}$ = 7.8 Hz, $J_{3',4'}$ = 3.3 Hz, H-3'); ^{13}C NMR (D_2O) δ 23.16 (NCO*C*H$_3$), 51.49 (C-2'), 56.27 (O*C*H$_3$), 67.74, 67.95, 69.46, 70.29, 71.71, 72.61, 74.21, 76.32, 76.85, 98.27 (C-1), 102.19 (C-1'), 175.44 (N*C*OCH$_3$).

Anal. Calcd for $C_{15}H_{27}O_{10}$: C, 47.24; H, 7.13. Found: C, 47.07; H, 7.32.

Methyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-galactopyranosyl-(1→6)-[2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl-(1→2)]-3,4-di-*O*-benzyl-β-D-galactopyranoside (11). To a soln of **1** (109 mg, 0.23 mmol), **8** (143 mg, 0.19 mmol), molecular sieves 4Å (0.5 g) in CH_2Cl_2 (15 mL) were added NIS (66 mg, 0.3 mmol) and TfOH[11] (61 µL, 0.07 mmol) and the mixture was stirred for 4 h at 0 °C. The workup was the same as described for the preparation of **9**. Column chromatography using 9:1 toluene-EtOAc gave pure **11** as syrup (133 mg, 61%); $[\alpha]_D$ -47.8° (*c* 0.46, $CHCl_3$); ^{1}H NMR δ 1.13 (d, 1H, J = 6.1 Hz, CH_3), 1.77, 1.98 and 2.12 (3s, 9H, 3 $OCOCH_3$), 3.41 (s, 3H, OCH_3), 3.60-3.68 (m, 2H, H-3, H-5), 3.87-3.95 (m, 3H, H-2, H-2', H-4'), 4.01-4.14 (m, 3H, H-5'', H-6'', H-3'), 4.35 (d, 1H, $J_{1,2}$ = 8.1 Hz, H-1), 4.59 (t, 1H, J = 10.7 Hz, H-2''), 5.38 (d, 1H, $J_{1'',2''}$ = 10.1 Hz, H-1''), 5.43 (d, 1H, $J_{1',2'}$ = 4.2 Hz, H-1'), 5.49 (d, 1H, J = 3.6 Hz, H-4''), 5.83 (m, 1H, H-3''), 7.16-7.33 (m, 30H, aromatic protons), 7.69-7.83 (m, 4H, NPhth); ^{13}C NMR δ 15.72 (CH_3), 20.99, 21.07 and 21.12 (3 $COCH_3$), 51.63 (C-2''), 55.78 (OCH_3), 61.25, 61.51 (C-6', C-6''), 66.27, 67.36, 67.84, 68.16, 69.15, 70.29, 72.65, 73.47, 74.93, 76.98, 77.42, 77.84, 79.09, 82.11, 84.78, 84.96, 98.36 (C-1'), 102.94 (C-1'''), 103.25 (C-1''), 125.47-136.62 (aromatic carbons), 165.27-168.16 (5 $COCH_3$).

Anal. Calcd for $C_{68}H_{73}O_{19}N$: C, 67.59; H, 6.08. Found: C, 66.82; H, 6.73.

Methyl 2-Acetamido-2-deoxy-β-D-galactopyranosyl-(1→6)-[α-L-fucopyranosyl-(1→2)]-β-D-galactopyranoside (12). To a soln of **11** (120 mg, 0.993 mmol) in 95% aq ethanol (10 mL) was added hydrazine hydrate (1 mL). The mixture was heated at 85 °C for 2 h and then concentrated. The residue was treated with pyridine (5 mL) and acetic anhydride (5 mL) at rt for 3 h and concentrated. The residue was purified by column chromatography using 3:1 toluene-EtOAc. The material after deacetylation[13] was purified by column chromatography (4:1 toluene-EtOAc). A soln of this product in AcOH (10 mL) was hydrogenolyzed for 48 h in presence of 10% Pd-C (30 mg) at 24 °C. The reaction mixture was filtered through a celite bed, purified by column chromatography and concentrated to give **12** as syrup (39 mg, 74%); $[\alpha]_D$ -12.7°(*c* 0.8, H_2O); ^{1}H NMR (D_2O) δ 1.11 (d, 1H, J = 6.5 Hz, CH_3), 2.01 (s, 3H, $NCOCH_3$), 3.46 (s, 3H, OCH_3), 3.64-3.71 (m, 2H, H-3, H-5), 3.93-3.96 (m, 3H, H-2, H-2', H-4'), 4.02-4.11 (m, 3H, H-3', H-5'', H-6''), 4.42 (d, 1H, $J_{1,2}$ = 7.3 Hz, H-1), 4.51 (t, 1H, $J_{2',3'}$ = 9.6 Hz, H-2''), 5.47 (d, 1H, $J_{1'',2''}$ = 9.2 Hz, H-1''), 5.48 (d, 1H, J = 3.9 Hz, H-4''), 5.89 (m, 1H, H-3''), 7.12-7.29 (m, 30H, aromatic protons); ^{13}C NMR (D_2O) δ 16.23 (CH_3), 23.31 ($NCOCH_3$), 52.05 (C-2'), 56.23 (OCH_3), 61.64, 61.70 (2 C-6), 66.35, 67.51, 67.92, 68.34, 69.29, 70.51, 72.83, 73.64, 75.26, 77.31, 77.65, 77.97, 79.32, 82.63, 84.91, 85.34, 99.03 (C-1'), 102.56 (C-1''), 103.45 (C-1), 123.45-140.46 (aromatic carbons), 176.32 ($NCOCH_3$).

Anal. Calcd for $C_{21}H_{37}O_{14}N$: C, 47.81; H, 7.06. Found: C, 47.25; H, 7.81.

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