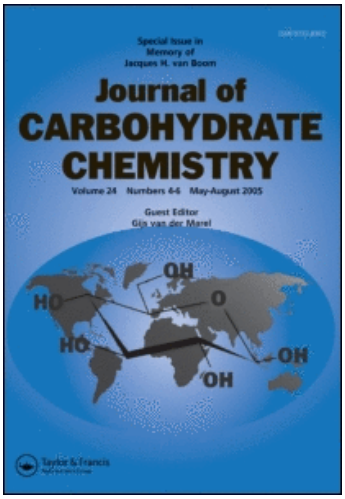

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SYNTHESIS OF AN ASPARAGINE-LINKED CORE PENTASACCHARIDE BY MEANS OF SIMULTANEOUS INVERSION REACTIONS

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ABSTRACT

A novel route for the synthesis of the asparagine-linked pentasaccharide **1**, the core unit of all asparagine-linked sugar chains, is described. To construct this pentasaccharide derivative, we first employed a regioselective coupling of a mannosyl donor to the C-3 and C-6 positions of a galactosyl chitobiose acceptor, and then by means of a conversion involving two simultaneous inversion reactions of the stereochemistry of the C-2 and C-4 hydroxyl groups of a galactose residue, a branched pentasaccharide containing the difficult to synthesize β-mannose unit was easily obtained.

INTRODUCTION

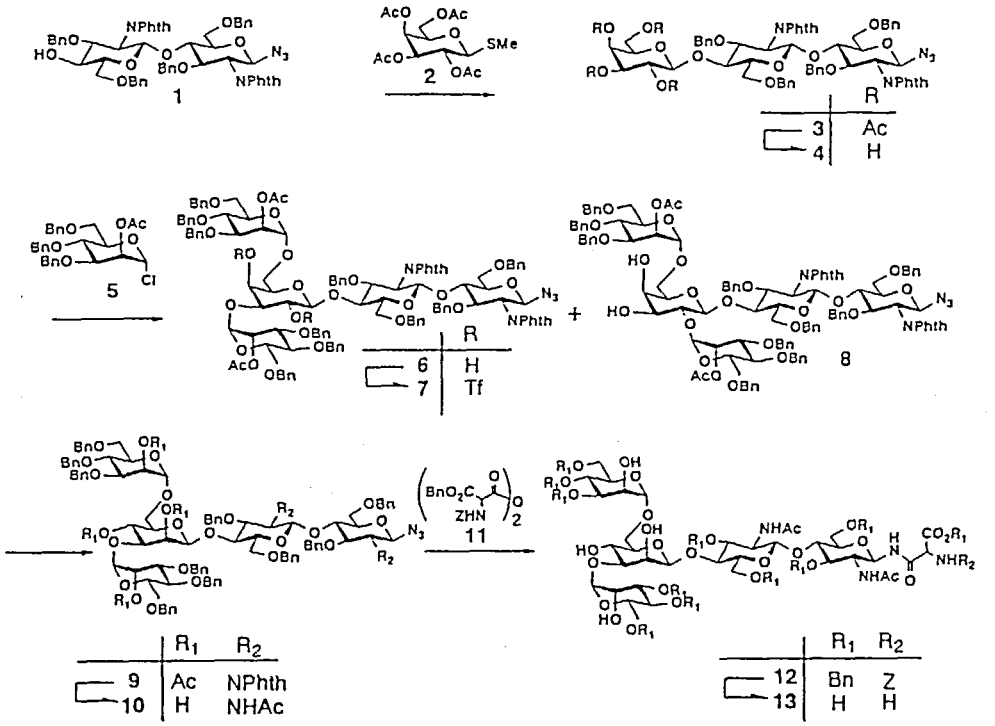
Glycoprotein synthesis is recognized to be one of the most challenging problems confronting present day synthetic organic chemists. Naturally occurring glycoproteins have complicated oligosaccharide structures which are linked to protein backbones via asparagine or serine/threonine residues.[1] In order to conduct synthetic studies of glycoproteins, efficient routes for the synthesis of these glycopeptides is necessary. Therefore, extensive efforts by many laboratories around the world have been devoted to the synthesis of

glycopeptides.[2] In our previous report, we described the synthesis of a core structure pentasaccharide common to all *N*-linked glycoprotein oligosaccharides containing the β-mannoside linkage.[3] In that study, the β-mannoside linkage was constructed by using a mannosyl bromide donor and silver silica-alumina[4] as the promoter. Since that reaction gave nearly equal amounts of the unwanted stereoisomer, we determined this method to be inappropriate for large scale preparation. Recently, selective inversion of configuration reactions have been applied to the synthesis of oligosaccharides allowing for the easy preparation of sequences containing β-mannoside linkages.[5,6] These methods avoid the non-selective glycosylation steps often associated with construction of β-mannoside bonds.

The novel aspect of the synthesis described in this report is that two simultaneous inversion reactions are performed on a branched oligosaccharide which has sugar residues at both the C-3 and C-6 positions of the β-D-galactopyranosyl derivative. The result represents an efficient synthetic approach to asparagine-linked pentasaccharides containing β-linked mannosyl residues.

RESULTS AND DISCUSSION

The synthetic route to the core pentasaccharide is shown in Scheme 1. Our strategy employs two key synthetic steps: 1) regioselective coupling of mannosyl donors to the C-3 and C-6 positions of a galactosyl chitobiose acceptor in which there are four unprotected hydroxyl groups (C-2, C-3, C-4, and C-6), and 2) inversion of the stereochemistry of the C-2 and C-4 hydroxyl groups of the galactose residue resulting in a branched pentasaccharide derivative possessing the desired β-manno configuration. Regioselective glycosylation can decrease the number of synthetic steps by eliminating the need for protection and deprotection steps. For construction of the branched pentasaccharide **6**, we prepared the galactosyl chitobiose acceptor **4** in which the hydroxyl groups at positions C-2, C-3, C-4, and C-6 of the galactosyl residue are unprotected. Generally, the primary hydroxyl group at C-6 and the secondary hydroxyl group at C-3 in galactose residues are more reactive than the secondary hydroxyl groups at C-2 and C-4. Taking this difference into account, mannosyl donors should react at the C-3 and C-6 positions regioselectively, after which the remaining hydroxyl groups at C-2 and C-4 are available for inversion of



Scheme 1

stereochemistry by nucleophilic substitution to provide the pentasaccharide **9** containing a β-mannoside bond.

First, we prepared trisaccharide **3** from known compounds. Coupling of the chitobiose acceptor **1**[5a] and the thioglycoside **2** using NIS / TfOH[7] as the promoter at -20 °C in CH_2Cl_2 for 2 h gave the trisaccharide **3** in quantitative yield. The β-configuration of the newly formed glycoside bond was confirmed by ^1H NMR spectroscopy. The observed coupling constant for $J_{1,2}$ was 8.0 Hz, which corresponds to the β-configuration. Deacetylation of **3** using NaOMe / MeOH in THF at 0 °C afforded the galactosyl chitobiose acceptor **4** (88%). Coupling of the glycosyl acceptor **4** and the mannosyl donor **5**[8] using silver triflate (AgOTf) as the promoter in CH_2Cl_2 at 4 °C, the mannosyl donor **5** was introduced to the C-3 and C-6 positions of the acceptor **4** regioselectively to give the pentasaccharide **6** in 63% yield; a small amount of the regioisomer **8** was also obtained (13% yield). The structure of **6** was confirmed by 2D NMR spectroscopy. The hmbc

spectrum of **6** showed cross peaks between the anomeric proton of the newly bound mannosyl residues and the C-3 and C-6 carbons of the galactosyl residue. The peaks corresponding to the H-2 and H-4 protons of the galactosyl residue shifted to lower fields following subjection of the compound to acetylation conditions, which also supports the assigned structure. After introduction of mannose residues at the C-3 and C-6 positions of the galactose residue in **4**, the remaining hydroxyl groups at C-2 and C-4 in the galactose residue of **6** were converted from the galacto configuration into the manno configuration by two simultaneous inversion reactions[6] of hydroxyl groups. The simultaneous inversion reaction of two hydroxyl groups was performed as follows: the pentasaccharide **6** was treated with triflic anhydride (Tf_2O) in dry pyridine at room temperature followed by nucleophilic substitution using CsOAc and 18-crown-6 in toluene under sonication at 40 °C.[5a] In spite of the fact that both hydroxyl groups were located in the interior of the oligosaccharide structure, inversion at both centers proceeded smoothly to give the pentasaccharide derivative **9** as the sole product (68% yield from **6**). The ^1H NMR spectrum of **9** and the acetylated compound **6** are shown in Figure 1. The coupling constants ($J_{1,2} < 0.5$ Hz, $J_{2,3} = 3.2$ Hz, and $J_{3,4} = 10.0$ Hz) of the β-mannose residue in **9**, support the mannose configuration.

In order to confirm the structure of the pentasaccharide derivative, pentasaccharide **9** was converted to the known compound **13**.[9] Dephthaloylation of **9** was cleanly achieved by use of $H_2NCH_2CH_2NH_2$/*n*-BuOH at 90 °C[10] and the product was acetylated to give **10** (88%). Introduction of asparagine residue were carried out by in situ trapping of the amine with acid anhydride **11**.[3] Benzyl carbamate (Z)[11] and benzyl[12] protecting groups were chosen for the amino and carboxyl groups of the asparagine residue, since they are both easily removed under mild conditions. Coupling of **10** and the aspartic acid anhydride **11** in the presence of Lindlar's catalyst under an atmosphere of hydrogen gave the glycopeptide **12**. Removal of the protecting groups in **12** was achieved by hydrogenolysis using Pd catalyst in 80% aq AcOH to give the *N*-linked core pentasacchride **13** in 53 % yield (2 steps). The NMR data of **13** was in good agreement with that of the natural product.[9]

CONCLUSION

An asparagine-linked pentasaccharide was synthesized by regioselective coupling to

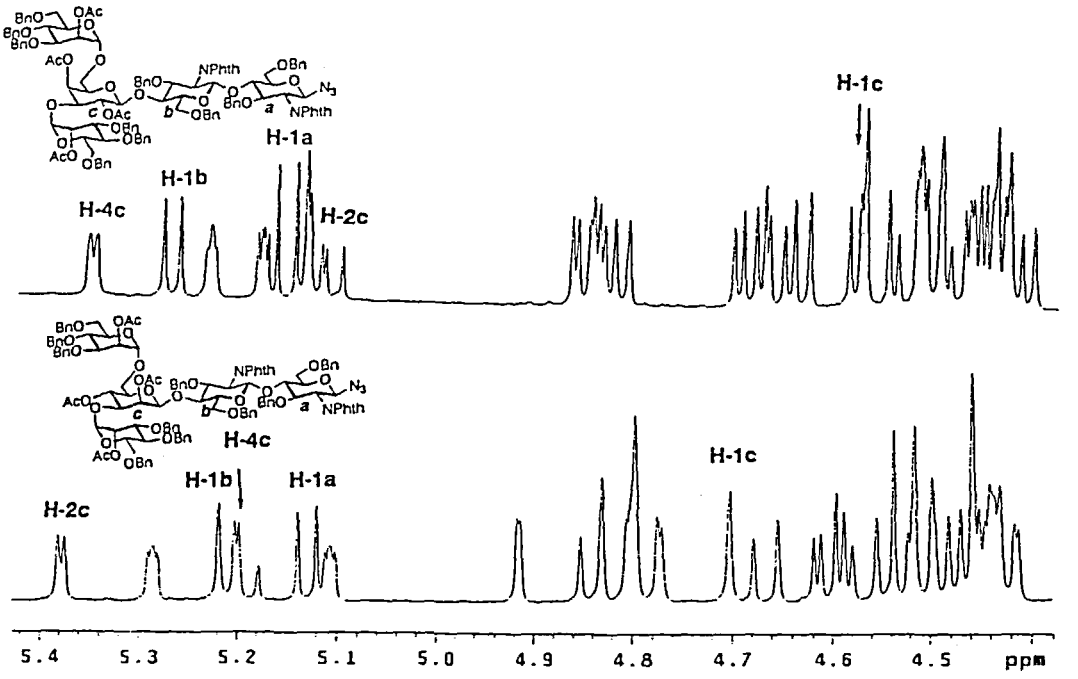


Figure 1

the C-3 and C-6 hydroxyl groups of the galactose residue in the trisaccharide acceptor followed by two simultaneous inversion reactions of the sterically congested C-2 and C-4 hydroxyl groups of the galactose residue in the resulting pentasaccharide derivative. This strategy eliminates many previously necessary synthetic steps and thus allows for the easy preparation of the β-mannoside. As a result, the core pentasaccharide was synthesized quickly and efficiently. This successful inversion of sterically hindered hydroxyl groups in the midst of a sizable oligosaccharide should greatly contribute to the synthetic options available to carbohydrate chemists.

EXPERIMENTAL

General methods. Optical rotations were measured at 25 °C with a HORIBA polarimeter SEPA-300. ^{1}H and ^{13}C NMR spectra were measured on a UNITY INOVA 500

spectrometer in $CDCl_3$ and were referenced to Me_4Si. Signal assignments such as 1c stand for a proton or carbon at C-1 of sugar residue c. Silica gel column chromatography was performed using BW300 (Fuji Silisia Co., Ltd., Aichi, Japan). Analytical TLC was performed on aluminum plates coated with silica gel 60 F_{254} (Merck). Preparative TLC was performed on glass plate coated with silica gel 60 F_{254} (Merck). Molecular sieves (type 4A) was purchased from Nacalai Tesque, INC., and activated at 180 °C under vacuum immediately prior to use. All glycosylation reactions were performed in anhydrous solvents under an atmosphere of dry Ar.

_O_-(2,3,4,6-Tetra-_O_-acetyl-β-D-galactopyranosyl)-(1→4)-_O_-(3,6-di-_O_-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-3,6-di-_O_-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl azide (3). A mixture of NIS (1.05 g, 4.67 mmol), TfOH (130 μL, 1.46 mmol) and molecular sieves (3.0 g, type 4A) in CH_2Cl_2 (5 mL) was stirred at 0 °C for 30 min, then cooled at -78 °C. To this mixture, a solution of glycosyl donor **2** (0.76 g, 2.01 mmol) and glycosyl acceptor **1** (1.53 g, 1.55 mmol) in CH_2Cl_2 (10 mL) was added dropwise over 10 min. The reaction mixture was stirred at -20 °C for 2 h. The reaction was quenched with sat. aq $NaHCO_3$. The reaction mixture was diluted with EtOAc and filtered through celite. The filtrate was washed with aq $Na_2S_2O_5$, brine. The solution was dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (toluene:EtOAc, 4:1) to afford the compound **3** (1.77 g, 86 %): Rf 0.26 (toluene:EtOAc, 4:1); $[\alpha]_D$ + 8° (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 5.29 (1H, d, *J* 8.6 Hz, H-1b), 5.26 (1H, dd, *J* 0.7 Hz, *J* 3.4 Hz, H-4c), 5.15 (1H, d, *J* 9.5 Hz, H-1a), 5.14 (1H, dd, *J* 10.5 Hz, H-2c), 4.62 (1H, d, *J* 8.1 Hz, H-1c), 2.04, 1.99, 1.962, 1.958 (3H×4, s, Ac); ^{13}C NMR (125 MHz, $CDCl_3$) δ 100.45 (C-1 c), 97.09 (C-1b), 85.62 (C-1a).

Anal. Calcd for $C_{70}H_{69}O_{21}N_5$: C, 63.87; H, 5.28; N 5.32. Found: C, 64.13; H, 5.31; N, 5.39.

_O_-(β-D-Galactopyranosyl)-(1→4)-_O_-(3,6-di-_O_-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-3,6-di-_O_-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl azide (4). To a stirred solution of **3** (134 mg, 0.102 mmol) in THF:MeOH (2:3, 5 mL) was added 1M NaOMe/MeOH (100 μL) at 0 °C. The mixture was stirred for 1 h, neutralized with Amberlyst 15 (H^+) resin, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography ($CHCl_3$:MeOH,

50:1~20;1) to give 4 (103 mg, 88%): Rf 0.33 ($CHCl_3$:MeOH, 15;1); $[\alpha]_D$ + 24° (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 5.32 (1H, d, *J* 7.9 Hz, H-1b), 5.16 (1H, d, *J* 9.5 Hz, H-1a); ^{13}C NMR (125 MHz, $CDCl_3$) δ 102.95 (C-1c), 97.08 (C-1b), 85.63 (C-1a), 73.76 (C-3c), 62.67 (C-6c).

Anal. Calcd for $C_{62}H_{61}O_{17}N_5$: C, 64.86; H, 5.35; N 6.10. Found: C, 64.33; H, 5.36; N, 6.11.

***O*-(2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-*O*-[(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→3)]-*O*-(β-D-galactopyranosyl)-(1→4)-*O*-(3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl azide (6).** To a stirred mixture of glycosyl acceptor 4 (232 mg, 0.202 mmol), AgOTf (140 mg, 0.545 mmol), and molecular sieves (1 g, type 4A) in CH_2Cl_2 (10 mL) was added a solution of glycosyl donor 5 (244 mg, 0.479 mmol) in CH_2Cl_2 (10 mL) at -40 °C. The mixture was gradually warmed up to ambient temperature and stirred for 12 h. Insoluble materials were removed by passage through celite, and the filtrate was then diluted with EtOAc, washed with brine, aq $NaHCO_3$, brine. The solution was dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (toluene:EtOAc, 7:1~3:1) to afford the compound **6** (266 mg, 63 %) and the compound **8** (44 mg, 10 %): compound **6**; Rf 0.56 (toluene:EtOAc, 2;1); $[\alpha]_D$ + 40° (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 5.42 (1H, m, H-2), 5.28 (1H, m, H-2), 5.27 (1H, d, *J* 8.2 Hz, H-1b), 5.15 (1H, d, *J* 9.3 Hz, H-1a), 5.06 (1H, bs, H-1), 2.15, 2.09 (3H×4, s, Ac); ^{13}C NMR (125 MHz, $CDCl_3$) δ 103.55 (C-1c), 98.26 (C-1), 96.90 (C-1b), 95.83 (C-1), 85.53 (C-1a), 79.44 (C-4c), 65.15 (C-6c).

Anal. Calcd for $C_{120}H_{121}O_{29}N_5$: C, 68.72; H, 5.81; N 3.34. Found: C, 69.12; H, 5.80; N, 3.37.

***O*-(2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-*O*-[(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→3)]-*O*-(2,4-di-*O*-acetyl-β-D-mannopyranosyl)-(1→4)-*O*-(3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl azide (9).** A mixture of compound **6** (46 mg, 0.022 mmol) and pyridine (60 μL) in dry CH_2Cl_2 (1 mL) was added Tf_2O (60 μL) at 0 °C. The mixture was stirred at room temperature for 2 h. The reaction mixture was diluted with

EtOAc and washed with aq $CuSO_4$, H_2O, aq $NaHCO_3$, and brine successively. The solution was dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (toluene:EtOAc, 4:1) to afford the compound **7** (38 mg, 74 %). A solution of compound **7** (58 mg, 0.025 mmol), CsOAc (93 mg, 0.485 mmol), and 18-crown-6 (128 mg, 0.484 mmol) in toluene (2 mL) was reacted under ultrasonication at 40 °C for 12 h. The reaction mixture was diluted with EtOAc, washed with brine, aq $NaHCO_3$, and brine. The solution was dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (toluene:EtOAc, 10:1~4:1) to afford the compound **9** (50 mg, 93 %): Rf 0.4 (toluene:EtOAc, 3:1); $[\alpha]_D$ + 20 ° (*c* 0.95, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 5.38 (1H, m, H-2c), 5.28 (1H, m, H-2), 5.21 (1H, d, *J* 7.8 Hz, H-1b), 5.219 (1H, t, *J* 9.9 Hz, H-4c), 5.13 (1H, d, *J* 9.4 Hz, H-1a), 5.10 (1H, m, H-2), 4.91 (1H, d, *J* 1.7 Hz, H-1), 4.79 (1H, bs, H-1), 4.70 (1H, bs, H-1c), 2.13, 2.10, 2.08, and 1.89 (3H×4, s, Ac); ^{13}C NMR (125 MHz, $CDCl_3$) δ 100.05 (C-1), 98.84 (C-1), 97.92 (C-1c), 96.94 (C-1b), 85.49 (C-1a).

Anal. Calcd for $C_{124}H_{125}O_{31}N_5$: C, 68.28; H, 5.78; N 3.21. Found: C, 67.82; H, 5.99; N, 3.10.

***O*-(3,4,6-Tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-*O*-[(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→3)]-*O*-(β-D-mannopyranosyl)-(1→4)-*O*-(2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)-(1→4)-2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranosyl azide (10).** A solution of compound **9** (17 mg, 0.0078 mmol) in 1-butanol containing 0.5 mL ethylenediamine was stirred at 90 °C for 15 h. Volatiles were removed by evaporation *in vacuo* and the residue was dissolved in pyridine (1 mL). The solution was treated at 0 °C with Ac_2O (0.5 mL) for 24 h and concentrated *in vacuo*. The residue was disolved in THF (1 mL) and 1M NaOMe/MeOH (500 μL) was added at 0 °C. The mixture was stirred for 12 h, neutralized with Amberlyst 15 (H^+) resin, and concentrated *in vacuo*. The residue was purified by preparative TLC ($CHCl_3$:MeOH, 20;1) to afford the compound **10** (9 mg, 63 %): Rf 0.57 ($CHCl_3$:MeOH, 15:1); $[\alpha]_D$ - 8 ° (*c* 0.5, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 6.17 (1H, bd, NH), 5.22 (1H, bd, NH), 5.07 (1H, d, *J* 1.6 Hz, H-1), 4.84 (1H, d, *J* 1.6 Hz, H-1) 4.74 (1H, d, *J* 8.5 Hz, H-1a), 4.40 (1H, d, *J* 8.1 Hz, H-1b), 1.88 and 1.72 (3H×2, s, Ac); ^{13}C NMR (125 MHz, $CDCl_3$) δ 100.67 (C-1), 99.87 (C-1 and C-1b), 99.38 (C-1), 88.29 (C-1a).

***N*-{*O*-(α-D-Mannopyranosyl)-(1→6)-*O*-[(α-D-mannopyranosyl)-(1→3)]-*O*-(β-D-mannopyranosyl)-(1→4)-*O*-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl}-L-asparagine (13).** To a stirred solution of Z-Asp-OBn (14 mg, 0.039 mmol) in CH_2Cl_2 (1 mL) was added DCC (4 mg, 0.019 mmol) at 0 °C. After being stirred for 30 min, the mixture was filtered through a membrane filter and the filtrate was concentrated *in vacuo*. Lindlar's catalyst (14 mg) was added to the residue and a solution of compound **10** (10 mg, 0.005 mmol) in THF/MeOH (1/1, 2 mL) was added. The mixture was then stirred under an atmosphere of hydrogen at room temperature. After 12 h, insoluble materials were filtered off, and the filtrate was concentrated *in vacuo*. The residue was disolved in 80 % acetic acid (2 mL) and hydrogenated over Pd black (1 mg) under atmospheric pressure. After 16 h, the mixture was filtered through a membrane filter, and the filtrate was concentrated *in vacuo*. The residue was purified by HPLC employing a size exclusion column (20 mm $\phi \times$ 100 mm, Asahipack GS-220, H_2O) to give compound **13** (3 mg, 54 %): ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.09 (1H, d, *J* 1.5 Hz, H-1), 5.06 (1H, d, *J* 8.1 Hz, H-1a), 4.90 (1H, d, *J* 1.7 Hz, H-1), 4.77 (1H, bs, H-1), 4.60 (1H, d, *J* 8.1 Hz, H-1b), 2.91 and 2.82 (1H, m, Asn of β-CH_2), 2.06 and 2.00 (3H×2, s, Ac).

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