Pseudosugars, 39[◇]

Synthesis of Methyl 5a′-Carba-β-lactoside and *N*-Acetyl-5a′-carba-β-lactosaminides, and Related 5a′-Carbadisaccharides

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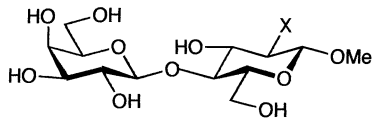
Construction of the ether-linked methyl 5a′-carba-β-lactoside (**3**) and *N*-acetyl-5a′-carba-β-lactosaminide (**4**) were carried out starting from the coupling products **15** and **16**, readily obtained by coupling between 1,2-anhydro-4,6-*O*-benzylidene-5a-carba-D-mannopyranose (**7**) and the oxide anions generated from methyl 2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (**8**) and methyl 2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside (**10**), respectively. Their 5a-carba-α-D-mannopyranose moieties were transformed into those of 5a-carba-β-D-galactopyranose by a sequence of reaction: Oxidation of the 2′-OH group, epimerization of the C-1′ with DBU, selective reduction of the carbonyl group, and epimerization of the C-4′ via oxidation and then reduction of 4′-OH or S_N2 reaction of the 4′-mesylate with an acetate anion. Reaction of 1,2-anhydro-6-*O*-benzyl-3,4-*O*-isopropylidene-5a-carba-α-D-galactopyranose (**6**), initially expected as the potential donor, with these oxide anions did not give any ether-linked products, rather resulting in elimination reaction of **7**. However, coupling of the epoxide **6** with methyl 2-acetamido-4-amino-2,4-dideoxy-β-D-glucopyranosides (**19**) easily gave rise to imino-linked 5a′-carbadisaccharide derivative **38**, which, after deprotection, gave the imino-linked congener **5**. On the other hand, two biologically interesting carbadisaccharides including methyl *N*,*N*′-diacetyl-5a′-carbachitobioside (**45**) were obtained from the versatile intermediate **24**.

In a family of pseudo-disaccharides, carbadisaccharides[2] bonded by an imino linkage have been shown to possess interesting biological activities: e.g. inhibitory potency against glycosidases as seen in α-glucosidase inhibitor α-methyl acarviosin,[3] trehalase inhibitor validoxylamine A,[4] 5a,5a′-dicarba-α,α-trehalose,[5] and so on. Whereas, ether-linked carbaoligosaccharides[6][7][8][9] have been shown to act rather as substrate analogs for some glycosyltransferases involved in oligosaccharide-chain biosynthesis.

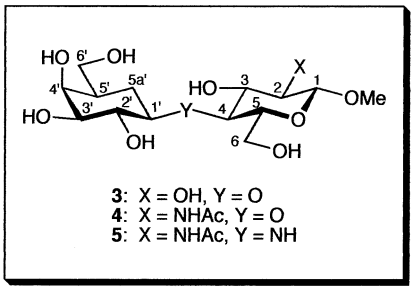
Synthesis[10] of biologically interesting ether-linked 5a′-carbadisaccharide analogs **3** of methyl β-lactoside **1**, together with the ether- and imino-linked analogs **4** and **5** of methyl *N*-acetyl-β-lactosaminide **2**, was reported herewith. These compounds have initially been designed and synthesized, being expected to act as disaccharide mimics useful as potential enzyme-inhibitors against β-galactosidases and/or galactosyl transferases involved in the biosynthesis of complex oligosaccharide-chains of glycolipids.

Construction of ether-linked carbadisaccharides **3** and **4** was carried out starting from the coupling products of carba-sugar donor 1,2-anhydro-4,6-*O*-benzylidene-5a-carba-β-D-mannopyranose[8] (**7**) and the respective *O*-benzylated sugar derivatives **8** and **10**, followed by consecutive epimerizations[9] at C-1 and 2 (α-*manno* → β-*gluco* configuration), and at C-4 (β-*gluco* → β-*galacto* configuration). On the other hand, synthesis of the imino-linked carbadisaccharide **5** has been conducted by direct coupling of 1,2-anhydro-6-*O*-benzyl-3,4-*O*-isopropylidene-5a-carba-α-D-galactopyranose[11] (**6**) and newly prepared methyl 2-acetamido-4-amino-2,4-dideoxy-β-D-glucopyranoside (**14**), followed by deprotection.

Scheme 1



1: X = OH
2: X = NHAc

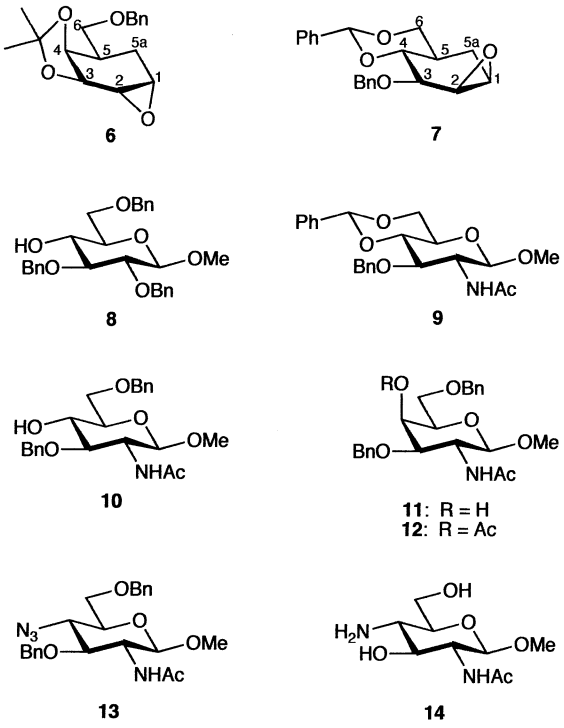


3: X = OH, Y = O
4: X = NHAc, Y = O
5: X = NHAc, Y = NH

[◇] Part 38: Ref.[1].

  1434–193X/98/0606–1099 $ 17.50+.50/0

Scheme 2



In addition, biologically interesting carbaoligosaccharides such as ether-linked methyl *N*,*N*′-diacetyl-5a′-carba-β-chitobioside **45** have been obtained from the present synthetic intermediate **28**.

Results and Discussion

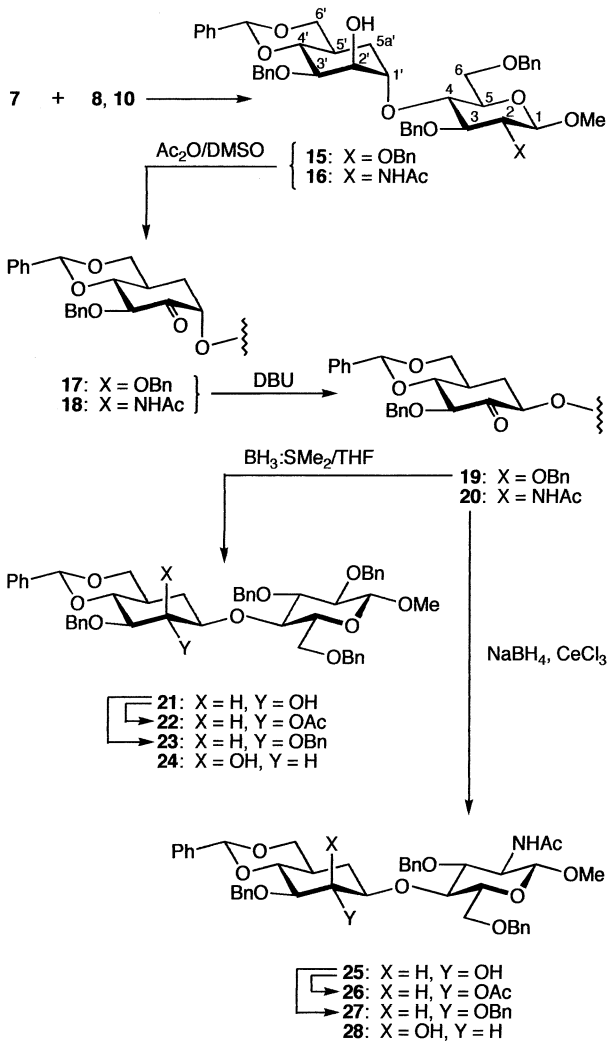
Synthesis of Ether-Linked Methyl 5a′-Carbalactoside (**3**) *and N-Acetyl-5a′-carbalactosaminide* (**4**): The 4-OH unprotected derivatives methyl 2,3,6-tri-*O*-benzyl-β-D-glucopyranoside[12] **8** and methyl 2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside **10** obtained by selective reduction of the 4,6-*O*-benzylidene derivative[13] **9** with sodium cyanoborohydride were employed as the acceptors for coupling reaction with the carba sugar epoxide as donor. Initially, direct incorporation of 5a-carba-β-galactopyranose residue into the acceptors was attempted by subjecting the appropriate 5a-carba-β-galactopyranosyl donor **6** to coupling reaction with the oxide anions generated from **8** and **10**. However, **6** has been shown to be a poor substrate for a nucleophilic attack of such bulky oxide anions and to be rather decomposed itself by elimination reaction between C-1 and C-5a, giving a complex mixture of side products containing the unsaturated cyclohexanol derivatives. Therefore, the 5a-carba-α-D-mannopyranosyl derivatives obtained by using the donor epoxide **7** were transformed into the corresponding β-D-galactopyranosyl derivatives by the following sequence: Oxidation of the 2-OH, base catalyzed epimeritation at C-1, selective reduction of the ketone, and finally epimerization at C-4. Very recently, attempts have been made to apply newly elaborated 1,2-anhydro-5a-carba-β-talopyranose derivatives as potential donors for incorpotation of 5a-carba-α-talopyranose residue as precursors of 5a-carba-β-galactopyranose and/or α-fucopyranose into oligosaccharide chains.

Compound **8** was initially treated with excess of sodium hydride in anhydrous DMF in the presence of 15-crown-5 ether to generate the oxide anion, which was then allowed to react in situ with the epoxide **7** under argon for 4 h at 70°C, giving selectively a 70% yield of the coupling product **15**. The proposed 1′,2′-*trans*-diaxial structure was supported by the ^{1}H-NMR spectrum which revealed a doublet of doublets (δ = 3.72, J = 2.6, 9.9 Hz) and a doublet of doublets of doublets (δ = 1.31, J = 1.4, 13.0, 13.0 Hz), being attributable to axial 3′-H and 5a′-H, respectively. Oxidation of the 2′-OH of **15** with acetic anhydride in DMSO gave the ketone **17** (95%), which was treated with DBU (2 molar equiv.) in toluene at 60°C, resulting in epimerization at C-1′ giving the β-isomer **19** (58%). Use of conventional strong base potassium tert-butoxide[9] has been shown to lead to a 1:1 equilibrium mixture of **17** and **19**, accompanying with a partial cleavage of the ether-bridge. Inversion of the C-1′ configuration was supported by their ^{1}H-NMR spectra which contained signals [δ = 1.03, $J_{1',5a'(ax)}$ = 2.6, $J_{5',5a'(ax)} = J_{5a'gem}$ = 14.3 Hz] and [δ = 0.95, $J_{1',5a'(ax)} = J_{5',5a'(ax)} = J_{5a'gem}$ = 12.6 Hz] due to the 5a′(ax)-H, respectively. Reduction of the ketone **19** under Luche conditions[14] with sodium borohydride in the presence of cerium chloride produced about 1:1 mixture of the 5a′-carbadisaccharides **21** (50%) and **24** (47%), having β-*gluco* and β-*manno* configurations. On the other hand, use of borane-THF complex improved selectivity, affording **21** in 78% yield. Compound **21** was further characterized by converting into the acetate **22** and the pentabenzyl ether **23** in the usual manner. Alternatively, attempted inversion of C-2 configuration was carried out through direct substitution of the mesylate **42** derived from **24** by treatment with sodium acetate in DMF, giving **22** in a poor yield (25%).

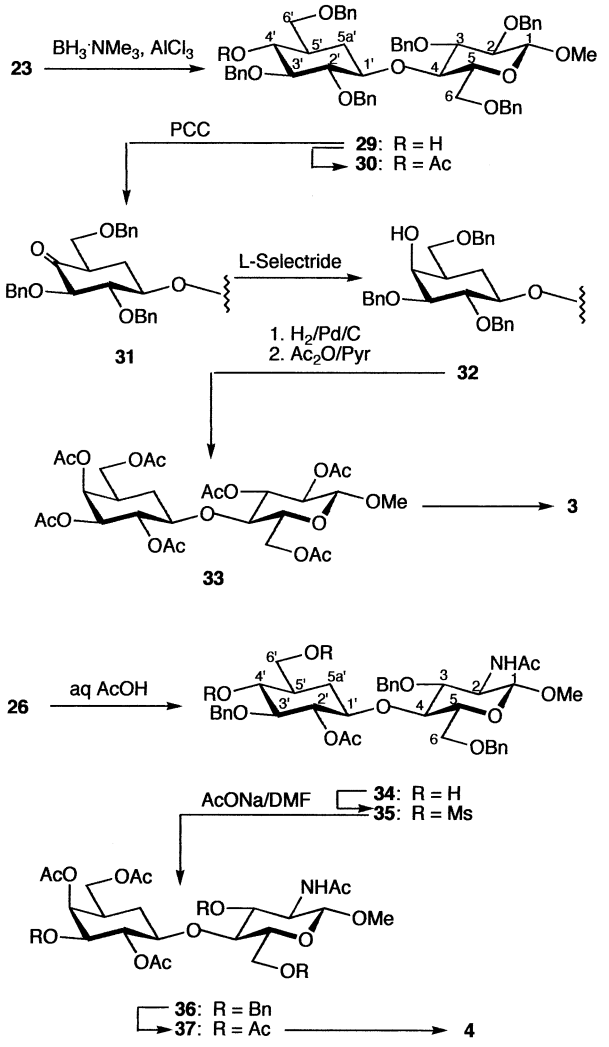
Similarly, coupling of **7** with the oxide anion derived from **10** was carried out in DMF for 4 h at 70°C to give 68% of the coupling product **16**. The structure was confirmed by the ^{1}H-NMR spectrum which revealed a doublet of doublets of doublets [δ = 1.34, $J_{1',5a'(ax)}$ = 2.2, $J_{5',5a'(ax)} = J_{5a'gem}$ = 13.6 Hz] ascribable to 5a′(ax)-H. Oxidation of **16** with acetic anhydride in DMSO gave the ketone **18** (90%), which was subsequently treated with DBU (2 molar equiv.) in a mixture of ethanol and toluene at 60°C to give the desired epimeric β-ketone **20** (81%). The ^{1}H-NMR ($CDCl_3$) spectra of **18** and **20** contained doublets of doublets (δ = 4.30, J = 2.6, 2.6 Hz) and (δ = 4.26, J = 6.4, 12.5 Hz) due to the 1′-H, respectively, demonstrating the configurational inversion at C-1′. Long range coupling ($J \approx 0.7$ Hz) between 1′-H and 3′-H of **20** was observed. Reduction of **20** under Luche conditions[14] produced an about 1:1 mixture of β-*gluco* **25** and β-*manno*-type disaccharides **28**. Compound **25** was characterized by converting into the acetate **26** and the tetrabenzyl ether **27**.

Inversion of the configuration at C-4′ (β-*gluco* → β-*galacto*) of each **23** and **26** was conducted by different manners. Thus, compound **23** was first reduced with borane trimethylamine complex and aluminium trichloride[15] in

Scheme 3



Scheme 4



THF to give selectively the 4′-OH unprotected derivative **29** (92%) as the major product. Oxidation of **29** with PCC gave the ketone **31**, which was selectively reduced with L-selectride in THF to give the axial alcohol **32** in 54% overall yield. Hydrogenolysis of **32** in the presence of 10% Pd/C followed by acetylation afforded the per-*O*-acetyl derivative **33** (76%) of the carbadisaccharide linked by an ether bridge. Zemplén de-*O*-acetylation[16] afforded methyl 5a′-carba-β-lactoside **3**.

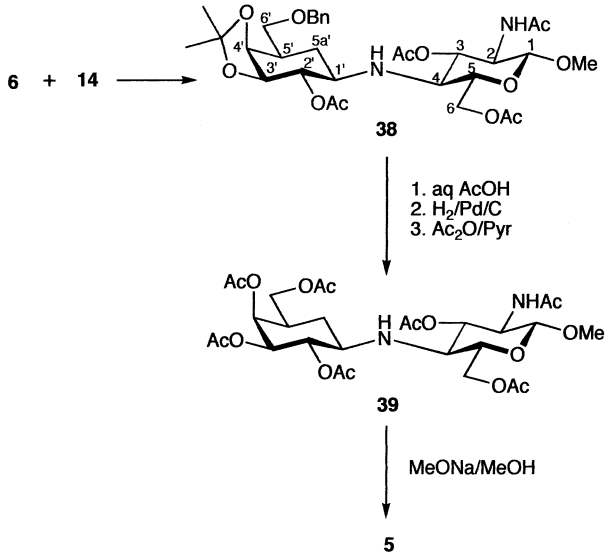
On the other hand, in the case of **26**, inversion of the configuration at C-4′ was carried out differently through S_N2 reaction of the 4′,6′-di-*O*-mesyl derivative **35** with sodium acetate. Compound **26** was de-*O*-benzylidenated with aqueous acetic acid and the resulting diol **34** was conventionally mesylated to **35** (65%). Treatment of **35** with excess sodium acetate in DMF for 3 days at 120°C, followed by acetylation, produced cleanly the 4′,6′-diacetate **36** (82%), having β-*galacto* configuration, through direct S_N2 reaction or the neighboring participation of the 6′-acetoxyl group initially formed. The structure was confirmed by transforming it into the hepta-*N*,*O*-acetyl derivative **37**, of which ^{1}H-NMR spectrum ($CDCl_3$) revealed a doublet of doublets (δ = 4.79, $J \approx 3$ and 10.5 Hz), a doublet of doublets (δ = 5.22, J = 10.5 Hz), and a narrow triplet (δ = 5.43, J ≈ 3 Hz), being attributable to 3′-H, 2′-H, and 4′-H, respectively. De-*O*-acetylation[16] gave the ether-linked methyl *N*-acetyl-5a′-carba-β-lactosaminide **4** (77%). Any side products conceivably derived by elimination reaction were not observed in the nucleophilic substitution at C-4′ of **35**. Therefore, the latter procedure seemed to be more convenient and effective, comparing to the former oxidation and reduction method, for epimerization at C-4′, transforming the 5a-carba-β-glucopyranose residue into the β-galactopyranose. Although, the epoxide **6** has been shown, disappointingly, not to be applicable as a donor substrate for incorporation of the ether-linked 5a-carba-β-galactopyranose residue into oligosaccharide chains, the present procedure has constituted a practical route using the versatile epoxide **7**.

Synthesis of Imino-Linked Methyl N-Acetyl-5a′-carbalactosaminide (**5**): Oxidation of **10** with acetic anhydride in DMSO gave the ketone, which was without purification reduced with L-selectride in THF to give the corresponding galactopyranoside **11** (49%), together with **10** (27%). The

structure of **11** was further confirmed by converting it into the acetate **12**. The mesylate derived from **11** was subjected to the S_N2 reaction with an azide anion in aqueous DMF to give the azide **13** (79%) with *gluco* configuration. Hydrogenolysis of **13** in the presence of 10% Pd/C gave methyl 2-acetamido-4-amino-2,4-dideoxy-β-D-glucopyranoside (**14**), which was used without purification for the coupling reaction with the epoxide **6**.

Coupling of the epoxide[11] **6** and **14** in 2-propanol in a sealed tube for 15 days at 120°C gave, after acetylation with acetic anhydride in pyridine, a 25% yield of a single coupling product **38**, which resulted from a preferential diequatorially-cleavage of the epoxide. The proposed structure was confirmed by the ^{1}H-NMR spectrum ($CDCl_3$) which revealed a doublet of doublets of doublets (δ = 2.27, *J* = 10.8, 11.7, 11.7 Hz) due to 1′-H. Interestingly, formation of the diaxially epoxide opening product was not observed in this reaction. The 3,4-dioxolane ring of **6** seemed to hamper an attack of the bulky amine at C-2. Removal of the ketal group with aqueous acetic acid, followed by hydrogenolysis in the presence of 10% Pd/C and conventional acetylation, afforded the per-*O*-acetyl 5a′-carbadisaccharide **39** (43%). De-*O*-acetylation[16] of **39** and purification by a column of Dowex 50W-X2 (H^+) resin gave imino-linked methyl *N*-acetyl-5a′-carba-β-lactosaminide **5** (90%).

Scheme 5

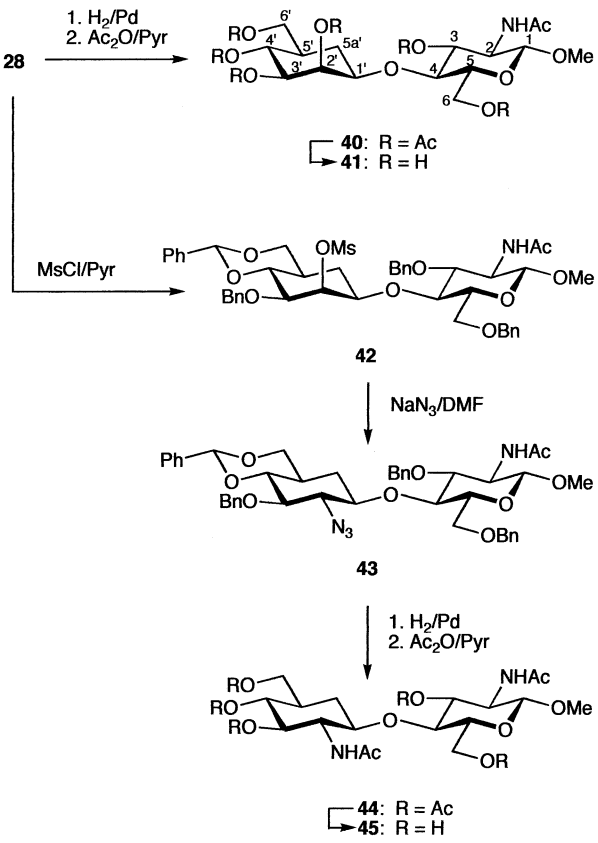


Synthesis of Ether-Linked Methyl N,N′-Diacetyl-5a′-carbachitobioside (**45**): In addition, in order to demonstrate a versatility of the intermediate **28**, chemical transformation into two biologically interesting 5a′-carbadisaccharides were carried out to give 5a-carba-β-Man*p*-(1→4)-β-Glc*p*NAc-OMe **41** and 5a-carba-β-Glc*p*NAc-(1→4)-β-Glc*p*NAc-OMe (methyl *N,N′*-diacetyl-5a′-carba-β-chitobioside) **45**, which are core structure-mimics of a common oligosaccharide chain of *N*-asparagine type glycoproteins.

Thus, hydrogenolysis of **28** in the presence of Pd/C produced after acetylation per-*N,O*-acetylated compound **40** (83%), which was de-*O*-acetylated to give **41**.

Conventional mesylation of **28** gave the mesylate **42**, which was treated with excess of sodium azide in DMF to give the azide **43** (57% over-all yield). Conventional hydrogenolysis of the azido, benzyl, and benzylidene functions in methanol in the presence of Pd/C catalyst and acetic anhydride, and subsequent acetylation gave the per-*N,O*-acetyl derivative **44** (54% over-all yield), which gave **45** in ≈ 80% yield.

Scheme 6



In summary, the present studies have constituted preparative route to these kinds of carba-sugar analogs of lactose and *N*-acetyl lactosamine, and related biologically interesting 5a-carbaoligosaccharides. Very recently, ether-linked *n*-octyl *N*-acetyl-5a′-carba-β-lactosaminide and 2-acetamido-3-*O*-(5a-carba-β-D-galactopyranosyl)-2-deoxy-β-D-glucopyranoside have been synthesized in a similar manner and subjected to biological test as substrate analogs toward human milk α-(1→3/4)-fucosyltransferase.[17]

The authors thank *K. Yaginuma* and *K. Hokazono* for performing elementary analyses and *Yamakawa Chemical Industry Co. Ltd.* (Tokyo) for providing us with optically resolving reagent. This work has partly been supported by a Grant-in-Aid for Science Research (B) from the *Ministry of Education, Science and Culture* (Japan).

Experimental Section

Melting points: Mel-Temp capillary melting-point apparatus, uncorrected. − Specific rotations: Jasco DIP-370 polarimeter, 1-dm cells. − IR: Jasco IR-810. − ^{1}H NMR: Jeol JNM GSX-270 f.t. (270 MHz) and Jeol JNM Lambda-300 (300 MHz); solvent $CDCl_3$ in-

ternal standard tetramethylsilane (TMS), D_2O internal acetone. – TLC: Silica Gel 60 GF (E. Merck, Darmstadt); detection by charring with concd. H_2SO_4. – Column chromatography: Wakogel C-300 (silica gel, 300 Mesh, Wako Chemical, Osaka). – Organic solutions, after drying with anhydrous Na_2SO_4, were concentrated <50°C at diminished pressure.

Methyl 2,3,6-Tri-O-benzyl-4-O-(3-O-benzyl-4,6-O-benzylidene-5a-carba-α-D-mannopyranosyl)-β-D-glucopyranoside (**15**): To a solution of methyl 2,3,6-tri-*O*-benzyl-β-D-glucopyranoside[12] (**8**, 515 mg, 1.11 mmol) in anhydrous DMF (16 ml) was added sodium hydride (438 mg, 11.0 mmol) and 15-crown-5 ether (2.2 ml, 11 mmol) under argon, and the mixture was stirred for 1 h at room temp. A solution of 1,2-anhydro-3-*O*-benzyl-4,6-*O*-benzylidene-5a-carba-β-D-mannopyranose[11] (**7**, 929 mg, 2.75 mmol) in DMF (14 ml) was added to it, and the mixture was stirred for 3 h at 70°C. After addition of small amount of methanol at 0°C and then ethyl acetate (200 ml), the solution was thoroughly washed with water, dried, and evaporated to dryness. The residual product was chromatographed on silica gel (100 g, ethyl acetate/hexane, 1:4) to give **15** (634 mg, 71%) as a hygroscopic syrup. R_f = 0.31 (ethyl acetate/hexane, 1:3). – $[\alpha]_D^{23} = -11$ (c = 1.3 in $CHCl_3$). – ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.55–7.20 (m, 25 H, 5 × Ph), 5.59 (s, 1 H, PhC*H*), 5.00 and 4.66 (2 d, J_{gem} = 11.0 Hz, each 1 H), 4.92 and 4.63 (2 d, J_{gem} 11.0 Hz, each 1 H), 4.69 and 4.38 (2 d, J_{gem} = 11.0 Hz, each 1 H), and 4.62 and 4.58 (2 d, J_{gem} = 12.5 Hz, each 1 H) (4 × PhCH_2), 4.30 (d, $J_{1,2}$ = 7.3 Hz, 1 H, 1-H), 4.12 (m, 2 H, 1′-H, 2′-H), 3.98 (dd, $J_{5',6'a}$ = 4.4, $J_{6'gem}$ = 11.0 Hz, 1 H, 6′a-H), 3.91 (dd, $J_{3',4'} = J_{4',5'}$ = 9.9 Hz, 1 H, 4′-H), 3.72 (dd, $J_{2',3'}$ = 2.6, $J_{3',4'}$ = 9.9 Hz, 1 H, 3′-H), 3.71 (m, 2 H, 6a-H, 6b-H), 3.60 (dd, $J_{3,4} = J_{4.5}$ = 8.4 Hz, 1 H, 4-H), 3.57 (s, 3 H, OMe), 3.55 (m, 1 H, 6′b-H), 3.52 (dd, 1 H, $J_{2,3} = J_{3,4}$ = 8.4 Hz, 1 H, 3-H), 3.44 (dd, $J_{1,2}$ = 7.3, $J_{2,3}$ = 8.4 Hz, 1 H, 2-H), 3.34 (ddd, $J_{4,5}$ = 9.2, $J_{5,6a} = J_{5,6b}$ = 2.9 Hz, 1 H, 5-H), 2.20–2.05 (m, 1 H, 5′-H), 1.47 [br d, $J_{5a'gem}$ = 13.0 Hz, 1 H, 5a′(eq)-H], 1.31 [ddd, $J_{1',5a'(ax)}$ = 1.4, $J_{5',5a'ax} = J_{5a'gem}$ = 13.0 Hz, 1 H, 5a′(ax)-H]. – $C_{49}H_{54}N_2O_{10}$ (803.0): calcd. C 73.30, H 6.78, N 4.30; found C 73.39, H 6.72, N 4.45.

Methyl 2-Acetamido-3,6-di-O-benzyl-2-deoxy-β-D-glucopyranoside (**10**): Methyl 2-acetamido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside[13] (**9**, 1.30 g, 3.14 mmol) was dissolved in THF (130 ml), and the solution was stirred with molecular sieves 4Å (5 g) and a trace of methyl orange for 30 min and then with sodium cyanoborohydride (2.5 g, 12 molar equiv.) for 1 h at room temp. The reaction mixture was acidified by addition of hydrochloric acid etherate and further stirred for 3.5 h. The mixture was treated with Dowex 50W-X2 (H^+) resin (1 g) for 1 h, and then diluted with chloroform (200 ml), washed with aqueous satd. sodium hydrogen carbonate and water, dried, and evaporated. The residue was chromatographed on silica gel (80 g, acetone/toluene, 1:4) to give **10** (0.97 g, 74%) as crystals, m.p. 170–172°C (from EtOH). – $[\alpha]_D^{20}$ = + 35 (c = 1.7, MeOH). – IR (neat): $\tilde{\nu}$ = 3500 cm^{-1} (OH), 1650 (amide). – ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.42–7.24 (m, 10 H, 2 × Ph), 5.66 (d, $J_{2,NH}$ = 7.9 Hz, 1 H, NH), 4.81 and 4.70 (2 d, J_{gem} = 11.6 Hz, PhCH_2), 4.74 (d, $J_{1,2}$ = 7.9 Hz, 1 H, H-1), 4.63 and 4.56 (2 d, J_{gem} = 11.9 Hz, each 1 H, PhCH_2), 3.96 (dd, $J_{2,3}$ = 10.3, $J_{3,4}$ = 8.6 Hz, 1 H, 3-H), 3.76 (m, 2 H, 6-H × 2), 3.68 (dd, $J_{3,4}$ = 8.6, $J_{4,5}$ = 9.5 Hz, 1 H, 4-H), 3.53 (m, 1 H, 5-H), 3.47 (s, 3 H, OMe), 3.32 (ddd, $J_{1,2}$ = 7.9, $J_{2,3}$ = 10.3, $J_{2,NH}$ = 7.9 Hz, 1 H, 2-H), 1.91 (s, 3 H, Ac).

Compound **10** (30 mg, 72 mmol) was acetylated with acetic anhydride (0.15 ml) in pyridine (0.3 ml) conventionally. The product was chromatographed on silica gel (2 g, acetone/toluene, 1:4) to give the 4-acetate (30 mg, 92%) as a white powder. – $[\alpha]_D^{20}$ = +6.2 (c = 1.2, MeOH). – IR (neat): $\tilde{\nu}$ = 3500 cm^{-1} (OH), 1740 (ester), 1650 (amide). – ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.38–7.20 (10 H, m, 2 × Ph), 5.81 (d, $J_{2,NH}$ = 7.3 Hz, 1 H, NH), 5.01 (dd, $J_{3,4}$ = 9.2, $J_{4,5}$ = 9.5 Hz, 1 H, 4-H), 4.90 (d, $J_{1,2}$ = 7.9 Hz, 1 H, 1-H), 4.64–4.48 (m, 4 H, 2 × PhCH_2), 4.31 (dd, $J_{2,3}$ = 10.3, $J_{3,4}$ = 9.2 Hz, 1 H, 3-H), 3.70–3.63 (m, 1 H, 5-H), 3.57–3.55 (m, 2 H, 6-H × 2), 3.50 (s, 3 H, OMe), 3.24 (ddd, $J_{1,2}$ = 7.9, $J_{2,3}$ = 10.3, $J_{2,NH}$ = 7.3 Hz, 1 H, 2-H), 1.87 and 1.90 (2 s, each 3 H, 2 × Ac). – $C_{25}H_{31}NO_7$ (457.5): calcd. C 65.63, H 6.83, N 3.06. found C 65.43, H 6.95, N 3.20.

Methyl 2-Acetamido-3,6-di-O-benzyl-4-O-(3-O-benzyl-4,6-O-benzylidene-5a-carba-α-D-mannopyranosyl)-2-deoxy-β-D-glucopyranoside (**16**): To a solution of **10** (50.6 mg, 0.122 mmol) in anhydrous DMF (1 ml) were added sodium hydride (29 mg, 0.73 mmol) and 15-crown-5 ether (120 µl, 0.60 mmol) under argon, and the mixture was stirred for 30 min at room temp. A solution of **7** (94 mg, 0.28 mmol) in DMF (2 ml) was added to it, and the mixture was stirred for 25 h at 70°C. The reaction mixture was processed as described in the preparation of **15**. The product was chromatographed on silica gel (15 g, acetone/toluene, 1:4) to give **16** (62 mg, 68%) as a syrup: R_f = 0.31 (acetone/toluene, 1:3). – $[\alpha]_D^{29}$ – 9.4 (c = 0.93, $CHCl_3$). – IR (neat): $\tilde{\nu}$ = 3440 cm^{-1} (OH), 3290 (NH), 1650 (amide). – ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.54–7.26 (m, 20 H, 4 × Ph), 5.70 (br d, 1 H, NH), 5.60 (s, 1 H, PhC*H*), 4.76 and 4.72 (2 d, J_{gem} = 11.7 Hz, each 1 H, PhCH_2), 4.74 (d, 1 H, $J_{1,2}$ = 7.3 Hz, H-1), 4.62 and 4.49 (2 d, $J_{6'gem}$ = 11.7 Hz, each 1 H) and 4.59 (s, 2 H) (2 × PhCH_2), 4.15–4.11 (m, 2 H, 1′-H, 2′-H), 4.03 (dd, $J_{2,3}$ = 8.4, $J_{3,4}$ = 8.8 Hz, 1 H, 3-H), 4.00 (dd, $J_{5',6'a}$ = 4.4, $J_{6'gem}$ = 11.0 Hz, 1 H, 6′a-H), 3.93 (dd, $J_{3',4'} = J_{4',5'}$ = 9.9 Hz, 1 H, 4′-H), 3.76–3.72 (m, 3 H, 6a-H, 6b-H, 3′-H), 3.65 (dd, $J_{3,4}$ = 8.8, $J_{4,5}$ = 8.4 Hz, 1 H, 4-H), 3.57 (dd, $J_{5',6'b} = J_{6'gem}$ = 11.0 Hz, 1 H, 6′b-H), 3.51–3.49 (m, 1 H, 5-H), 3.47 (s, 3 H, OMe), 3.42 (ddd, $J_{1,2}$ = 7.3, $J_{2,3} = J_{2,NH}$ = 8.8 Hz, 1 H, 2-H), 2.12 (m, 1 H, 5′-H), 1.88 (s, 3 H, Ac), 1.51 [br d, $J_{5a'gem}$ = 13.6 Hz, 1 H, 5a′(eq)-H], 1.34 [ddd, $J_{1',5a'(ax)}$ = 2.2, $J_{5',5a'(ax)} = J_{5a'gem}$ = 13.6 Hz, 1 H, 5a′(ax)-H]. – $C_{44}H_{51}NO_{10}$ (753.9): calcd. C 70.10, H 6.82, N 1.86; found C 69.97, H 6.66, N 1.84.

Methyl 2,3,6-Tri-O-benzyl-4-O-(3-O-benzyl-4,6-O-benzylidene-5a-carba-α-D-arabino-hex-2-ulopyranosyl)-β-D-glucopyranoside (**17**): Compound **15** (79.6 mg, 0.10 mmol) was treated with acetic anhydride (0.28 ml, 3.0 mmol) in anhydrous DMSO (2.5 ml) for 4 h at room temp. The mixture was diluted with ethyl acetate (30 ml), and the solution was washed thorougly with water, dried, and evaporated. The product was purified by preparative TLC (ethyl acetate/hexane, 1:4) to give **17** (58.6 mg, 74%) as a hygroscopic syrup. R_f = 0.32 (ethyl acetate/hexane, 1:8). – IR (neat): $\tilde{\nu}$ = 1740 cm^{-1} (C=O). – $[\alpha]_D^{23} = -19$ (c = 1.4 in $CHCl_3$). – ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.55–7.20 (m, 25 H, 5 × Ph), 5.53 (s, 1 H, PhC*H*), 4.91 and 4.70 (2 d, J_{gem} = 10.6 Hz, each 1 H), 4.87 and 4.62 (2 d, J_{gem} = 11.0 Hz, each 1 H), and 4.67 and 4.56 (2 d, J_{gem} = 12.1 Hz, each 1 H) (3 × PhCH_2), 4.65 (d, $J_{3',4'}$ = 9.9 Hz, 1 H, 3′-H), 4.57 and 4.27 (2 d, J_{gem} = 11.7 Hz, each 1 H, PhCH_2), 4.31 [dd, $J_{1',5a'(ax)} = J_{1',5a'(eq)}$ = 2.6 Hz, 1 H, 1′-H], 4.29 (d, $J_{1,2}$ = 7.3 Hz, 1 H, 1-H), 4.10 (dd, $J_{5',6'a}$ = 4.2, $J_{6'gem}$ = 11.1 Hz, 1 H, 6′a-H), 3.72 (m, 2 H, 6-H × 2), 3.66 (dd, $J_{3,4} = J_{4,5}$ = 9.0 Hz, 1 H, 4-H), 3.62 (dd, $J_{2,3} = J_{3,4}$ = 9.0 Hz, 1 H, 3-H), 3.56 (s, 3 H, OMe), 3.59 (dd, $J_{3',4'} = J_{4',5'}$ = 10.3 Hz, 1 H, 4′-H), 3.54 (dd, $J_{5',6'b} = J_{6'gem}$ = 11.1 Hz, 1 H, 6′b-H), 3.43 (dd, $J_{1,2}$ = 7.7, $J_{2,3}$ = 8.8 Hz, 1 H, 2-H), 3.34 (ddd, $J_{4,5}$ = 9.5, $J_{5,6a} = J_{5,6b}$ = 2.7 Hz, 1 H, 5-H), 2.52 (m, 1 H, 5′-H), 1.81 [ddd, $J_{1',5a'(eq)} = J_{5',5a'(eq)}$ = 2.7, $J_{5a'gem}$ = 14.3 Hz, 1 H, 5a′(eq)-H], 1.03 [ddd, $J_{1',5a'(ax)}$ = 2.6, $J_{5',5a'(ax)} = J_{5a'gem}$ = 14.3 Hz, 1 H, 5a′(ax)-H]. – $C_{49}H_{52}O_{10}$ (800.9): calcd. C 73.48, H 6.54; found C 73.54, H 6.40.

Methyl 2,3,6-Tri-O-benzyl-4-O-(3-O-benzyl-4,6-O-benzylidene-5a-carba-β-D-arabino-hex-2-ulopyranosyl)-β-D-glucopyranoside (**19**): A 83 mg (0.104 mmol) portion of **17** was treated with DBU (31 µl, 0.21 mmol) in toluene (1.6 ml) for 20 min at 80°C. The reaction mixture was evaporated and the residue was chromatographed on silica gel (7 g, ethyl acetate/toluene, 1:8) to give **17** (16.5 mg, 20%) and **19** (48 mg, 58%) as a hygroscopic syrup. − $[\alpha]_D^{22}$ = + 12 (*c* = 0.95 in $CHCl_3$). − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.49−7.22 (m, 25 H, 5 × Ph), 5.45 (s, 1 H, PhC*H*), 5.02 and 4.70 (2 d, J_{gem} = 11.0 Hz, each 1 H), 4.94 and 4.56 (2 d, J_{gem} = 11.4 Hz, each 1 H), 4.79 and 4.54 (2 d, J_{gem} = 12.1 Hz, each 1 H), 4.63 and 4.50 (2 d, J_{gem} = 12.1 Hz, each 1 H) (4 × PhCH_2), 4.32 (d, $J_{1,2}$ = 7.7 Hz, 1 H, 1-H), 4.27 [br dd, $J_{1',5a'(ax)}$ = 12.8, $J_{1',5a'(eq)}$ = 6.6 Hz, 1 H, 1′-H], 4.04 (d, J_{6gem} = 11.0 Hz, 1 H, 6a-H), 3.90 (dd, $J_{5,6b}$ = 3.5, J_{6gem} = 10.8 Hz, 1 H, 6b-H), 3.88 (m, 1 H, 6′a-H), 3.84 (br d, $J_{3',4'}$ = 10.2 Hz, 1 H, 3′-H), 3.59 (s, 3 H, OMe), 3.59 (m, 1 H, 5-H), 3.55−3.50 (m, 2 H, 3-H, 4-H), 3.50 (dd, $J_{3',4'}$ = $J_{4',5'}$ = 10.2 Hz, 1 H, 4′-H), 3.40 (dd, $J_{1,2}$ = 7.7, $J_{2,3}$ = 8.4 Hz, 1 H, 2-H), 3.38 (dd, $J_{5',6'b}$ = $J_{6'gem}$ = 11.0 Hz, 1 H, 6′b-H), 1.76 [ddd, $J_{1',5a'(eq)}$ = 6.4, $J_{5',5a'(eq)}$ = 3.1, $J_{5a'gem}$ = 12.8 Hz, 1 H, 5a′(eq)-H], 1.64 (m, 1 H, 5′-H), 0.95 [ddd, $J_{1',5a'(ax)}$ = $J_{5',5a'(ax)}$ = $J_{5a'gem}$ = 12.6 Hz, 1 H, 5a′(ax)-H]. − $C_{49}H_{52}O_{10}$ (800.9): calcd. C 73.48, H 6.54; found C 73.54, H 6.38.

Methyl 2-Acetamido-3,6-di-O-benzyl-4-O-(3-O-benzyl-4,6-O-benzylidene-5a-carba-α-D-arabino-hex-2-ulopyranosyl)-2-deoxy-β-D-glucopyranoside (**18**): Compound **16** (63.8 mg, 85 mmol) was treated with acetic anhydride (0.25 ml, 2.6 mmol) in anhydrous DMSO (2.0 ml) for 18 h at room temp. The mixture was processed as in the preparation of **19** to give, after chromatography on silica gel (3.5 g, acetone/toluene, 1:5), **18** (57 mg, 90%) as a syrup. R_f = 0.34 (acetone/toluene, 1:3). − $[\alpha]_D^{22}$ = −23.6 (*c* = 0.92 in $CHCl_3$). − IR (neat): $\tilde{\nu}$ = 3260 (NH) cm^{-1}, 1730 (C=O), 1650 (amide). − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.55−7.22 (m, 20 H, 4 × Ph), 5.54 (s, 1 H, PhC*H*), 5.45 (br d, 1 H, NH), 4.76 (d, $J_{1,2}$ = 7.7 Hz, 1 H, 1-H), 4.76 and 4.41 (2 d, J_{gem} = 11.4 Hz, each 1 H), 4.67 and 4.55 (2 d, J_{gem} = 12.5 Hz, each 1 H), 4.66 and 4.41 (2 d, J_{gem} = 12.1 Hz, each 1 H) (3 × PhCH_2), 4.63 (d, $J_{3',4'}$ = 9.9 Hz, 1 H, 3′-H), 4.30 [dd, $J_{1',5a'(ax)}$ = $J_{1',5a'(eq)}$ = 2.6 Hz, 1 H, 1′-H], 4.10 (dd, $J_{5',6'a}$ = 4.4, $J_{6'gem}$ = 11.0 Hz, 1 H, 6′a-H), 4.09 (dd, 1 H, $J_{2,3}$ = 9.5, $J_{3,4}$ = 8.6 Hz, 1 H, 3-H), 3.78 (dd, $J_{5,6a}$ = 3.7, J_{6gem} = 11.0 Hz, 1 H, 6a-H), 3.69 (dd, $J_{3,4}$ = $J_{4,5}$ = 8.6 Hz, 1 H, 4-H), 3.61 (dd, $J_{3',4'}$ = 9.9, $J_{4',5'}$ = 11.0 Hz, 1 H, 4′-H), 3.55 (dd, 1 H, $J_{5',6'b}$ = 11.4, $J_{6'gem}$ = 11.0 Hz, 1 H, 6′b-H), 3.48 (m, 1 H, 5-H), 3.46 (s, 3 H, OMe), 3.32 (ddd, $J_{1,2}$ = $J_{2,NH}$ = 7.7, $J_{2,3}$ = 9.5 Hz, 1 H, 2-H), 2.51 (m, 1 H, 5′-H), 1.90−1.83 [m, 1 H, 5a′(eq)-H], 1.07 [br dd, $J_{5',5a'(ax)}$ = $J_{5a'gem}$ = 13.8 Hz, 1 H, 5a′(ax)-H]. − $C_{44}H_{49}NO_{10}$ (751.9): calcd. C 70.29, H 6.57, N 1.86; found C 70.39, H 6.75, N 1.90.

Methyl 2-Acetamido-3,6-di-O-benzyl-4-O-(3-O-benzyl-4,6-O-benzylidene-5a-carba-β-D-arabino-hex-2-ulopyranosyl)-2-deoxy-β-D-glucopyranoside (**20**): Compound **18** (57 mg, 0.076 mmol) was treated with DBU (20 µl, 0.15 mmol) in a mixture of ethanol (1 ml) and toluene (1 ml) for 1 h at 80°C. The product was chromatographed on silica gel (5 g, acetone/toluene, 1:2) to give **20** (46 mg, 81%) as a white solid. − $[\alpha]_D^{25}$ = −12.6 (*c* = 0.36 in $CHCl_3$). − IR (neat): $\tilde{\nu}$ = 3440 cm^{-1} (NH), 1730 (C=O), 1650 (amide). − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.52−7.24 (m, 20 H, 4 × Ph), 5.66 (d, $J_{2,,NH}$ = 8.1 Hz, NH), 5.47 (s, 1 H, PhC*H*), 4.82 and 4.57 (2 d, J_{gem} = 12.1 Hz, each 1 H) and, 4.75 and 4.62 (2 d, J_{gem} = 11.7 Hz, each 1 H) (2 × PhCH_2), 4.67 (d, $J_{1,2}$ = 7.3 Hz, 1 H, 1-H), 4.62 and 4.47 (2 d, J_{gem} = 12.1 Hz, each 1 H, PhCH_2), 4.26 [ddd, $J_{1',3'}$ = 0.7, $J_{1',5a'(ax)}$ = 12.5, $J_{1',5a'(eq)}$ = 6.4 Hz, 1 H, 1′-H], 3.97 (dd, $J_{5',6'a}$ = 4.6, $J_{6'gem}$ = 10.9 Hz, 1 H, 6′a-H), 3.86 (br d, $J_{3',4'}$ = 10.3 Hz, 1 H, 3′-H), 4.05−3.83 (m, 3 H, 3-H, 6a-H, 6b-H), 3.54 (dd, $J_{5',6'b}$ = $J_{6'gem}$ = 10.9 Hz, 1 H, 6′b-H), 3.52 (ddd, $J_{1,2}$ = 7.3 Hz, 1 H, 2-H), 3.49 (s, 3 H, OMe), 3.43 (dd, 1 H, $J_{3',4'}$ = 10.3, $J_{4',5'}$ = 11.0 Hz, 1 H, 4′-H), 3.64−3.47 (m, 2 H, 4-H, 5-H), 1.93 (s, 3 H, Ac), 1.84 [ddd, $J_{1',5a'(eq)}$ = 6.4, $J_{5',5a'(eq)}$ = 3.3, $J_{5a'gem}$ = 12.5 Hz, 1 H, 5a′(eq)-H], 1.72 (m, 1 H, 5′-H), 1.26 [ddd, $J_{1',5a'(ax)}$ = $J_{5',5a'(ax)}$ = 12.5 Hz, 1 H, 5a′(ax)-H]. − $C_{44}H_{49}NO_{10}$ (751.9): calcd. C 70.29, H 6.57, N 1.86; found C 70.54, H 6.75, N 1.84.

Methyl 2,3,6-Tri-O-benzyl-4-O-(3-O-benzyl-4,6-O-benzylidene-5a-carba-β-D-gluco- (**21**) *and -mannopyranosyl)-β-D-glucopyranoside* (**24**): (a) To a solution of **19** (446 mg, 0.557 mmol) in methanol (5 ml) and dichloromethane (5 ml) were added in turn $CeCl_3 \cdot 7H_2O$ (1.24 g, 3.34 mmol) and sodium borohydride (0.128 g, 3.05 mmol), and the mixture was stirred for 30 min at room temp. The mixture was then neutralized with acetic acid, and diluted with ethyl acetate (150 ml). The solution was thoroughly washed with water, dried, and evaporated. The product was chromatographed on silica gel (15 g, ethyl acetate/toluene, 1:6) to give first **21** (225 mg, 50%) and then **24** (210 mg, 47%) as a hygroscopic syrup. (b) To a solution of **19** (171 mg, 0.213 mmol) in THF (3.5 ml) was added a 1 M solution of borane dimethylsulfide-THF (0.60 ml, 0.60 mmol) at 0°C, and the mixture was stirred for 18 h at room temp. After addition of small amount of methanol, the mixture was evaporated and the residue was chromatographed on silica gel (18 g, ethyl acetate/toluene, 1:10) to give **21** (134 mg, 78%) and **24** (26 mg, 15%).

21: R_f = 0.21 (ethyl acetate/toluene, 1:5). − $[\alpha]_D^{24}$ = + 3.6 (*c* = 0.80 in $CHCl_3$). − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.49−7.22 (m, 25 H, 5 × Ph), 5.45 (s, 1 H, PhC*H*), 5.04 and 4.70 (2 d, J_{gem} = 11.4 Hz, each 1 H), 4.94 and 4.58 (2 d, J_{gem} = 11.4 Hz, each 1 H), 4.91 and 4.68 (2 d, J_{gem} = 11.0 Hz, each 1 H), 4.67 and 4.56 (2 d, J_{gem} = 12.1 Hz, each 1 H) (4 × PhCH_2), 4.29 (d, $J_{1,2}$ = 7.3 Hz, 1 H, 1-H), 3.96 (dd, $J_{5,6a}$ = 4.0, J_{6gem} = 11.0 Hz, 1 H, 6a-H), 3.82 (dd, $J_{5,6b}$ = 1.8, J_{6gem} = 11.0 Hz, 1 H, 6b-H), 3.78 (dd, $J_{5',6'a}$ = 4.6, $J_{6'gem}$ = 11.2 Hz, 1 H, 6′a-H), 3.73 (dd, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, 1 H, 4-H), 3.57 [ddd, $J_{1',5a'(eq)}$ = 4.8, $J_{1',5a'(ax)}$ = $J_{5a'gem}$ = 12.3 Hz, 1 H, 1′-H], 3.57 (s, 3 H, OMe), 3.48 (dd, $J_{2,3}$ = $J_{3,4}$ = 9.2 Hz, 1 H, 3-H), 3.42 (dd, $J_{3',4'}$ = 7.9, $J_{4',5'}$ = 9.3 Hz, 1 H, 4′-H), 3.42 (m, 1 H, 5-H), 3.40 (dd, $J_{1',2'}$ = $J_{2',3'}$ = 8.4 Hz, 1 H, 2′-H), 3.40 (dd, $J_{1,2}$ = 7.3, $J_{2,3}$ = 9.6 Hz, 1 H, 2-H), 3.34 (dd, $J_{2',3'}$ = $J_{3',4'}$ = 7.9 Hz, 1 H, 3′-H), 3.27 (dd, $J_{5',6'b}$ = $J_{6'gem}$ = 10.4 Hz, 1 H, 6′b-H), 1.64 [ddd, $J_{1',5a'(eq)}$ = $J_{5',5a'(eq)}$ = 4.0, $J_{5a'gem}$ = 12.3 Hz, 1 H, 5a′(eq)-H], 1.38 (m, 1 H, 5′-H), 0.72 [ddd, $J_{1',5a'(ax)}$ = $J_{5',5a'(ax)}$ = $J_{5a'gem}$ = 12.3 Hz, 1 H, 5a′(ax)-H]. − $C_{49}H_{54}O_{10}$ (803.0): calcd. C 73.30, H 6.78; found C 73.59, H 6.68.

24: R_f = 0.10 (ethyl acetate/toluene, 1:5). − $[\alpha]_D^{24}$ = + 26 (*c* = 1.04 in $CHCl_3$). − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.50−7.25 (m, 25 H, 5 × Ph), 5.52 (s, 1 H, PhC*H*), 4.99 and 4.70 (2 d, J_{gem} = 11.0 Hz, each 1 H), 4.93 and 4.58 (2 d, J_{gem} = 12.4 Hz, each 1 H), 4.70 and 4.63 (2 d, J_{gem} = 11.0 Hz, each 1 H), 4.67 and 4.54 (2 d, J_{gem} = 12.1 Hz, each 1 H) (4 × PhCH_2), 4.30 (d, $J_{1,2}$ = 7.7 Hz, 1 H, 1-H), 4.23 (dd, $J_{1',2'}$ = $J_{2',3'}$ = 2.4 Hz, 1 H, 2′-H), 3.89 (dd, $J_{5,6a}$ = 3.7, J_{6gem} = 11.0 Hz, 1 H, 6a-H), 3.75 (dd, $J_{5,6b}$ = 2.4, J_{6gem} = 11.0 Hz, 1 H, 6b-H), 3.65 (m, 1 H, 1′-H), 3.59 (m, 1 H, 4-H), 3.58 (s, 3 H, OMe), 3.48 (dd, $J_{5',6'b}$ = $J_{6'gem}$ = 10.6 Hz, 1 H, 6′b-H), 3.70−3.37 (m, 1 H, 3-H), 3.41 (dd, $J_{1,2}$ = 7.7, $J_{2,3}$ = 8.8 Hz, 1 H, 2-H), 3.40 (m, 1 H, 5-H), 3.27 (dd, $J_{2',3'}$ = 2.6, $J_{3',4'}$ = 9.5 Hz, 1 H, 3′-H), 1.43−1.32 [m, 3 H, 5′-H, 5a′(ax)-H, 5a′(eq)-H]. − $C_{49}H_{54}O_{10}$ (803.0): calcd. C 73.30, H 6.78; found C 73.32, H 6.71.

Methyl 2,3,6-Tri-O-benzyl-4-O-(2-O-acetyl-3-O-benzyl-4,6-O-benzylidene-5a-carba-β-D-glucopyranosyl)-β-D-glucopyranoside (**22**): To a solution of **21** (19 mg, 0.024 mmol) in pyridine (0.4 ml) was added methanesulfonyl chloride (10 ml, 0.13 mmol), and the

mixture was stirred for 3 h at room temp. After the usual processing, the product was purified by preparative TLC (silica gel, ethyl acetate/toluene, 1:6) to give the mesylate **42** (10.2 mg). A mixture of **42** (10 mg, 0.012 mmol) and anhydrous sodium acetate (8.4 mg, 0.1 mmol) in aqueous 80% DMF was stirred for 6 days at 100°C. Then the mixture was diluted with ethyl acetate (30 ml), washed with water, dried, and evaporated. The product was purified by preparative TLC (silica gel, ethyl acetate/hexane, 2:5) to give **22** (5.0 mg, 25%) as a syrup. R_f = 0.60 (ethyl acetate/toluene, 1:3). − $[\alpha]_D^{23}$ = +3 (*c* = 1.4, $CHCl_3$). − IR (neat): $\tilde{\nu}$ = 1750 cm^{-1} (ester). − ^1H NMR (270 MHz, $CDCl_3$): δ = 7.49−7.23 (m, 25 H, 5 × Ph), 5.44 (s, 1 H, PhC*H*), 4.97 and 4.59 (2 d, J_{gem} = 11.0 Hz, PhCH_2), 4.93 (dd, $J_{1',2'}$ = $J_{2',3'}$ = 9.5 Hz, 1 H, 2′-H), 4.90 and 4.68 (2 d, J_{gem} = 9.5 Hz, 11.0 Hz, each 1 H), 4.86 and 4.57 (2 d, J_{gem} = 11.7 Hz, each 1 H), and 4.70 and 4.47 (2 d, J_{gem} = 12.1 Hz, each 1 H) (3 × PhCH_2), 4.26 (d, $J_{1,2}$ = 7.3 Hz, 1 H, 1-H), 3.83 (dd, $J_{5',6'a}$ = 4.4, $J_{6'gem}$ = 11.0 Hz, 1 H, 6′a-H), 3.75−3.73 (m, 2 H, 6a-H, 6b-H), 3.56 (s, 3 H, OMe), 3.50−3.27 (m, 7 H, 2-H, 3-H, 4-H, 5-H, 1′-H, 3′-H, 4′-H), 3.18 (dd, $J_{5',6'b}$ = $J_{6'gem}$ = 11.0 Hz, 1 H, 6′b-H), 1.91 (s, 3 H, Ac), 1.84 [ddd, $J_{1',5a'(eq)}$ = 4.4, $J_{5',5a'(eq)}$ = 3.3, $J_{5a'gem}$ = 13.2 Hz, 1 H, 5a′(eq)-H], 1.43 (m, 1 H, 5′-H), 0.68 [ddd, $J_{1',5a'(ax)}$ = $J_{5a'gem}$ = 13.2, $J_{5',5a'(ax)}$ = 11.4 Hz, 1 H, 5a′(ax)-H]. − $C_{51}H_{56}O_{11}$ (845.0): calcd. C 72.49, H 6.68; found C 72.44, H 6.64. This compound was identical with the acetate obtained from **21** in all respects.

Methyl 2,3,6-Tri-O-benzyl-4-O-(2,3-di-O-benzyl-4,6-O-benzylidene-5a-carba-β-D-glucopyranosyl)-β-D-glucopyranoside (**23**): To a solution of **21** (128 mg, 0.160 mmol) in anhydrous DMF (2.5 ml) were added in turn sodium hydride (26 mg, 0.65 mmol) and benzyl bromide (30 µl, 0.25 mmol), and the mixture was stirred for 24 h at room temp. After the usual processing, the product was chromatographed on silica gel (15 g, ethyl acetate/toluene, 1:20) to give **23** (131 mg, 92%) as a white solid. R_f = 0.69 (ethyl acetate/toluene, 1:5). − $[\alpha]_D^{30}$ = −7.8 (*c* = 1.2, $CHCl_3$).− ^1H NMR (270 MHz, $CDCl_3$): δ = 7.35−7.23 (m, 30 H, 6 × Ph), 5.45 (s, 1 H, PhC*H*), 4.95 and 4.77 (2 d, J_{gem} = 11.4 Hz), 4.91 and 4.73 (2 d, J_{gem} = 11.4 Hz), 4.90 and 4.70 (2 d, J_{gem} = 11.0 Hz), 4.85 and 4.63 (2 d, J_{gem} = 11.0 Hz), and 4.52 and 4.37 (2 d, J_{gem} = 12.1 Hz) (each 1 H, 5 × PhCH_2), 4.28 (d, $J_{1,2}$ = 7.3 Hz, 1 H, 1-H), 3.87 (dd, $J_{5',6'a}$ = 4.2, $J_{6'gem}$ = 11.0 Hz, 1 H, 6′a-H), 3.87 (dd, $J_{5,6a}$ = 4.2, J_{6gem} = 10.6 Hz, 1 H, 6a-H), 3.69 (dd, $J_{5,6b}$ = 1.5, J_{6gem} = 10.6 Hz, 1 H, 6b-H), 3.56 (s, 3 H, OMe), 3.53−3.27 (m, 6 H, 3-H, 4-H, 1′-H, 2′-H, 3′-H, 4′-H), 3.37 (dd, $J_{1,2}$ = 7.3, $J_{2,3}$ = 8.8 Hz, 1 H, 2-H), 3.29 (br d, $J_{4,5}$ = 7.7 Hz, 1 H, 5-H), 3.19 (dd, $J_{5',6'b}$ = $J_{6'gem}$ = 11.0 Hz, 1 H, 6′b-H), 1.86 [m, 1 H, 5a′(eq)-H], 1.45 (m, 1 H, 5′-H), 0.64 [ddd, $J_{1',5a'(ax)}$ = 13.2, $J_{5',5a'(ax)}$ = $J_{5a'gem}$ = 11.0 Hz, 1 H, 5a′(ax)-H]. − $C_{56}H_{60}O_{10}$ (893.1): calcd. C 75.31, H 6.77; found C 75.13, H 6.94.

Methyl 2-Acetamido-3,6-di-O-benzyl-4-O-(3-O-benzyl-4,6-O-benzylidene-5a-carba-β-D-gluco- (**25**) *and -mannopyranosyl)-2-deoxy-β-D-glucopyranoside* (**28**): (a) To a solution of **20** (27.3 mg, 0.0363 mmol) in methanol (0.5 ml) and dichloromethane (5 ml) were added $CeCl_3 \cdot 7H_2O$ (74 mg, 0.20 mmol) and sodium borohydride (12.8 mg, 0.305 mmol), and the mixture was stirred for 20 min at 0°C. The mixture was then neutralized with acetic acid, and diluted with ethyl acetate (30 ml). The solution was thoroughly washed with water, dried, and evaporated. The product was chromatographed on silica gel (3 g, acetone/toluene, 1:2) to give first **25** (12 mg, 44%) and then **28** (14.3 mg, 52%) as a hygroscopic syrup. (b) To a solution of **20** (45.3 mg, 0.0602 mmol) in THF (4.5 ml) was added a 1 M solution of borane dimethylsulfide-THF (0.30 ml, 0.30 mmol) at 0°C, and the mixture was stirred for 18 h at room temp. After addition of small amount of methanol, the mixture was evaporated and the residue was chromatographed on silica gel (5 g, acetone/chloroform, 1:6) to give **25** (18 mg, 40%) and **28** (13.4 mg, 30%).

25: R_f = 0.29 (acetone/toluene, 1:2). − $[\alpha]_D^{26}$ = −25 (*c* = 0.31 in $CHCl_3$). − IR (neat): $\tilde{\nu}$ = 3450 cm^{-1} (OH, NH), 1650 (amide). − ^1H NMR (270 MHz, $CDCl_3$): δ = 7.50−7.25 (m, 20 H, 4 × Ph), 5.56 (d, $J_{2,NH}$ = 9.2 Hz, 1 H, NH), 5.47 (s, 1 H, PhC*H*), 4.95 and 4.67 (2 d, J_{gem} = 11.4 Hz, each 1 H), 4.73 and 4.66 (2 d, J_{gem} = 11.7 Hz, each 1 H), 4.71 and 4.55 (2 d, J_{gem} = 11.7 Hz, each 1 H) (3 × PhCH_2), 4.70 (d, $J_{1,2}$ = 7.3 Hz, 1 H, 1-H), 3.99 (dd, $J_{5,6a}$ = 3.3, J_{6gem} = 11.4 Hz, 1 H, 6a-H), 3.98 (dd, $J_{2,3}$ = $J_{3,4}$ = 9.2 Hz, 1 H, 3-H), 3.88 (dd, $J_{5',6'a}$ = 4.4, $J_{6'gem}$ = 11.0 Hz, 6′a-H), 3.82 (dd, $J_{5,6b}$ = 2.0, J_{6gem} = 11.0 Hz, 1 H, 6b-H), 3.78 (dd, $J_{1',2'}$ = $J_{2',3'}$ = 8.8 Hz, 1 H, 2′-H), 3.58 (ddd, $J_{1',2'}$ = 8.8, $J_{1'.5a'(ax)}$ = 9.2 Hz, 1 H, 1′-H), 3.49 (m, 1 H, 5-H), 3.48 (s, 3 H, OCH_3), 3.48−3.29 (m, 3 H, 4-H, 3′-H, 6′b-H), 3.40 (ddd, $J_{1,2}$ = 7.3, $J_{2,3}$ = $J_{2,NH}$ = 9.2 Hz, 1 H, 2-H), 3.35 (dd, $J_{3',4'}$ = $J_{4',5'}$ = 10.8 Hz, 1 H, 4′-H), 1.88 (s, 3 H, Ac), 1.74 [br d, $J_{5a'gem}$ = 13.1 Hz, 1 H, 5a′(eq)-H], 1.43 (m, 1 H, 5′-H), 0.78 [ddd, $J_{1',5a'(ax)}$ = 9.2, $J_{5',5a'(ax)}$ = 13.1 Hz, 5a′(ax)-H]. − $C_{44}H_{51}NO_{10}$ (753.9): calcd. C 70.10, H 6.82, N 1.86; found C 69.84, H 6.78, N 2.06.

28: R_f = 0.24 (acetone/toluene, 1:2). − $[\alpha]_D^{26}$ = + 15 (*c* = 0.45 in $CHCl_3$). − IR (neat): $\tilde{\nu}$ = 3440 cm^{-1}(OH, NH), 1660 (amide). − ^1H NMR (270 MHz, $CDCl_3$): δ = 7.50−7.26 (m, 20 H, 4 × Ph), 5.63 (d, 1 H, $J_{2,NH} \approx$ 9 Hz, 1 H, NH), 5.53 (s, 1 H, PhC*H*), 4.71 and 4.60 (2 d, J_{gem} = 12.1 Hz, each 1 H), 4.70 (s, 2 H) (2 × PhCH_2), 4.68 (d, $J_{1,2}$ = 7.3 Hz, 1 H, 1-H), 4.66 and 4.52 (2 d, J_{gem} = 12.1 Hz, each 1 H, PhCH_2), 4.24 (dd, $J_{1',2'}$ = 2.2, $J_{2',3'}$ = 2.6 Hz, 1 H, 2′-H), 4.00 (dd, $J_{2,3}$ = 9.2, $J_{3,4}$ = 8.4 Hz, 1 H, 3-H), 3.93 (dd, $J_{5',6'a}$ = 4.4, $J_{6'gem}$ = 11.4 Hz, 1 H, 6′a-H), 3.91 (dd, $J_{3',4'}$ = 9.9, $J_{4',5'}$ = 10.3 Hz, 1 H, 4′-H), 3.86 (dd, $J_{5,6a}$ = 3.7, J_{6gem} = 10.5 Hz, 1 H, 6a-H), 3.75 (dd, $J_{5,6b}$ = 2.6, J_{6gem} = 10.5 Hz, 1 H, 6b-H), 3.65 (dd, $J_{3,4}$ = 8.4, $J_{4,5}$ = 8.8 Hz, 1 H, 4-H), 3.62 [br d, $J_{1',5a'(ax)}$ = 12.4 Hz, 1 H, 1′-H], 3.53−3.42 (m, 3 H, 2-H, 5-H, 6′b-H), 3.48 (s, 3 H, OMe), 3.29 (dd, $J_{2',3'}$ = 2.6, $J_{3',4'}$ = 9.9 Hz, 1 H, 3′-H), 1.91 (s, 3 H, Ac), 1.43−1.39 [m, 3 H, 5′-H, 5a′(ax)-H, 5a′(eq)-H]. − $C_{44}H_{51}NO_{10}$ (753.9): calcd. C 70.10, H 6.82, N 1.86; found C 70.39, H 6.55, N 2.02.

Methyl 2-Acetamido-4-O-(2-O-acetyl-3-O-benzyl-4,6-O-benzylidene-5a-carba-β-D-glucopyranosyl)-3,6-di-O-benzyl-2-deoxy-β-D-glucopyranoside (**26**): Compound **25** (8.4 mg, 11 mmol) was treated with acetic anhydride (0.5 ml) and pyridine (1 ml) for 2 h at room temp. After addition of methanol (0.2 ml), the mixture was evaporated. The product was purified by preparative TLC (silica gel, acetone/toluene, 1:2) to give **26** (8.6 mg, 97%) as a syrup. − $[\alpha]_D^{29}$ = −46 (*c* = 0.49 in $CHCl_3$). − IR (neat): $\tilde{\nu}$ = 3380 cm^{-1} (NH), 1740 (ester), 1650 (amide). − ^1H NMR (270 MHz, $CDCl_3$): δ = 7.49−7.25 (m, 25 H, 5 × Ph), 5.87 (d, $J_{2,NH}$ = 8.8 Hz, 1 H, NH), 5.50 (s, 1 H, PhC*H*), 4.96 (dd, $J_{1',2'}$ = 9.2, $J_{2',3'}$ = 9.5 Hz, 1 H, 2′-H), 4.88 and 4.62 (2 d, J_{gem} = 11.7 Hz, each 1 H), 4.73 and 4.49 (2 d, J_{gem} = 11.7 Hz, each 1 H), and 4.60 (s, 2 H) (3 × PhCH_2), 4.60−4.50 (m, 1 H, 1-H), 4.01 (dd, $J_{5',6'a}$ = 4.4, $J_{6'gem}$ = 11.0 Hz, 1 H, 6′a-H), 3.87−3.38 (m, 7 H, 2-H, 3-H, 4-H, 5-H, 6-H × 2, 1′-H), 3.56 (dd, $J_{3',4'}$ = 9.2, $J_{4',5'}$ = 9.5 Hz, 1 H, 4′-H), 3.46 (dd, $J_{2',3'}$ = 9.5, $J_{3',4'}$ = 9.2 Hz, 1 H, 3′-H), 3.43 (s, 3 H, OMe), 3.41 (dd, $J_{5',6'b}$ = 10.6, $J_{6'gem}$ = 11.0 Hz, 1 H, 6′b-H), 1.97 and 1.93 (2 s, each 3 H, 2 × Ac), 1.79 [ddd, $J_{1',5a'(eq)}$ = $J_{5',5a'(eq)}$ = 3.5 Hz, $J_{5a'gem}$ = 12.8 Hz, 1 H, 5a′(eq)-H], 1.55 (m, 1 H, 5′-H), 0.83 [ddd, $J_{1',5a'(ax)}$ = 11.4, $J_{5',5a'(ax)}$ = $J_{5a'gem}$ = 12.8 Hz, 1 H, 5a′(ax)-H]. − $C_{46}H_{53}NO_{11}$ (795.9): calcd. C 69.42, H 6.71, N 1.76; found C 69.29, H 6.81, N 1.67.

Methyl 2-Acetamido-3,6-di-O-benzyl-4-O-(2,3-di-O-benzyl-4,6-O-benzylidene-5a-carba-β-D-glucopyranosyl)-2-deoxy-β-D-

glucopyranoside (**27**): To a solution of **25** (21.7 mg, 29 μmol) in DMF (1.0 ml) were added sodium hydride (3.2 mg, 80 μmol) and benzyl bromide (4 ml, 34 μmol), and the mixture was stirred for 18 h at room temp. After the usual processing, the product was chromatographed on silica gel (3 g, acetone/toluene, 1:5), and further purified by preparative TLC (silica gel, acetone/chloroform, 1:4) to give **25** (5.6 mg, 26%) remained unchanged, and **27** (10.5 mg, 43%) as a white powder. R_f = 0.43 (acetone/toluene, 1:3). − $[\alpha]_D^{25}$ = −10 (*c* = 0.53 in $CHCl_3$). − IR (neat): $\tilde{\nu}$ = 3280 cm^{-1} (NH), 1650 (amide). − ^1H NMR (270 MHz, $CDCl_3$): δ = 7.50−7.26 (m, 25 H, 5 × Ph), 5.53 (d, 1 H, $J_{2,NH}$ = 7.7 Hz, 1 H, NH), 5.47 (s, 1 H, PhC*H*), 4.90 and 4.74 (2 d, J_{gem} = 11.0 Hz, each 1 H), 4.85 and 4.80 (2 d, J_{gem} = 11.4 Hz, each 1 H), 4.72 and 4.66 (2 d, J_{gem} = 11.7 Hz, each 1 H), and 4.55 and 4.39 (2 d, J_{gem} = 12.1 Hz, each 1 H) (4 × PhCH_2), 4.01−3.94 (m, 2 H, 3-H, 6′a-H), 3.92 (dd, $J_{5,6a}$ = 3.7, J_{6gem} = 10.6 Hz, 1 H, 6a-H), 3.66 (dd, $J_{5,6b}$ = 1.8, J_{6gem} = 10.6 Hz, 1 H, 6b-H), 3.57 (dd, $J_{3,4}$ = 9.2, $J_{4,5}$ = 8.8 Hz, 1 H, 4-H), 3.46 (s, 3 H, OMe), 3.50−3.23 (m, 7 H, 2-H, 5-H, 1′-H, 2′-H, 3′-H, 4′-H, 6′b-H), 1.86 (s, 3 H, Ac), 1.86 [m, 1 H, 5a′(eq)-H], 1.45 (m, 1 H, 5′-H), 0.74 [ddd, $J_{1',5a'(ax)}$ = $J_{5',5a'(ax)}$ = $J_{5a'gem}$ = 11.5 Hz, 1 H, 5a′(ax)-H]. − $C_{51}H_{57}NO_{10}$ (844.0): calcd. C 72.58, H 6.81, N 1.66; found C 72.51, H 7.01, N 1.89.

Methyl 2,3,6-Tri-O-benzyl-4-O-(2,3,6-tri-O-benzyl-5a-carba-β-D-glucopyranosyl)-β-D-glucopyranoside (**29**) *and Its 4′-Acetate* (**30**): A mixture of **23** (98 mg, 0.11 mmol), boran trimethylamine (87 mg, 1.20 mmol) and molecular sieves 4Å (160 mg) in THF (2 ml) was stirred for 30 min at room temp. Aluminium chloride (161 mg, 1.20 mmol) was added to it, and the mixture was stirred for 2 h at room temp. After treatment with Dowex 50X-2 (H^+) resin, an insoluble material was removed by filtration through a Celite bed and the filtrate was evaporated. The residue was dissolved in ethyl acetate (30 ml) and solution was washed with saturated sodium hydrogen carbonate and water, dried, and evaporated. The residual products were chromatographed on silica gel (8 g, ethyl actate/toleune, 1:12) to give **29** (91 mg, 92%) as a colorless syrup. A 19 mg (0.022 mmol) portion of **29** was acetylated in the usual manner and the product was chromatographed on silica gel (1 g, ethyl acetate/toluene, 1:10) to give **30** (19 mg, 92%) as a syrup.

29: R_f = 0.46 (ethyl acetate/toluene, 1:8). − $[\alpha]_D^{26}$ = + 6.5 (*c* = 0.97 in $CHCl_3$). − ^1H NMR (270 MHz, $CDCl_3$): δ = 7.38−7.19 (m, 30 H, 6 × Ph), 4.89 and 4.81 (2 d, J_{gem} = 11.0 Hz, each 1 H), 4.88 and 4.68 (2 d, J_{gem} = 11.0 Hz, each 1 H), 4.85 and 4.72 (2 d, J_{gem} = 11.0 Hz, each 1 H), 4.78 (s, 2 H), and 4.55 and 4.40 (2 d, J_{gem} = 11.0 Hz, each 1 H) (6 × PhCH_2), 3.89 (dd, $J_{5,6a}$ = 4.4, J_{6gem} = 10.6 Hz, 1 H, 6a-H), 3.71 (dd, $J_{5,6b}$ = 1.5, J_{6gem} = 10.6 Hz, 1 H, 6b-H), 3.55 (s, 3 H, OMe), 3.55−3.13 (m, 6 H, 3-H, 4-H, 5-H, 1′-H, 2′-H, 3′-H), 3.42 (dd, $J_{3',4'}$ = $J_{4',5'}$ = 8.8 Hz, 1 H, 4′-H), 3.37 (dd, $J_{1,2}$ = 7.3, $J_{2,3}$ = 8.8 Hz, 1 H, 2-H), 3.29 (dd, $J_{5',6'a}$ = 4.6, $J_{6'gem}$ = 9.2 Hz, 1 H, 6′a-H), 3.20 (dd, $J_{5',6'b}$ = 6.0, $J_{6'gem}$ = 9.2 Hz, 1 H, 6′b-H), 2.02 [ddd, $J_{1',5a'(eq)}$ or $J_{5',5a'(eq)}$ = 3.3 or 3.7, $J_{5a'gem}$ = 13.2 Hz, 1 H, 5a′(eq)-H], 1.45 (m, 1 H, 5′-H), 0.92 [ddd, $J_{1',5a'(ax)}$ or $J_{5',5a'(ax)}$ = 11.7 or 12.8, $J_{5a'gem}$ = 13.2 Hz, 1 H, 5a′(ax)-H]. − $C_{56}H_{62}O_{10}$ (895.1): calcd. C 75.14, H 6.98; found C 75.01, H 7.00.

30: R_f = 0.42 (ethyl acetate/toluene, 1:10). − $[\alpha]_D^{23}$ = + 13.8 (*c* = 0.78 in $CHCl_3$). − ^1H NMR (270 MHz, $CDCl_3$): δ = 7.38−7.18 (m, 30 H, 6 × Ph), 4.88 (dd, $J_{3',4'}$ = $J_{4',5'}$ = 9.9 Hz, 1 H, 4′-H), 4.90 and 4.77 (2 d, J_{gem} = 11.0 Hz, each 1 H), 4.88 and 4.71 (2 d, J_{gem} = 11.0 Hz, each 1 H), 4.69 and 4.57 (2 d, J_{gem} = 11.0 Hz, each 1 H), 4.56 and 4.43 (2 d, J_{gem} = 12.3 Hz, each 1 H), and 4.30 and 4.24 (2 d, J_{gem} = 12.2 Hz, each 1 H) (6 × PhCH_2), 4.28 (dd, $J_{1,2}$ = 7.3 Hz, 1 H, 1-H), 3.90 (dd, $J_{5,6a}$ = 4.2, J_{6gem} = 10.6 Hz, 1 H, 6a-H), 3.73 (dd, $J_{5,6b}$ = 1.8, J_{6gem} = 10.6 Hz, 1 H, 6b-H), 3.58−3.27 (m, 4 H, 3-H, 4-H, 1′-H, 2′-H), 3.56 (s, 3 H, OMe), 3.38 (dd, $J_{1,2}$ = 7.3, $J_{2,3}$ = 9.5 Hz, 1 H, 2-H), 3.26 (dd, $J_{2',3'}$ = $J_{3',4'}$ = 9.2 Hz, 1 H, 3′-H), 3.16 (dd, $J_{5',6'a}$ = 4.8, $J_{6'gem}$ = 9.2 Hz, 1 H, 6′a-H), 3.01 (dd, $J_{5',6'b}$ = 5.1, $J_{6'gem}$ = 9.2 Hz, 1 H, 6′b-H), 2.23 [br d, 1 H, $J_{5a'gem}$ = 13.9 Hz, 1 H, 5a′(eq)-H], 1.80 (s, 3 H, Ac), 1.54 (m, 1 H, 5′-H), 1.11 [ddd, 1 H, $J_{1',5a'(ax)}$ = $J_{5',5a'(ax)}$ = $J_{5a'gem}$ = 13.9 Hz, 1 H, 5a′(ax)-H]. − $C_{58}H_{64}O_{11}$ (937.1): calcd. C 74.34, H 6.88; found C 74.04, H 7.16.

Methyl 4-O-(2,3,6-Tri-O-benzyl-5a-carba-β-D-galactopyranosyl)-2,3,6-tri-O-benzyl-β-D-glucopyranoside (**32**): To a solution of **29** (93 mg, 0.104 mmol) in dichloromethane (2 ml) were added PCC (69 mg, 0.32 mmol) and molecular sieves 4Å (70 mg), and the mixture was stirred for 3 h at room temp. Then the mixture was taken up on a silica gel column and eluted with diethyl ether thoroughly to give, after evaporation, a crude ketone **31** (≈92 mg). To a solution of the ketone in THF (1.5 ml) was added 1 M THF solution of L-selectride (0.36 ml, 0.36 mmol) and the mixture was stirred for 30 min at 0°C. After the usual processing, the product was purified by preparative TLC (silica gel, ethyl acetate/toluene, 1:15) to give **32** (50 mg, 54%) as a syrup. R_f = 0.32 (ethyl acetate/toluene, 1:8). − $[\alpha]_D^{20}$ = + 14.6 (*c* = 0.69 in $CHCl_3$). − ^1H NMR (270 MHz, $CDCl_3$): δ = 7.39−7.18 (m, 30 H, 6 Ph), 4.90 and 4.76 (2 d, J_{gem} = 11.0 Hz, each 1 H), 4.88 and 4.73 (2 d, J_{gem} = 10.6 Hz, each 1 H), 4.81 and 4.68 (2 d, J_{gem} = 11.4 Hz, each 1 H), 4.65 (s, 2 H), 4.49 and 4.36 (2 d, J_{gem} = 12.1 Hz, each 1 H), and 4.44 and 4.38 (2 d, J_{gem} 11.9 Hz, each 1 H) (6 × PhCH_2), 4.28 (d, $J_{1,2}$ = 7.3 Hz, 1 H, 1-H), 4.13 (br d, $J_{4',5'}$ = 2.2 Hz, 1 H, 4′-H), 3.87 (dd, $J_{5,6a}$ = 4.4, J_{6gem} = 10.6 Hz, 1 H, 6a-H), 3.74 (dd, $J_{5,6b}$ = 1.5, J_{6gem} = 10.6 Hz, 1 H, 6b-H), 3.62 (dd, $J_{1',2'}$ = $J_{2',3'}$ = 9.2 Hz, 1 H, 2′-H), 3.57−3.28 (m, 3 H, 3-H, 4-H, 6′a-H), 3.55 (s, 3 H, OMe), 3.37 (dd, $J_{1,2}$ = 7.3, $J_{2,3}$ = 8.4 Hz, 1 H, 2-H), 3.36 [br dd, $J_{1',2'}$ = 9.2, $J_{1',5a'(ax)}$ = 8.1 Hz, 1 H, 1′-H], 3.19 (dd, $J_{2',3'}$ = 9.3, $J_{3',4'}$ = 2.9 Hz, 1 H, 3′-H), 3.11 (dd, $J_{5',6'b}$ = 4.1, $J_{6'gem}$ = 9.0 Hz, 1 H, 6′b-H), 2.02 (m, 1 H, 5′-H), 1.82 [m, 1 H, 5a′(eq)-H], 1.47 [m, 1 H, 5a′(ax)-H]. − $C_{56}H_{62}O_{10}$ (895.1): calcd. C 75.14, H 6.98; found C 74.86, H 7.17.

Methyl 4-O-(2,3,4,6-Tetra-O-acetyl-5a-carba-β-D-galactopyranosyl)-2,3,6-tri-O-acetyl-β-D-glucopyranoside (**33**): To a solution of **32** (40 mg, 45 μmol) in ethanol (1 ml) were added 10% Pd/C (10 mg) and 1 N HCl (0.1 ml), and the mixture was stirred under hydrogen atmosphere for 3 h at room temp. The catalyst was removed by filtration and the filtrate was evaporated. The residue was acetylated with acetic anhydride and pyridine in the usual manner, and the product was chromatographed on silica gel (4 g, acetone/toluene, 1:8) to give **33** (22 mg, 76%) as a syrup. R_f = 0.38 (acetone/toluene, 1:5). − $[\alpha]_D^{20}$ = −17 (*c* = 1.1 in $CHCl_3$). − ^1H NMR (270 MHz, $CDCl_3$): δ = 5.42 (br s, 1 H, 4′-H), 5.22 (dd, $J_{1',2'}$ = 9.9, $J_{2',3'}$ = 10.6 Hz, 1 H, 2′-H), 5.11 (dd, $J_{2,3}$ = 9.5, $J_{3,4}$ = 8.4 Hz, 1 H, 3-H), 4.83 (dd, $J_{1,2}$ = 8.1, $J_{2,3}$ = 9.5 Hz, 1 H, 2-H), 4.75 (dd, $J_{2',3'}$ = 10.6, $J_{3',4'}$ = 2.9 Hz, 1 H, 3′-H), 4.53 (dd, $J_{5,6a}$ = 1.6, J_{6gem} = 11.7 Hz, 1 H, 6a-H), 4.39 (d, $J_{1,2}$ = 8.1 Hz, 1 H, 1-H), 4.19 (dd, $J_{5,6b}$ = 4.8, J_{6gem} = 11.7 Hz, 1 H, 6b-H), 3.97 (dd, $J_{5',6'a}$ = 8.2, $J_{6'gem}$ = 11.4 Hz, 1 H, 6′a-H), 3.87 (dd, $J_{5',6'b}$ = 6.2, $J_{6'gem}$ = 11.4 Hz, 1 H, 6′b-H), 3.60−3.45 (m, 3 H, 4-H, 5-H, 1′-H), 3.47 (s, 3 H, OMe), 2.13, 2.12, 2.06, 2.05, 2.04 and 1.96 (6 s, 3, 3, 3, 6, 3, 3 H, 7 × Ac), 2.14−1.94 [m, 2 H, 5-H, 5a′(eq)-H], 1.38 [ddd, $J_{1',5a'(ax)}$ = $J_{5',5a'(ax)}$ = $J_{5a'gem}$ = 13.1 Hz, 1 H, 5a′(ax)-H]. − $C_{28}H_{40}O_{17}$ (648.6): calcd. C 51.85, H 6.22; found C 51.77, H 6.85.

Methyl 4-O-(5a-Carba-β-D-galactopyranosyl)-β-D-glucopyranoside (Methyl 5a′-carba-β-lactoside) (**3**): Compound **33** (19 mg, 0.029 mmol) was treated with methanolic sodium methoxide con-

ventionally. After neutralization, the reaction mixture was evaporated to gvie **3** (10 mg, ≈100%) as a syrup. R_f = 0.24 (chloroform/methanol, 1:2). − $[\alpha]_D^{28}$ = −38 (*c* = 0.3, H_2O). − ^{1}H NMR (270 MHz, D_2O): δ = 4.34 (d, $J_{1,2}$ = 8.1 H, 1 H, 1-H), 4.02 (br d, J_{6gem} = 11.7 Hz, 1 H, 6a-H), 3.99 (br s, 1 H, 4′-H), 3.83 (dd, $J_{5,6b}$ = 3.3, J_{6gem} = 11.7 Hz, 6b-H), 3.67−3.40 (m, 8 H, 3-H, 4-H, 5-H, 1′-H, 2′-H, 3′-H, 6′-H × 2), 3.54 (s, 3 H, OMe), 1.98 [br d, $J_{5a'gem}$ = 12.1 Hz, 1 H, 5a′(eq)-H], 1.68 (m, 1 H, 5′-H), 1.37−1.20 [m, 1 H, 5a′(ax)-H]. − $C_{14}H_{26}O_{10}$ (354.4): calcd. C 47.45, H 7.40; found C 47.17, H 7.70.

Methyl 2-Acetamido-4-O-(2-O-acetyl-3-O-benzyl-4,6-di-O-methanesulfonyl-5a-carba-β-D-glucopyranosyl)-3,6-di-O-benzyl-2-deoxy-β-D-glucopyranoside (**35**): A solution of **26** (47.4 mg, 59.6 μmol) in 60% aqueous acetic acid (0.7 ml) was stirred for 11 h at 55°C, and then evaporated to dryness. The residual crude diol **34** was dissolved in anhydrous pyridine (0.7 ml) and the solution was treated with methanesulfonyl chloride (27.7 μl) for 5 h at room temp. The solution was diluted with ethyl acetate and the solution was washed with 1 M hydrochloric acid, saturated aqueous sodium hydrogen carbonate, water, and dried. The product was chromatographed on silica gel (4 g, acetone/toluene, 1:2) to give **35** (34 mg, 65%) as a syrup. R_f = 0.55 (acetone/toluene, 1:1). − $[\alpha]_D^{23}$ = −14 (*c* = 0.9, $CHCl_3$). − IR (neat): $\tilde{\nu}$ = 3500 cm^{-1} (NH), 1740 (ester), 1650 (amide). − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.42−7.19 (m, 15 H, 3 × Ph), 5.97 (d, $J_{2,NH}$ = 7.7 Hz, 1 H, NH), 5.02 (dd, $J_{1',2'}$ or $J_{2',3'}$ = 9.5 or 9.9 Hz, 1 H, 2′-H), 4.71 and 4.62, 4.71 and 4.48, and 4.64 and 4.58 (3 × 2 d, J_{gem} = 11.7 Hz, each 1 H, 3 × PhCH_2), 4.56 (d, $J_{1,2}$ = 7.9 Hz, 1 H, 1-H), 4.45 (dd, $J_{3',4'}$ or $J_{4',5'}$ = 8.4 or 11.7 Hz, 1 H, 4′-H), 4.16 (m, 2 H, 6′-H × 2), 3.88−3.38 (m, 8 H, 2-H, 3-H, 4-H, 5-H, 6a-H, 6b-H, 1′-H, 3′-H), 3.43 (s, 3 H, OMe), 3.00 and 2.80 (2 s, each 3 H, 2 × OMs), 2.06 [m, 1 H, 5a′(eq)-H], 1.97 and 1.95 (2 s, each 3 H, 2 × OAc), 1.73 (m, 1 H, 5′-H), 1.32 [m, 1 H, 5a′(ax)-H]. − $C_{41}H_{53}NO_{15}S_2$ (864.0): calcd. C 57.00, H 6.18, N 1.62; found C 56.76, H 6.30, N 1.91.

Methyl 2-Acetamido-3,6-di-O-benzyl-2-deoxy-4-O-(2,4,6-tri-O-acetyl-3-O-benzyl-5a-carba-β-D-galactopyranosyl)-β-D-glucopyranoside (**36**): A mixture of **35** (20 mg, 23 μmol), anhydr. sodium acetate (75 mg, 40 molar equiv), and aqueous 80% DMF (0.4 ml) was stirred for 3 d at 120°C. The mixture was then diluted with ethyl acetate (50 ml), washed with saline, and dried. Evaporation of the solvent left the residue which was acetylated with acetic anhydride (0.5 ml) and pyridine (1 ml) for 5 h at room temp. The product was chromatographed on silica gel (2 g, butanone/hexane, 1:2) to give **36** (15 mg, 82%) as a white solid. R_f = 0.53 (acetone/hexane, 1:1). − $[\alpha]_D^{22}$ = −17 (*c* = 0.33, $CHCl_3$), − IR (neat): $\tilde{\nu}$ = 3500 cm^{-1} (NH), 1740 (ester), 1650 (amide). − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.38−7.17 (m, 15 H, 3 × Ph), 5.92 (d, $J_{2,NH}$ = 8.8 Hz, 1 H, NH), 5.52 (br t, *J* = 3 Hz, 1 H, 4′-H), 5.09 (dd, $J_{1',2'}$ = 9.9, $J_{2',3'}$ = 9.9 Hz, 1 H, 2′-H), 4.68 and 4.36 (2 d, J_{gem} = 12.1 Hz, each 2 H), 4.61 and 4.46 (2 d, J_{gem} = 12.1 Hz, each 1 H, 3 × PhCH_2), 4.55 (d, $J_{1,2}$ = 7.9 Hz, 1 H, 1-H), 3.88−3.31 (m, 9 H, 2-H, 3-H, 4-H, 5-H, 6-H × 2, 1′-H, 6′-H × 2), 3.43 (s, 3 H, OMe), 3.20 (dd, $J_{2',3'}$ = 9.9, $J_{3',4'}$ = 3.1 Hz, 1 H, 3′-H), 2.09, 2.06, 2.01, and 1.97 (4 s, each 3 H, 4 × Ac), 1.83 (m, 1 H, 5′-H), 1.61 [m, 1 H, 5a′(eq)-H], 1.34 [m, 1 H, 5a′(ax)-H]. After elucidation of the structure based on the ^{1}H-NMR spectrum, this compound was used directly in the next reaction.

Methyl 2-Acetamido-3,6-di-O-acetyl-4-O-(2,3,4,6-tetra-O-acetyl-5a-carba-β-D-galactopyranosyl)-2-deoxy-β-D-glucopyranoside (**37**): A solution of **36** (15 mg, 19 μmol) in ethanol (1 ml) was hydrogenated in the presence of 10% Pd/C and one drop of 1 M hydrochloric acid for 3.5 h at room temp. The mixture was filtered and the filtrate was evaporated and the residue was acetylated with acetic anhydride in pyridine conventionally. The product was chromatographed on silica gel (1.5 g, acetone/toluene, 2:3) to give **37** (7 mg, 57%) as a white powder. R_f = 0.30 (acetone/hexane, 1:1). − $[\alpha]_D^{23}$ = −18 (*c* = 0.3 in $CHCl_3$). − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 5.65 (d, $J_{2,NH}$ = 8.4 Hz, 1 H, NH), 5.43 (br s, 1 H, 4′-H), 5.22 (dd, $J_{1',2'}$ = $J_{2',3'}$ = 10.5 Hz, 1 H, 2′-H), 4.91 (dd, $J_{2,3}$ = $J_{3,4}$ = 9.2 Hz, 1 H, 3-H), 4.79 (dd, $J_{2',3'}$ = 10.5, $J_{3',4'}$ = Hz, 1 H, 3′-H), 4.56 (dd, $J_{5,6}$ = 2.6, J_{6gem} = 11.4 Hz, 1 H, 6a-H), 4.33 (d, $J_{1,2}$ = 7.0 Hz, 1 H, 1-H), 4.21 (dd, $J_{5,6b}$ = 5.0, J_{6gem} = 11.4 Hz, 1 H, 6b-H), 4.07 (ddd, $J_{1,2}$ = 7.0, $J_{2,3}$ = 9.2, $J_{2,NH}$ = 8.4 Hz, 1 H, 2-H), 4.01−3.87 (m, 2 H, 6′-H × 2), 3.55−3.47 (m, 3 H, 4-H, 5-H, 1′-H), 3.44 (s, 3 H, OMe), 2.11 (m, 1 H, 5′-H), 2.13, 2.11, 2.08, 2.07, 2.06, 1.98, 1.96 (7 s, each 3 H, 7 × Ac), 1.64 [m, 1 H, 5a′(eq)-H], 1.43 [m, 1 H, 5a′(ax)-H]. − $C_{28}H_{41}NO_{16}$ (647.6): calcd. C 51.93, H 6.38, N 2.16; found C 52.10, H 6.72, N 2.15.

Methyl 2-Acetamido-4-O-(5a-carba-β-D-galactopyranosyl)-2-deoxy-β-D-glucopyranoside (Methyl N-acetyl-5a′-carba-β-lactosaminide) (**4**): Compound **37** (5.5 mg, 8.5 μmol) was treated with methanolic 1 M sodium methoxide (10 μl) in methanol (0.1 ml) for 8 h at room temp. After neutralization with Dowex 50W × 2 (H^+) resin, the filtrate was evaporated and the residue was crystallized from ethanol to give **4** (2.6 mg, 77%) as a hygroscopic powder. R_f = 0.40 (chloroform/methanol, 1:1). − IR (neat): $\tilde{\nu}$ = 3500 cm^{-1} (OH), 1650 (amide). − $[\alpha]_D^{21}$ = + 24 (*c* = 0.1 in $CHCl_3$). − ^{1}H NMR (270 MHz, D_2O): δ = 4.29 (d, $J_{1,2}$ = 8.4 Hz, 1 H, 1-H), 3.94−3.72 (m, 2 H, 6a-H, 4′-H), 3.75 (dd, $J_{5,6b}$ = 3.0, J_{6gem} = 12.5 Hz, 1 H, 6b-H), 3.57−3.21 (9 H, 2-H, 3-H, 4-H, 5-H, 1′-H, 2′-H, 3′-H, 6′-H × 2), 3.37 (s, 3 H, OMe), 2.09 (s, 3 H, Ac), 1.89 (m, 1 H, 5′-H), 1.62−1.53 [m, 1 H, 5a′(eq)-H], 1.19−1.12 [m, 1 H, 5a′(ax)-H].

Methyl 2-Acetamido-3,6-di-O-benzyl-2-deoxy-β-D-galactopyranoside (**11**): To a solution of **10** (215 mg, 0.052 mmol) in DMSO (6.5 ml) was added acetic anhydride (1.5 ml), and the mixture was stirred for 20 h at room temp. The mixture was diluted with chloroform (30 ml), and the solution was washed thoroughly with saline, dried, and evaporated to give a crude ketone. Without further purification, the ketone was treated with 1 M L-selectride-THF (2.1 ml, ≈ 4 molar equiv.) in THF (4.3 ml) and the mixture was allowed to stand in a refrigerator for 7 h. After usual treatment with aq. saturated ammonium chloride and magnesium sulfate, the mixture was filtered through Celite bed and the filtrate was evaporated. The products were chromatographed on silica gel (20 g, acetone/toluene, 1:4) to give **10** (57 mg, 27%) and **11** (104 mg, 49%) as a white powder. R_f = 0.33 (acetone/toluene, 1:2). − IR (neat): $\tilde{\nu}$ = 3500 cm^{-1} (OH and NH), 1650 (amide). − $[\alpha]_D^{26}$ = + 16.2 (*c* = 0.42 in $CHCl_3$). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38−7.25 (m, 10 H, 2 × Ph), 5.59 (d, $J_{2,NH}$ = 7.1 Hz, 1 H, NH), 4.47 (d, $J_{1,2}$ = 8.3 Hz, 1 H, 1-H), 4.68 and 4.50 (2 d, *J* = 11.7 Hz, each 1 H, PhCH_2), 4.59 (s, 2 H, PhCH_2), 4.21 (dd, $J_{2,3}$ = 10.1, $J_{3,4}$ = 2.9 Hz, 1 H, 3-H), 4.08 (br t, $J_{3,4}$ = $J_{4,5}$ = 2.9 Hz, 1 H, 4-H), 3.83−3.65 (m, 3 H, H-5, H-6a, H-6b), 3.49 (s, 3 H, OMe), 3.39 (ddd, $J_{1,2}$ = 8.3, $J_{2,3}$ = 10.1, $J_{2,NH}$ = 7.1 Hz, 1 H, 2-H), 1.92 (s, 3 H, Ac).

Methyl 2-Acetamido-4-O-acetyl-3,6-di-O-benzyl-2-deoxy-β-D-galactopyranoside (**12**): Compound **11** (20 mg, 48 μmol) was treated with acetic anhydride and pyridine conventionally. The product was chromatographed on silica gel (2 g, ethyl acetate/toluene, 1:5) to give **12** (21 mg, 97%) as a white powder. R_f = 0.30 (acetone/toluene, 1:3). − IR (neat): $\tilde{\nu}$ = 3500 cm^{-1} (NH), 1740 (ester), 1650 (amide). − $[\alpha]_D^{26}$ = + 26.3 (*c* = 1.0 in $CHCl_3$). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40−7.23 (m, 10 H, 2 × Ph), 5.62 (br t, $J_{3,4}$ = $J_{4,5}$ = 3.2 Hz, 1 H, 4-H), 5.53 (br d, $J_{2,NH}$ = 7.6 Hz, 1 H, NH), 4.92 (d,

$J_{1,2}$ = 8.3 Hz, 1 H, 1-H), 4.72 and 4.34 (2 d, J = 11.0 Hz, each 1 H, PhCH_2), 4.58 and 4.48 (2 d, J = 12.0 Hz, each 1 H, PhCH_2), 4.30 (dd, $J_{2,3}$ = 10.7, $J_{3,4}$ = 3.2 Hz, 1 H, 3-H), 3.85 (m, 1 H, 5-H), 3.62−3.52 (m, 2 H, H-6a, H-6b), 3.49 (s, 3 H, OMe), 3.31 (ddd, $J_{1,2}$ = 8.3, $J_{2,3}$ = 10.7, $J_{2,NH}$ = 7.6 Hz, 1 H, 2-H), 2.60 (s, 3 H, OAc), 1.90 (s, 3 H, NAc). − $C_{25}H_{31}NO_7$ (457.5): calcd. C 65.62, H 6.83, N 3.06; found C 65.66, H 6.87, N 3.01.

Methyl 2-Acetamido-4-azido-3,6-di-O-benzyl-2,4-dideoxy-β-D-glucopyranoside (**13**): To a solution of **12** (77.2 mg, 18.6 μmol) in pyridine (1.5 ml) was added methanesulfonyl chloride (43 μl, 56 μmol) at 0°C, and the mixture was stirred for 30 min at room temp. After dilution with chloroform (30 ml), the solution was washed with 1 M hydrochloric acid, aqueous satd. sodium hydrogen carbonate, and water, dried, and evaporated. The mesylate was roughly purified by a silica gel column (2.5 g, acetone/toluene, 1:4). A mixture of the mesylate and sodium azide (0.12 g) in aqueous 80% DMF (3 ml) was stirred for 32 h at 100°C. After the usual processing, the product was chromatographed on silica gel (7 g, acetone/toluene, 1:4) to give **13** (65 mg, 79%) as a white powder. R_f = 0.55 (acetone/toluene, 1:1). − IR (neat): $\tilde{\nu}$ = 3500 cm^{-1} (NH), 2100 (N_3), 1650 (amide). − $[\alpha]_D^{26}$ = + 53.4 (c = 0.38 in $CHCl_3$). − ^1H NMR (300 MHz, $CDCl_3$): δ = 7.34 (m, 10 H, 2 × Ph), 5.57 (d, $J_{2,NH}$ = 7.1 Hz, 1 H, NH), 4.87 and 4.62 (2 d, J_{gem} = 11.5 Hz, each 1 H, PhCH_2), 4.82 (d, $J_{1,2}$ = 8.0 Hz, 1 H, 1-H), 4.66 and 4.56 (2 d, J_{gem} = 12.0 Hz, each 1 H, PhCH_2), 4.15 (dd, $J_{2,3}$ = 9.9, $J_{3,4}$ = 9.5 Hz, 1 H, 3-H), 3.73 (m, 2 H, 6-H × 2), 3.63 (dd, $J_{3,4}$ = 9.5, $J_{4,5}$ = 10.5 Hz, 1 H, 4-H), 3.47 (s, 3 H, OMe), 3.39 (m, 1 H, 5-H), 3.16 (ddd, $J_{1,2}$ = 8.0, $J_{2,3}$ = 9.9, $J_{2,NH}$ = 7.1 Hz, 1 H, 2-H), 1.88 (s, 3 H, Ac).− $C_{23}H_{28}N_4O_5$ (440.5): calcd. C 62.71, H 6.41, N 12.72; found C 62.78, H 6.53, N 12.94.

Methyl 2-Acetamido-4-amino-2,4-dideoxy-β-D-glucopyranoside (**14**): A solution of **13** (5.0 mg, 11 μmol) in ethanol (2 ml) was hydrogenolyzed in the presence of 10% Pd/C (5 mg) under atmospheric hydrogen pressure for 8.5 h at room temp. The catalyst was removed by filtration and the filtrate was evaporated. The residue was chromatographed on a column of Dowex 50W × 2 (H^+) resin (2.5 g), and it was eluted with MeOH/H_2O (1:1) and then 28% ammonia/MeOH (1:27) to give (2.1 mg, 81%) as a white powder. R_f = 0.20 (H_2O/CH_3CN, 1:3). − IR (neat): $\tilde{\nu}$ = 3450 cm^{-1} (NH, OH), 1650 (amide). − $[\alpha]_D^{22}$ = −28 (c = 0.10 in H_2O). − ^1H NMR (300 MHz, D_2O): δ = 4.42 (d, $J_{1,2}$ = 8.2 Hz, 1 H, 1-H), 3.90 (dd, $J_{5,6a}$ = 2.4, J_{6gem} = 12.4 Hz, 1 H, 6a-H), 3.74 (dd, 1 H, $J_{5,6b}$ = 6.3 Hz, J_{6gem} = 12.4 Hz, 1 H, 6b-H), 3.66 (dd, $J_{1,2}$ = 8.2, $J_{2,3}$ = 10.5 Hz, 1 H, 2-H), 3.49 (s, 3 H, OMe), 3.39 (dd, $J_{2,3}$ = 10.5, $J_{3,4}$ = 9.7 Hz, 1 H, 3-H), 3.44−3.38 (m, 1 H, 5-H), 2.76 (dd, $J_{3,4}$ = 9.7, $J_{4,5}$ = 9.7 Hz, 1 H, 4-H), 2.02 (s, 3 H, Ac).

Methyl 2-Acetamido-3,6-di-O-acetyl-4-(2-O-acetyl-6-O-benzyl-3,4-O-isopropylidene-5a-carba-β-D-galactopyranosyl)amino-2,4-dideoxy-β-D-glucopyranoside (**38**): A mixture of 1,2-anhydro-6-*O*-benzyl-3,4-*O*-isopropylidene-5a-carba-α-D-galactopyranose[11] (**6**, 144 mg, 0.496 mmol) and the free base (**14**, 107 mg, 0.458 mmol) in 2-propanol (1.0 ml) was heated in a sealed tube for 15 d at 120°C, and then concentrated. After conventional acetylation, the products were chromatographed on silica gel (30 g, acetone/toluene, 1:3) to give **38** (75.3 mg, 25%) as a syrup. R_f = 0.26 (acetone/ethyl acetate, 1:2). − $[\alpha]_D^{23}$ = + 13 (c = 0.9 in $CHCl_3$). − ^1H NMR (270 MHz, $CDCl_3$): δ = 7.49 (m, 5 H, Ph), 5.62 (m, 1 H, NH), 4.76 (dd, $J_{1',2'}$ = 10.8, $J_{2',3'}$ = 7.7 Hz, 1 H, 2′-H), 4.74 (dd, $J_{2,3}$ = $J_{3,4}$ = 9.9 Hz, 1 H, 3-H), 4.56 and 4.51 (2 d, J_{gem} = 12.1 Hz, each 1 H, PhCH_2), 4.53 (m, 1 H, 6a-H), 4.31 (d, $J_{1,2}$ = 8.4 Hz, 1 H, 1-H), 4.26 (dd, $J_{3',4'}$ = $J_{4',5'}$ = 5.1 Hz, 1 H, 4′-H), 4.18 (dd, $J_{5,6b}$ = 5.7, J_{6gem} = 11.5 Hz, 1 H, 6b-H), 3.95 (dd, $J_{2',3'}$ = 7.7, $J_{3',4'}$ = 5.1 Hz, 1 H, 3′-H), 3.44 (s, 3 H, OMe), 3.33 (m, 1 H, 5-H), 2.69 (dd, $J_{3,4}$ = $J_{4,5}$ = 9.9 Hz, 1 H, 4-H), 2.27 (m, 1 H, 1′-H), 2.09, 2.08, 2.04, and 1.94 (4 s, each 3 H, 4 × Ac), 2.09−1.94 [m, 2 H, 5′-H, 5a′(eq)-H], 1.05 [ddd, $J_{1',5a'(ax)}$ = $J_{5a'gem}$ 11.7 Hz, 1 H, 5a′(ax)-H]. − $C_{32}H_{46}N_2O_{12}\cdot 0.5H_2O$ (659.7): calcd. C 58.26, H 7.18, N 4.25; found C 58.15, H 7.43, N 4.32.

Methyl 2-Acetamido-3,6-di-O-acetyl-2,4-dideoxy-4-(2,3,4,6-tetra-O-acetyl-5a-carba-β-D-galactopyranosyl)amino-β-D-glucopyranoside (**39**): A mixture of **38** (44 mg, 0.068 mmol) and aqueous 80% acetic acid (2 ml) was stirred for 30 min at 80°C and then evaporated. The residue was dissolved in methanol (2 ml) and the solution was hydrogenated in the presence of 10% Pd/C and trace of hydrochloric acid for 30 min at room temp. The product was acetylated conventionally and purified by a silica gel column (3 g, acetone/toluene, 2:3) to give **39** (20 mg, 43%) as a syrup. R_f = 0.56 (acetone/toluene, 1:1). − $[\alpha]_D^{23}$ = −4.3 (c = 0.8 in $CHCl_3$). − IR (neat): $\tilde{\nu}$ = 3450 cm^{-1} (OH), 1740 (ester), 1670 (amide). − ^1H NMR (270 MHz, $CDCl_3$): δ = 5.91 (br d, 1 H, NH), 5.46 (br s, 1 H, 4′-H), 5.01 (dd, $J_{1',2'}$ = $J_{2',3'}$ = 10.3 Hz, 1 H, 2′-H), 4.81 (dd, $J_{2',3'}$ = 10.3, $J_{3',4'}$ = 2.9 Hz, 1 H, 3′-H), 4.73 (dd, $J_{2,3}$ = $J_{3,4}$ = 9.9 Hz, 1 H, 3-H), 4.58 (dd, $J_{5,6a}$ = 1.8, J_{6gem} = 11.7 Hz, 1 H, 6a-H), 4.34 (d, $J_{1,2}$ = 8.4 Hz, 1 H, 1-H), 4.15 (dd, $J_{5,6b}$ = 5.9, J_{6gem} = 11.7 Hz, 1 H, 6b-H), 4.04−3.94 (m, 2 H, 2-H, 6′a-H), 3.86 (dd, $J_{5',6'b}$ = 5.9, $J_{6'gem}$ = 11.0 Hz, 6′b-H), 3.45 (s, 3 H, OMe), 3.33 (m, 1 H, 5-H), 2.70 (dd, $J_{3,4}$ = $J_{4,5}$ = 9.9 Hz, 1 H, 4-H), 2.51 (m, 1 H, 1′-H), 2.10, 2.08, 2.05, and 1.94 (4 s, 3, 9, 3, 6 H, 7 × Ac), 2.10−1.94 [m, 2 H, 5′-H, 5a′(eq)-H], 1.23 [m, 1 H, 5a′(ax)-H]. − $C_{28}H_{42}N_2O_{15}$ (646.6): calcd. C 52.01, H 6.55, N 4.33; found C 52.65, H 6.95, N 4.30.

Methyl 2-Acetamido-4-(5a-carba-β-D-galactopyranosyl)amino-2,4-dideoxy-β-D-glucopyranoside (Methyl N-Acetyl-5a′-carba-β-lactosaminide) (**5**): Compound **39** (17.9 mg, 28 μmol) was treated with methanolic sodium methoxide in the usual manner and the product was purified by a resin column as described for the preparation of **3** to give **5** (9.8 mg, 90%) as a hygroscopic syrup. R_f = 0.17 (chloroform/methanol, 1:1). − $[\alpha]_D^{23}$ = −56 (c = 0.45 in MeOH). − ^1H NMR (270 MHz, D_2O): δ = 4.40 (d, $J_{1,2}$ = 8.4 Hz, 1 H, 1-H), 4.04−3.99 (m, 2 H, 6a-H, 4′-H), 3.80 (dd, $J_{5,6b}$ = 5.5, J_{6gem} = 12.1 Hz, 6b-H), 3.68 (dd, $J_{1,2}$ = 8.4, $J_{2,3}$ = 10.3 Hz, 1 H, 2-H), 3.49 (s, 3 H, OMe), 2.66 (dd, $J_{3,4}$ = $J_{4,5}$ = 9.9 Hz, 1 H, 4-H), 2.57 (m, 1 H, 1′-H), 2.03 (s, 3 H, Ac), 1.87 [br d, $J_{5a'gem}$ = 11.7 Hz, 1 H, 5a′(eq)-H], 1.73 (m, 1 H, 5′-H), 1.14 [ddd, $J_{1',5a'(ax)}$ = $J_{5',5a'(ax)}$ = $J_{5a'gem}$ = 11.7 Hz, 1 H, 5a′(ax)-H]. −$C_{16}H_{30}N_2O_9\cdot H_2O$ (412.4): calcd. C 46.59, H 7.82, N 6.79; found C 46.88, H 7.79, N 6.88.

Methyl 2-Acetamido-3,6-di-O-acetyl-2-deoxy-4-O-(2,3,4,6-tetra-O-acetyl-5a-carba-β-D-mannopyranosyl)-β-D-glucopyranoside (**40**): A solution of **28** (30 mg, 40 μmol) in a mixture of ethanol (1 ml) and ethyl acetate (1 ml) was hydrogenated in the presence of catalytic amount of 10% Pd/C for 4 h at room temp. The catalyst was removed by filtration and the filtrate was evaporated. The residue was acetylated conventionally to give, after chromatogreaphy on silica gel (3 g, acetone/toluene, 1:3), **40** (21 mg, 83%) as a powder. R_f = 0.54 (ethanol/toluene, 1:5). − $[\alpha]_D^{23}$ = −9 (c = 0.6 in $CHCl_3$). − IR (neat): $\tilde{\nu}$ = 3400 cm^{-1} (NH), 1740 (ester), 1650 (amide). − ^1H NMR (270 MHz, $CDCl_3$): δ = 5.56 (br s, 1 H, 2′-H), 5.43 (d, $J_{2,NH}$ = 9.2 Hz, 1 H, NH), 5.13 (dd, $J_{3',4'}$ = $J_{4',5'}$ = 10.3, 1 H, 4′-H), 5.07 (dd, $J_{2,3}$ = 10.3, $J_{3,4}$ = 9.0 Hz, 1 H, 3-H), 4.77 (dd, $J_{2',3'}$ = 2.8, $J_{3',4'}$ = 10.3 Hz, 1 H, 3′-H), 4.47 (2 d, $J_{5,6a}$ = 2.2, J_{6gem} = 12.4 Hz, 1 H, 6a-H), 4.36 (d, $J_{1,2}$ = 8.1 Hz, 1 H, 1-H), 4.00−3.93 (m, 4 H, 2-H, 6b-H, 6′a-H, 6′b-H), 3.75 (m, 1 H, 1′-H), 3.70 (dd, $J_{3,4}$ = 9.0, $J_{4,5}$ = 9.2 Hz, 1 H, 4-H), 3.49 (m, 1 H, 5-H), 3.45 (s, 3 H, OMe), 2.35, 2.13, 2.12, 2.07, 2.03, 1.96, and 1.95 (7 s, each 3 H,

7 × Ac), 1.89−1.81 [m, 2 H, 5′-H, 5a′(eq)-H], 1.75 [m, 1 H, 5a′(ax)-H]. − $C_{28}H_{41}NO_{16}$ (647.6): calcd. C 51.93, H 6.38, N 2.16. found: C, 51.68; H, 6.63; N, 1.90.

Methyl 2-Acetamido-4-O-(5a-carba-β-D-mannopyranosyl)-2-deoxy-β-D-glucopyranoside (**41**): Compound **40** (11 mg, 17 μmol) was treated with methanolic sodium methoxide as described in the preparation of **4** to give **41** (≈ 6 mg, quantitative) as a white powder. − $[\alpha]_D^{22}$ = − 14 (*c* = 0.3 in H_2O). − ^{1}H NMR (270 MHz, D_2O): δ = 4.29 (d, 1 H, $J_{1,2}$ = 8.1 Hz, 1 H, 1-H), 4.06 (br s, 1 H, 2′-H), 3.85−3.28 (m, 12 H, 1-H, 2-H, 3-H, 4-H, 5-H, 6a-H, 6b-H, 1′-H, 3′-H, 4′-H, 6′a-H, 6′b-H), 3.36 (s, 3 H, OMe), 1.90 (s, 3 H, Ac), 1.85 (m, 1 H, 5′-H), 1.41 [m, 2 H, 5a′(ax)-H, 5a′(eq)-H].

Methyl 2-Acetamido-3,6-di-O-benzyl-4-O-(3-O-benzyl-4,6-O-benzylidene-2-O-methanesulfonyl-5a-carba-β-D-mannopyranosyl)-2-deoxy-β-D-glucopyranoside (**42**): A solution of **28** (62 mg, 82 μmol) in pyridine (1.2 ml) was treated with methanesulfonyl chloride (27 μl, 4 molar equiv) in the presence of catalytic amount of 4-dimethylaminopyridine for 30 h at room temp. The solution was diluted with ethyl acetate, washed with 1 M hydrochloric acid , saturated sodium hydrogen carbonate, and water. The solution was evaporated and the residue was chromatographed on silica gel (7 g, acetone/toluene, 1:3) to give **42** (40 mg, 77%), together with **28** (14 mg) recovered. R_f = 0.58 (acetone/toluene, 1:1). − $[\alpha]_D^{22}$ = + 45 (*c* = 0.5 in $CHCl_3$). − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.30 (4 s, 20 H, 4 × Ph), 5.63 (d, $J_{2,NH}$ = 7.3 Hz, 1 H, NH), 5.53 (s, 1 H, PhC*H*), 5.13 (br s, 1 H, 2′-H), 4.56 (d, $J_{1,2}$ = 7.0 Hz, 1 H, 1-H), 4.76 and 4.67 (2 d, J_{gem} = 12.1 Hz, each 1 H), 4.74 and 4.65 (2 d, J_{gem} = 11.7 Hz, each 1 H), and 4.64 and 4.45 (2 d, J_{gem} = 12.1 Hz, each 1 H) (3 × PhCH_2), 3.96−3.49 (m, 10 H, 2-H, 3-H, 4-H, 5-H, 6a-H, 6b-H, 1′-H, 4′-H, 6′a-H, 6′b-H), 3.46 (s, 3 H, OMe), 3.05 (s, 3 H, Ms), 1.87 (s, 3 H, Ac), 1.72−1.60 [m, 2 H, 5′-H, 5a′(eq)-H], 1.35−1.23 [m, 1 H, 5a′(ax)-H]. This compound was without further purification used in the next reaction.

Methyl 2-Acetamido-4-O-(2-azido-3-O-benzyl-2-deoxy-4,6-O-benzylidene-5a-carba-β-D-glucopyranosyl)-3,6-di-O-benzyl-2-deoxy-β-D-glucopyranoside (**43**): A mixture of the mesylate **42** (68 mg, 82 μmol), aqueous 80% DMF (1.4 ml), and sodium azide (53 mg, 10 molar equiv) was stirred for 19 h at 120°C. The reaction mixture was diluted with ethyl acetate (10 ml), washed with water, and dried. The solution was evaporated and the residue was chromatographed on silica gel (8 g, acetone/toluene, 2:5) to give **43** (36 mg, 57%) as a syrup. R_f = 0.68 (acetone/toluene, 1:1). − $[\alpha]_D^{21}$ = −46 (*c* = 0.5 in $CHCl_3$). − IR (neat): $\tilde{\nu}$ = 3300 cm^{-1} (NH), 2100 (N_3), 1680 (amide). − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 5.54 (d, $J_{2,NH}$ = 7.7 Hz, 1 H, NH), 4.89 and 4.73 (2 d, J_{gem} = 11.0 Hz, each 1 H, PhCH_2), 4.70 (d, $J_{1,2}$ = 7.3 Hz, 1 H, 1-H), 4.69 and 4.53 (2 d, J_{gem} = 11.9 Hz, each 1 H) and 4.67 (br s, 2 H) (2 × PhCH_2), 4.00 (dd, $J_{5,6a}$ = 3.7, J_{6gem} = 10.8 Hz, 1 H, 6a-H), 3.92 (dd, $J_{1',2'}$ = 9.2, $J_{2',3'}$ = 8.4 Hz, 1 H, 2′-H), 3.89 (dd, $J_{5,6b}$ = 4.4, J_{6gem} = 10.8 Hz, 1 H, 6b-H), 3.84 (dd, $J_{3',4'}$ = 9.2, $J_{4',5'}$ = 9.2 Hz, 1 H, 4′-H), 3.65 (dd, $J_{2',3'}$ = 8.4 Hz, $J_{3',4'}$ = 9.2 Hz, 1 H, 3′-H), 3.56−3.21 (m, 7 H, 2-H, 3-H, 4-H, 5-H, 1′-H, 6a′-H, 6′b-H), 3.48 (s, 3 H, Me), 1.87 (s, 3 H, Ac), 1.84−1.78 [m, 1 H, 5a′(eq)-H], 1.39−1.32 (m, 1 H, H-5′), 0.69 [ddd, $J_{1',5a'(ax)}$ = $J_{5',5a'(ax)}$ = 10.6, $J_{5a'gem}$ = 13.0, Hz, 1 H, 5a′(ax)-H]. − $C_{44}H_{50}N_4O_9$ (778.9): calcd. C 67.85; H 6.47; N 7.19; found C 67.72, H 6.35, N 7.03.

Methyl 2-Acetamido-4-O-(2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-5a-carba-β-D-glucopyranosyl)-3,6-di-O-acetyl-2-deoxy-β-D-glucopyranoside (**44**): A solution of **43** (36 mg, 47 μmol) in a mixture of ethanol (1.5 ml) and ethyl acetate (1.5 ml) was hydrogenated in the presence of 10% Pd/C for 30 h at room temp. The catalyst was removed by filtration and the filtrate was evaporated. The residue was acetylated with acetic anhydride in pyridine conventionally to give, after chromatography on silica gel (2 g, acetone/toluene, 1:1), **44** (16 mg, 54%) as a white powder. R_f = 0.44 (ethanol/toluene, 1:5). − $[\alpha]_D^{22}$ = −21 (*c* = 0.2 in $CHCl_3$). − IR (neat): $\tilde{\nu}$ = 3300 cm^{-1} (NH), 1740 (ester), 1660 (amide). − ^{1}H NMR (270 MHz): δ = 6.02 (m, 2 H, NH × 2), 5.02 (dd, $J_{3',4'}$ = $J_{4',5'}$ = 10.1 Hz, 1 H, 4′-H), 4.92 (dd, $J_{2',3'}$ = $J_{3',4'}$ = 10.1 Hz, 1 H, 3′-H), 4.89 (dd, $J_{2,3}$ = $J_{3,4}$ = 10.3 Hz, 1 H, 3-H), 4.45−4.37 (m, 2 H, 6a-H, 6b-H), 4.33 (d, 1 H, $J_{1,2}$ = 7.0 Hz, 1 H, 1-H), 4.17−3.92 (m, 4 H, 2-H, 2′-H, 6′a- H, 6′b-H), 3.62 (m, 1 H, 5-H), 3.49 (dd, $J_{3,4}$ = $J_{4,5}$ = 10.3 Hz, 1 H, 4-H), 3.45 (s, 3 H, OMe), 3.34 (m, 1 H, 1′-H), 2.28 [ddd, $J_{1',5a'(eq)}$ = $J_{5',5a'(eq)}$ = 4.0, $J_{5a'gem}$ = 11.7 Hz, 1 H, 5a′(eq)-H], 2.13, 2.07, 2.06, 2.02, 2.00, 1.98, and 1.96 (7 s, each 3 H, 7 × Ac), 1.36 [ddd, $J_{1',5a'(ax)}$ = $J_{5',5a'(ax)}$ = $J_{5a'gem}$ = 11.7 Hz, 1 H, 5a′(ax)-H]. − $C_{28}H_{42}N_2O_{15}$ (646.7): calcd. C 52.01, H 6.55, N 4.33; found C 52.22, H 6.70, N 4.26.

Methyl 2-Acetamido-4-O-(2-acetamido-2-deoxy-5a-carba-β-D-glucopyranosyl)-2-deoxy-β-D-glucopyranoside (**45**): Compound **44** (16 mg, 25 μmol) was treated with 1 M methanolic sodium methoxide (16 μl) in methanol (0.16 ml) for 4 h at room temp. After neutralization with Dowex 50W × 2 (H^+) resin, the solution was evaporated and the residue was crystallized from ethanol to give **45** (3.6 mg, 33%) as hygroscopic crystals (ethanol). The mother liquor was chromatographed on silica gel (methanol/chlorofrom, 2:3) to give additional crystals (4.5 mg, total ≈ 80%). − $[\alpha]_D^{20}$ = −33 (*c* = 0.18 in $CHCl_3$). − IR (neat): $\tilde{\nu}$ = 3300 cm^{-1} (NH), 1654, 1627 (amide). − ^{1}H NMR (270 MHz, D_2O): δ = 4.26 (d, $J_{1,2}$ = 8.4 Hz, 1 H, 1-H), 3.78 (br d, J_{6gem} 11.4 Hz, 1 H, 6a-H), 3.66−3.16 (m, 11 H, 2-H, 3-H, 4-H, 5-H, 6b-H, 1′-H, 2′-H, 3′-H, 4′-H, 6′a-H, 6′b-H), 3.36 (s, 3 H, OMe), 2.18 (m, 1 H, 5′-H), 1.93 and 1.89 (2 s, each 3 H, 2 × Ac), 1.40 [m, 1 H, 5a′(eq)-H], 1.15 [m, 1 H, 5a′(ax)-H].

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