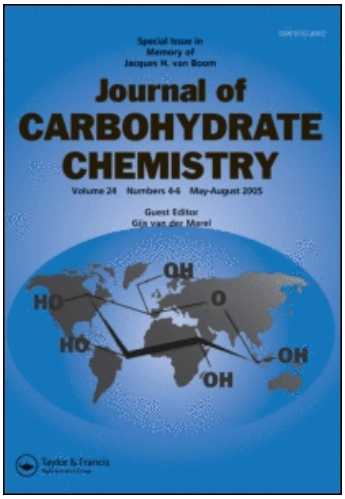

Journal of Carbohydrate Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713617200

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Online publication date: 30 November 2001

To cite this Article Viodé, Cécile and Vogel, Pierre(2001) 'SYNTHESIS OF THE *C*-DISACCHARIDE α-*C*(1→3)-L-FUCOPYRANOSIDE OF *N*-ACETYLGALACTOSAMINE[1]', Journal of Carbohydrate Chemistry, 20: 7, 733 — 746
To link to this Article: DOI: 10.1081/CAR-100108286
URL: http://dx.doi.org/10.1081/CAR-100108286

J. CARBOHYDRATE CHEMISTRY, 20(7&8), 733–746 (2001)

SYNTHESIS OF THE *C*-DISACCHARIDE α-*C*(1→3)-L-FUCOPYRANOSIDE OF *N*-ACETYLGALACTOSAMINE[1]

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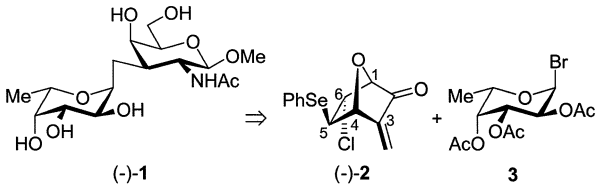
ABSTRACT

Radical *C*-glycosidation of racemic 5-*exo*-benzeneselenyl-6-*endo*-chloro-3-methylidene-7-oxabicyclo[2.2.1]heptan-2-one ((±)-**2**) with α-acetobromofucose (**3**) provided a mixture of α-*C*-fucosides that were reduced with $NaBH_4$ to give two diastereomeric alcohols that were separated readily. One of them ((−)-**6**) was converted into (−)-methyl 2-acetamido-4-*O*-acetyl-2,3-dideoxy-3-*C*-(3′,4′,5′-tri-*O*-acetyl-2′,6′-anhydro-1′,7′-dideoxy-α-L-*glycero*-D-*galacto*-heptitol-1′-*C*-yl)-α -D-galactopyranuronate ((−)-**11**) and then into (−)-methyl 2-acetamido-2,3-dideoxy-3-*C*-(2′,6′-anhydro-1′,7′-dideoxy-α-L-*glycero*-D-*galacto*-heptitol-1′-*C*-yl)-β -D-galactopyranoside ((−)-**1**), a new α-*C*(1→3)-L-fucopyranoside of *N*-acetylgalactosamine. Its ^1H NMR data shows that this *C*-disaccharide (α-L-Fuc*p*-(1→3)CH_2-β-D-GalNAc-OMe) adopts a major conformation in solution similar to that expected for the corresponding *O*-linked disaccharide, i.e., with antiperiplanar σ(C-3′,C-2′) and σ(C-1′,C-3) bonds.

INTRODUCTION

Carbohydrate mimetics are potentially useful molecular tools for biology,[3] and may become leads for drug discovery.[4] In particular, *C*-linked disaccharides and oligosaccharides containing them offer the advantage of being resistant to acidic and enzymatic hydrolysis.[5] They are potential inhibitors of glycosidases and glycosyltransferases.[6] They represent non-hydrolyzable epitopes.[7] Kishi and co-workers have prepared blood group mimics involving α-*C*(1→2)-L-fucopyranosides of D-galactopyranosides and analogs.[8] The first examples of α-*C*(1→3)-L-



Scheme 1.

fucopyranosides have been prepared by Sinaÿ and co-workers; they did not describe the corresponding non-protected derivatives.[9] Applying our first method to the synthesis of *C*-disaccharides[10] based on Giese's radical *C*-glycosidation[11] of 3-methylidene-7-oxabicyclo[2.2.1]heptan-2-one derivatives (Scheme 1) we have now obtained the disaccharide mimic (−)-**1** (α-L-Fuc*p*-(1→3)CH_2-β-D-GalNAc*p*-OMe) for the first time in which α-L-fucopyranose is *C*-linked at *C*-3 of methyl β-D-*N*-acetylgalactosaminepyranoside.[12] The ^{1}H NMR data recorded for (−)-**1** allow us to define its preferred conformation in methanolic solution.

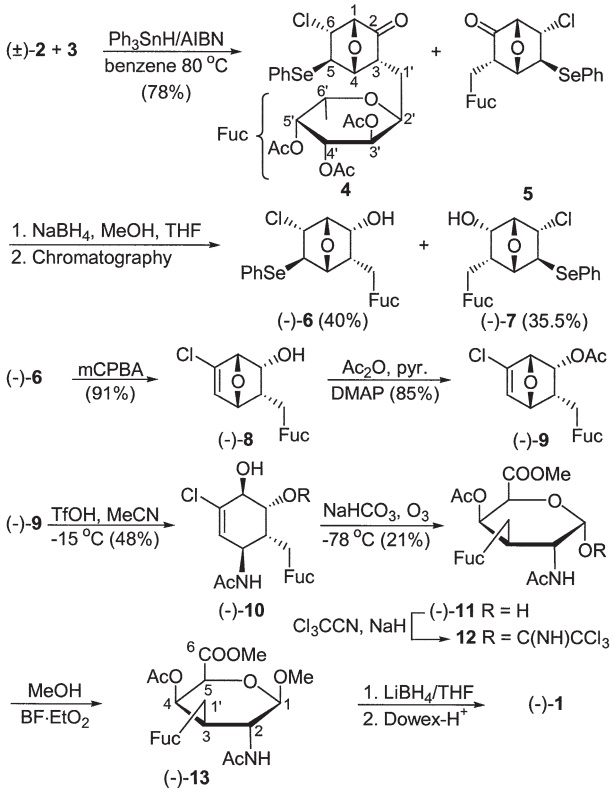
SYNTHESIS

Following the procedure of Pasquarello *et al.*[6d] utilizing enone concentrations of ca. 0.16 molar and Ph_3SnH as reducing agent, Giese's radical fucosidation of racemic enone (±)-**2** (derived[12a] from the Diels-Alder adduct of furan to 1-cyanovinyl acetate[13]) with α-L-bromoacetofucose (**3**), obtained from L-fucose via peracetylation and subsequent treatment with HBr in AcOH,[14] provided the expected mixture of diastereomeric α-*C*-fucosides **4** and **5** in low yield (less than 26%). Using Bu_3SnH/AIBN instead of Ph_3SnH/AIBN was less successful. We finally found that the radical *C*-fucosidation could give a reproducible yield of 78% when a 1:1 mixture of Ph_3SnH/AIBN was added slowly (syringe, 90 min) to a boiling 0.64 molar solution of a 1:1 mixture of (±)-**2** and AIBN in benzene. The *C*-fucosides **4** and **5** could not be separated by the usual chromatographic techniques, thus the crude reaction mixture was directly submitted to the ketone reduction with $NaBH_4$ in methanol and tetrahydrofuran. This provided a 1:1 mixture (95%) of *endo*-alcohols (−)-**6** and (−)-**7** that were readily separated by flash chromatography on silica gel and isolated pure in 40 and 35.5% yield, respectively. In order to assign the structures of these diastereomeric *C*-fucosides we repeated the *C*-fucosidation with the enantiomerically enriched enone (−)-**2** (50% e.e., obtained by incomplete resolution of (±)-**2** with (1*R*,2*R*)-diphenylethylenediamine[15]) that led to a 3:1 mixture of *C*-fucosides **4** and **5** and then to a 3:1 mixture of (−)-**6** and (−)-**7** (Scheme 2).

Oxidative elimination of the benzeneselenyl group of (−)-**6** with metachloroperbenzoic acid in CH_2Cl_2 provided the chloroalkenol (−)-**8** (91%) that was acetylated under standard conditions (Ac_2O/pyridine, DMAP) to give *endo* acetate (−)-**9** in 85% yield. Acid-promoted ring opening of (−)-**9** with trifluo-

romethanesulfonic acid in acetonitrile led to a chloroallylic cation intermediate[6] that was quenched with MeCN to give, after aqueous work-up, the acetamide (−)-**10** (Ritter reaction) in 48% yield, together with several products of decomposition. Ozonolysis of the chloroalkene moiety of (−)-**10** was troublesome, leading to untractable polymeric material in the absence of $NaHCO_3$. When the ozonolysis was carried out with a 1:1 mixture of (−)-**10** and $NaHCO_3$ at–78°C, the methyl uronic ester (−)-**11** was obtained in modest yield (21%).

Since we wanted to avoid the formation of galactofuranuronic derivatives during the protection of the hemiacetal (−)-**11**, we applied Schmidt's glycosidation method[16] for its conversion into the methyl galactopyranoside derivative (−)-**13**. Thus, treatment of (−)-**11** with Cl_3CCN and NaH generated the corresponding trichloroacetimidate **12** (^{1}H NMR:δ_H = 8.82 ppm (NH); 5.54 ppm/doublet, H-C(1)) that was not isolated but directly treated with anhydrous methanol and $BF_3{\cdot}Et_2O$ in CH_2Cl_2 at 0°C. This furnished the totally protected *C*-disaccharide (—)-**13** in 79% yield. Its ^{1}H NMR data confirmed its structure and especially the methyl β-D-galactopyranoside configuration. The reduction of (−)-**13** with an excess of $LiBH_4$ in THF provided, after treatment with DOWEX 50x8 acidic ion exchange resin, the desired *C*-fucoside (−)-**1** in 70% yield.



Scheme 2.

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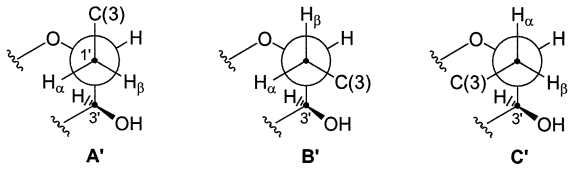

Figure 1. Newman Projections for (−)-**1** along C-1′, C-2!

CONFORMATIONAL STUDIES

For *C*(1→2)-α -fucosides, Kishi and co-workers[8] have found that the major conformers have antiperiplanar orientation of the (σ(C-2′,C-3′) bond of the fucose moiety with the σC(C-1′,C-2) bond of the *C*-disaccharide. Depending on substitution of the "aglycone" part, various conformers or rotamers about bond σ(C-1′,C-2) are possible, all of them can be suited in a diamond lattice (optimal staggered conformations). The ^{1}H NMR spectrum (400 MHz, CD_3OD) of (−)-**1** shows for the proton signals assigned to H_α-1′ (δ_H = 1.94 ppm) and H_β-1′ (δ_H = 1.70 ppm) of the methano linker that H_α-1′ is antiperiplanar with H-2′ and with H-3 as the vicinal coupling constants $^3J(H_\alpha\text{-}1',H\text{-}2') = 11\pm0.5$ Hz and $^3J(H_\alpha\text{-}1',H\text{-}3) = 9\pm1$ Hz were measured (double irradiation experiments). For proton H_β-1′ much smaller vicinal coupling constants $^3J(H_\beta\text{-}1',H\text{-}3) \simeq {}^3J(H_\beta\text{-}1',H\text{-}2') = 3\pm0.3$ Hz were found, with a geminal coupling constant $^2J(H_\alpha\text{-}1',H_\beta\text{-}1') = 14.6\pm0.2$ Hz. These data are consistent with both rotamers **A**′ and **B**′ about the σ(C-2′,C-1′) bond (Figure 1), not with conformer **C**′. Nuclear Overhauser Effects were required to distinguish between conformers **A**′ and **B**′ and for the assignment of configuration of protons H_α and H_β. Strong NOE's were observed in the 2D NOESY ^{1}H NMR spectrum of (−)-**1** between the signal pairs assigned to H_α-1′/H-6′ (δ_H = 3.96 ppm) H_α-1′/H-4 (3.77 ppm), and H_β-1′/H-3 (1.76 ppm), H-1 (4.28 ppm)/H-5 (3.56 ppm) H-1/H-3, H-1/H-5 and H-4 (3.67 ppm)/H-6′ (3.96 ppm) thus confirming chair conformations for both the α-L-fucopyranoside and β-D-galactopyranosyl moieties. The data were consistent only with the conformation represented in Figure 2 for which H_α-1′ is proR and H_α-1′ proS, and in which the bonds σ(C-3′,

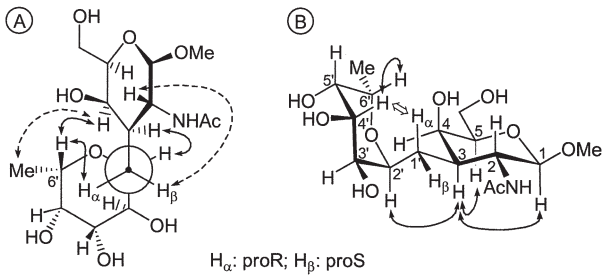

Figure 2. Representations of the most stable conformer of (−)-**1** ↔ strong NOE, ⇔medium NOE, ←→ weak NOE)

C-2′) and σ(C-1′,C-3) are antiperiplanar. The large NOE observed for signals of H-6′ and H-4 as well as the vicinal coupling constants that H-3′ has with H_α-1′ and H_β-1′ confirmed that H-3 is antiperiplanar or nearly antiperiplanar with H_α-1′ (Figure 2). If other conformers are equilibrating with that shown in Figure 2, their proportion must not represent more than 15–20%.

CONCLUSION

Giese radical α-L-fucosidation of racemic 5-*exo*-benzeneselenyl-6-*endo*-chloro-3-methylidene-7-oxabicyclo[2.2.1]heptan-2-one ((±)-**2**) with α-acetobromofucose (**3**) is a more delicate reaction than the corresponding *C*-glucosidation, *C*-galactosidation and *C*-mannosidation. A good yield in the *C*-fucosidation of (±)-**2** can be obtained if one uses Ph_3SnH and high concentrations of (±)-**2** and **3**. One of the diastereomeric *C*-fucosides so obtained has been converted into various (1→3)-*C*-linked disaccharides linking α-L-fucopyranose and 2-acetamido-2-deoxy-D-galactopyranuronic and–D-galactopyranoside derivatives though a methano linker. The preferred conformation of the new *C*-disaccharide (−)-**1** (α-L-Fuc*p*-(1→3)CH_2-β-D-GalNAc*p*-OMe) in solution is similar to that expected for the corresponding *O*-linked disaccharide and similar to that reported by Kishi and co-workers for *C*-disaccharides linking α-L-fucopyranose at C-2 of hexoses through methano linkers. In particular, it implies antiperiplanar σ(C-3′,C-2′) and σ(C-1′,C-3) bonds.

EXPERIMENTAL

General methods. Most procedures were not optimized. All solvents were distilled prior to use: THF from Na and benzophenone; CH_2Cl_2 and pyridine form CaH_2; MeOH from Mg. Solutions after reactions and extractions were concentrated on a rotatory evaporator under reduced pressure. Liquid/solid flash chromatography (FC): columns of silica gel (0.040–0.64 μm, Merck No. 9385 silica gel 60, 240–400 mesh) or Lobar columns (Merck SiO_2, or RP-8). Thin-layer chromatography (TLC) for reaction monitoring: Merck silica gel 60 F_{254} plates; detection by UV light. Pancaldi reagent ($(NH_4)_6MoO_4$, $Ce(SO_4)_2$, H_2SO_4, H_2O), or $KMnO_4$. Reagents were from Fluka or Aldrich and used without purification. Melting points are reported uncorrected; Tottoli (Büchi SMP-20) apparatus. Optical rotations: Jasco-DIP-370 polarimeter. UV/VIS spectra: Kontron-Uvikon-811 or Hewlett-Packard-HP8450 A spectrometer; λin nm (ε [$dm^3mol^{-1}cm^{-1}$]). IR spectra: Perkin-Elmer-1420 or Beckman-IR4230 spectrometer; $\tilde{\nu}$ in cm^{-1}. ^1H NMR spectra: Bruker-DPX-400, or Bruker-ARX-400 spectrometer, δ in ppm rel to internal Me_4Si (0.00 ppm) or to the solvent's residual ^1H signals ($CHCl_3$, δ 7.27; C_6HD_5, δ 7.16; CHD_2COCD_3, δ 1.95; CD_2HCN, δ 2.50; CHD_2SOCD_3, δ 2.50; CHD_2OD, δ 3.31) as internal reference; in D_2O, internal reference $Me_3SiCH_2CH_2CH_2SO_3Na$ (δ(Me_3Si) 0), all ^1H signal assignments were confirmed

by double irradiation experiments or by 2D COSY-DQF or COSY-45 spectra. ^{13}C NMR spectra: same instruments as above (100.61 MHz); δ in ppm rel to internal Me_4Si (0.00 ppm) or to the solvent's C signal ($CDCl_3$, δ 77.0; C_6D_6, δ 128.4; $(CD_3)_2CO$, δ 29.8; CD_3CN, δ 1.3; $(CD_3)_2SO$, δ 39.5; CD_3OD, δ 49.2) as internal reference, coupling constants J in Hz (±0.5 Hz). MS (Nermag R-10–10C, chemical ionization (NH_3) mode, *m/z* (amu) (% rel. base peak (100%)). Elemental analysis: Ilse Beetz, D-96301 Kronach, Germany.

(+)-(1*S*,3*S*,4 *R*,5*R*,6*R*)-5-*exo*-Benzeneselenyl-6-*endo*-chloro-3-*endo*-[(3′,4′,5′-tri-*O*-acetyl-2′,6′-anhydro-1′,7′-dideoxy-α-L-*glycero*-D-*galacto*-heptitol-1′-*C*-yl)]-7-oxabicyclo[2.2.1]hept-2-one (4) and (+)-(1*R*,3*R*,4*S*,5*S*,6*S*)-5-*exo*-benzeneselenyl-6-*endo*-chloro-3-*endo*-[(3′,4′,5′-tri-*O*-acetyl-2′,6′-anhydro-1′,7′-dideoxy-α-L-*glycero*-D-*galacto*-heptitol-1′-*C*-yl)]-7-oxabicyclo[2.2.1]hept-2-one (5). A solution of Ph_3SnH (1.89 g, 5.39 mmol), AIBN (68 mg, 0.65 mmol) in benzene (12 mL) was added slowly in 90 min (syringe) to a boiling solution of (±)-**2**[12a] (1.3 g, 4.15 mmol) **3**[14] (1.9 g, 5.39 mmol) in anhydrous benzene (4 mL). After the end of the addition boiling was continued for 1 h. The solution was cooled to 20°C and KF (1.8 g) was added. The mixture was boiled overnight, cooled to 20°C and the solid residue was filtered off (Celite). The solution was concentrated *in vacuo* and purified by FC (Ø = 6.5 cm, h = 18 cm, 1:3 EtOAc/light petroleum ether): 1.9 g (78%), 1:1 mixture of **4** and **5**, white powder, mp 65°C.

3:1 Mixture of **4** and **5**: same procedure as above using (−)-**2** with 50% e.e. Yield: 78%, R_f (1:3 EtOAc/light petroleum ether) = 0.45, white powder. UV (MeCN): λ_{max} = 196 (ϵ = 4500), 217 (1950). IR (KBr): υ 2985, 1750, 1630, 1480, 1440, 1370, 1245, 1225, 1110, 1055, 915, 740, 695, 465 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) of **4**:δ_H 7.63–7.62 (m, 2H), 7.40–7.35 (m, 3H), 5.30–5.15 (m, 3H, H-3′,4′,5′), 4.88 (d, 1H, ^3J = 6.1 Hz, H-4), 4.53 (d, 1H, ^3J = 5.7 Hz, H-1), 4.34 (dd, 1H, ^3J = 5.7, 3.3 Hz, H-6), 4.02 (qd, 1H, ^3J = 6.4, 1.5 Hz, H-6′), 3.95 (ddd, 1H, ^3J = 10.5, 6.1, 4.4 Hz, H-3), 3.44 (d, 1H, ^3J = 3.3 Hz, H-5), 2.80 (ddd, 1H, ^3J = 12.7, 6.1, 3.3 Hz, H-2′), 2.30 (ddd, 1H, ^2J = 15.6, ^3J = 12.7, 4.4 Hz, H-1′a), 2.18, 2.02, 2.00 (3s, 9H, 3 AcO), 1.28 (ddd, 1H, ^2J = 15.6, ^3J = 10.5, 3.3 Hz, H-1′b), 1.15 (d, 3H, ^3J = 6.4 Hz, H-7′). ^{13}C NMR (100.6 MHz, $CDCl_3$) of **4**:δ_C 207.1 (s, C-2), 173.4, 173. 1, 172.8 (3s, 3 COO), 134.8 (d, ^1J(C,H) = 161 Hz), 129.7 (d, ^1J(C,H) = 158 Hz), 128.8 (d, ^1J(C,H) = 161 Hz), 85.0 (d, ^1J(C,H) = 164 Hz, C-4), 83.4 (d, ^1J(C,H) = 173 Hz, C-1), 70.5 (d, ^1J(C,H) = 153 Hz, C-2′), 70.3 (d, ^1J(C,H) = 150 Hz, C-6′), 68.2, 67.8 (2d, ^1J(C,H) = 141 Hz, C-3′,4′), 65.9 (d, ^1J(C,H) = 143 Hz, C-5′), 58.4 (d, ^1J(C,H) = 168 Hz, C-6), 49.3 (d, ^1J(C,H) = 133 Hz, C-3), 46.7 (d, ^1J(C,H) = 149 Hz, C-5), 22.3 (t, ^1J(C,H) = 132 Hz), 20.7 (3q, ^1J(C,H) = 130 Hz, Ac), 16.1 (q, ^1J(C,H) = 128 Hz, C-7′). CI-MS (NH_3): *m/z* 606 (100, $[M+NH_4]^+$), 589 (44, $[M+H]^+$), 553 (29), 395 (45), 353 (11), 251 (51), 157 (10), 111 (15), 77 (19).

Anal. Calcd for $C_{25}H_{29}ClO_9Se$ (588.07): C 51.07, H 4.97; Found: C 51.13, H 5.04.

(−)-(1*S*,2*R*,3*S*,4*R*,5*R*,6*R*)-5-*exo*-Benzeneselenyl-6-*endo*-chloro-3-*endo*-[(3′,4′,5′-tri-*O*-acetyl-2′,6′-anhydro-1′,7′-dideoxy-α-L-*glycero*-D-*galacto*-heptitol-1′-*C*-yl)]-7-oxabicyclo[2.2.1]hept-2-*endo*-ol ((−)-6) and (−)-(1*R*,2*S*,3*R*,4*S*,5*S*,6*S*)-5-*exo*-benzeneselenyl-6-*endo*-chloro-3-*endo*-[(3′,4′,5′-tri-*O*-acetyl-2′,6′-anhydro-1′,7′-dideoxy-α-L-*glycero*-D-*galacto*-heptitol-1′-*C*-yl)]-7-oxabicyclo[2.2.1]hept-2-*endo*-ol ((−)-7). $NaBH_4$ (83 mg, 2.2 mmol) was added portionwise to a stirred solution of a 1:1 mixture of **4** and **5** (0.5 g, 0.85 mmol) in 1:1 MeOH/THF (20 mL) cooled to 0°C. After the end of the reduction (control by TLC, ca. 5 min), 1 N aq HCl (6.5 mL) was added. The solvent was evaporated, and the residue was extracted with CH_2Cl_2 (30 mL, 3 times). The combined org. extracts were dried ($MgSO_4$), and the solvent was evaporated giving 477 mg (95%) of a 1:1 mixture of (−)-**6** and (−)-**7**. FC (Ø = 6.5 cm, h = 20 cm, 7:3 Et_2O/light petroleum ether) gave a first fraction of (−)-**7** (498 mg, 35.5 %) and a second fraction of (−)-**6** (564 mg, 40%).

Data of (−)-**6**: white powder, mp 132°C (Et_2O/pentane), R_f (7:3 Et_2O/light petroleum ether) = 0.17. $[\alpha]_D^{25} = -54$, $[\alpha]_{577}^{25} = -57$, $[\alpha]_{546}^{25} = -65$, $[\alpha]_{435}^{25} = -110$, $[\alpha]_{405}^{25} = -131$ (*c* 1.0, CH_2Cl_2). UV (MeCN): 198 (11100), 217 (6200), 273 (1650). IR (KBr): υ 3475, 2985, 1750, 1635, 1440, 1370, 1225, 1055, 915 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$):δ_H 7.63–7.61 (m, 2H), 7.35–7.32 (m, 3H), 5.27–5.25, 5.23–5.19 (2m, 3H, H-3′,4′,5′), 4.58 (d, 1H, ^3J = 5.2 Hz, H-4), 4.49–4.46 (m, 2H, H-1,2), 4.29 (m, 1H, H-6), 4.08 (qd, 1H, ^3J = 6.8, 2.8 Hz, H-6′), 3.96 (ddd, 1H, ^3J = 12.0, 5.5, 2.8 Hz, H-2′), 3.45 (d, 1H, ^3J = 4.9 Hz, H-5), 2.90 (br. s, 1H, OH), 2.30 (m, 1H, H-3), 2.10–2.00 (2s, + m, 7H, 2 Ac, H-1′b), 1.34 (ddd, 1H, ^2J = 14.8, ^3J = 8.6, 3.0 Hz, H-1′a), 1.15 (d, 3H, ^3J = 6.8 Hz, H-7′). ^{13}C NMR (100.6 MHz, $CDCl_3$):δ_C 170.4, 170.0, 169.8 (3s, COO), 135.2, 129.4, 128.6 (3d, ^1J(C,H) ≅161 Hz), 129.0 (s), 88.3 (d, ^1J(C,H) = 163 Hz, C-4), 78.9 (d, ^1J(C,H) = 142 Hz, C-1), 73.3 (d, ^1J(C,H) = 159 Hz, C-2), 17.2 (d, ^1J(C,H) = 145 Hz, C-2′), 69.9 (d, ^1J(C,H) = 148 Hz, C-3′), 68.6 (2d, ^1J(C,H) = 155 Hz, C-4′,5′), 66.8 (d, ^1J(C,H) = 141 Hz, C-6′), 62.9 (d, ^1J(C,H) = 164 Hz, C-6), 46.6 (d, ^1J(C,H) = 150 Hz, C-5), 41.3 (d, ^1J(C,H) = 132 Hz, C-3), 21.1 (t, ^1J(C,H) = 124 Hz, C-1′), 20.8, 20.75, 20.7 (3q, ^1J(C,H) = 130 Hz, CH_3CO), 15.6 (q, ^1J(C,H) = 127 Hz, C-7′). CI-MS (NH_3): *m/z* 608 (73, $[M+NH_4]^+$), 591 (46, $[M+H]^+$), 590 (34, $M^{+\bullet}$), 416 (100).

Anal. Calcd for $C_{25}H_{31}ClO_9Se$ (589.92): C 50.90, H 5.30; Found: C 50.91, H 5.25.

Data of (−)-**7**: white powder, mp 116°C (Et_2O/pentane). R_f (7:3 Et_2O/light petroleum ether) = 0.25. $[\alpha]_D^{25} = -34$, $[\alpha]_{577}^{25} = -37$, $[\alpha]_{546}^{20} = -42$, $[\alpha]_{435}^{25} = -67$, $[\alpha]_{405}^{25} = -78$ (*c* 0.55, CH_2Cl_2). UV (MeCN): 198 (11000), 216 (5700), 238 (2050), 273 (1630). IR (KBr): υ 3480, 3060, 2985, 2940, 1745, 1635, 1480, 1440, 1370, 1225, 1130, 1055, 1025, 905, 740, 695, 470 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$):δ_H 7.67–7.65 (m, 2H), 7.38–7.34 (m, 3H), 5.24 (dd, 1H, ^3J = 9.0, 5.5 Hz, H-3′), 5.17 (dd, 1H, ^3J = 3.2, 2.7 Hz, H-5′), 5.11 (dd, 1H, ^3J = 9.0, 3.2 Hz, H-4), 4.55 (d, 1H, ^3J = 5.5 Hz, H-4), 4.45 (m, 2H, H-1,2), 4.32 (m, 1H, H-6), 4.24 (ddd, 1H, ^3J = 11.0, 5.5, 2.8 Hz, H-2′), 3.71 (qd, 1H, ^3J = 6.0, 2.5 Hz, H-6′), 3.65

(d, 1H, ^3J = 5.5 Hz, H-5), 2.55 (br. s, 1H, OH), 2.46 (m, 1H, H-3), 2.14, 2.07, 2.04 (3s, 9H, 3 Ac), 1.82 (ddd, 1H, ^2J = 14.5, ^3J = 8.0, 2.8 Hz, H-1′b), 1.50 (ddd, 1H, ^2J = 14.5, ^3J = 11.0, 7.0 Hz, H-1′a), 1.45 (d, 3H, ^3J = 6.0 Hz, H-7′).^{13}C NMR (100.6 MHz, $CDCl_3$):δ_C = 170.4, 170.0, 169.3 (3s, COO), 135.0, 129.4, 128.5 (3d), 128.0 (s), 89.1 (d), 78.5 (d), 73.2 (d), 71.1 (d), 69.9, 68.6, 68.4, 66.5 (4d, C-3′,4′,5′,6′), 63.2 (d, C-6), 46.5 (d, C-3), 41.2 (d, C-5), 21.1 (t, C-1′), 20.8, 20.75, 20.7 (3q, Ac), 15.7 (q, C-7′). CI-MS (NH_3): *m/z* 608 (73, $[M+NH_4]^+$), 591 (46, $[M+H]^+$), 590 (34, $M^{\bullet+}$), 416 (100).

(−)-(1*S*,2*R*,3*S*,4*R*)-6-Chloro-3-*endo*-[(3′,4′,5′-tri-*O*-acetyl-2′,6′-anhydro-1′,7′-dideoxy-α-L-*glycero*-D-*galacto*-heptitol-1′-*C*-yl)]-7-oxabicyclo[2.2.1]hept-5-en-2-*endo*-ol ((−)-8). Metachloroperbenzoic acid (145 mg, 0.59 mmol) was added portionwise to a solution of (−)-**6** (316 mg, 0.535 mmol) in anhydrous CH_2Cl_2 stirred at −78°C. After stirring at −78°C for 3 h, then at 20°C for 15 h, CH_2Cl_2 (20 mL) was added. The solution was washed with sat aq solution of $NaHCO_3$ (30 mL), then with brine (30 mL). After drying ($MgSO_4$) the solvent was evaporated. The crude yellowish oil was purified by FC (Ø = 2.8 cm, h = 12 cm, 9:1 Et_2O/light petroleum ether) to give 210 mg (91%) of (−)-**8**, white powder, mp 58°C, R_f (Et_2O/(light petroleum ether) = 9:1) = 0.54. $[\alpha]_D^{25}$ = −71, $[\alpha]_{577}^{25}$ = −63, $[\alpha]_{546}^{25}$ = −96, $[\alpha]_{435}^{25}$ = −161 $[\alpha]_{405}^{25}$ = −192 (*c* 0.2, $CHCl_3$). UV (MeCN): 208 (4150). IR (KBr): υ 3745, 3480, 2985, 1745, 1645, 1595, 1435, 1375, 1230, 1055, 910, 600, 465 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$):δ_H 6.21 (d, 1H, ^3J = 1.9 Hz, H-5), 5.27 (dd, 1H, ^3J = 3.7, 3.6 Hz, H-5′), 5.16 (d, 1H, ^3J = 6.7 Hz, H-4′), 5.14 (d, 1H, ^3J = 6.7 Hz, H-3′), 4.87–4.85 (m, 1H, H-4), 4.74 (d, 1H, ^3J = 4.6 Hz, H-1), 4.56 (dd, 1H, ^3J = 7.8, 4.6 Hz, H-2), 4.21–4.13 (m, 2H, H-2′,6′), 2.53–2.41 (br. s, 1H, OH), 2.36–2.27 (m, 1H, H-3), 2.12, 2.10, 2.05 (3s, 9H, 3 Ac), 1.69–1.61 (ddd, 1H, ^2J = 15.0, ^3J = 11.6, 8.3 Hz, H-1′b), 1.24 (d, 3H, ^3J = 6.7 Hz, H-7′), 1.22–1.16 (m, 1H, H-1′a). ^{13}C NMR (100.6 MHz, $CDCl_3$):δ_C 170.2, 169.9, 169.7 (3s, COO), 138.7 (s, C-6), 128.0 (d, ^1J(C,H) = 180 Hz, C-5), 83.7 (d, ^1J(C,H) = 161 Hz, C-1), 83.1 (d, ^1J(C,H) = 165 Hz, C-4), 70.9 (d, C-2′), 69.9 (d, C-2), 69.5 (d, C-3′), 69.0 (d, C-5′), 68.5 (d, C-4′), 67.7 (d, ^1J(C,H) = 131 Hz, C-6′), 41.5 (d, ^1J(C,H) = 138 Hz, C-3), 23.8 (t, ^1J(C,H) = 130 Hz, C-1′), 20.8, 20.7, 20.6 (3q, 3Ac), 15.1 (q, ^1J(C,H) = 128 Hz, C-7′). CI-MS (NH_3): *m/z* 452 (40, $[M+NH_4]^+$), 435 (20, $[M+H]^+$), 434 (21, $M^{\bullet+}$), 450 (100), 433 (54), 373 (11), 273 (10), 102 (65), 83 (22).

Anal. Calcd for $C_{19}H_{25}ClO_9$ (432.12): C 52.72, H 5.82; Found: C 52.63, H 5.83.

(−)-(1*S*,2*R*,3*S*,4*R*)-6-Chloro-3-*endo*-[(3′,4′,5′-tri-*O*-acetyl-2′,6′-anhydro-1′,7′-dideoxy-ga-L-*glycero*-D-*galacto*-heptitol-1′-*C*-yl)]-7-oxabicyclo[2.2.1]hept-5-en-2-*endo*-yl Acetate ((−)-9). A mixture of (−)-**8** (360 mg, 0.83 mmol), anhydrous pyridine (39 mL), acetic anhydride (0.35 mL) and 4-dimethylaminopyridine (5 mg) was stirred at 20°C for 15 h. The solvent was evaporated *in vacuo* to dryness and the residue taken in Et_2O (20 mL). The solution was washed with aq 1 N HCl (20 mL), dried ($MgSO_4$) and the solvent evaporated to give

336 mg (85%) of (−)-**9** as a colorless powder, mp 104°C, R_f (1:1 EtOAc/light petroleum ether) = 0.45. $[\alpha]_D^{25} = -65$, $[\alpha]_{577}^{25} = -67$, $[\alpha]_{546}^{25} = -75$, $[\alpha]_{435}^{25} = -122$, $[\alpha]_{405}^{25} = -144$ (*c* 1.0, $CHCl_3$). UV (MeCN): 205 (2050), 287 (220). IR (KBr): υ 2975, 1745, 1635, 1590, 1435, 1375, 1230, 1115, 1070, 1035, 912, 465 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$):δ_H 6.22 (d, 1H, ^3J = 1.9 Hz, H-5), 5.28–5.24 (m, 4H, H-4,3,5′), 5.19–5.15 (dd, 1H, ^3J = 10.2, 3.3 Hz, H-4′), 4.97 (d, 1H, ^3J = 4.3 Hz, H-2), 4.22–4.15 (ddd, 1H, ^3J = 12.1, 5.7, 3.5 Hz, H-2′), 3.99–3.92 (qd, 1H, ^3J = 6.4, 1.8 Hz, H-6′), 2.61–2.52 (m, 1H, H-3), 2.17, 2.08, 2.02 (3s, 12H, 4 Ac), 1.85–1.74 (ddd, 1H, ^2J = 16.0, ^3J = 12.1, 4.9 Hz, H-1′b), 1.18 (d, 3H, ^3J = 6.4 Hz, H-7′), 1.08–0.97 (ddd, 1H, ^2J = 16.0, ^3J = 11.4, 3.5 Hz, H-1′a). ^{13}C NMR (100.6 MHz, $CDCl_3$):δ_C 170.7, 170.5, 170.2, 170.0 (4s, 4 COO), 137.9 (s, C-6), 128.4 (d, C-5), 82.2 (d, C-1), 81.8 (d, C-4), 71.2 (d, C-2), 70.7 (d, C-2′), 70.5 (d, C-3′), 68.4 (d, C-5′), 68.3 (d, C-4′), 65.8 (d, C-6′), 38.4 (d, C-3), 22.9 (t, C-1′), 20.8, 20.7, 20.75, 20.6 (4q, 4 Ac), 16.1 (q, C-7′). CI-MS (NH_3): *m/z* 492 (55, $[M+NH_4]^+$), 475 (20, $[M+H]^+$), 415 (12), 330 (6), 273 (100), 111 (50), 102 (32), 83 (44).

Anal. Calcd for $C_{21}H_{27}ClO_{10}$ (474.89): C 53.11, H 5.73; Found: C 53.02, H 5.80.

(−)-(1*R*,2*S*,5*R*,6*R*)-5-Acetamido-3-chloro-2-hydroxy-6-[(3′,4′,5′-tri-*O*-acetyl-2′,6′-anhydro-1′,7′-dideoxy-α-L-*glycero*-D-*galacto*-heptitol-1′-*C*-yl)]cyclohex-3-en-1-yl Acetate ((−)-10). CF_3SO_3H (0.2 mL, 2.3 mmol) was added dropwise to a stirred solution of (−)-**9** (200 mg) in anhydrous MeCN (10 mL) cooled to −15°C. After stirring at −15°C for 30 min, CH_2Cl_2 (10 mL) was added and the solution washed with an ice-cold sat aq solution of $NaHCO_3$ (15 mL, 3 times). Drying ($MgSO_4$), solvent evaporation gave 228 mg of a yellowish oil FC (Ø = 2.2 cm, h = 15 cm, 7:3 EtOAc/light petroleum ether): 108 mg (48%) of (−)-**10**, colorless powder, mp 117°C, R_f (7:3 EtOAc/light petroleum ether) = 0.29. $[\alpha]_D^{25} = -61$, $[\alpha]_{577}^{25} = -54$ $[\alpha]_{546}^{25} = -59$, $[\alpha]_{435}^{25} = -98$, $[\alpha]_{405}^{25} = -123$ (*c* 1.0, $CHCl_3$). UV (MeCN): 206 (4300), 260 (250), 281 (260). IR (KBr): υ 3560, 2985, 2940, 1750, 1655, 1535, 1435, 1375, 1230, 1110, 1060, 1030, 915, 600, 560 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$):δ_H 6.43 (d, 1H, ^3J = 9.4 Hz, NH), 5.81 (d, 1H, ^3J = 2.4 Hz, H-4), 5.20 (dd, 1H, ^3J = 3.2, 1.9 Hz, H-5′), 5.15 (dd, 1H, ^3J = 10.2, 5.6 Hz, H-3′), 5.07 (dd, 1H, ^3J = 10.2, 3.2 Hz, H-4′), 5.02 (dd, 1H, ^3J = 3.1, 2.7 Hz, H-1), 4.58 (ddd, 1H, ^3J = 9.4, 9.3, 2.4 Hz, H-5), 4.33 (br. s, 1H, OH), 4.21 (ddd, ^3J = 11.3, 5.6, 3.2 Hz, H-2′), 4.00 (d, 1H, ^3J = 2.76 Hz, H-2), 3.88 (qd, 1H, ^3J = 6.5, 1.9 Hz, H-6′), 2.61–2.52 (m, 1H, H-3), 2.10, 2.09, 2.03, 2.00, 1.96 (5s, 15H, 5 Ac), 2.06 (m, H-6), 1.75 (m, 1H, H-1′b), 1.56 (m, 1H, H-1′a), 1.10 (d, 3H, ^3J = 6.5 Hz, H-7′). ^{13}C NMR (100.6 MHz, $CDCl_3$):δ_C 170.8, 170.4, 170.3, 170.2, 170.1 (5s, 5 COO), 132.6 (s, C-3), 129.3 (d, ^1J(C,H) = 169 Hz, C-4), 75.4 (d, ^1J(C,H) = 152 Hz, C-1), 72.8 (d, ^1J(C,H) = 145 Hz, C-2′), 70.5 (d, ^1J(C,H) = 153 Hz, C-5′), 69.8 (d, ^1J(C,H) = 150 Hz, C-2), 68.1 (d, ^1J(C,H) = 154 Hz, C-3′), 68.05 (d, ^1J(C,H) = 154 Hz, C-4′), 65.7 (d, ^1J(C,H) = 139 Hz, C-6′), 48.7 (d, ^1J(C,H) = 145 Hz, C-5), 35.4 (d, ^1J(C,H) = 128 Hz, C-6), 23.0 (t, ^1J(C,H) = 128 Hz, C-1′), 23.0 (q, ^1J(C,H) = 128 Hz, AcNH), 21.8, 20.7, 20.6, 20.5 (4q, ^1J(C,H) = 130 Hz, 5 AcO), 15.8 (q, ^1J(C,H) = 128 Hz, C-7′).

Anal. Calcd for $C_{23}H_{32}ClO_{11}$ (533.17): C 51.74, H 6.04; Found: 51.56, H 6.12.

(−)-Methyl 2-Acetamido-4-*O*-acetyl-2,3-dideoxy-3-*C*-(3′,4′,5′-tri-*O*-acetyl-2′,6′-anhydro-1′,7′-dideoxy-α-L-*glycero*-D-*galacto*-heptitol-1′-*C*-yl)-α-D-galactopyranuronate ((−)-11). Ozone (3% in O_2) was bubbled through a mixture of (−)-**10** (54 mg, 0.1 mmol), MeOH (2 mL), THF (2 mL), $NaHCO_3$ (48 mg, 0.56 mmol) cooled to −78°C. After 10 min, Me_2S (two drops) was added and the mixture stirred at −78°C for 10 min, then at 20°C for 6 h. Water (5 mL) was added and the mixture was extracted with CH_2Cl_2 (20 mL, twice). Drying, solvent evaporation, FC (Ø = 1 cm, h = 12 cm, 48.5:48.5:3 EtOAc/CH_2Cl_2/MeOH) gave 12 mg (21%) of (−)-**11**, colorless powder, R_f (48.5:48.5:3 EtOAc/CH_2Cl_2/MeOH) = 0.11. $[\alpha]_D^{25} = -45$, $[\alpha]_{577}^{25} = -14.5$, $[\alpha]_{546}^{25} = -32$, $[\alpha]_{435}^{25} = -54$, $[\alpha]_{405}^{25} = -62$ (*c* 0.2, CH_2Cl_2). IR (KBr): υ 3385, 2960, 1750, 1660, 1540, 1440, 1375, 1230, 1110, 1045, 915, 805, 600 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$):δ_H 5.77 (d, 1H, ^3J = 9.8 Hz, NH), 5.39 (br. s, 1H, H-4), 5.26, 5.25 (d, 1H, ^3J = 3.5 Hz, H-1), 5.25–5.24 (dd, 1H, ^3J = 4.0, 2.0 Hz, H-5′), 5.18 (dd, 1H, ^3J = 10.2, 6.0 Hz, H-3′), 5.08 (dd, 1H, ^3J = 10.2, 4.0 Hz, H-4′), 4.75 (br. s, 1H, H-5), 4.39 (ddd, 1H, ^3J = 12.0, 10.0, 3.5 Hz, H-2), 4.24 (ddd, 1H, ^3J = 10.6, 6.0, 4.0 Hz, H-2′) 3.95 (qd, 1H, ^3J = 6.6, 2.0 Hz, H-6′), 3.74 (s, 3H, COOMe), 2.26 (m, 1H, H-3), 2.15, 2.08, 2.00, 1.98 (5s, 15H, 3 Ac), 1.67 (ddd, 1H, ^2J = 15.4, ^3J = 10.6, 4.4 Hz, H-1′a), 1.57 (ddd, 1H, ^2J = 15.4, ^3J = 4.6, 4.3 Hz, H-1′b), 1.17 (d, 3H, ^3J = 6.6 Hz, H-7′). ^{13}C NMR (100.6 MHz, $CDCl_3$):δ_C 170.5, 170.4, 170.3, 170.0, 168.9 (5s), 91.8 (d, ^1J(C,H) = 172 Hz, C-1), 72.6 (d, ^1J(C,H) = 146 Hz, C-6′), 70.8 (d, ^1J(C,H) = 148 Hz, C-5′), 70.5 (d, ^1J(C,H) = 151 Hz, C-4′), 69.6 (d, ^1J(C,H) = 138 Hz, C-3′), 68.2 (d, ^1J(C,H) = 138 Hz, C-2′), 68.1 (d, ^1J(C,H) = 138 Hz, C-4), 65.8 (d, ^1J(C,H) = 141 Hz, C-5), 52.6 (q, ^1J(C,H) = 148 Hz, MeO), 48.2 (d, ^1J(C,H) = 143 Hz, C-2), 35.5 (d, ^1J(C,H) = 130 Hz, C-3), 24.0 (q, ^1J(C,H) = 128 Hz, MeCONH), 23.3 (q, ^1J(C,H) = 130 Hz, C-1′), 20.8, 20.7, 20.6 (3q, ^1J(C,H) = 130 Hz, 3 Ac), 16.0 (q, ^1J(C,H) = 128 Hz, C-7′). CI-MS (NH_3): *m/z* 579 (9, $[M+NH_4]^+$), 562 (100, $[M+H^+]$), 561 (8, $M^{(+)}$), 502 (27), 442 (12).

Anal. Calcd for $C_{23}H_{32}ClO_{11}$ (533.17): C 51.33, H 6.28; Found: C 51.23, H 6.35.

(−)-Methyl 2-Acetamido-4-*O*-acetyl-2,3-dideoxy-1-*O*-methyl-3-*C*-(3′,4′,5′-tri-*O*-acetyl-2′,6′-anhydro-1,7′-dideoxy-α-L-*glycero*-D-*galacto*-heptitol-1′-*C*-yl)-β-D-galactopyranuronate ((−)-13). A mixture of (−)-**11** (21 mg, 0.037 mmol), anhydrous CH_2Cl_2 (5 mL), Cl_3CCN (60 μL) and NaH (3 mg) was stirred under Ar atmosphere at 20°C for 4 h. Brine (5 mL) was added and the mixture extracted with CH_2Cl_2 (10 mL, 3 times). The combined org. extracts were dried ($MgSO_4$). Solvent evaporation provided **12** (^1H NMR,δ_H = 8.82 ppm (NH), 5.54 ppm (d, H-1)) that was directly taken in anhydrous CH_2Cl_2 (4 mL) and MeOH (0.1 mL). After cooling to 0°C, $BF_3{\cdot}Et_2O$ (0.02 mL) in solution in anhydrous CH_2Cl_2 (1 mL) was then added slowly under stirring. After 10 min at 0°C, the mixture was stirred at 20°C for 15 h. A sat aq solution of $NaHCO_3$ (4 mL) was added and the mixture extracted with CH_2Cl_2 (10 mL, 3 times). The combined org. extracts were

dried ($MgSO_4$). Solvent evaporation, FC (Ø = 1 cm, h = 15 cm, 50:48:2 EtOAc/CH_2Cl_2/MeOH) gave 17 mg (79%) of (−)-**13**, colorless powder, R_f (50:48:2 EtOAc/CH_2Cl_2/MeOH) = 0.19. $[\alpha]_D^{25} = -143$, $[\alpha]_{577}^{25} = -150$, $[\alpha]_{546}^{25} = -173$, $[\alpha]_{435}^{25} = -283$, $[\alpha]_{405}^{25} = -327$ (*c* 0.03, EtOH). IR (KBr): υ 2960, 1745, 1655, 1375, 1230, 1060 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$):δ_H 5.51 (d, 1H, ^3J = 8.0 Hz, NH), 5.33 (d, 1H, ^3J = 2.0 Hz, H-4), 5.22 (dd, 1H, $^3J \cong 3.0$, 2.0 Hz, H-5′), 5.15 (dd, 1H, ^3J = 10.0, 6.0 Hz, H-3′), 5.07 (dd, 1H, ^3J = 10.0, 3.0 Hz, C-4′), 4.52 (d, 1H, ^3J = 8.0 Hz, H-1), 4.28 (d, 1H, ^3J = 2.0 Hz, H-5), 4.24 (ddd, 1H, ^3J = 10.0, 5.0, 4.9 Hz, H-2′), 3.94 (qd, 1H, ^3J = 6.5, 2.0 Hz, H-6′), 3.76 (m, 1H, H-2), 3.53 (s, 3H, MeO), 2.35 (m, 1H, H-3), 2.13, 2.07, 2.04, 2.00, 1.96 (5s, 15H, 5 Ac), 1.68 (ddd, 1H, ^2J = 15.4, ^3J = 10.0, 4.9 Hz, H-1′a), 1.61 (ddd, 1H, ^2J = 15.4, ^3J = 5.0, 4.4 Hz, H-1′b), 1.16 (d, 3H, ^3J = 6.5 Hz, H-7′). ^{13}C NMR (100.6 MHz, $CDCl_3$):δ_C 170.6, 170.5, 170.4, 170.0 (5s, 4 COO + CONH), 167.7 (s, C-6), 102.7 (d, ^1J(C,H) = 170 Hz, C-1), 75.2 (d, ^1J(C,H) = 142 Hz, C-5), 72.1 (d, ^1J(C,H) = 149 Hz, C-2′), 70.2 (2d, ^1J(C,H) = 153 Hz, C-4,5′), 68.3, 68.1 (2d, ^1J(C,H) = 162 Hz, C-3,4′), 66.1 (d, ^1J(C,H) = 145 Hz, C-2), 40.0 (d, ^1J(C,H) = 127 Hz, C-3), 23.5 (t, ^1J(C,H) = 126 Hz, C-1′), 20.8, 20.7 (5q, ^1J(C,H) = 130 Hz, 5 Ac), 15.7 (q, ^1J(C,H) = 126 Hz, C-7′). CI-MS (NH_3): *m/z* 593 (9, $[M+NH_4]^+$), 576 (56, $[M+H]^+$), 575 (25, $M^{(+)}$), 544 (27, $[M+H\text{-}MeOH]^+$), 424 (12), 179 (9).

Anal. Calcd for $C_{25}H_{37}NO_{14}$ (575.56): C 52.17, H 6.48; Found: C 52.36, H 6.32.

(−)-Methyl 2-Acetamido-2,3-dideoxy-3-*C*-(2′,6′-anhydro-1′,7′-dideoxy-α-L-*glycero*-D-*galacto*-heptitol-1′-*C*-yl)-β -D-galactopyranoside ((−)-1). A 2 M solution of $LiBH_4$ in anhydrous THF (0.3 mL) was added dropwise under Ar atmosphere to a stirred solution of (−)-**13** (47.3 mg, 0.082 mmol) in anhydrous THF (8 mL) cooled at 0°C. After stirring at 0°C for 1 h, then at 20°C for 15 h, H_2O (4 mL) was added and the solvent was evaporated to dryness (lyophilisation). The residue was taken in MeOH (2 mL) and filtered through a column (Ø = 1 cm, h = 5 cm) of DOWEX 50x8 (acidic) prewashed with 1:10 HCl/H_2O (20 mL), then H_2O (20 mL, 3 times) and MeOH (20 mL, twice). Elution with MeOH provided 22 mg (70%) of (−)-**1**, colorless powder, mp 134–138°C (dec.). $[\alpha]_D^{25} = -78$, $[\alpha]_{577}^{25} = -74$, $[\alpha]_{546}^{25} = -86$, $[\alpha]_{435}^{25} = -130$, $[\alpha]_{405}^{25} = -158$ (*c* 0.05, EtOH). IR (KBr): υ 3745, 3445, 2985, 1745, 1650, 1540, 1455, 1395, 1080 cm^{-1}. ^1H NMR (400 MHz, MeOH-d_4):δ_H 4.28 (d, 1H, ^3J = 8.4 Hz, H-1), 3.97 (ddd, 1H, ^3J(H-1′(proR),H-2′) = 8.5–10, ^3J(H-2′,H-3′) = 5.0, ^3J(H-1′(proS) = 3.0 Hz, H-2′), 3.96 (qd, 1H, ^3J = 6.5, 3.0 Hz, H-6′), 3.90 (dd, 1H, ^3J(H-1,H-2) = 8.4, ^3J(H-2,H-3) = 9.0 Hz, H-2), 3.86 (br. dd, 1H, ^3J(H-3′,H-4′) = 8.8, ^3J(H-2′,H-3′) = 5.0 Hz, H-3′), 3.77 (dd, 1H, ^3J(H-3,H-4) = 6.5, ^3J(H-4,H-5) = 4.5 Hz, H-4), 3.73 (dd, 1H, ^3J(H-5′,H-6′) $\cong {}^3J$(H-4′,H-5′) ≅3.0 Hz, H-5′), 3.67 (dd, 1H, ^3J(H-3′,H-4′) = 8.8, ^3J(H-4′,H-5′) = 3.0 Hz, H-4′), 3.56 (dd, 1H, ^3J = 6.5, 4.5 Hz, H-5), 3.50 (br. s, 2H, H-6), 3.39 (s, 3H, MeO), 2.01 (s, 3H, AcNH), 1.94 (m, 1H, H-1′(proR)), 1.76 (m, 1H, ^3J(H-1′(proR),H-3) = 11.0, ^3J(H-2,H-3) = 9.0, ^3J(H-3,H-4) = 6.5, ^3J(H-1′(proS),H-3) = 3.0 Hz, H-3), 1.70 (m, 1H, ^2J = 14.6, ^3J(H-1′(proS),H-2′) $\cong {}^3J$(H-1′(proS),H-3) = 3.0 Hz, H-1′(proS)), 1.26 (d, 3H, ^3J = 6.5 Hz, H-7′). ^{13}C NMR (100.6 MHz, MeOH-d_4):δ_C 174.3 (1s, CONH), 105.6 (d, ^1J(C,H) = 174 Hz, C-1), 84.9, 79.7,

72.2, 70.3, 69.4, 68.2, 56.7 (7d, C-2′,3′,4′,4,5,5′,6′), 63.0 (t, C-6), 52.3 (d, ^1J(C,H) = 138 Hz, C-2), 49.8 (q, MeO), 45.2 (d, ^1J(C,H) = 129 Hz, C-3), 23.5 (t, C-1′), 22.6 (q, ^1J(C,H) = 128 Hz, MeCONH), 16.5 (q, ^1J(C,H) = 128 Hz, C-7′). CI-MS (NH_3): *m/z* 347 (23, $[M\text{-}MeOH]^+$), 77 (100). electrospray MS: *m/z* 380 $[M+H^+]$, 348 $[M+H\text{-}MeOH]^+$. HRMS calcd for $C_{16}H_{29}NO_9Na$: 402.174002; found: 402.173143

ACKNOWLEDGMENTS

We thank the Swiss National Science Foundation, the Fonds Herbette (Lausanne) and the Office Fédéral de l'enseignement et de la Science (European project COSTD13/0001/99) for financial support. We thank Prof. I. Robina, Mr. M. Rey and F. Sepúlveda for technical help.

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Accepted September 18, 2001

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