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# SYNTHESIS OF A MUCIN-TYPE *O*-GLYCOSYLATED AMINO ACID, β-Gal-(1→3)-[α-Neu5Ac-(2→6)]-α-GalNAc-(1→3)-Ser*

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ABSTRACT

Total synthesis of *O*-β-D-galactopyranosyl-(1→3)-*O*-[(5-acetamido-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonic acid)-(2→6)]-*O*-(2-acetamido-2-deoxy-α-D-galactopyranosyl)-(1→3)-L-serine was achieved by use of the key glycosyl donor *O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→3)-*O*-[methyl (5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosyl)onate-(2→6)]-4-*O*-acetyl-2-azido-2-deoxy-α-D-galactopyranosyl trichloroacetimidate and the key glycosyl acceptor *N*-(benzyloxycarbonyl)-L-serine benzyl ester in a regiocontrolled way.

## INTRODUCTION

A sialic acid-containing trisaccharide linked to either L-serine or L-threonine has been proposed for a partial structure of various glycoproteins[2]. In the course of our synthetic studies on glycopeptides[3], mucin-type glycopeptides have been chosen for the synthetic targets, and a synthesis of disaccharide-L-serine **1** was recently[4] reported. The $^1$H- and $^{13}$C-n.m.r. data of synthetic **1** were in good agreement with those of the natural ovine submaxillary mucin reported recently by Gerken and Dearborn[5]. Herein is described a synthetic approach to serine-trisaccharide **2**.

## RESULTS AND DISCUSSION

Synthesis design for compound **2** is shown in Scheme 1. Compound **2** was "disconnected" into a trisaccharide donor **3** that may be obtained either by route A or B, and a properly protected L-serine derivative **4**. In the case of route A, the known disaccharide **9** (ref. 4) was employed as a synthetic equivalent of the glycosyl acceptor **5**, while, in the case of route B, a known sialic acid donor **19** (ref. 6) was used as a synthetic equivalent of the glycosyl donor **7**.

Silver triflate-promoted glycosylation of protected disaccharide **9** with

*Part 56 in the series "Synthetic Studies on Cell-Surface Glycans". For Part 55, see ref. 1.
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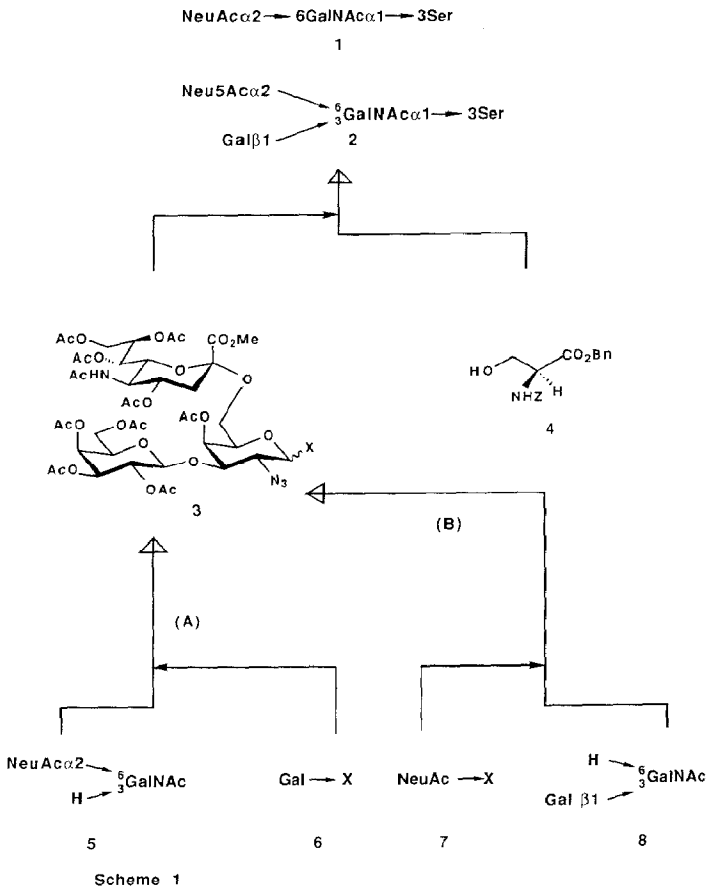
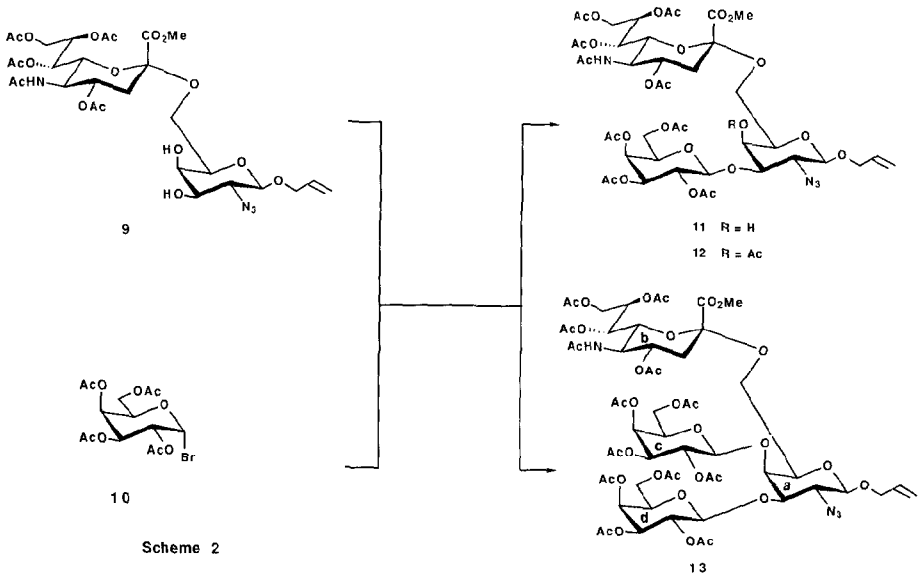



Scheme 1

galactopyranosyl bromide **10** in 1,2-dichloroethane was performed in the presence of activated powdered molecular sieves 4A, to give a 61% yield of a mixture of the desired trisaccharide **11** and the tetrasaccharide **13** (in the ratio of ~2:1), which was readily separated by flash chromatography on silica gel. The configuration of compound **11** at C-1c was assigned by $^1$H-n.m.r. data, which contained a signal for H-1c as a doublet with $^3J_{HH}$ 8.1 Hz at $\delta$ 4.759. In order to assign the regiochemistry of the newly introduced glycosidic linkage between the 2-azido-2-deoxy-D-galactopyranosyl residue and the $\beta$-D-galactopyranosyl residue, compound **11** (see Scheme 2) was acetylated, to give the deca-*O*-acetyl derivative **12**. From inspection of the 400-MHz $^1$H-n.m.r. data of **12**, a deshielded signal for H-4a could not be unambiguously assigned, due to the presence of overlapped signals at $\delta$ ~5.35. However the regiochemistry of **11** was determined through comparison with the glycosylation product obtainable in a regiocontrolled way by route B as described later. Structure of the by-product **13** was assigned by the presence in the $^1$H-n.m.r. data of the signals of two anomeric protons with $\beta$-D configuration for two D-galactopyranosyl residues. The formation of the tetrasaccharide **13** may proceed



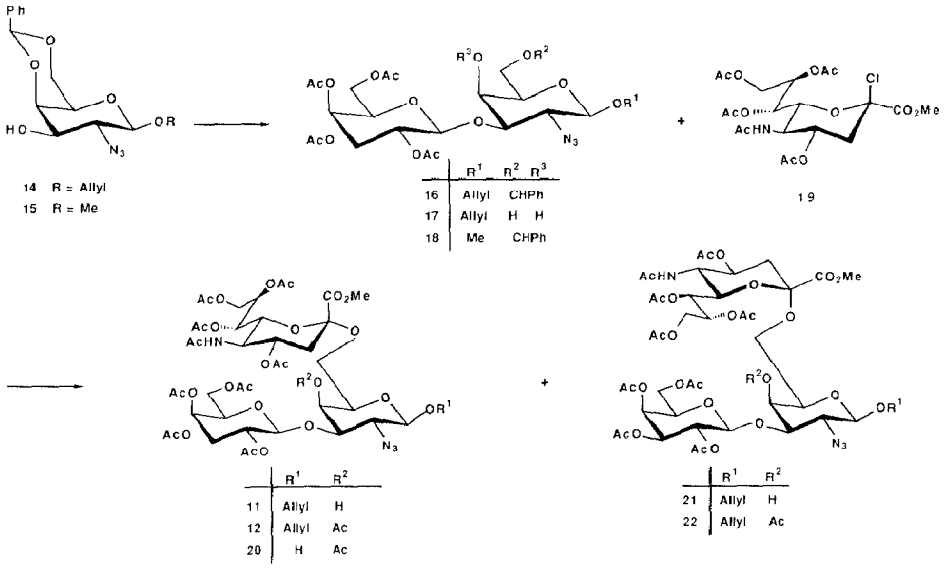

Scheme 2

through the intermediacy of the trisaccharide **11**, as no (1→4) regioisomer of **11** was isolated.

A second approach (B) was next studied (see Scheme 3). According to the reported observations that mercuric salt promoted glycosylation[7] of methyl glycoside **15** with bromide **10** gave none of the desired disaccharide **18**, while silver triflate–collidine-promoted glycosylation of allyl glycoside **14** with the same bromide **10** afforded the desired disaccharide **16** (ref. 8), glycosylation of **14** with **10** was performed in the presence of silver triflate and molecular sieves 4A, to give **16** in 80% yield. Removal of the benzylidene group of compound **16** gave an 89% yield of the diol **17**. Mercuric salt-promoted glycosylation of compound **17** with the chloride **19** afforded the desired trisaccharide **11** and the C-2b $\beta$ anomer **21**, in 44 and 41% yield, respectively, based on compound **17**. The configurations at C-2b for compounds **11** and **21** were assigned by the following $^1$H-n.m.r. data[9]. In the case of compound **11**, a signal for H-4b was observed at $\delta$ 4.861. In the case of compound **21**, the signal for H-4b was overlapped with other signals, but was assigned at $\delta$ 5.240 through double-irradiation experiments. The compound **11** was identified with the product obtained by route A.

Further transformation of the trisaccharide **11** into a 4:1 mixture of the $\alpha$- and $\beta$-trichloroacetimidate **23** was achieved in three steps: (*1*) acetylation, (*2*) palladium(II)-promoted deallylation, and (*3*) treatment with base and trichloroacetonitrile[10] (see Scheme 4).

Crucial glycosylation of the serine derivative **4** was examined by using the imidate **23** as a 4:1 mixture of $\alpha$ and $\beta$ isomers in the presence of trimethylsilyl triflate and powdered molecular sieves 4A, to give a 1:2 mixture of compounds **24** and **27**. The structure of **24** was deduced from $^1$H-n.m.r. data. The signals for H-1a and H-2a were observed at $\delta$ 4.856 and 3.547 as a doublet with $J$ 3.4 Hz, and as a




Scheme 3

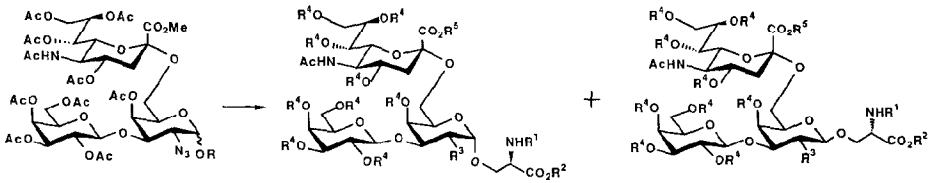
doublet of doublets with $J$ 3.4 and 10.7 Hz, respectively. The structure assignment for compound **27** from $^1$H-n.m.r. data was not straightforward due to the presence of overlapping signals, but was confirmed after further chemical transformations. It is to be noted that similar low stereoselectivity was recently reported for the coupling between an oligosaccharide[11] imidate and a serine derivative. Reduction of the azide of the minor product **24** in the presence of Lindlar catalyst, and acetylation of the product, afforded a 74% yield of the acetamido derivative **25**, which was treated with 10% palladium–carbon under hydrogen, and the product with methanolic sodium hydroxide; purification by gel filtration with Sephadex G-10 in $H_2O$ afforded the target compound **2** in 53% overall yield.

The transformation of compound **27** into the acetamide **28** was performed as described for compound **25**. The $^1$H-n.m.r. data of compound **28** contained a signal for H-1a at $\delta$ 4.630 as a doublet with $J$ 8.1 Hz, proving the $\beta$-D-configuration at C-1a for compound **28** as well as **27**. Deprotection of compound **28** afforded the unnatural isomer **30** of the target compound **2**.

In conclusion, a typical branching trisaccharide-serine, compound **2**, was synthesized for the first time by using the imidate **23** as a key intermediate, although the low stereoselectivity for the coupling between trisaccharide imidate **23** and the protected serine **4** remains to be improved.

## EXPERIMENTAL

*General.* — Melting points were determined with a Yanagimoto micro



23 R = CNHCCl$_3$

| | $R^1$ | $R^2$ | $R^3$ | $R^4$ | $R^5$ |
|---|---|---|---|---|---|
| 24 | $CO_2Bn$ | Bn | $N_3$ | Ac | Me |
| 25 | $CO_2Bn$ | Bn | NHAc | Ac | Me |
| 26 | H | H | NHAc | Ac | Me |
| 2 | H | H | NHAc | H | H |

| | $R^1$ | $R^2$ | $R^3$ | $R^4$ | $R^5$ |
|---|---|---|---|---|---|
| 27 | $CO_2Bn$ | Bn | $N_3$ | Ac | Me |
| 28 | $CO_2Bn$ | Bn | NHAc | Ac | Me |
| 29 | H | H | NHAc | Ac | Me |
| 30 | H | H | NHAc | H | H |

Scheme 4

melting-point apparatus and are uncorrected. Optical rotations were determined with a Perkin–Elmer Model 241 MC polarimeter, for solutions in $CHCl_3$ at 25°, unless noted otherwise. Column chromatography was performed on Silica Gel (Merck 70–230 mesh). Flash chromatography was performed on columns of Wako gel C-300 (200–300 mesh). T.l.c. and high-performance (h.p.) t.l.c. were performed on Silica Gel 60 $F_{254}$ (Merck). Molecular sieves were purchased from Nakarai Chemicals. N.m.r. spectra were recorded with either a JEOL GX400 [$^1H$ (400 MHz)] or a FX90Q [$^{13}C$ (22.50 MHz)] spectrometer. The values of $\delta_H$ and $\delta_C$ are expressed in p.p.m. downward from the signal for internal $Me_4Si$, for solutions in $CDCl_3$, unless noted otherwise. Values of $\delta_H$ ($D_2O$) and $\delta_C$ ($D_2O$) are expressed in p.p.m. downward from the signal for $Me_4Si$, by reference to internal $Me_2CO$ (2.225) or $Me_3COH$ (1.230), and 1,4-dioxane (67.4) or MeOH (49.8), respectively.

*Allyl* O-*(2,3,4,6-tetra*-O-*acetyl-β*-D-*galactopyranosyl)-(1→3)-2-azido-4,6*-O-*benzylidene-2-deoxy-β*-D-*galactopyranoside* (**16**). — To a stirred mixture of compound **14** (100 mg, 300 μmol), $AgOSO_2CF_3$ (116 mg, 450 μmol), and powdered molecular sieves 4A (910 mg) in $Cl(CH_2)_2Cl$ (3 mL) was added dropwise a solution of compound **10** (148 mg, 360 μmol) in $Cl(CH_2)_2Cl$ (1.5 mL) at −15°. The mixture was stirred for 2 h at −15°, diluted with $CHCl_3$, and filtered through Celite. The filtrate was successively washed with aq. $NaHCO_3$ and aq. NaCl, dried ($MgSO_4$), and evaporated. The residue was chromatographed over $SiO_2$ in 1:1 EtOAc–toluene, to give **16** (160 mg, 80%); m.p. 140–142° (from MeOH), $[\alpha]_D$ +13.6° (*c* 1.3); $R_F$ 0.48 in 1:1 EtOAc–toluene; n.m.r. data: $\delta_H$ 7.55–7.30 (m, 5 H, Ph), 5.98–5.90 (m, 1 H, C*H*=$CH_2$), 5.560 (s, 1 H, PhC*H*), 5.396 (d, 1 H, *J* 3.4 Hz, H-4b), 5.340 (m, 1 H, CH=C$H_2$), 5.268 (dd, 1 H, *J* 8.1, 10.5 Hz, H-2b), 5.250 (m, 1 H, CH=C$H_2$), 5.034 (dd, 1 H, *J* 3.4, 10.3 Hz, H-3b), 4.810 (d, 1 H, *J* 7.8 Hz, H-1b), 4.45 and 4.14 (2 m, 2 H, OC$H_2$CH=$CH_2$), 4.353 (d, 1 H, *J* 8.1 Hz, H-1a), 3.847 (dd, 1 H, *J* 8.1, 10.7 Hz, H-2a), 3.480 (dd, 1 H, *J* 3.2, 10.7 Hz, H-3a), 3.380 (m, 1 H, H-5a), and 2.165, 2.079, 2.052, and 1.991 (4 s, 12 H, 4 OCOC$H_3$).

*Anal.* Calc. for $C_{30}H_{37}N_3O_{14}$: C, 54.30; H, 5.62; N, 6.33. Found: C, 54.56; H, 5.55; N, 6.56.

*Allyl* O-*(2,3,4,6-tetra*-O-*acetyl-β*-D-*galactopyranosyl)-(1→3)-2-azido-2-*

*deoxy-β-D-galactopyranoside* (**17**). — A solution of **5** (118 mg, 0.18 mmol) in dichloromethane (5 mL) plus 60% aqueous trifluoroacetic acid (0.2 mL) was stirred for 6 h at 20°. To the solution was added aq. $NaHCO_3$ (15 mL), and the mixture was extracted with dichloromethane (15 mL × 2). The extracts were combined, dried ($MgSO_4$), and evaporated, and the residue was chromatographed over $SiO_2$ in 4:1 EtOAc–toluene, to give **6** (90 mg, 89%); m.p. 151–152° (from toluene), $[\alpha]_D$ −0.8° (*c* 1.0); $R_F$ 0.13 in 1:1 EtOAc–toluene; n.m.r. data: $\delta_H$ 5.990–5.900 (m, 1 H, C*H*=$CH_2$), 5.400 (dd, 1 H, *J* 3.4 and 1.0 Hz, H-4b), 5.340 (m, 1 H, CH=C*H*$_2$), 5.263 (dd, 1 H, *J* 7.8, *J* 10.5 Hz, H-2b), 5.233 (m, 1 H, CH=C*H*$_2$), 5.038 (dd, 1 H, *J* 3.4 and 10.5 Hz, H-3b), 4.682 (d, 1 H, *J* 7.8 Hz, H-1b), 4.422 and 4.163 (2 m, 2 H, OC*H*$_2$CH=$CH_2$), 4.320 (d, 1 H, *J* 8.1 Hz, H-1a), 4.178 (dd, 1 H, *J* 7.1 and 11.2 Hz, H-6b), 4.085 (dd, 1 H, *J* 6.1 and 11.2 Hz, H-6'b), 4.017 (d, 1 H, *J* 3.4 Hz, H-4a), 3.976 (dd, 1 H, *J* 6.6 and 11.7 Hz, H-6a), 3.929 (t, 1 H, *J* 6.5 Hz, H-5b), 3.822 (dd, 1 H, *J* 4.9 and 11.7 Hz, H-6'a), 3.653 (dd, 1 H, *J* 8.1 and 10.0 Hz, H-2a), 3.488 (t, 1 H, *J* 5.4 Hz, H-5a), and 3.402 (dd, 1 H, *J* 3.4 and 10.1 Hz, H-3a).

*Anal.* Calc. for $C_{23}H_{33}N_3O_{14}$: C, 48.00; H, 5.78; N, 7.30. Found: C, 47.64; H, 5.70; N, 7.20.

*Allyl* O-*(2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl)-(1→3)-*O*-[methyl (5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-*D*-glycero-α-*D*-galacto-2-nonulopyranosyl)onate-(2→6)]-2-azido-2-deoxy-β-*D*-galactopyranoside* (**11**) *and allyl* O-*(2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl)-(1→3)-*O*-[methyl (5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-*D*-glycero-β-*D*-galacto-2-nonulopyranosyl)onate-(2→6)]-2-azido-2-deoxy-β-*D*-galactopyranoside* (**21**). — To a stirred mixture of powdered molecular sieves 4A (0.52 g), **17** (50 mg, 87 μmol), $Hg(CN)_2$ (106 mg, 416 μmol), and $HgBr_2$ (75 mg, 208 μmol) in $Cl(CH_2)_2Cl$ (1.5 mL) was added dropwise a solution of **19** (212 mg, 416 μmol) in $Cl(CH_2)_2Cl$ (0.5 mL) under argon at −15°. The mixture was stirred for 1 h at −15° and then for 24 h at room temperature, diluted with EtOAc, and filtered through a bed of Celite. The filtrate was successively washed with aq. $NaHCO_3$ and brine, and evaporated to a residue which was chromatographed on $SiO_2$ in 20:20:1 EtOAc–toluene–MeOH, to give **11** (40 mg, 44%) and **21** (37 mg; 41%, based on **17**).

Compound **11** had $[\alpha]_D$ −4.9° (*c* 0.29); $R_F$ 0.52 in 10:10:1 EtOAc–toluene–MeOH; n.m.r. data: $\delta_H$ 5.97–5.89 (m, 1 H, C*H*=$CH_2$), 5.408 (d, 1 H, *J* 2.5 Hz, H-4c), 5.38–5.31 (m, 3 H, H-7b, H-8b, CH=C*H*$_2$), 5.262 (dd, 1 H, *J* 8.1 and 10.5 Hz, H-2c), 5.220 (m, 1 H, CH=C*H*$_2$), 5.165 (d, 1 H, *J* 9.5 Hz, N*H*), 5.047 (dd, 1 H, *J* 3.4 and 10.5 Hz, H-3c), 4.861 (ddd, 1 H, *J* 4.5, 10.5, and 12.1 Hz, H-4b), 4.759 (d, 1 H, *J* 8.1 Hz, H-1c), 4.410 (m, 1 H, OC*H*$_2$CH=$CH_2$), 4.348 (dd, 1 H, *J* 12.2 and 2.7 Hz, H-6b), 4.309 (d, 1 H, *J* 8.1 Hz, H-1a), 4.200–4.050 (m, 6 H, H-5b,9b,9'b,6c, 6'c, and OC*H*$_2$CH=$CH_2$), 3.976 (d, 1 H, *J* 2.9 Hz, H-4a), 3.947 (t, 1 H, *J* 7.6 Hz, H-5c), 3.877 (dd, 1 H, *J* 5.9 and 9.8 Hz, H-6a), 3.814 (s, 3 H, COOC*H*$_3$), 3.676 (dd, 1 H, *J* 7.3 and 9.8 Hz, H-6'a), 3.619 (dd, 1 H, *J* 8.1 and 10.3 Hz, H-2a), 3.522 (t, 1 H, *J* 6.7 Hz, H-5a), 3.411 (dd, 1 H, *J* 3.4 and 10.3 Hz, H-3a), 2.588 (dd, 1 H, *J* 4.6 and 12.9 Hz, H-3b*eq*), 2.176, 2.141, 2.134, 2.100, 2.054,

2.038, 2.029, 2.002, 1.883 (9 s, 27 H, 8 OCOC$H_3$ and NCOC$H_3$), and 1.945 (t, 1 H, *J* 12.6 Hz, H-3b*ax*).

*Anal.* Calc. for $C_{43}H_{60}N_4O_{26}\cdot H_2O$: C, 48.41; H, 5.86; N, 5.25. Found: C, 48.61; H, 5.61; N, 5.12.

Compound **21** had $[\alpha]_D$ −14.4° (*c* 0.54, MeOH); $R_F$: 0.54 in 10:10:1 EtOAc–toluene–MeOH; n.m.r. data: $\delta_H$ 6.560 (d, 1 H, *J* 10.0 Hz, N*H*), 5.97–5.87 (m, 1 H, C*H*=$CH_2$), 5.456 (dd, 1 H, *J* 2.2 and 4.2 Hz, H-7b), 5.436 (d, 1 H, *J* 2.7 Hz, H-4c), 5.35–5.19 (m, 4 H, H-4b,8b, CH=C$H_2$), 5.268 (dd, 1 H, *J* 8.1 and 10.5 Hz, H-2c), 5.067 (dd, 1 H, *J* 10.5 and 3.4 Hz, H-3c), 4.774 (d, 1 H, *J* 8.1 Hz, H-1c), 4.733 (dd, 1 H, *J* 12.5 and 2.2 Hz, H-9b), 4.369 (ddt, *J* 1.7, 5.1, and 12.9 Hz, OC$H_2$CH=$CH_2$), 4.280 (d, 1 H, *J* 8.1 Hz, H-1a), 4.106 (d, 1 H, *J* 3.7 Hz, H-4a), 4.008 (q, 1 H, *J* 10.0 Hz, H-5b), 3.944 (t, 1 H, *J* 6.8 Hz, H-5a), 3.819 (s, 3 H, COOC$H_3$), 3.658 (dd, 1 H, *J* 8.1 and 10.3 Hz, H-2a), 3.427 (dd, 1 H, *J* 3.4 and 10.3 Hz, H-3a), 2.447 (dd, 1 H, *J* 4.9 and 12.9 Hz, H-3b*eq*), 2.189, 2.143, 2.122, 2.103, 2.056 (6 H), 2.018, 1.973, 1.874 (8 s, total 27 H, 8 OCOC$H_3$ and NCOC$H_3$), and 1.835 (t, 1 H, *J* 11.5 Hz, H-3b*ax*).

*Anal.* Calc. for $C_{43}H_{60}N_4O_{26}\cdot H_2O$: C, 48.41; H, 5.86; N, 5.25. Found: C, 48.47; H, 5.60; N, 5.20.

*Allyl* O-*(2,3,4,6-tetra*-O-*acetyl*-β-D-*galactopyranosyl)-(1→3)*-O-[*methyl (5-acetamido-4,7,8,9-tetra*-O-*acetyl-3,5-dideoxy*-D-glycero-α-D-galacto-*2-nonulopyranosyl)onate-(2→6)*]-*2-azido-2-deoxy*-β-D-*galactopyranoside* (**11**) *and allyl* O-*(2,3,4,6-tetra*-O-*acetyl*-β-D-*galactopyranosyl)-(1→3)*-O-[*(2,3,4,6-tetra*-O-*acetyl*-β-D-*galactopyranosyl)-(1→4)*]-O-[*methyl (5-acetamido-4,7,8,9-tetra*-O-*acetyl-3,5-dideoxy*-D-glycero-α-D-galacto-*2-nonulopyranosyl)onate-(2→6)*]-*2-azido-2-deoxy*-β-D-*galactopyranoside* (**13**). — To a stirred mixture of powdered molecular sieves 4A (0.49 g), **9** (140 mg, 195 μmol), and $AgOSO_2CF_3$ (76 mg, 292 μmol) in $Cl(CH_2)_2Cl$ (1.5 mL) was added dropwise a solution of **10** (96 mg, 234 μmol) in $Cl(CH_2)_2Cl$ (1 mL) under argon at −15°. The mixture was stirred for 1 h at −15° and then for 24 h at room temperature, diluted with ethyl acetate, and filtered through a bed of Celite. The filtrate was successively washed with aq. $NaHCO_3$ and brine, dried ($MgSO_4$), and evaporated to a residue which was chromatographed on $SiO_2$ in 8:1 *i*-$Pr_2O$–MeOH, to give **11** (79 mg, 39%) and **13** (60 mg, 22%). Product **11** was identified with that obtained by the reaction between **17** and **19**.

Compound **13** had $[\alpha]_D$ −11.1° (*c* 1.96); $R_F$ 0.29 in 8:1 *i*-$Pr_2O$–MeOH (for compound **11**, $R_F$ 0.31); n.m.r. data: $\delta_H$ 5.99–5.89 (m, 1 H, C*H*=$CH_2$), 5.423 and 5.391 (2 d, 2 H, *J* 2.7 and 2.4 Hz, H-4c,4d), 5.060 (d, 1 H, *J* 7.6 Hz, H-1c), 4.860 (m, 1 H, H-4b), 4.796 (d, 1 H, *J* 7.8 Hz, H-1d), 4.315 (d, 1 H, *J* 7.3 Hz, H-1a), 3.855 (s, 3 H, COOC$H_3$), 2.573 (dd, 1 H, *J* 4.6 and 12.7 Hz, H-3b*eq*), 2.222, 2.148, 2.131, 2.125, 2.106, 2.084, 2.084, 2.027, 2.027, 2.027, 2.005, 1.991, and 1.877 (13 s, 39 H, 12 OCOC$H_3$ and NCOC$H_3$).

*Anal.* Calc. for $C_{57}H_{78}N_4O_{35}$: C, 49.64; H, 5.70; N, 4.06. Found: C, 49.28; H, 5.64; N, 3.95.

*Allyl* O-*(2,3,4,6-tetra*-O-*acetyl*-β-D-*galactopyranosyl)-(1→3)*-O-[*methyl (5-*

*acetamido-4,7,8,9-tetra*-O-*acetyl-3,5-dideoxy*-D-glycero-α-D-galacto-*2-nonulopyranosyl)onate-(2→6)*]-*4*-O-*acetyl-2-azido-2-deoxy*-β-D-*galactopyranoside* (**12**). — Compound **11** (50 mg, 48 μmol) was dissolved in pyridine (1 mL) and $Ac_2O$ (0.5 mL). The solution was stirred for 24 h at room temperature, and then evaporated *in vacuo*. The residue was chromatographed on $SiO_2$ in 10:10:1 EtOAc–toluene–MeOH, to give **12** (51 mg, 98%); $[\alpha]_D$ −3.9° (*c* 0.18); $R_F$ 0.54 in 40:1 $CHCl_3$–MeOH; n.m.r. data: $\delta_H$ 6.01–5.93 (m, 1 H, C*H*=$CH_2$), 5.40–5.24 (m, 6 H, H-4a,7b,8b,4c, CH=C$H_2$), 5.145 (dd, 1 H, *J* 7.8 and 10.5 Hz, H-2c), 5.145 (d, 1 H, *J* 10.5 Hz, N*H*), 5.011 (dd, 1 H, *J* 3.4 and 10.5 Hz, H-3c), 4.850 (m, 1 H, H-4b), 4.763 (d, 1 H, *J* 7.8 Hz, H-1c), 4.480 and 4.160 (2 m, 2 H, OC$H_2$CH=$CH_2$), 4.343 (d, 1 H, *J* 7.8 Hz, H-1a), 4.308 (dd, 1 H, *J* 2.5 and 12.3 Hz, H-6b), 3.879 (t, 1 H, *J* 6.5 Hz, H-5c), 3.794 (s, 3 H, COOC$H_3$), 3.657 (t, 1 H, *J* 6.5 Hz, H-5a), 3.354 (dd, 1 H, *J* 5.7 and 10.1 Hz, H-6'a), 2.574 (dd, 1 H, *J* 4.6 and 12.9 Hz, H-3b*eq*), 2.158, 2.146, 2.119, 2.116, 2.080, 2.049, 2.035, 2.024, 1.982, and 1.878 (10 s, 30 H, 9 OCOC$H_3$ and NCOC$H_3$).

*Anal.* Calc. for $C_{45}H_{62}N_4O_{27}$: C, 49.54; H, 5.73; N, 5.14. Found: C, 49.19; H, 5.69; N, 5.05.

*Allyl* O-*(2,3,4,6-tetra*-O-*acetyl*-β-D-*galactopyranosyl)-(1→3)*-O-[*methyl (5-acetamido-4,7,8,9-tetra*-O-*acetyl-3,5-dideoxy*-D-glycero-β-D-galacto-*2-nonulopyranosyl)onate-(2→6)*]-*4*-O-*acetyl-2-azido-2-deoxy*-β-D-*galactopyranoside* (**22**). — Compound **21** (50 mg, 48 μmol) was dissolved in pyridine (1 mL) and acetic anhydride (0.5 mL). The solution was stirred for 24 h at room temperature, and then processed as for **12**, to give **22** (51 mg, 98%); $[\alpha]_D$ −16.2° (*c* 0.1); $R_F$ 0.59 in 40:1 $CHCl_3$–MeOH; n.m.r. data: $\delta_H$ 6.173 (d, 1 H, *J* 10.2 Hz, N*H*), 5.99–5.89 (m, 1 H, C*H*=$CH_2$), 5.565 (d, 1 H, *J* 3.2 Hz, H-4a), 5.416 (d, 1 H, *J* 2.7 Hz, H-4c), 5.360 and 5.260 (2 m, 2 H, CH=C$H_2$), 5.300 (m, 1 H, H-4b), 5.205 (dd, 1 H, *J* 7.8 and 10.5 Hz, H-2c), 5.028 (dd, 1 H, *J* 3.4 and 10.1 Hz, H-3c), 4.761 (dd, 1 H, *J* 2.4 and 12.2 Hz, H-9b), 4.701 (d, 1 H, *J* 7.8 Hz, H-1c), 4.410 and 4.250 (2 m, 2 H, OC$H_2$CH=$CH_2$), 4.342 (d, 1 H, *J* 8.1 Hz, H-1a), 3.816 (s, 3 H, COOC$H_3$), 3.652 (dd, 1 H, *J* 8.1 and 10.3 Hz, H-2a), 3.531 (dd, 1 H, *J* 3.2 and 10.3 Hz, H-3a), 2.423 (dd, 1 H, *J* 4.9 and 12.9 Hz, H-3b*eq*), 2.291, 2.159 (6 H), 2.095, 2.069, 2.037, 2.001, 1.998, 1.959, 1.922 (9 s, total 30 H, 9 OCOC$H_3$ and NCOC$H_3$), 1.789 (t, 1 H, *J* 12.1 Hz, H-3b*ax*).

*Anal.* Calc. for $C_{45}H_{62}N_4O_{27}$: C, 49.54; H, 5.73; N, 5.14. Found: C, 49.22; H, 5.63; N, 5.01.

O-*(2,3,4,6-Tetra*-O-*acetyl*-β-D-*galactopyranosyl)-(1→3)*-O-[*methyl (5-acetamido-4,7,8,9-tetra*-O-*acetyl-3,5-dideoxy*-D-glycero-α-D-galacto-*2-nonulopyranosyl)onate-(2→6)*]-*4*-O-*acetyl-2-azido-2-deoxy*-β-D-*galactopyranose* (**20**). — A mixture of **12** (570 mg, 520 μmol), $PdCl_2$ (131 mg, 730 μmol), and AcONa (176 mg, 2.13 mmol) in $H_2O$ (1 mL) and AcOH (19 mL) was stirred for 12 h at room temperature, diluted with AcOEt, poured into aq. $NaHCO_3$, the suspension filtered through Celite, and the filtrate evaporated *in vacuo*, to give an oil which was purified by chromatography over $SiO_2$ in 10:10:1 EtOAc–toluene–MeOH to

give **20** (450 mg, 82%); $[\alpha]_D$ +10.4° (*c* 0.1); $R_F$ 0.40 in 10:10:1 EtOAc–toluene–MeOH; n.m.r. data: $\delta_H$ 3.80 and 3.79 (2 s, 3 H, 2 COOC$H_3$); $\delta_C$ 100.9 (C-1c), 98.6 (C-2b), 98.3 (C-1a$\beta$), and 91.9 (C-1a$\alpha$).

*Anal.* Calc. for $C_{42}H_{58}N_4O_{27}$: C, 48.00; H, 5.56; N, 5.33. Found: C, 48.20; H, 5.50; N, 5.11.

O-*(2,3,4,6-Tetra*-O-*acetyl-β*-D-*galactopyranosyl)-(1→3)*-O-[*methyl (5-acetamido-4,7,8,9-tetra*-O-*acetyl-3,5-dideoxy*-D-glycero-*α*-D-galacto-*2-nonulopyranosyl)onate-(2→6)*]-*4*-O-*acetyl-2-azido-2-deoxy-α*-D-*galactopyranosyl trichloroacetimidate* (**23**). — A mixture of **20** (231 mg, 0.22 mmol), $Cl_3CCN$ (160 mg, 1.10 mmol), and DBU 76 mg (0.11 mmol) in dry $CH_2Cl_2$ (2 mL) was stirred for 45 min at −15°. The reaction mixture was directly chromatographed over $SiO_2$ in 10:10:1 EtOAc–toluene–MeOH, to give a 4:1 mixture of **23** and the β-isomer (115 mg, 43%); $[\alpha]_D$ +18.8° (*c* 5.5); $R_F$ 0.44 in 10:10:1 EtOAc–toluene–MeOH; n.m.r. data: $\delta_H$ 8.793 (s, 1 H, C=N*H*), 6.522 (d, 0.8 H, *J* 3.4 Hz, H-1a$\alpha$), 5.656 (d, 0.2 H, *J* 8.6 Hz, H-1a$\beta$), 5.524 and 5.377 (2 dd, 2 H, *J* 3.4 Hz, H-4a,4c), 5.204 (dd, 1 H, *J* 7.8 and 10.5 Hz, H-2c), 5.137 (d, 1 H, *J* 9.8 Hz, N*H*), 5.020 (dd, 1 H, *J* 3.4 and 10.5 Hz, H-3c), 4.840 (m, 1 H, H-4b), 4.762 (d, 1 H, *J* 7.8 Hz, H-1c), 3.791 (s, 3 H, COOC$H_3$), 3.347 (dd, 1 H, *J* 4.4 and 10.5 Hz, H-6'a), 2.571 (dd, 0.2 H, *J* 4.6 and 12.7 Hz, H-3b*eq*), 2.519 (dd, 0.8 H, *J* 4.6 and 12.7 Hz, H-3b*eq*), 2.166, 2.161, 2.143, 2.101, 2.071, 2.053, 2.041, 2.018, 1.984, and 1.867 (10 s, 30 H, 9 OCOC$H_3$ and NCOC$H_3$).

*Anal.* Calc. for $C_{44}H_{58}Cl_3N_5O_{27}$: C, 44.21; H, 4.89; N, 5.86. Found: C, 44.01; H, 5.20; N, 5.49.

N-*(Benzyloxycarbonyl)*-O-*(2,3,4,6-tetra*-O-*acetyl-β*-D-*galactopyranosyl)-(1→3)*-O-[*methyl (5-acetamido-4,7,8,9-tetra*-O-*acetyl-3,5-dideoxy*-D-glycero-*α*-D-galacto-*2-nonulopyranosyl)onate-(2→6)*]-O-*(4*-O-*acetyl-2-azido-2-deoxy-α*-D-*galactopyranosyl)-(1→3)*-L-*serine benzyl ester* (**24**) *and* N-*(benzyloxycarbonyl)*-O-*(2,3,4,6-tetra*-O-*acetyl-β*-D-*galactopyranosyl)-(1→3)*-O-[*methyl (5-acetamido-4,7,8,9-tetra*-O-*acetyl-3,5-dideoxy*-D-glycero-*α*-D-galacto-*2-nonulopyranosyl)onate-(2→6)*]-O-*(4*-O-*acetyl-2-azido-2-deoxy-β*-D-*galactopyranosyl)-(1→3)*-L-*serine benzyl ester* (**27**). — To a stirred mixture of powdered molecular sieves AW-300 (0.3 g) and *N*-Cbz-L-serine benzyl ester (96 mg, 288 μmol) in $Cl(CH_2)_2Cl$ (1 mL) was added a solution of **23** (115 mg, 96 μmol) in dichloroethane (1 mL). To this mixture was added dropwise $Me_3SiOSO_2CF_3$ (27.0 μL, 31 mg, 144 μmol) at −15° under argon. After being stirred for 30 min, the mixture was diluted with EtOAc, filtered through Celite, and the filtrate successively washed with aq. $NaHCO_3$ and water, dried ($MgSO_4$); and evaporated *in vacuo,* and the residue chromatographed on $SiO_2$ in 10:10:1 EtOAc–toluene–MeOH, to give **24** (20 mg, 15%) and **27** (43 mg, 33%).

Compound **24** had $[\alpha]_D$ +22.7° (*c* 0.5); $R_F$ 0.51 in 10:10:1 EtOAc–toluene–MeOH; n.m.r. data: $\delta_H$ 7.42–7.29 (m, 10 H, 2 Ph), 5.794 (d, 1 H, *J* 8.3 Hz, N*H*cbz), 4.986 (dd, 1 H, *J* 3.2 and 10.5 Hz, H-3c), 4.856 (d, 1 H, *J* 3.4 Hz, H-1a), 4.648 (d, 1 H, *J* 8.1 Hz, H-1c), 4.620 (m, 1 H, H-1Ser), 3.764 (s, 3 H, COOC$H_3$), 3.547 (dd,

1 H, *J* 3.4 and 10.7 Hz, H-2a), 3.296 (dd, 1 H, *J* 3.4 and 10.3 Hz, H-6a'), 2.554 (dd, 1 H, *J* 4.6 and 12.6 Hz, H-3b*eq*), 2.142, 2.121, 2.096, 2.094, 2.057, 2.013 (9 H), 1.979, and 1.870 (8 s, total 30 H, 9 OCOC$H_3$ and NCOC$H_3$).

*Anal.* Calc. for $C_{60}H_{75}N_5O_{31}$: C, 52.90; H, 5.55; N, 5.14. Found: C, 52.68; H, 5.42; N, 4.95.

Compound **27** had $[\alpha]_D$ +7.3° (*c* 0.9); $R_F$ 0.49 in 10:10:1 EtOAc–toluene–MeOH; n.m.r. data: $\delta_H$ 7.44–7.78 (m, 10 H, 2 Ph), 5.870 (d, 1 H, *J* 9.2 Hz, N*H*-Ser), 4.740 (d, 1 H, *J* 7.8 Hz, H-1c), 3.776 (s, 3 H, COOC$H_3$), 3.359 (dd, 1 H, *J* 5.9 and 10.3 Hz, H-6'a), 2.554 (dd, 1 H, *J* 4.9 and 12.7 Hz, H-3b*eq*), 2.159, 2.124, 2.120, 2.105, 2.049, 2.037, 2.024, 2.015, 1.982, and 1.875 (10 s, 30 H, 9 OCOC$H_3$ and NCOC$H_3$).

*Anal.* Calc. for $C_{60}H_{75}N_5O_{31}$: C, 52.90; H, 5.55; N, 5.14. Found: C, 52.62; H, 5.39; N, 4.91.

N-*(Benzyloxycarbonyl)*-O-*(2,3,4,6-tetra*-O-*acetyl-β*-D-*galactopyranosyl)-(1→3)*-O-[*methyl (5-acetamido-4,7,8,9-tetra*-O-*acetyl-3,5-dideoxy*-D-glycero-*α*-D-galacto-*2-nonulopyranosyl)onate-(2→6)*]-O-*(2-acetamido-4*-O-*acetyl-2-deoxy-α*-D-*galactopyranosyl)-(1→3)*-L-*serine benzyl ester* (**25**). — A mixture of **24** (9 mg) and Lindlar catalyst (15 mg) in methanol was stirred under hydrogen at 40°. After stirring for 12 h, **24** had disappeared in t.l.c. The mixture was diluted with MeOH, filtered through Celite, and the filtrate evaporated *in vacuo*, to give a syrupy residue which was dissolved in pyridine (0.5 mL) and $Ac_2O$ (0.3 mL). The solution was stirred for 12 h at room temperature, evaporated *in vacuo*, and the residue chromatographed over $SiO_2$ in 70:1 $CHCl_3$–MeOH, to give **25** (6.7 mg, 74%); $[\alpha]_D$ +23.9° (*c* 0.3); $R_F$ 0.39 in 30:10:1 EtOAc–toluene–MeOH; n.m.r. data: $\delta_H$ 7.44–7.29 (m, 10 H, 2 Ph), 5.840 and 5.740 (2 d, 2 H, *J* 7.3 and 8.8 Hz, N*H*-Ser and N*H*-2a), 4.952 (dd, 1 H, *J* 3.4 and 10.5 Hz, H-3c), 4.854 (ddd, 1 H, *J* 4.4, 9.5, and 12.0 Hz, H-4b), 4.806 (d, 1 H, *J* 3.7 Hz, H-1a), 4.580 (d, 1 H, *J* 7.6 Hz, H-1c), 4.441 (ddd, 1 H, *J* 3.4, 9.3, and 10.7 Hz, H-2a), 4.302 (dd, 1 H, *J* 2.4 and 12.2 Hz, H-9b), 3.770 (s, 3 H, COOC$H_3$), 3.310 (dd, 1 H, *J* 4.6 and 10.0 Hz, H-6'a), 2.552 (dd, 1 H, *J* 4.6 and 12.7 Hz, H-3b*eq*), 2.142, 2.126, 2.112, 2.095, 2.069, 2.027, 2.020, 2.013, 1.972, 1.964, and 1.872 (11 s, 33 H, 9 OCOC$H_3$ and 2 NCOC$H_3$).

*Anal.* Calc. for $C_{62}H_{79}N_3O_{32}\cdot H_2O$: C, 53.33; H, 5.85; N, 3.01. Found: C, 53.51; H, 5.68; N, 3.01.

N-*(Benzyloxycarbonyl)*-O-*(2,3,4,6-tetra*-O-*acetyl-β*-D-*galactopyranosyl)-(1→3)*-O-[*methyl (5-acetamido-4,7,8,9-tetra*-O-*acetyl-3,5-dideoxy*-D-glycero-*α*-D-galacto-*2-nonulopyranosyl)onate-(2→6)*]-*(2-acetamido-4*-O-*acetyl-2-deoxy-β*-D-*galactopyranosyl)-(1→3)*-L-*serine benzyl ester* (**28**). — A mixture of **27** (19 mg) and Lindlar catalyst (30 mg) in MeOH was stirred under hydrogen at 40°, and then processed as for **25**, to give **28** (13 mg, 68%); $[\alpha]_D$ −7.6° (*c* 0.2); $R_F$ 0.37 in 30:10:1 EtOAc–toluene–MeOH; n.m.r. data: $\delta_H$ 7.43–7.29 (m, 10 H, 2 Ph), 5.914 and 5.746 (2 d, 2 H, *J* 8.6 and 7.6 Hz, N*H*-Ser and N*H*-2a), 5.444 and 5.348 (2 dd, 2 H, *J* 3.2 and 2.4 Hz, H-4a,4c), 5.310 (m, 1 H, H-8b), 5.255 (bd, 1 H, *J* 8.3 Hz, H-7b), 4.951 (dd, 1 H, *J* 3.4 and 10.5 Hz, H-3c), 4.932 (d, 1 H, *J* 7.6 Hz, H-1c), 4.870 (m,

1 H, H-4b), 4.630 (d, 1 H, *J* 8.1 Hz, H-1a), 4.540 (m, 1 H, H-1Ser), 3.781 (s, 3 H, $COOCH_3$), 3.367 (dd, 1 H, *J* 6.1 and 10.3 Hz, H-6'a), 2.561 (dd, 1 H, *J* 4.6 and 13.2 Hz, H-3b*eq*), 2.158, 2.140, 2.114, 2.106, 2.043, 2.043, 2.021, 1.998, 1.966, 1.882, and 1.860 (11 s, 33 H, 9 $OCOCH_3$ and 2 $NCOCH_3$).

*Anal.* Calc. for $C_{62}H_{79}N_3O_{32}$: C, 54.03; H, 5.78; N, 3.05. Found: C, 53.70; H, 5.68; N, 3.01.

O-*(2,3,4,6-Tetra*-O-*acetyl-β*-D-*galactopyranosyl)-(1→3)*-O-[*methyl (5-acetamido-4,7,8,9-tetra*-O-*acetyl-3,5-dideoxy*-D-glycero-*α*-D-galacto-*2-nonulopyranosyl)-onate-(2→6)*]-O-*(2-acetamido-4*-O-*acetyl-2-deoxy-α*-D-*galactopyranosyl)-(1→3)*-L-*serine* (**26**). — A mixture of **25** (6.7 mg) and 10% Pd–C (10 mg) in MeOH (0.5 mL) was stirred under hydrogen for 3.5 h at room temperature, diluted with methanol, filtered through Celite, and the filtrate evaporated *in vacuo*, to give **26** (5.2 mg, 92%); $[\alpha]_D$ +40.4° (*c* 0.26, MeOH); $R_F$ 0.56 in 2:1:1 1-butanol–EtOH–$H_2O$; n.m.r. data: $\delta_H$ ($CD_3OD$) 5.42–5.34 (m, 3 H, H-4a,8b,4c), 5.323 (dd, 1 H, *J* 2.2 and 8.7 Hz, H-7b), 5.059 (dd, 1 H, *J* 3.4 and 10.5 Hz, H-3c), 4.992 (dd, 1 H, *J* 7.6 and 10.5 Hz, H-2c), 4.816 (d, 1 H, *J* 3.7 Hz, H-1a), 4.769 (d, 1 H, *J* 7.8 Hz, H-1c), 4.429 (dd, 1 H, *J* 3.7 and 11.2 Hz, H-2a), 3.820 (s, 3 H, $COOCH_3$), 2.646 (dd, 1 H, *J* 4.8 and 12.8 Hz, H-3b*eq*), 2.137, 2.135, 2.117, 2.101, 2.034 (6 H), 2.024, 2.007, 1.974, 1.929, and 1.825 (10 s, total 33 H, 9 $OCOCH_3$ and 2 $NCOCH_3$).

O-*(2,3,4,6-Tetra*-O-*acetyl-β*-D-*galactopyranosyl)-(1→3)*-O-[*methyl (5-acetamido-4,7,8,9-tetra*-O-*acetyl-3,5-dideoxy*-D-glycero-*α*-D-galacto-*2-nonulopyranosyl)-onate-(2→6)*]-O-*(2-acetamido-4*-O-*acetyl-2-deoxy-β*-D-*galactopyranosyl)-(1→3)*-L-*serine* (**29**). — A mixture of **28** (3.4 mg) and 10% Pd–C (6 mg) in MeOH (0.3 mL) was stirred under hydrogen at room temperature, and then processed as for **26**, to give **29** (2.2 mg, 77%); $[\alpha]_D$ +15.0° (*c* 0.1, methanol); $R_F$ 0.55 in 2:1:1 BuOH–EtOH–$H_2O$; n.m.r. data: $\delta_H$ ($CD_3OD$) 3.806 (s, 3 H, $COOCH_3$), 2.142, 2.137, 2.122, 2.110, 2.036, 2.019, 2.019, 2.019, 2.007, 1.976, and 1.886 (11 s, 33 H, 9 $OCOCH_3$ and 2 $NCOCH_3$).

O-*β*-D-*Galactopyranosyl-(1→3)*-O-[*(5-acetamido-3,5-dideoxy*-D-glycero-*α*-D-galacto-*2-nonulopyranosylonic acid)-(2→6)*]-O-*(2-acetamido-2-deoxy-α*-D-*galactopyranosyl)-(1→3)*-L-*serine* (**2**). — To solution of **26** (5.2 mg) in MeOH (0.6 mL) was added dropwise M aq. NaOH (72 μL). The mixture was stirred for 3 h at room temperature, made neutral with Amberlyst-15 ($H^+$) resin in cold $H_2O$ (10 mL), filtered through Celite, and the filtrate evaporated *in vacuo*, the residue was purified by gel filtration with Sephadex G-10 in $H_2O$, to give **2** (2.5 mg, 72%); m.p. 201°, $[\alpha]_D$ +65.6° (*c* 0.09, $H_2O$); $R_F$ 0.21 in 2:1:1 BuOH–EtOH–$H_2O$; n.m.r. data: $\delta_H$ ($D_2O$) 4.863 (d, 1 H, *J* 3.7 Hz, H-1a), 4.451 (d, 1 H, *J* 7.8 Hz, H-1c), 4.228 (d, 1 H, *J* 2.9 Hz, H-4a), 4.037 (dd, 1 H, *J* 2.9 and 11.2 Hz, H-3a), 4.030 (m, 1 H, H-1Ser), 3.984 (dd, 1 H, *J* 3.2 and 10.5 Hz, H-6a), 3.558 (dd, 1 H, *J* 1.7 and 8.5 Hz, H-7b), 3.495 (dd, 1 H, *J* 7.8 and 9.8 Hz, H-2c), 2.719 (dd, 1 H, *J* 4.6 and 12.2 Hz, H-3b*eq*), 2.021 and 2.010 (2 s, 6 H, 2 $NCOCH_3$), and 1.664 (t, 1 H, *J* 12.0 Hz, H-3b*ax*).

*Anal.* Calc. for $C_{28}H_{47}N_3O_{23} \cdot 4\ H_2O$: C, 38.84; H, 6.40; N, 4.85. Found: C, 39.19; H, 6.01; N, 4.50.

O-*Deacetylation of* **29**. — To solution of **29** (2.0 mg) in MeOH (0.3 mL) was added dropwise M aq. NaOH (30 μL). Processing as for **2** gave *O*-β-D-galactopyranosyl-(1→3)-*O*-[(5-acetamido-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nulopyranosylonic acid)-(2→6)]-*O*-(2-acetamido-2-deoxy-β-D-galactopyranosyl)-(1→3)-L-serine (**30**; 0.9 mg, 68%); m.p. 202.5°, $[\alpha]_D$ +22.2° (*c* 0.05, $H_2O$); $R_F$ 0.18 in 2:1:1 BuOH–EtOH–$H_2O$); n.m.r. data: $\delta_H$ ($D_2O$, 40°), 4.518 (d, 1 H, *J* 7.8 Hz, H-1a), 4.420 (d, 1 H, *J* 7.6 Hz, H-1c), 2.717 (dd, 1 H, *J* 4.2 and 12.2 Hz, H-3b*eq*), 2.020 (2 s, 6 H, 2 NCO$CH_3$), and 1.683 (t, 1 H, *J* 12.0 Hz, H-3b*ax*).

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