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Synthetic mucin fragments: synthesis of *O*-sulfo and *O*-methyl derivatives of allyl *O*-(β-D-galactopyranosyl)-(1 → 3)-2-acetamido-2-deoxy-α-D-galactopyranoside as potential compounds for sulfotransferases ☆

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Abstract

Allyl 2-acetamido-4,6-*O*-(4-methoxybenzylidene)-2-deoxy-α-D-galactopyranoside (**1**) was condensed with either 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide (**2**) or 2,3,4-tri-*O*-benzoyl-6-*O*-bromoacetyl-α-D-galactopyranosyl bromide (**14**) in the presence of mercuric cyanide. Selective substitution with methyl, sulfo or both at desired positions, followed by the removal of protecting groups, afforded allyl *O*-(β-D-galactopyranosyl)-(1 → 3)-2-acetamido-2-deoxy-6-*O*-methyl-α-D-galactopyranoside (**5**), allyl *O*-(6-*O*-sulfo-β-D-galactopyranosyl sodium salt)-(1 → 3)-2-acetamido-2-deoxy-6-*O*-methyl-α-D-galactopyranoside (**10**), allyl *O*-(β-D-galactopyranosyl)-(1 → 3)-2-acetamido-2-deoxy-6-*O*-sulfo-α-D-galactopyranoside sodium salt (**13**), allyl *O*-(6-*O*-sulfo-β-D-galactopyranosyl sodium salt)-(1 → 3)-2-acetamido-2-deoxy-α-D-galactopyranoside (**17**) and allyl *O*-(3-*O*-sulfo-β-D-galactopyranosyl sodium salt)-(1 → 3)-2-acetamido-2-deoxy-α-D-galactopyranoside (**22**). The structures of compounds **5**, **10**, **13**, **17** and **22** were established by ^{13}C NMR and FAB mass spectroscopy.

Keywords: Mucin fragments; Sulfotransferases; ^{13}C NMR; FAB mass spectroscopy

☆ Synthetic Studies in Carbohydrates, Part 97. For Part 96 see ref. [1].

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1. Introduction

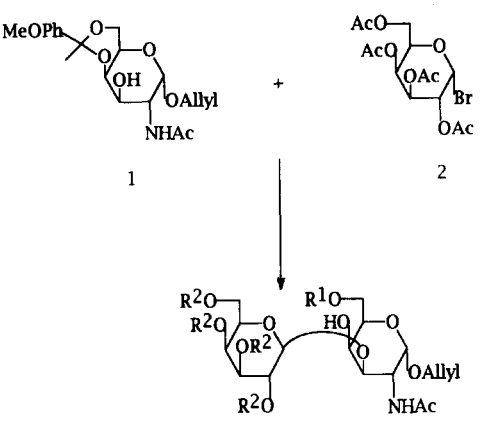
During the past few years we have seen a great deal of interest in studies concerning the structure and function of sulfate containing glycoproteins [2–7]. GLYCAM-1 and CD_{34}, two HEV-associated ligands for L-selectin, have been identified as mucin-like glycoproteins [8–11]. These two ligands are sulfated, fucosylated and sialylated glycoproteins [9]. These three elements are now generally recognized as important and/or even essential for binding with L-selectin. This knowledge has further stimulated our interest in the study of sulfotransferases involved in the biosynthesis of the sulfated mucin structures. In the past we have reported the synthesis of various acceptors and expected reference compounds for identification and characterization of glycosyltransferases such as the β-*N*-acetylglucosaminyltransferases involved in the assembly of core structures in *O*-linked glycoproteins. In this report we describe the synthesis of a series of *O*-sulfated and *O*-methylated β-Gal-(1 → 3)-α-GalNAc-(1 → *O*-allyl) disaccharide derivatives desired for the study of sulfotransferases. We have already observed that allyl 2-acetamido-2-deoxy-3-*O*-β-D-galactopyranosyl-α-D-galactopyranoside acts as an acceptor for sulfotransferases present in ovarian tissue (unpublished results). In this regard, we have accomplished the synthesis of allyl *O*-(β-D-galactopyranosyl)-(1 → 3)-2-acetamido-2-deoxy-6-*O*-methyl-α-D-galactopyranoside (**5**), allyl *O*-(6-*O*-sulfo-β-D-galactopyranosyl sodium salt)-(1 → 3)-2-acetamido-2-deoxy-6-*O*-methyl-α-D-galactopyranoside (**10**), allyl *O*-(β-D-galactopyranosyl)-(1 → 3)-2-acetamido-2-deoxy-6-*O*-sulfo-α-D-galactopyranoside sodium salt (**13**), allyl *O*-(6-*O*-sulfo-β-D-galactopyranosyl sodium salt)-(1 → 3)-2-acetamido-2-deoxy-α-D-galactopyranoside (**17**) and allyl *O*-(3-*O*-sulfo-β-D-galactopyranosyl sodium salt)-(1 → 3)-2-acetamido-2-deoxy-α-D-galactopyranoside (**22**).

2. Results and discussion

A common intermediate, namely, allyl *O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-(1 → 3)-2-acetamido-2-deoxy-α-D-galactopyranoside (**3**) was utilized for the synthesis of target compounds **5**, **10** and **13**. Glycosylation of allyl 2-acetamido-2-deoxy-4,6-*O*-(4-methoxybenzylidene)-α-D-galactopyranoside (**1**) with 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide in 1 : 1 benzene–nitromethane and in the presence of $Hg(CN)_2$, followed by hydrolysis of the product mixture with 70% aq acetic acid, afforded, in 69% yield, disaccharide derivative **3** (Scheme 1).

The selective methylation of **3** with trimethyloxonium tetrafluoroborate–2,6-di-(*tert*-butyl)-4-methylpyridine [12] in dichloromethane gave the 6-*O*-methyl derivative **4** in 69% yield. De-*O*-acetylation of **4** with methanolic sodium methoxide furnished compound **5** in 69% yield. The structure of **5** was established by ^{13}C NMR and FAB mass spectroscopy (see Table 1; Experimental section).

Allyl *O*-(2-*O*-acetyl-3,4-*O*-isopropylidene-β-D-galactopyranosyl)-(1 → 3)-2-acetamido-4-*O*-acetyl-2-deoxy-6-*O*-methyl-α-D-galactopyranoside (**9**) was the intermediate of choice for obtaining compound **10** (Scheme 2). Treatment of **5** with *tert*-butyl chlorodiphenylsilane [13] in *N*,*N*-dimethylformamide, in the presence of imidazole,



3 $R^1 = H$; $R^2 = Ac$

4 $R^1 = Me$; $R^2 = Ac$

5 $R^1 = Me$; $R^2 = H$

Scheme 1.

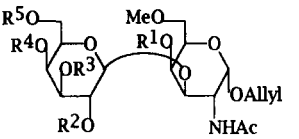
afforded the 6-*O*-*tert*-butyldiphenylsilyl derivative **6** in 93% yield. Compound **6** was converted into 3,4-*O*-isopropylidene derivative **7**.

Acetylation of **7** with pyridine–acetic anhydride (2 : 1, v/v) followed by removal of the *tert*-butyldiphenylsilyl group with a molar solution of tetrabutylammonium fluoride [13] in oxolane gave **9** in 80% yield. The ^1H NMR spectrum of **9** showed three resonances at 2.17, 2.10 and 1.99 ppm which correspond to two *O*-acetyl and one

Table 1
Proposed ^{13}C NMR data [a]

Residue	Compound	Carbon atom								
		C-1	C-2	C-3	C-4	C-5	C-6	NAc	OMe	Allyl
β-D-Gal-(1 → 3)		103.67	69.60	70.81	67.70	73.97	59.98	—	—	—
6-*O*-Me-GalNAc α-OR	**5**	95.44	47.51	76.04	67.95	71.52	67.57	20.97	57.35	132.60, 116.88
6-*O*-SO_3Na-β-D-Gal-(1 → 3)		103.57	69.48	71.05	67.75	71.57	67.39	—	—	—
6-*O*-Me-GalNAc-α-OR	**10**	95.39	47.47	76.41	67.98	71.44	67.51	20.98	53.32	132.64, 116.86
β-D-Gal-(1 → 3)		103.69	69.62	69.74	67.58	73.95	59.93	—	—	—
6-*O*-SO_3Na-GalNAc-α-OR	**13**	95.41	47.49	76.06	67.58	71.55	67.49	20.99	—	132.64, 117.12
6-*O*-SO_3Na-β-D-Gal-(1 → 3)		103.52	69.49	69.81	67.35	71.53	67.35	—	—	—
GalNAc-α-OR	**17**	95.34	47.55	76.49	67.75	71.42	60.44	20.98	—	132.72, 116.83
3-*O*-SO_3Na-β-D-Gal-(1 → 3)		103.35	67.72	79.22	67.43	73.54	59.87	—	—	—
GalNAc-α-OR	**22**	95.43	47.53	76.68	67.61	69.66	60.19	20.99	—	132.72, 116.84

[a] For solutions in D_2O; Me_4Si as the external standard; R = $CH_2CH{=}CH_2$.



6 $R^1 = R^2 = R^3 = R^4 = H$; $R^5 = {}^tBuPh_2Si$

7 $R^1 = R^2 = H$; $R^3, R^4 = CMe_2$; $R^5 = {}^tBuPh_2Si$

8 $R^1 = R^2 = Ac$; $R^3, R^4 = CMe_2$; $R^5 = {}^tBuPh_2Si$

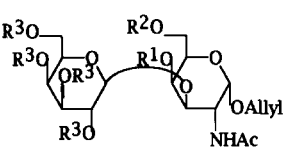
9 $R^1 = R^2 = Ac$; $R^3, R^4 = CMe_2$; $R^5 = H$

10 $R^1 = R^2 = R^3 = R^4 = H$; $R^5 = SO_3Na$

Scheme 2.

N-acetyl group. Reaction of **9** with SO_3–pyridine complex in *N*,*N*-dimethylformamide followed by removal of 3,4-*O*-isopropylidene and de-*O*-acetylation with methanolic sodium methoxide produced the sodium salt of the 6′-*O*-sulfate compound **10** after passage through a cation exchange (Na^+) resin column. The structure of **10** was confirmed by ^{13}C NMR and FAB mass spectroscopy (see Table 1 and Experimental section).

Treatment of **3** with *tert*-butylchlorodimethylsilane under similar reaction conditions as described for the preparation of **6** (from **5**) gave **11** in 74% yield. Acetylation of **11** with pyridine–acetic anhydride followed by removal of the *tert*-butyldimethylsilyl group with pyridinium *p*-toluenesulfonate–ethanol [14] provided compound **12** in 56% overall yield. The ^1H NMR spectrum of **12** showed doublets at δ5.37 ($J = 3.4$ Hz, H-4′) and 5.34 ($J = 2.5$ Hz, H-4) and the ^{13}C NMR spectrum showed signals at 61.16 (C-6′) and 60.28 (C-6) ppm, confirming the presence of a free 6-OH group. Similarly, sulfation of compound **12** (Scheme 3), as described for the preparation of **10**, followed by de-*O*-acetylation with methanolic sodium methoxide furnished compound **13** in 54% yield;

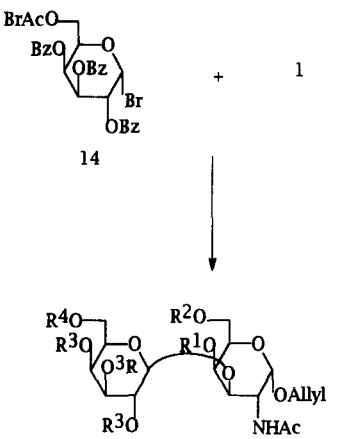


11. $R^1 = H$; $R^2 = {}^tBuMe_2Si$; $R^3 = Ac$

12. $R^1 = R^3 = Ac$; $R^2 = H$

13. $R^1 = R^3 = H$; $R^2 = SO_3Na$

Scheme 3.



15 R^1, R^2 = MeO·PhCH; R^3 = Bz; R^4 = BrAc

16 R^1, R^2 = MeO·PhCH; R^3 = Bz; R^4 = H

17 $R^1 = R^2 = R^3$ = H; $R^4 = SO_3Na$

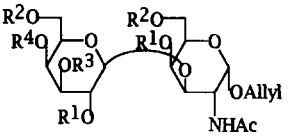
Scheme 4.

^{13}C-NMR and FAB mass spectra of **13** were in accord with the structure assigned (see Table 1 and Experimental section).

Similarly, mercuric cyanide catalyzed glycosylation of **1** with 2,3,4-tri-*O*-benzoyl-6-*O*-bromoacetyl-α-D-galactopyranosyl bromide [15] as described for the preparation of **3** (from **1**) afforded, in 74% yield, the fully protected disaccharide **15** (Scheme 4). Selective removal of the bromoacetyl group from **15** was achieved by treatment with thiourea in pyridine–ethanol to provide compound **16** in 80% yield.

Conventional transformation of **16** into the 6′-*O*-sulfo derivative **17** was performed by a similar reaction sequence as was described for the preparation of **10** from **9**. The structure of **17** was confirmed by ^{13}C NMR and FAB mass spectroscopy (see Table 1 and Experimental section).

For the synthesis of 3′-*O*-sulfo disaccharide **22** (Scheme 5), the readily accessible allyl *O*-(β-D-galactopyranosyl)-(1 → 3)-2-acetamido-2-deoxy-α-D-galactopyranoside (**18**) was the chosen starting material. Compound **18** was treated with *tert*-butylchlorodiphenylsilane in *N*,*N*-dimethylformamide under reaction conditions similar to those described for the preparation of **6** to give **19** in 94% yield. Isopropylidenation of compound **19** with 2,2-dimethoxypropane–acetone in the presence of 4-toluenesulfonic acid afforded the 3′,4′-*O*-isopropylidene derivative which, after acetylation with pyridine–acetic anhydride followed by the hydrolysis of isopropylidene group with $CHCl_3$–TFA–H_2O, afforded the diol **20** in 75% yield. The ^{1}H NMR spectrum of **20** exhibited signals at δ5.33 (d, J = 3.2 Hz, H-4), 2.14, 2.12, 2.08, 2.06 (4 × OAc) and 1.99 (NAc) showing that compound **20** had four acetyl groups. The diol **20** was converted into its



18. $R^1 = R^2 = R^3 = R^4 = H$

19. $R^1 = R^3 = R^4 = H$; $R^2 = {}^tBuPh_2Si$

20. $R^1 = R^2 = Ac$; $R^3 = R^4 = H$

21. $R^1 = R^2 = R^4 = Ac$; $R^3 = H$

22. $R^1 = R^2 = R^4 = H$; $R^3 = SO_3Na$

Scheme 5.

3′,4′-(ethyl orthoacetate), which was hydrolyzed to give a key intermediate **21** in 93% yield. The ^1H NMR spectrum of **21** exhibited low field chemical shifts at δ5.36 (d, $J = 2.7$ Hz, H-4′) and 5.30 (d, $J = 3.6$ Hz, H-4) and high field chemical shifts at δ2.19, 2.15, 2.12, 2.07 and 2.06 (5 × OAc) and 2.00 (NAc), confirming that compound **20** had been acetylated at O-4′. Sulfation of compound **21** in *N*,*N*-dimethylformamide with SO_3–pyridine complex at room temperature followed by de-*O*-acetylation with methanolic sodium methoxide afforded compound **22** in 81% yield. The structural assignment of **22** was confirmed by ^{13}C NMR and FAB mass spectroscopy.

^{13}C NMR assignment.—In the ^{13}C NMR spectra of compounds **5**, **10**, **13**, **17** and **22** the resonances for C-1 of the Gal residue (δ103.35-103.69) were all in the region characteristic of β-glycoside linkages. Similarly, the resonances of C-1 of the GalNAc residue were observed at δ95.34–95.44 which confirms an α-configuration. The resonances for C-3 of the GalNAc residue displayed downfield shifts (δ76.04–76.68), confirming the site of glycosylation in these compounds.

In the ^{13}C NMR spectra of compounds **5**, **10** and **13**, the resonance for C-6 of α-GalNAc-*O*-allyl exhibited a downfield shift (δ67.49–67.57) confirming this position as the site of substitution in these compounds. Similarly, the resonance of C-6 of the Gal residue in compounds **10** and **17** displayed a downfield shift (δ67.35 and 67.39) confirming this position as the site of sulfation. Also, the resonance of C-3 of the Gal residue in compound **22** showed a downfield shift at δ79.22, indicating that O-3′ was the site of sulfation.

3. Experimental

General methods.—Optical rotations were measured at ~ 25°C with a Perkin–Elmer 241 Polarimeter. TLC was conducted on glass plates, precoated with 0.25 mm layers of silica gel 60F-254 (Analtech GHLF uniplates). The compounds were located by exposure to UV light or by spraying with 5% H_2SO_4 in EtOH and charring, or by both techniques. The silica gel used for column chromatography was Baker Analyzed

(60–200 mesh). NMR spectra were recorded at ~25°C; ^{1}H spectra with a Varian EM-390 at 90 MHz and with a Bruker AM-400 at 400 MHz and ^{13}C spectra with a Bruker AM-400 at 100.6 MHz. All chemical shifts are referenced to tetramethylsilane. Solutions in organic solvents were generally dried with anhydrous Na_2SO_4. Dichloromethane, *N,N*-dimethylformamide, 1,2-dichloroethane, benzene and 2,2-dimethoxypropane were kept dried over 4 Å molecular sieves. Elemental analyses were performed by the Robertson Laboratory, Madison, New Jersey, USA.

*Allyl 2-acetamido-2-deoxy-4,6-*O*-(4-methoxybenzylidene)-α-*D*-galactopyranoside* (**1**). —To a stirred solution of allyl 2-acetamido-2-deoxy-α-D-galactopyranoside (8.0 g, 30.7 mmol) in *N,N*-dimethylformamide (250 mL) were added 4-toluenesulfonic acid monohydrate (1.5 g) and anisaldehyde dimethyl acetal (20 mL). The stirring was continued for 16 h at room temperature. The acid was neutralized with triethylamine, and the solution concentrated under reduced pressure. The residue was purified in a column of silica gel with 10% methanol in chloroform as the eluent to give **1** as an amorphous solid (6.9 g, 77%), $[\alpha]_D$ +94° (*c* 1.2, Me_2SO), ^{1}H NMR ($CDCl_3$ + CD_3OD): δ7.80–6.77 (m, 4 H, arom.), 5.93–5.63 (m, 1 H, =CH), 5.50 (s, 1 H, CH), 4.93 (d, *J* = 3 Hz, 1 H, H-1), 3.77 (s, 3 H, OMc), 1.97 (s, 3 H, NAc).

Anal. Calcd for $C_{19}H_{25}NO_7$: C, 60.14; H, 6.64; N, 3.69. Found: C, 60.23; H, 6.61; N, 3.42.

Allyl O-*(2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl)-(1 → 3)-2-acetamido-2-deoxy-α-*D*-galactopyranoside* (**3**).—A stirred mixture of **1** (6.0 g, 15.8 mmol) and powdered $Hg(CN)_2$ (6.0 g, 24 mmol) in 1 : 1 benzene–nitromethane (600 mL) was boiled until 100 mL of the solvent had distilled off. The temperature was then adjusted to ~55°C and 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide (**2**, 14 g, 33 mmol) was added and stirring continued for 16 h at 55°C. The mixture was then concentrated under reduced pressure. The residue was dissolved in chloroform and successively washed with saturated aq $NaHCO_3$, 10% aq KI solution and water, dried and evaporated to a syrup. This residue in 70% aq acetic acid (150 mL) was stirred for 1 h at 70°C. The acetic acid was evaporated under diminished pressure, the last traces being removed by coevaporation with several added portions of toluene. The residue was purified in a column of silica gel using a solvent gradient consisting of 5% to 7% methanol in chloroform as the eluent, to afford amorphous **3** (6.5 g, 69%); $[\alpha]_D$ +71° (*c* 1.2 $CHCl_3$); ^{1}H NMR ($CDCl_3$): 5.97–5.63 (m, 1 H, =CH), 4.89 (d, *J* = 3 Hz, 1 H, H-1), 4.67 (d, *J* = 8 Hz, 1 H, H-1′), 2.17–2.02 (cluster of s, 15 H, 4 × OAc and NAc).

Anal. Calcd for $C_{25}H_{37}NO_{15}$: C, 50.75; H, 6.30; N, 2.37. Found: C, 50.82; H, 6.39; N, 2.31.

Allyl O-*(2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl)-(1 → 3)-2-acetamido-2-deoxy-6-*O*-methyl-α-*D*-galactopyranoside* (**4**).—To a cold (0°) bath stirred solution of **3** (0.5 g, 0.85 mmol) in dichloromethane (20 mL) was added 2,6-di-(*tert*-butyl)-4-methylpyridine (0.31 g, 1.5 mmol) and trimethyloxonium tetrafluoroborate (0.19 g, 1.3 mmol). Stirring was continued for 5 h at room temperature. The mixture was diluted with chloroform, successively washed with saturated aq $NaHCO_3$ and water, dried and concentrated under reduced pressure. The residue was applied to a column of silica gel and eluted with a solvent gradient consisting of 20% to 30% acetone in chloroform to give **4** (0.35 g, 69%); $[\alpha]_D$ +76° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ5.94–5.86 (m, 1 H, =CH), 5.50

(d, $J = 9.4$ Hz, 1 H, NH), 5.37 (d, $J = 3.3$ Hz, 1 H, H-4′), 5.27 (dd, $J = 16.6$ and 1.4 Hz, 1 H, vinylic H), 5.22 (dd, $J = 10.2$ and 1.5 Hz, 1 H, vinylic H), 5.19 (dd, 1 H, H-2′), 4.98 (dd, 1 H, H-3′), 3.39 (s, 3 H, OMe), 2.16, 2.07, 2.05 and 1.98 (each s, 12 H, 4 × OAc), 1.97 (s, 3 H, NAc); ^{13}C NMR ($CDCl_3$): δ133.62 and 118.04 (allylic C, 101.61 (C-1′), 97.14 (C-1), 78.15 (C-3), 68.11 (C-6), 61.33 (C-6′), 59.30 (OMe), 47.83 (C-2).

Anal. Calcd for $C_{26}H_{39}NO_{15}$: C, 51.56; H, 6.49; N, 2.31. Found: C, 51.48; H, 6.41; N, 2.22.

Allyl O-*(β-D-galactopyranosyl)-(1 → 3)-2-acetamido-2-deoxy-6-*O*-methyl-α-D-galactopyranoside* (**5**).—Compound **4** (0.3 g) in 0.05 M methanolic sodium methoxide (20 mL) was stirred at room temperature for 16 h. The base was neutralized with Amberlite IR-120 (H^+) cation-exchange resin, filtered and concentrated under reduced pressure. The residue on trituration with hot ethanol gave pure **5** (0.15 g, 69%); $[\alpha]_D$ +128° (*c* 1.1, H_2O); ^{1}H NMR (D_2O): δ6.19–5.95 (m, 1 H, =CH), 5.40 (bd, $J = 17.2$ Hz, 1 H, vinylic H), 5.31 (bd, $J = 10.4$ Hz, 1 H, vinylic H), 4.97 (bs, 1 H, H-1), 4.51 (d, $J = 7.7$ Hz, 1 H, H-1′), 4.09 (dd, 2 H, H-6), 3.79 (d, 1 H, H-4′), 3.61 (dd, 1 H, H-3′), 3.44 (s, 3 H, OMe), 2.07 (s, 3 H, NAc), For ^{13}C NMR data, see Table 1; *m/z*: 438.3 $(M + H)^+$, 460.1 $(M + Na)^+$, 436.5 $(M - H)^-$.

Anal. Calcd for $C_{18}H_{31}NO_{11}$: C, 49.42; H, 7.14; N, 3.20. Found: C, 49.69; H, 7.27; N, 3.10.

Allyl O-*(6-*O*-tert-butyldiphenylsilyl-β-D-galactopyranosyl)-(1 → 3)-2-acetamido-2-deoxy-6-*O*-methyl-α-D-galactopyranoside* (**6**).—To an ice cold, stirred solution of **5** (0.7 g, 1.6 mmol) and imidazole (0.26 g, 3.8 mmol) in dry *N,N*-dimethylformamide (10 mL) was added *tert*-butylchlorodiphenylsilane (0.5 mL, 1.8 mmol), and stirring continued for 2 h at 0°C. The reaction mixture was then diluted with chloroform and washed with water, dried over Na_2SO_4 and concentrated. The residue was purified in a column of silica gel with 10–15% methanol in chloroform as the eluent to give **6** (1.0 g, 93%); $[\alpha]_D$ +46° (*c* 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ7.67–7.38 (m, 10 H, arom.), 5.94–5.87 (m, 1 H, =CH), 5.28 (bd, $J = 17.1$ Hz, 1 H, vinylic H), 5.21 (bd, $J = 10.4$ Hz, 1 H, vinylic H), 4.86 (d, $J = 3.6$ Hz, 1 H, H-1), 4.25 (d, $J = 7.6$ Hz, 1 H, H-1′), 3.27 (s, 3 H, OMe), 1.99 (s, 3 H, NAc), 1.03 (s, 9 H, CMe_3).

Anal. Calcd for $C_{34}H_{49}NO_{11}Si$: C, 60.42; H, 7.31; N, 2.07. Found: C, 60.36; H, 7.43; N, 2.18.

Allyl O-*(2-*O*-acetyl-6-*O*-tert-butyldiphenylsilyl-3,4-*O*-isopropylidene-β-D-galactopyranosyl)-(1 → 3)-2-acetamido-4-*O*-acetyl-2-deoxy-6-*O*-methyl-α-D-galactopyranoside* (**8**).—To a cold solution of **6** (0.9 g, 1.3 mmol) in dry acetone (20 mL) were added 2,2-dimethoxypropane (20 mL) and 4-toluenesulfonic acid monohydrate (0.15 g). The mixture was stirred at room temperature for 1 h, made neutral by the addition of triethylamine, and evaporated under reduced pressure to give the intermediate **7**. It was acetylated with pyridine–acetic anhydride (2:1 (v/v); 45 mL) and *N,N*-dimethyl-4-aminopyridine (30 mg) for 16 h. After usual workup, it was purified by silica gel column chromatography using a gradient consisting of 10–15% acetone in chloroform as the eluent to give **8** (0.85 g, 80%); $[\alpha]_D$ +77° (*c* 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ7.71–7.40 (m, 10 H, arom.), 5.84 (m, 1 H, =CH), 5.59 (d, $J = 8.8$ Hz, 1 H, NH), 5.34 (d, $J = 2.8$ Hz, 1 H, H-4), 5.26 (bd, $J = 17.2$ Hz, 1 H, vinylic H), 5.20 (bd, $J = 10.3$

Hz, 1 H, vinylic H), 4.96 (d, $J = 3.6$ Hz, 1 H, H-1), 4.85 (dd, $J = 7.9$ and 7.5 Hz, 1 H, H-2'), 4.43 (d, $J = 7.8$ Hz, 1 H, H-1'), 3.27 (s, 3 H, OMe), 2.11 and 2.08 (each s, 6 H, 2 × OAc), 1.95 (s, 3 H, NAc), 1.52 and 1.31 (each s, 6 H, CMe_2), 1.06 (s, 9 H, CMe_3).

Anal. Calcd for $C_{41}H_{57}NO_{13}Si$: C, 61.55; H, 7.18; N, 1.75. Found: C, 61.35; H, 7.26; N, 1.71.

Allyl O-*(2-O-acetyl-3,4-O-isopropylidene-β-D-galactopyranosyl)-(1 → 3)-2-acetamido-4-O-acetyl-6-2-deoxy-O-methyl-α-D-galactopyranoside* (**9**).—A stirred solution of **8** (0.8 g, 1 mmol) in anhydrous oxolane (30 mL) was treated with a 1 M solution of tetrabutylammonium fluoride in oxolane (1.5 mL), and the stirring was continued for 1.5 h at room temperature. The mixture was evaporated to dryness and the residue purified in a column of silica gel using a solvent gradient consisting of 30–35% acetone in chloroform as the eluent to give **9** (0.43 g, 77%); $[\alpha]_D$ +150° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ5.89–5.85 (m, 1 H, = CH), 5.62 (d, $J = 8.4$ Hz, 1 H, NH), 5.50 (d, $J = 3.1$ Hz, 1 H, H-4), 5.27 (bd, $J = 17.1$ Hz, 1 H, vinylic H), 5.25 (bd, $J = 10.7$ Hz, 1 H, vinylic H), 5.06 (d, $J = 3.6$ Hz, 1 H, H-1), 4.86 (dd, $J = 7.1$ and 7.2 Hz, 1 H, H-2'), 4.46 (d, $J = 7.6$ Hz, 1 H, H-1'), 3.32 (s, 3 H, OMe), 2.17 and 2.10 (each s, 6 H, 2 × OAc), 1.99 (s, 3 H, NAc), 1.52 and 1.30 (each s, 6 H, CMe_2); ^{13}C NMR ($CDCl_3$): δ101.75 (C-1'), 96.81 (C-1), 77.31 (C-3), 68.45 (C-6), 62.18 (C-6'), 59.26 (OMe), 48.99 (C-2).

Anal. Calcd for $C_{25}H_{39}NO_3$: C, 53.47; H, 7.00; N, 2.49. Found: C, 53.42; H, 6.96; N, 2.57.

Allyl O-*(6-O-sulfo-β-D-galactopyranosyl sodium salt)-(1 → 3)-2-acetamido-2-deoxy-6-O-methyl-α-D-galactopyranoside* (**10**).—To a stirred solution of **9** (0.4 g, 0.7 mmol) in dry *N,N*-dimethylformamide (20 mL) was added SO_3–pyridine complex (0.28 g, 1.7 mmol). Stirring was continued for 1 h at room temperature, then excess reagent was decomposed by the addition of methanol. The solvent was evaporated and residue was passed through a small silica gel column with 20–30% methanol in chloroform as eluent. The fractions corresponding to the product were concentrated and heated with 60% aq acetic acid (30 mL) for 2 h at 60°C. Acetic acid was evaporated under diminished pressure, the last traces being removed by coevaporation with several added portions of toluene. This residue was de-*O*-acetylated with 0.05 M methanolic sodium methoxide (50 mL) for 16 h at room temperature. The solution was de-ionized with Amberlite IR-120 (H^+) cation-exchange resin, filtered and concentrated under reduced pressure. The residue was purified on a column of silica gel with 13:6:1 (v/v) chloroform–methanol–water as the eluent. The fractions corresponding to the product were combined and concentrated, and the residue so obtained was dissolved in water and passed through Amberlite IR-120 (Na^+) cation-exchange resin. Lyophilization of the fractions corresponding to **10** gave an amorphous solid (0.24 g, 62.5%); $[\alpha]_D$ +91° (*c* 1.6, H_2O); ^1H NMR (D_2O): δ6.15–5.95 (m, 1 H, = CH), 5.41 (d, $J = 16.1$ Hz, 1 H, vinylic), 5.53 (d, $J = 10.7$ Hz, 1 H, vinylic), 4.99 (d, $J = 3$ Hz, 1 H, H-1), 3.45 (s, 3 H, OMe), 2.08 (s, 3 H, NAc); For ^{13}C NMR data see Table 1; *m/z* 562.0 $(M + Na)^+$, 538.3 $(M - H)^-$, 516.3 $(M - Na)^-$.

Anal. Calcd for $C_{18}H_{30}NNaO_{14}S \cdot 1.5H_2O$: C, 40.27; H, 5.87; N, 2.47. Found: C, 40.00; H, 5.62; N, 2.57.

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

butyldimethylsilyl-2-deoxy-α-D-galactopyranoside (**11**).—To a cold (0°C, bath) solution of **3** (0.48 g, 0.9 mmol) in anhydrous *N,N*-dimethylformamide (10 mL) containing imidazole (0.24 g, 3 mmol) was added *tert*-butylchlorodimethylsilane (0.22 g, 1.4 mmol), and the stirring was continued for 0.5 h at room temperature. After processing as described for the preparation of **6** (from **5**), followed by column chromatographic purification with a solvent gradient consisting of 10–15% acetone in chloroform, **11** was obtained as an amorphous solid (0.5 g, 74%); $[\alpha]_D$ +60° (*c* 0.6, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ5.92–5.89 (m, 1 H, = CH), 5.48 (d, J = 9.4 Hz, 1 H, NH), 5.39 (d, J = 3.3 Hz, 1 H, H-4′), 5.3 (dd, 1 H, H-2), 5.23 (dd, 1 H, H-2′), 4.99 (dd, 1 H, H-3′), 4.86 (d, J = 3.8 Hz, 1 H, H-1), 4.62 (d, J = 7.9 Hz, 1 H, H-1′), 2.16, 2.07, 2.04 and 1.98 (each s, 12 H, 4 × OAc), 1.97 (s, 3 H, NAc), 0.90 (s, 9 H, CMe_3), 0.09 and 0.08 (each s, 6 H, $SiMe_2$); ^{13}C NMR ($CDCl_3$): δ101.69 (C-1′), 97.02 (C-1), 78.34 (C-3), 61.10 (C-6′), 47.95 (C-2).

Anal. Calcd for $C_{31}H_{51}NO_{15}Si$: C, 52.75; H, 7.28; N, 1.98. Found: C, 52.78; H, 7.03; N, 2.12.

Allyl O-*(2,3,4,6-tetra*-O-*acetyl-β-D-galactopyranosyl)-(1 → 3)-2-acetamido-4*-O-*acetyl-2-deoxy-α-D-galactopyranoside* (**12**).—Compound **11** (0.48 g) was stirred overnight in 1:2 acetic anhydride–pyridine (30 mL) at room temperature. The pyridine and acetic anhydride were evaporated under diminished pressure, the last traces being removed by coevaporation with several added portions of toluene. Product residue was taken up in absolute ethanol (10 mL), pyridinium *p*-toluenesulfonate (220 mg) was added and the mixture was stirred for 16 h at room temperature. The solvent was evaporated under reduced pressure and residue was applied to a column of silica gel and eluted with 25–30% acetone in chloroform to give **12** (0.24 g, 56%); $[\alpha]_D$ +82° (*c* 0.7, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ5.94–5.84 (m, 1 H, =CH), 5.55 (d, J = 9.0 Hz, 1 H, NH), 5.37 (d, J = 3.4 Hz, 1 H, H-4′), 5.34 (d, J = 2.5 Hz, 1 H, H-4), 5.28 (dd, 1 H, H-2), 5.14 (dd, J = 7.8 Hz, 1 H, H-2′), 4.96 (dd, 1 H, H-3), 4.90 (d, J = 3.6 Hz, 1 H, H-1), 4.59 (d, J = 7.8 Hz, 1 H, H-1′), 2.19, 2.15, 2.07, 2.05 and 2.00 (each s, 15 H, 5 × OAc), 1.97 (s, 3 H, NAc); ^{13}C NMR ($CDCl_3$): δ101.25 (C-1′), 97.01 (C-1), 77.78 (C-3), 61.16 (C-6′), 60.28 (C-6), 48.84 (C-2).

Anal. Calcd. for $C_{27}H_{39}NO_{16}$: C, 51.18; H, 6.20; N, 2.21. Found: C, 51.33; H, 6.14; N, 2.14.

Allyl O-*(β-D-galactopyranosyl)-(1 → 3)-2-acetamido-2-deoxy-6*-O-*sulfo-α-D-galactopyranoside sodium salt* (**13**).—Compound **12** (0.2 g, 0.3 mmol) was treated with SO_3–pyridine complex (0.24 g, 1.5 mmol) exactly as described for the preparation of **10**, followed by de-*O*-acetylation with methanolic sodium methoxide to provide **13** as its sodium salt after passing through IR-120 (Na^+) cation-exchange resin (0.09 g, 54%); $[\alpha]_D$ +93° (*c* 1.0, H_2O); ^{1}H NMR (D_2O): δ6.08–6.01 (m, 1 H, = CH), 5.42 (d, J = 17.3 Hz, 1 H, vinylic H), 5.33 (d, J = 10.3 Hz, 1 H, vinylic H), 5.00 (d, J = 3.8 Hz, 1 H, H-1), 4.52 (d, J = 7.7 Hz, 1 H, H-1), 4.28 (dd, 2 H, H-6), 3.97 (d, 1 H, H-4), 3.68 (dd, 1 H, H-4′), 3.58 (dd, 1 H, H-3′), 2.08 (s, 3 H, NAc); For ^{13}C NMR data see Table 1; *m/z*: 548.0 $(M + Na)^+$, 524.3 $(M - H)^-$, 502.3 $(M - Na)^-$.

Anal. Calcd for $C_{17}H_{28}NNaO_{14}S \cdot H_2O$: C, 37.56; H, 5.56; N, 2.58. Found: C, 37.47; H, 5.30; N, 2.49.

Allyl O-*(2,3,4-tri*-O-*benzoyl-6*-O-*bromoacetyl-β-D-galactopyranosyl)-(1 → 3)-2-acetamido-2-deoxy-4,6*-O-*(4-methoxybenzylidene)-α-D-galactopyranoside* (**15**).—Allyl

2-acetamido-2-deoxy-4,6-*O*-(4-methoxybenzylidene)-α-D-galactopyranoside (**1**; 0.76 g, 2 mmol) was condensed with 2,3,4-tri-*O*-benzoyl-6-*O*-bromoacetyl-α-D-galactopyranosyl bromide (**14**; 2.0 g, 3 mmol) in benzene–nitromethane 1 : 1 (v/v) in the presence of $Hg(CN)_2$ (0.76 g, 3 mmol) in a manner analogous to that described for the preparation of **3** (from **1**). After processing as described earlier, the crude reaction product was applied to a column of silica gel and eluted with a solvent gradient consisting of 10–15% acetone in chloroform. Evaporation of the fractions corresponding to the product yielded **15** (1.2 g, 74%); $[\alpha]_D$ +148° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ8.06–6.80 (m, 19 H, arom.), 5.89–5.81 (m, 1 H, =CH), 5.76 (dd, J = 7.7 and 7.5 Hz, 1 H, H-2′), 5.57 (d, J = 3.4 Hz, 1 H, H-4′), 5.53 (dd, J = 3.5 and 8.0 Hz, 1 H, H-3′), 5.44 (s, 1 H, CH), 5.24 (bd, J = 16.8 Hz, 1 H, vinylic H), 5.19 (bd, J = 7.3 Hz, 1 H, vinylic H), 5.13 (d, J = 3.6 Hz, 1 H, H-1), 3.79 (s, 5 H, CH_2Br and OMe), 1.53 (s, 3 H, NAc); ^{13}C NMR ($CDCl_3$): δ101.58 (CH), 100.79 (C-1′), 97.47 (C-1), 77.31 (C-3), 68.69 (C-6), 63.04 (C-6′), 55.29 (OMe), 48.33 (C-2), 25.16 (CH_2Br), 22.68 (NAc).

Anal. Calcd for $C_{48}H_{48}NO_{16}Br$: C, 59.14; H, 4.96; N, 1.44. Found: C, 58.96; H, 4.96; N, 1.64.

Allyl O-*(2,3,4-tri-*O*-benzoyl-β-*D*-galactopyranosyl)-(1 → 3)-2-acetamido-2-deoxy-4,6-*O*-(4-methoxybenzylidene)-α-*D*-galactopyranoside* (**16**).—Compound **15** (0.6 g, 0.75 mmol) in pyridine–ethanol (4.1 (v/v); 30 mL) containing thiourea (0.15 g, 2.1 mmol) was stirred for 1 h at 70°C. The solvents were evaporated under reduced pressure, and the residue was taken up in chloroform, washed with water, dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified on a column of silica gel using a solvent gradient consisting of 20–30% acetone in chloroform to give **16** (0.4 g, 80%); $[\alpha]_D$ +218° (*c* 0.7, $CHCl_3$); ^1H NMR ($CDCl_3$): δ8.07–6.87 (m, 19 H, arom.), 5.86–5.74 (m, 1 H, =CH), 5.68 (d, J = 8.4 Hz, 1 H, NH), 5.52 (d, J = 3.4 Hz, 1 H, H-4′), 5.47 (dd, J = 3.4 Hz and 7.8 Hz, 1 H, H-3′), 5.38 (s, 1 H, CH), 5.22 (bd, J = 17.2 Hz, 1 H, vinylic H), 5.15 (bd, J = 10.2 Hz, 1 H, vinylic H), 5.08 (d, J = 3.6 Hz, 1 H, H-1), 3.83 (s, 3 H, OMe), 1.79 (s, 3 H, NAc); ^{13}C NMR ($CDCl_3$): δ100.74 (CH), 99.81 (C-1′), 97.64 (C-1), 77.31 (C-3), 61.55 (C-6′), 55.35 (OMe), 48.30 (C-2), 22.68 (NAc).

Anal. Calcd for $C_{46}H_{47}NO_{15}$: C, 64.70; H, 5.55; N, 1.64. Found: C, 64.53; H, 5.72; N, 1.71.

Allyl O-*(6-*O*-sulfo-β-*D*-galactopyranosyl sodium salt)-(1 → 3)-2-acetamido-2-deoxy-α-*D*-galactopyranoside* (**17**).—Compound **16** (0.3 g, 0.45 mmol) was treated with SO_3–pyridine complex (0.3 g, 2 mmol) as described for the preparation of **10** (from **9**) to give **17** (0.1 g, 43%); $[\alpha]_D$ +91° (*c* 1.2, H_2O); ^1H NMR (D_2O); δ6.04–5.96 (m, 1 H, =CH), 5.40 (bd, J = 17.4 Hz, 1 H, vinylic H), 5.16 (bd, J = 10.4 Hz, 1 H, vinylic H), 5.00 (d, J = 3.7 Hz, 1 H, H-1), 4.53 (d, J = 7.8 Hz, 1 H, H-1′), 3.94 (dd, 1 H, H-6′), 3.69 (dd, 1 H, H-4′), 3.59 (dd, 1 H, H-3′), 2.07 (s, 3 H, NAc); For ^{13}C NMR data see Table 1; *m/z*: 548.0 $(M + Na)^+$, 502.3 $(M - Na)^-$, 524.3 $(M - H)^-$.

Anal. Calcd for $C_{17}H_{28}NNaO_{14}S$: C, 38.86; H, 5.37; N, 2.67. Found: C, 38.75; H, 5.41; N, 2.60.

Allyl O-*(6-*O*-tert-butyldiphenylsilyl-β-*D*-galactopyranosyl)-(1 → 3)-2-acetamido-6-*O*-tert-butyldiphenylsilyl-2-deoxy-α-*D*-galactopyranoside* (**19**).—To a cold (0°, bath), stirred solution of allyl *O*-(β-D-galactopyranosyl)-(1 → 3)-2-acetamido-2-deoxy-α-D-

galactopyranoside (**18**; 1.2 g, 2.8 mmol) in anhydrous *N,N*-dimethylformamide (20 mL) containing imidazole (1.5 g, 21 mmol) was added *tert*-butylchlorodiphenylsilane (2.0 mL, 6.9 mmol) and stirring was continued for 1 h at the same temperature. The mixture was then poured into ice–water and extracted with chloroform. The chloroform solution was washed with water, saturated aq $NaHCO_3$ and water, dried over Na_2SO_4, and evaporated to dryness. The residue was applied to a column of silica gel and eluted with a solvent gradient consisting of 5–10% methanol in chloroform. On evaporation, the fractions corresponding to the product afforded **19** (2.2 g, 94%); $[\alpha]_D$ +26° (*c* 1.1, $CHCl_3$); ^1H NMR ($CDCl_3$): δ7.65–7.26 (m, 20 H, arom.), 5.90–5.86 (m, 1 H, =CH), 5.83 (d, $J = 9.5$ Hz, 1 H, NH), 5.26 (bd, $J = 18.5$ Hz, 1 H, vinylic H), 5.20 (bd, $J = 10.3$ Hz, 1 H, vinylic H), 4.84 (d, $J = 3.9$ Hz, 1 H, H-1), 4.23 (d, $J = 7.7$ Hz, 1 H, H-1′), 1.99 (s, 3 H, NAc), 1.01 and 0.95 (each s, 18 H, 2 × CMe_3).

Anal. Calcd for $C_{49}H_{65}NO_{11}Si_2$: C, 65.37; H, 7.28; N, 1.56. Found: C, 65.28; H, 7.31; N, 1.53.

Allyl O-*(2,6-di-*O*-acetyl-β-*D*-galactopyranosyl)-(1 → 3)-2-acetamido-4,6-di-*O*-acetyl-2-deoxy-α-*D*-galactopyranoside* (**20**).—This compound was obtained from **19** (2.0 g) by the same reaction sequence described for the preparation of **9** (from **6**), followed by the hydrolysis of the isopropylidene group with $CHCl_3$–TFA–H_2O to give amorphous **20** (1.0 g, 75%); $[\alpha]_D$ +82° (*c* 0.8, $CHCl_3$); ^1H NMR ($CDCl_3$): δ5.93–5.86 (m, 1 H, =CH), 5.77 (d, $J = 8.7$ Hz, 1 H, NH), 5.33 (d, $J = 3.2$ Hz, 1 H, H-4), 5.30 (bd, $J = 17.1$ Hz, 1 H, vinylic H), 5.25 (bd, $J = 8.6$ Hz, 1 H, vinylic H), 4.98 (d, $J = 3.7$ Hz, 1 H, H-1), 4.94 (dd, $J = 8.0$ Hz, 1 H, H-2′), 4.52 (d, $J = 7.9$ Hz, 1 H, H-1′), 2.14, 2.12, 2.08 and 2.06 (each s, 12 H, 4 × OAc), 1.99 (s, 3 H, NAc); ^{13}C NMR ($CDCl_3$): δ100.28 (C-1′), 97.03 (C-1), 77.31 (C-3), 62.69 (C-6′), 62.54 (C-6), 48.81 (C-2).

Anal. Calcd for $C_{25}H_{37}NO_{15}$: C, 50.75; H, 6.30; N, 2.37. Found: C, 50.63; H, 6.51; N, 2.14.

Allyl O-*(2,4,6-tri-*O*-acetyl-β-*D*-galactopyranosyl)-(1 → 3)-2-acetamido-4,6-di-*O*-acetyl-2-deoxy-α-*D*-galactopyranoside* (**21**).—To a solution of **20** (0.8 g, 1.4 mmol) in dry benzene (50 mL) were added triethyl orthoacetate (12 mL) and 4-toluenesulfonic acid monohydrate (50 mg). After stirring for 1 h at room temperature, triethylamine was added and the solution was washed with cold water and concentrated under reduced pressure. The residue was taken up in 80% aq acetic acid (50 mL) and stirred for 1 h at room temperature. Acetic acid was evaporated under diminished pressure, the last traces being removed by coevaporation with several added portions of toluene. The crude product was purified on a silica gel column using 5% methanol in chloroform as the eluent to give **21**; amorphous solid (0.8 g, 93%); $[\alpha]_D$ +91° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ5.93–5.86 (m, 1 H, =CH), 5.68 (d, $J = 8.6$ Hz, 1 H, NH), 5.36 (d, $J = 2.7$ Hz, 1 H, H-4′), 5.30 (d, $J = 3.6$ Hz, 1 H, H-4), 5.25 (bd, $J = 16.7$ Hz, 1 H, vinylic H), 5.22 (bd, $J = 10.5$ Hz, 1 H, vinylic H), 4.99 (d, $J = 3.6$ Hz, 1 H, H-1), 4.92 (dd, $J = 7.9$ Hz, 1 H, H-2′), 4.58 (d, $J = 7.8$ Hz, 1 H, H-1′), 2.19, 2.15, 2.12, 2.07 and 2.06 (each s, 15 H, 5 × OAc), 2.00 (s, 3 H, NAc).

Anal. Calcd for $C_{27}H_{39}NO_{16}$: C, 51.18; H, 6.20; N, 2.21. Found: C, 51.24; H, 6.11; N, 2.04.

Allyl O-*(3-*O*-sulfo-β-*D*-galactopyranosyl sodium salt)-(1 → 3)-2-acetamido-2-deoxy-*

α-D-*galactopyranoside* (**22**).—Compound **21** (0.7 g, 1.1 mmol) on treatment with SO_3–pyridine complex (0.8 g, 5.0 mmol) in *N*,*N*-dimethylformamide, followed by de-*O*-acetylation with methanolic sodium methoxide, provided the title compound **22** (0.47 g, 81%); $[\alpha]_D$ +89° (*c* 0.8, H_2O); ^1H NMR (D_2O): δ6.04–5.97 (m, 1 H, =CH), 5.42 (d, $J = 17.4$ Hz, 1 H, vinylic H), 5.32 (d, $J = 10.4$ Hz, 1 H, vinylic H), 5.01 (d, $J = 3.6$ Hz, 1 H, H-1), 4.64 (d, $J = 7.8$ Hz, 1 H, H-1′), 4.30 (dd, 1 H, H-3′), 4.26 (d, 1 H, H-4′), 3.78–3.77 (m, H-2′, H-5′, H-6′, H-5 and H-6), 2.09 (s, 3 H, NAc); For ^{13}C NMR data see Table 1; *m/z*: 548.0 $(M + Na)^+$, 502.4 $(M - Na)^-$.

Anal. Calcd for $C_{17}H_{28}NNaO_{14}S \cdot H_2O$: C, 37.56; H, 5.56; N, 2.58. Found: C, 37.68; H, 5.25; N, 2.45.

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