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Synthesis of monosulfated saccharides in the spacered form

Tatyana V. Ovchinnikova, Ekaterina V. Shipova, Marina A. Sablina, Galina V. Pazynina, Inna S. Popova, Aleksandr B. Tuzikov and Nicolai V. Bovin*

M. M. Shemyakin–Yu. A. Ovchinnikov Institute of Bioorganic Chemistry, Russian Academy of Sciences, 117997 Moscow, Russian Federation. Fax: +7 095 330 5592; e-mail: bovin@carb.siobc.ras.ru

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The sulfated (Su) saccharides 3-Su-Galβ, 3-Su-GalNAcβ, 4-Su-GalNAcβ, 6-Su-GalNAcα, 6-Su-GlcNAcβ, 6-Su-LacNAcβ, 6′-Su-LacNAcβ, 3′-Su-Galβ1-3GlcNAcβ and 3′-Su-Galβ1-3GalNAcα, all monosaccharides in D-configuration, have been synthesised in the form of 3-aminopropyl or 3-trifluoroacetamidopropyl glycosides.

Various glycoproteins, especially mucins, are known to bear sulfated oligosaccharides.[1,2] The sulfo group endows these molecules with special biological properties. The sulfate moiety can mask antigenic and lectin-binding sites, protect them from premature degradation and regulate the biosynthesis and biological functions of glycoproteins and proteoglycans. Sulfates are usually attached to terminal saccharides, but they can also occur in the core region. The most typical positions for the sulfo groups in glycoprotein glycans are 3-Gal, 6-Gal, 4-GlcNAc, 6-GlcNAc, 4-GalNAc and 6-GalNAc.[3–6] The discovery of many new objects containing sulfated oligosaccharides and clarifying new biologically relevant events involving these compounds require the design of molecular tools appropriate for their elucidation.

Here, we describe a practical synthesis of the 3-aminopropyl glycoside forms of nine mono- and disaccharides with one sulfate group to be used for preparing neoglycoconjugate probes.[7]

Syntheses of partially protected saccharides **1**–**9** (Table 1) were described earlier,[8–11,†] and the only sulfation step followed by deprotection is herein reported. The amounts of hydroxyl groups in the starting molecules served as a criterion for the choice of the sulfation conditions. Galactosamines **1** and **2**, galactose **5**, and lactosamines **6** and **7** with one free hydroxyl group were sulfated with a threefold excess of the SO_3·Py complex in Py at room temperature.[12] After the completion of reaction (usually, 24 h), the unreacted SO_3·Py was quenched with a fourfold excess of $NaHCO_3$ (protocol A). The resulting sodium salts of sulfated saccharides were deprotected either without isolation (in the case of **1** and **5**) or after chromatographic purification (in the case of **2**, **6** and **7**). The target sulfated saccharides were finally obtained as aminopropyl glycosides **10**, **11**, **14**, **15** and **16**, respectively.[‡]

The sulfation of disaccharides **8** and **9** at the 3′-position of the galactose unit occurred with high regiospecificity when using a large (fivefold) excess of SO_3·Py and cooling (protocol B).[13] The secondary equatorial hydroxyl group at this position exhibits a higher reactivity; thus, we succeeded in obtaining sulfates **17** and **18** in high yields.

For sulfation of the primary hydroxyl groups of triols **3** and **4**, the SO_3·Et_3N complex generated *in situ*[14] was used (protocol C). The sulfation of triols **3** and **4** by method C resulted in 6-sulfated **12** and **13** in good yields, the negligible amounts of disulfated derivatives (2–5%, TLC data) were detected, and a small amount of the starting material was recovered.

The structure and purity of final compounds were confirmed by ^{1}H NMR spectroscopy. Sulfation of the hydroxyl function resulted in the downfield shift of the signals of neighbouring protons: 4.2–4.4 ppm in the case of H-6 and H-6′, 4.3–4.4 ppm for H-3, and 4.7 ppm for H-4 (bold faced in the spectral data[8]).

General sulfation protocols. *Protocol A*. The SO_3·Py complex (3 mmol) was suspended in a saccharide solution (1 mmol) in Py (1 ml). The reaction mixture was stirred at room temperature for 24 h. Solid $NaHCO_3$ (5 mmol) was added, the mixture was stirred for 30 min and filtered, and the residue was washed with DMF or MeOH. The combined filtrate was concentrated *in vacuo* and chromatographed on silica gel using a suitable eluent containing 2% Py.[‡]

Protocol B. A solution of a saccharide (0.1 mmol) in Py (1 ml) was cooled to –20 °C, and SO_3·Py (0.5 mmol) was added with stirring. The reaction mixture was stirred for 6–7 h at –10 °C. After the completion of reaction (TLC control), solid $NaHCO_3$ (2 mmol) was added. The reaction mixture was allowed to reach room temperature for 30 min and filtered, and the residue was washed with DMF. The combined filtrate was

† Galactosamine **2** was synthesised from saccharide **1** by O-acetylation and subsequent opening of the 4,6-*O*-benzylidene ring by treating with $NaCNBH_3$/HCl in THF to yield the 6-*O*-benzyl derivative.

3-Trifluoroacetamidopropyl 2-acetamido-3-O-*acetyl-6*-O-*benzyl-2-deoxy-β-D-galactopyranoside* **2**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.79 and 1.88 (2m, 2×1H, CCH_2C), 1.96 and 2.12 (2s, 2×3H, 2Ac), 2.87 (d, 1H, OH, $J_{4,OH}$ 3.9 Hz), 3.29 (m, 1H, NCH), 3.58–3.64 (m, 2H, NCH and OCH), 3.70 (ddd ≈ br. t, 1H, H-5, $J_{4,5}$ < 1 Hz, $J_{5,6a}$ 5.2 Hz, $J_{5,6b}$ 5.4 Hz), 3.73 (dd, 1H, H-6a, $J_{5,6a}$ 5.2 Hz, $J_{6a,6b}$ 9.8 Hz), 3.77 (dd, 1H, H-6b, $J_{5,6b}$ 5.4 Hz, $J_{6a,6b}$ 9.8 Hz), 3.98 (m, 1H, OCH), 4.08 (ddd ≈ br. t, 1H, H-4, $J_{3,4}$ 2.9 Hz, $J_{4,5}$ < 1 Hz, $J_{4,OH}$ 3.9 Hz), 4.23 (ddd, 1H, H-2, $J_{2,NH}$ 8.8 Hz, $J_{1,2}$ 8.6 Hz, $J_{2,3}$ 11 Hz), 4.56 (d, 1H, H-1, $J_{1,2}$ 8.6 Hz), 4.55 and 4.58 (2d, 2×1H, CH_2Ph, J_{AB} 12.0 Hz), 5.03 (dd, 1H, H-3, $J_{2,3}$ 11 Hz, $J_{3,4}$ 2.9 Hz), 5.84 (d, 1H, NHAc, $J_{2,NH}$ 8.8 Hz), 7.28–7.36 (m, 5H, Ph), 7.48 (m, 1H, $NHCOCF_3$).

Lactosamine **6** was synthesised by the condensation of 3-trifluoroacetamidopropyl 2-acetamido-3-*O*-acetyl-6-*O*-benzyl-2-deoxy-β-D-glucopyranoside with 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl trichloroacetimidate followed by hydrogenolysis over 10% Pd/C in MeOH.

3-Trifluoroacetamidopropyl 2-acetamido-3-O-*acetyl-2-deoxy-4*-O-*(2,3,4,6-tetra*-O-*acetyl-β-D-galactopyranosyl)-β-D-glucopyranoside* **6**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.84 and 1.89 (2m, 2×1H, CCH_2C), 1.90, 1.91, 2.03, 2.07, 2.14 and 2.17 (6s, 6×3H, 6Ac), 3.23 (m, 1H, CHN), 3.34 (m, 1H, H-5), 3.52 (m, 1H, OCH), 3.62 (m, 1H, CHN), 3.68 (m, 1H, H-6a), 3.82–3.90 (m, 4H, H-6b, H-5′, H-4 and OCH), 3.94 (ddd, 1H, H-2, $J_{1,2} = J_{2,NHAc}$ = 9 Hz, $J_{2,3}$ 11 Hz), 4.03–4.12 (m, 2H, H-6′a and H-6′b), 4.33 (d, 1H, H-1, $J_{1,2}$ 9 Hz), 4.60 (d, 1H, H-1′, $J_{1',2'}$ 9 Hz), 4.96 (dd, 1H, H-3′, $J_{3',2'}$ 11 Hz, $J_{3',4'}$ 4 Hz), 5.02 (dd, 1H, H-3, $J_{2,3}$ 11 Hz, $J_{3,4}$ 11 Hz), 5.08 (dd, 1H, H-2′, $J_{1',2'}$ 9 Hz, $J_{2',3'}$ 11 Hz), 5.33 (dd, 1H, H-4′, $J_{3',4'}$ 4 Hz, $J_{4',5'}$ 1 Hz), 5.75 (d, 1H, NHAc, $J_{2,NHAc}$ 9 Hz), 7.3 (m, 1H, $NHCOCF_3$).

Lactosamine **7** was synthesised from **6** by sequential de-O-acetylation, benzylidenation, O-acetylation, 4,6-*O*-benzylidene conversion into 6-*O*-benzyl, acetylation and hydrogenolysis.

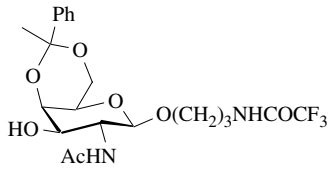
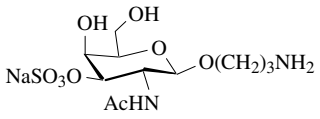
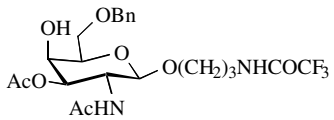
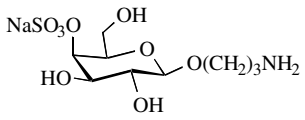
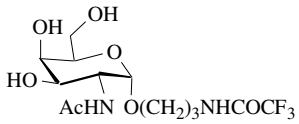
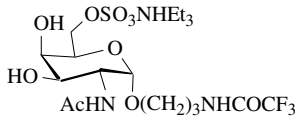
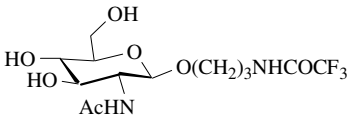
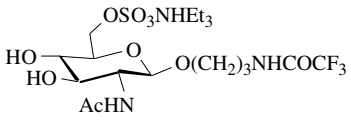
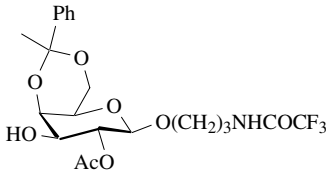
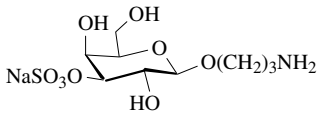
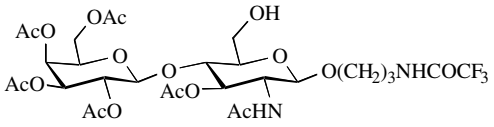
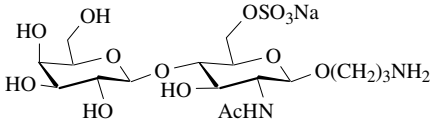
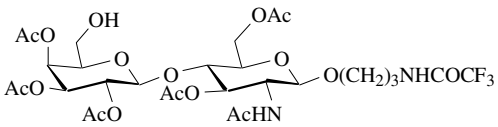
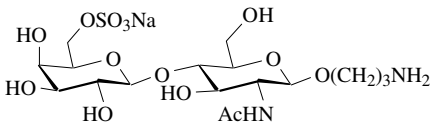
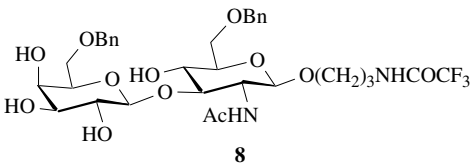
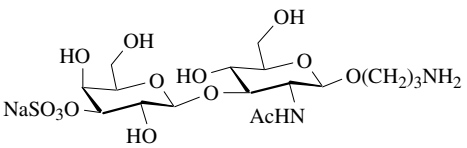
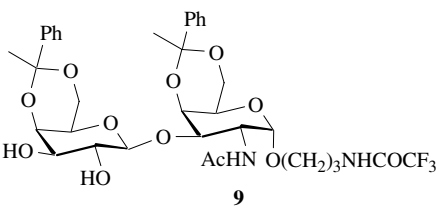
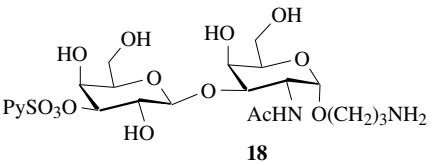
3-Trifluoroacetamidopropyl 2-acetamido-2-deoxy-3,6-di-O-*acetyl-4*-O-*(2,3,4-tri*-O-*acetyl-β-D-galactopyranosyl)-β-D-glucopyranoside* **7**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.81 and 1.89 (2m, 2×1H, CCH_2C), 1.98, 1.99, 2.07, 2.09, 2.11 and 2.17 (6s, 6×3H, 6Ac), 3.26 (m, 1H, CHN), 3.49–3.67 (m, 4H, H-6′a, H-5, CHN and OCH), 3.69–3.77 (m, 2H, H-6′b and H-5′), 3.82 (dd, 1H, H-4, $J_{3,4} = J_{4,5}$ = 8 Hz), 3.90 (m, 1H, OCH), 4.03 (ddd, 1H, H-2, $J_{2,3} = J_{2,NHAc}$ = 9 Hz, $J_{1,2}$ 7 Hz), 4.1 (dd, 1H, H-6a), 4.45 (d, 1H, H-1, $J_{1,2}$ 7 Hz), 4.55 (dd, 1H, H-6b), 4.58 (d, 1H, H-1′, $J_{1',2'}$ 8 Hz), 5.03 (dd, 1H, H-3′, $J_{2',3'}$ 10 Hz, $J_{3',4'}$ 3 Hz), 5.11 (dd, 1H, H-3, $J_{2,3}$ 9 Hz, $J_{3,4}$ 8 Hz), 5.5 (dd, 1H, H-2′, $J_{1',2'}$ 8 Hz, $J_{2',3'}$ 10 Hz), 5.37 (dd, 1H, H-4′, $J_{3',4'}$ 3 Hz, $J_{4',5'}$ < 1 Hz), 5.93 (d, 1H, NHAc, $J_{2,NHAc}$ 9 Hz), 7.3 (m, 1H, $NHCOCF_3$).

‡ The protective groups were removed by the routine procedures: the 4,6-*O*-benzylidene moiety was removed by treating with 80% aq. AcOH at 80 °C; the *O*-acetyl group was removed by treating with 2 M NaOMe in MeOH; the benzyl group was removed by hydrogenolysis over 10% Pd/C in MeOH in the presence of 1 equiv. of NaOAc and 2 equiv. of acetic acid per SO_3 group; and the *N*-trifluoroacetyl group was removed by treating with 0.05 equiv. of triethylamine in aq. MeOH or with 2 M NaOMe in 50% aq. MeOH. Deprotected sulfates obtained according to protocol A or B were purified by gel filtration and isolated as sodium salts.

concentrated *in vacuo* and chromatographed on silica gel using a suitable eluent containing 2% Py.‡

Protocol C. A solution of SO_3·Py (0.75 mmol) in a mixture of DMF (0.6 ml) and triethylamine (0.3 ml) was added portionwise to a saccharide solution (0.05 mmol) in DMF (0.6 ml) for 1–1.5 h, and the reaction mixture was stirred at room temperature for 24–72 h. After the completion of sulfation (TLC control), the reaction mixture was chromatographed on silica gel using a suitable eluent containing 2% triethylamine. The sulfated derivatives were isolated as triethylammonium salts.

Table 1 Synthesis of monosulfated saccharides.

Starting compound	Product	Protocol	Sulfation yield (%)
 **1**	 **10**	A	56[a]
 **2**	 **11**	A	95
 **3**	 **12**	C	64/85[b]
 **4**	 **13**	C	57
 **5**	 **14**	A	56[a]
 **6**	 **15**	A	68[a]
 **7**	 **16**	A	60[a]
 **8**	 **17**	B	52[a]
 **9**	 **18**	B	70[a]

[a]Yield after complete deprotection. [b]For reacted material.

References

1 I. Brockhausen and W. Kuhns, *Trends Glycosci. Glycotechnol*., 1997, **9**, 379.

doi> 2 Q.-W. Fun, K. Uchimura, Yu. Yuzawa, S. Matsuo, C. Mitsuoka, R. Kannagi, H. Muramatsu, K. Kadomatsu and T. Muramatsu, *Glycobiology*, 1999, **9**, 947.

3 L. V. Hooper, S. M. Manzella and J. U. Baenziger, in *Glycosciences*, eds. H.-J. Gabius and S. Gabius, Chapman & Hall, Weinheim, 1997, p. 261.

4 J.-M. Lo-Guidice, H. Herz, G. Lamblin, Y. Plancke, P. Roussel and M. Lhermitte, *Glycoconjugate J*., 1997, **14**, 113.

doi> 5 T. P. Mawhinney, D. C. Lamdrum, D. C. Gayer and G. J. Barbero, *Carbohydr. Res*., 1992, **235**, 179.

6 Y. Imai and S. D. Rosen, *Glycoconjugate J*., 1993, **10**, 34.

doi> 7 N. V. Bovin, *Glycoconjugate J*., 1998, **15**, 431.

8 T. V. Ovchinnikova, A. G. Ter-Grigoryan, G. V. Pazynina and N. V. Bovin, *Bioorg. Khim*., 1997, **23**, 61 (*Russ. J. Bioorg. Chem*., 1997, **23**, 55).

9 N. V. Bovin, T. V. Zemlyanukhina and A. Ya. Khorlin, *Bioorg. Khim*., 1986, **12**, 533 (*Sov. J. Bioorg. Chem*., 1986, **12**, 282).

10 E. Yu. Korchagina and N. V. Bovin, *Bioorg. Khim*., 1992, **18**, 283 (*Russ. J. Bioorg. Chem*., 1992, **18**, 153).

11 N. E. Nifant'ev, A. S. Shashkov, Yu. E. Tsvetkov, A. B. Tuzikov, I. V. Abramenko, D. F. Gluzman and N. V. Bovin, in *ACS Symp. Ser. Synthetic Oligosaccharides: Indispensable Probes for the Life Sciences*, ed. P. Kovac, ACS, Washington, DC, 1994, vol. 560, p. 267.

doi> 12 R. A. Field, A. Otter, W. Fu and O. Hindsgaul, *Carbohydr. Res*., 1995, **276**, 347.

13 T. V. Zemlyanukhina, N. E. Nifant'ev, A. S. Shashkov, Yu. E. Tsvetkov and N. V. Bovin, *Carbohydr. Lett*., 1995, **1**, 277.

14 S. Futaki, T. Taike, T. Yagami, T. Ogawa, T. Akita and K. Kitagawa, *J. Chem. Soc., Perkin Trans. 1*, 1990, 1739.

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§ Selected ^{1}H NMR data (500 MHz, D_2O).

3-Aminopropyl 2-acetamido-2-deoxy-3-O-*sulfo-β-D-galactopyranoside (sodium salt)* **10**: 1.97 (m, 2H, CCH_2C), 2.06 (s, 3H, NAc), 3.11 (m, 2H, CH_2N), 3.74–3.79 (m, 1H, OCH), 3.76 (dd, 1H, H-5, $J_{5,6a}$ 4.6 Hz, $J_{5,6b}$ 7.6 Hz), 3.81 (dd, 1H, H-6a, $J_{5,6a}$ 4.6 Hz, $J_{6a,6b}$ 11.7 Hz), 3.84 (dd, 1H, H-6b, $J_{5,6b}$ 7.6 Hz, $J_{6a,6b}$ 11.7 Hz), 4.03–4.08 (m, 1H, OCH), 4.07 (dd, 1H, H-2, $J_{1,2}$ 8.6 Hz, $J_{2,3}$ 11 Hz), 4.27 (br. d, 1H, H-4, $J_{3,4}$ 3 Hz, $J_{4,5}$ < < 1 Hz), 4.43 (dd, 1H, **H-3**, $J_{2,3}$ 11 Hz, $J_{3,4}$ 3 Hz), 4.61 (d, 1H, H-1, $J_{1,2}$ 8.6 Hz).

3-Aminopropyl 2-acetamido-2-deoxy-4-O-*sulfo-β-D-galactopyranoside (sodium salt)* **11**: 1.98 (m, 2H, CCH_2C), 2.07 (s, 3H, NAc), 3.13 (m, 2H, CH_2N), 3.76 (m, 1H, OCH), 3.81–3.87 (m, 3H, H-5, H-6a and H-6b), 3.9 (dd, 1H, H-3, $J_{2,3}$ 11 Hz, $J_{3,4}$ 2.7 Hz), 3.93 (dd, 1H, H-2, $J_{1,2}$ 7.6 Hz, $J_{2,3}$ 11 Hz), 4.06 (m, 1H, OCH), 4.51 (d, 1H, H-1, $J_{1,2}$ 7.6 Hz), 4.72 (br. d, 1H, **H-4**, $J_{3,4}$ 2.7 Hz, $J_{4,5}$ < 1 Hz).

3-Trifluoroacetamidopropyl 2-acetamido-2-deoxy-6-O-*sulfo-α-D-galactopyranoside (triethylammonium salt)* **12**: 1.30 (t, 9H, $NCH_2\mathit{Me}$, *J* 7.3 Hz), 1.92 (m, 2H, CCH_2C), 2.07 (s, 3H, NAc), 3.21 (q, 6H, $NC\mathit{H}_2Me$, *J* 7.3 Hz), 3.34 (m, 1H, CHN), 3.48–3.55 (m, 2H, CHN and OCH), 3.80 (m, 1H, OCH), 3.95 (dd, 1H, H-3, $J_{2,3}$ 11 Hz, $J_{3,4}$ 3.2 Hz), 4.05 (br. d, 1H, H-4, $J_{3,4}$ 3.2 Hz, $J_{4,5}$ < 1 Hz), 4.16–4.24 (m, 4H, H-2, H-5, **H-6a**, **H-6b**), 4.91 (d, 1H, H-1, $J_{1,2}$ 3.7 Hz).

3-Trifluoroacetamidopropyl 2-acetamido-2-deoxy-6-O-*sulfo-β-D-glucopyranoside (triethylammonium salt)* **13**: 1.30 (t, 9H, $NCH_2\mathit{Me}$, *J* 7.3 Hz), 1.87 (m, 2H, CCH_2C), 2.06 (s, 3H, NAc), 3.20 (q, 6H, $NC\mathit{H}_2Me$, *J* 7.3 Hz), 3.34 and 3.44 (2m, 2×1H, CH_2N), 3.52 (dd ≈ br. t, 1H, H-4, $J_{3,4}$ 9.3 Hz, $J_{4,5}$ 9.5 Hz), 3.58 (dd ≈ br. t, 1H, H-3, $J_{3,4}$ 9.3 Hz, $J_{2,3}$ 9.8 Hz), 3.68 (ddd, 1H, H-5, $J_{4,5}$ 9.5 Hz, $J_{5,6a}$ 5.4 Hz, $J_{5,6b}$ 1.7 Hz), 3.70–3.64 (m, 1H, OCH), 3.73 (dd, 1H, H-2, $J_{1,2}$ 8.6 Hz, $J_{2,3}$ 9.8 Hz), 3.96 (m, 1H, OCH), 4.24 (dd, 1H, **H-6a**, $J_{5,6a}$ 5.4 Hz), 4.37 (dd, 1H, **H-6b**, $J_{5,6b}$ 1.7 Hz), 4.54 (d, 1H, H-1, $J_{1,2}$ 8.6 Hz).

3-Aminopropyl 3-O-*sulfo-β-D-galactopyranoside (sodium salt)* **14**: 2.03 (m, 2H, CCH_2C), 3.18 (m, 2H, CH_2N), 3.68 (dd, 1H, H-2, $J_{1,2}$ 8.1 Hz, $J_{2,3}$ 9.6 Hz), 3.74–3.80 (m, 3H, H-5, H-6a and H-6b), 3.94 and 4.01 (2m, 2×1H, OCH_2), 4.29 (br. d, 1H, H-4, $J_{3,4}$ 2.9 Hz, $J_{4,5}$ < 1 Hz), 4.33 (dd, 1H, **H-3**, $J_{2,3}$ 9.6 Hz, $J_{3,4}$ 3.9 Hz), 4.54 (d, 1H, H-1, $J_{1,2}$ 8.1 Hz).

3-Aminopropyl 2-acetamido-2-deoxy-4-O-*(β-D-galactopyranosyl)-6*-O-*sulfo-β-D-glucopyranoside (sodium salt)* **15**: 1.94 (m, 2H, CCH_2C), 2.03 (s, 3H, NAc), 3.09 (m, 2H, CH_2N), 3.52 (dd, 1H, H-2′, $J_{1',2'}$ 7.8 Hz, $J_{2',3'}$ 10 Hz), 3.66 (dd, 1H, H-3′, $J_{2',3'}$ 10 Hz, $J_{3',4'}$ 3.4 Hz), 3.68–3.80 (m, 8H, OCH, H-2, H-3, H-4, H-5, H-5′, H-6′a and H-6′b), 3.91 (br. d, 1H, H-4′, $J_{3',4'}$ 3.4 Hz, $J_{4',5'}$ < 1 Hz), 3.98 (m, 1H, OCH), 4.32 (dd, 1H, **H-6a**, $J_{6a,6b}$ 11 Hz, $J_{5,6a}$ 4 Hz), 4.41 (dd, 1H, **H-6b**, $J_{6a,6b}$ 11 Hz, $J_{5,6b}$ 1.7 Hz), 4.51 (d, 1H, H-1′, $J_{1',2'}$ 7.8 Hz), 4.54 (d, 1H, H-1, $J_{1,2}$ 8.1 Hz).

3-Aminopropyl 2-acetamido-2-deoxy-4-O-*(6-O-sulfo-β-D-galactopyranosyl)-β-D-glucopyranoside (sodium salt)* **16**: 1.95 (m, 2H, CCH_2C), 2.07 (s, 3H, NAc), 3.09 (m, 2H, CH_2N), 3.57 (dd, 1H, H-2′, $J_{1',2'}$ 8.1 Hz, $J_{2',3'}$ 10 Hz), 3.65 (ddd, 1H, H-5, $J_{4,5}$ 9.5 Hz, $J_{5,6a}$ 5.1 Hz, $J_{5,6b}$ 2.2 Hz), 3.71 (dd, 1H, H-3′, $J_{2',3'}$ 10 Hz, $J_{3',4'}$ 3.4 Hz), 3.70–3.78 (m, 4H, H-2, H-3, H-4 and OCH), 3.85 (dd, 1H, H-6a, $J_{6a,6b}$ 11.2 Hz, $J_{5,6a}$ 5.1 Hz) 3.98–4.07 (m, 4H, H-4′, H-5′, H-6b and OCH), 4.22 (m, 2H, **H-6'a** and **H-6'b**), 4.53 (d, 1H, H-1, $J_{1,2}$ 7.8 Hz), 4.54 (d, 1H, H-1′, $J_{1',2'}$ 8.1 Hz).

3-Aminopropyl 2-acetamido-2-deoxy-3-O-*(3-O-sulfo-β-D-galactopyranosyl)-β-D-glucopyranoside (sodium salt)* **17**: 1.87 (m, 2H, CCH_2C), 2.05 (s, 3H, NAc), 3.10 (m, 2H, CH_2N), 3.51 (ddd, 1H, H-5, $J_{4,5}$ 9.7 Hz, $J_{5,6a}$ 5.4 Hz, $J_{5,6b}$ 2.2 Hz), 3.57 (dd, 1H, H-4, $J_{3,4}$ 8.1 Hz, $J_{4,5}$ 9.7 Hz), 3.67 (m, 1H, OCH), 3.68 (dd, 1H, H-2′, $J_{1',2'}$ 8.1 Hz, $J_{2,3}$ 9.5 Hz), 3.78 (dd, 1H, H-6a, $J_{5,6a}$ 5.4 Hz, $J_{5,6a,6b}$ 12.5 Hz), 3.77–3.88 (m, 4H, H-3, H-4, H-6′a and H-6′b), 3.84 (dd, 1H, H-2, $J_{1',2'}$ 7.8 Hz, $J_{2',3'}$ 9.5 Hz), 3.94 (m, 1H, H-6b), 3.96 (m, 1H, OCH), 4.31 (br. d, 1H, H-4′, $J_{3',4'}$ 3.4 Hz, $J_{4',5'}$ < 1 Hz), 4.33 (dd, 1H, **H-3′**, $J_{2',3'}$ 9.5 Hz, $J_{3',4'}$ 3.4 Hz), 4.565 (d, 1H, H-1, $J_{1,2}$ 7.8 Hz), 4.57 (d, 1H, H-1′, $J_{1',2'}$ 8.1 Hz).

3-Aminopropyl 2-acetamido-2-deoxy-3-O-*(3-O-sulfo-β-D-galactopyranosyl)-α-D-galactopyranoside (pyridinium salt)* **18**: 1.95 (m, 2H, CCH_2C), 2.01 (s, 3H, NAc), 3.12 (m, 2H, CH_2N), 3.56 (m, 1H, OCH), 3.65 (dd, 1H, H-2′, $J_{1',2'}$ 7.8 Hz, $J_{2',3'}$ 8.8 Hz), 3.68–3.85 (m, 6H, OCH, H-5′, H-6a, H-6b, H-6′a and H-6′b), 3.96 (m, 1H, H-5), 4.03 (dd, 1H, H-3, $J_{2,3}$ 11.1 Hz, $J_{3,4}$ 2.9 Hz), 4.25 (br. d, 1H, H-4, $J_{3,4}$ 3 Hz, $J_{4,5}$ < 1 Hz), 4.27 (m, 2H, **H-3′**, H-4′), 4.33 (dd, 1H, H-2, $J_{1,2}$ 3.7 Hz, $J_{2,3}$ 11.1 Hz), 4.56 (d, 1H, H-1′, $J_{1',2'}$ 7.8 Hz), 4.90 (d, 1H, H-1, $J_{1,2}$ 3.7 Hz), 8.09 (m, 2H, Py), 8.63 (m, 1H, Py), 7.79 (m, 2H, Py).