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Note

Multigram syntheses of the disaccharide repeating units of chondroitin 4- and 6-sulfates

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Abstract

The multigram syntheses of β-D-glucopyranosyluronic acid-(1→3)-2-acetamido-2-deoxy-4- and 6-*O*-sulfo-D-galactopyranose disodium salt, the disaccharide repeating units of chondroitin 4- and 6-sulfates, are described. The disaccharide benzyl methyl 2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyluronate-(1→3)-2-acetamido-2-deoxy-α-D-galactopyranoside was used as a common intermediate. Selective benzoylation at O-6 followed by O-sulfonation at C-4 of the aminosugar moiety, saponification and catalytic hydrogenation afforded the 4-*O*-sulfo derivative, whereas selective O-sulfonation at C-6 followed by similar deprotection steps provided the 6-*O*-sulfo derivative in high yield.

Keywords: Oligosaccharide synthesis; Chondroitin sulfates; Glycosaminoglycans

Chondroitin sulfate proteoglycans (ChS) are found in various body fluids, at the cell surface or in the extracellular matrix, or intracellularly in secretory granules [1]. Structural studies showed chondroitins to be essentially linear copolymers built from dimeric units composed of D-glucuronic acid (GlcA) and 2-acetamido-2-deoxy-D-galactose (GalNAc), namely [4)-β-D-Glc*p*A-(1→3)-β-D-GalNAc-(1→]$_n$. In the major variants, the 4-*O*- and 6-*O*-positions of the GalNAc residue are found sulfonated, but several types of ChS having one or more sulfate groups at various positions are also known. These sulfation patterns give rise to biologically important functions deeply related to the position and the number of sulfate groups. For example, ChS play a role in cellular recognition [2], inhibition of human $C1_q$ factor [3], blood-coagulation system [4], and in many other, still poorly understood, biological processes. The use of ChS for the treatment of human osteoarthritis has also been reported [5]. Determination of the precise structure of sequences having biological effects is, however, complicated by the microheterogeneity of the polymers. Controlled chemical degradation affords complex mixtures of products in low yield, and enzymatic hydrolysis provides unsaturated derivatives for which the geometry of the

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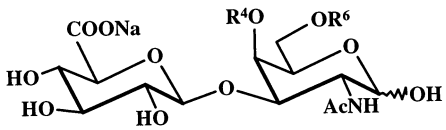
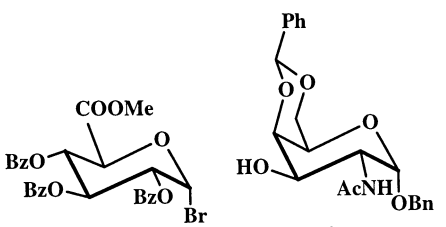
non-reducing GlcA unit is modified. The basic disaccharides of the 4- and 6-sulfate series are commercially available and are obtained by degradation of natural polymers. However, as homogeneous pure 4- or 6-sulfated polymers are not found in nature, the chemical purity of these products cannot exceed 90%, and the exact role of each isomer cannot be determined with precision. Thus, there is a need for chemically pure samples to further study in detail the different biological functions of these molecules.

Several syntheses of derivatives of the basic disaccharides of the 4- and 6-sulfate series have been reported, such as methyl glycosides [6,7] or 4-methoxyphenyl glycosides [8], but the preparation of the corresponding reducing disaccharides has never been described. We now report on expeditious and stereocontrolled multigram syntheses of both 4-*O*-sulfo (**1**) and 6-*O*-sulfo (**2**) species using the disaccharide diol **6** as a common intermediate.



	R4	R6
1	SO_3Na	H
2	H	SO_3Na

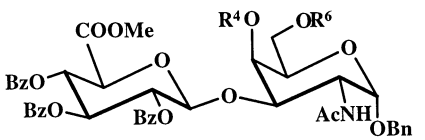
For the construction of the disaccharide skeleton, bromide **3**, easily prepared [9] from commercial D-glucurono-6,3-lactone was selected as the donor, and known galactosaminide **4** [10], prepared in 4 steps [11] from easily available benzyl 2-acetamido-2-deoxy-α-D-glucopyranoside was used as the acceptor.



3 4

Condensation of **3** (1.4 equiv) with **4** in dichloromethane at room temperature (rt) promoted by silver triflate afforded the crystalline disaccharide derivative **5** in 70% yield. It is to be noted that addition of a base (*sym*-collidine) in the reaction mixture caused extensive formation of the corresponding *ortho*-disaccharide derivative which could not be transformed easily into **5**. Treatment of **5** with aqueous acetic acid at 100 °C gave the crystalline diol **6**, the common intermediate, in 87% yield.

Preparation of the target molecule **1** was achieved as follows. Treatment of diol **6** with benzoyl cyanide [12] in pyridine at rt afforded the crystalline 6-*O*-benzoyl derivative **7** in 93% yield. The free hydroxyl group in **7** was then O-sulfonated by treatment with the sulfur trioxide–trimethylamine complex in *N*,*N*-dimethylformamide at 50 °C, followed by ion-exchange chromatography (Na^+ resin) to give the crystalline sodium salt **8** in 90% yield.



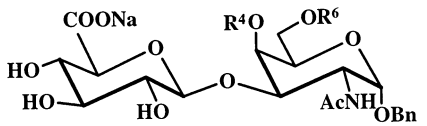
	R4	R6
5	PhCH	
6	H	H
7	H	Bz
8	SO_3Na	Bz
9	H	SO_3Na

Comparison of the ^1H NMR spectra of **8** and **7** (Table 1) showed the expected [7] downfield shift (0.88 ppm) of the signal for H-4 in **8**. Saponification of the ester groups was achieved by treatment of **8** with lithium hydroperoxide [13] in aqueous tetrahydrofuran followed by methanolic sodium hydroxide to give the crystalline disodium salt **10** in 83% yield. Hydrogenolysis (Pd–C) of **10** in aqueous methanol afforded the target molecule **1** in 97% yield. The ^1H (Table 1) and ^{13}C NMR spectra for **1** are in full agreement with the expected structure, and in accord with those reported for synthetic disaccharide derivatives [7] and for polymeric chondroitin 4-sulfate [14].

Preparation of the second target molecule **2** was then achieved as follows. Regioselective O-sulfonation at C-6 in diol **6** was examined. Treatment of **6** with the sulfur trioxide–

trimethylamine complex (3 equiv) in *N*,*N*-dimethylformamide at 50 °C, followed by ion-exchange chromatography, gave the crystalline sodium salt **9** in 90% yield. A very small amount (< 2%) of the corresponding 4,6-disulfated derivative was also obtained, but easily separated from **9** by simple chromatography. Attempted tin-mediated regioselective sulfation [15–17] proceeded in much lower yield due to the difficulty in removing completely the tin salts. Comparison of the ^{1}H NMR spectra of **9** and **6** (Table 1) also showed the expected downfield shifts (0.31 and 0.42 ppm) of the signals for H-6a and H-6b, respectively, in **9**, and no change of the signal for H-4, demonstrating that monosulfation occurred at C-6.

Saponification of **9**, as described for the preparation of **10**, gave crystalline **11** in 82% yield, and final catalytic hydrogenation (Pd–C) afforded the second target molecule **2** in 96% yield. The ^{1}H (Table 1) and ^{13}C NMR spectra of **2** are in full agreement with the expected structure, and also accord with those reported for synthetic [7] and natural [14] products.



	R^4	R^6
10	SO_3Na	H
11	H	SO_3Na

Table 1
^{1}H NMR data for disaccharide derivatives **5**–**11** and **1**–**2**[a]

Chemical shifts (δ, ppm)	Compounds								
	5	**6**	**7**	**8**[b]	**9**[b]	**10**[c]	**11**[c]	**1**[c]	**2**[c]
H-1^{I}	5.18	5.02	5.00	4.81	4.82	4.99	5.00	5.23, 4.74	5.24, 4.73
H-2^{I}	4.64	4.60	4.60	4.42	4.37	4.39	4.36	4.38, 4.30	4.38, 4.34
H-3^{I}	4.25	3.90	3.90	4.01	3.92	4.23	4.07	4.24, 4.23	4.05, 3.88
H-4^{I}	4.37	4.28	4.30	5.18	4.33	4.89	4.33	4.87, 4.81	4.31, 4.30
H-5^{I}	3.68	3.89	4.20	4.29	4.24	4.19	4.15	4.08	4.15
H-6^{I}a	4.21	3.98	4.60	4.77	4.29	3.82	4.27	3.78	4.28
H-6^{I}b	3.98	3.82	4.60	4.69	4.24	3.73	4.21	3.78	4.28
N*H*	5.81	5.43	5.39						
CH_3CO	1.65	1.50	1.43	1.42	1.32	2.01	2.01	2.06, 2.05	2.05, 2.04
H-1^{II}	5.28	5.07	5.09	5.03	5.11	4.52	4.57	4.54, 4.49	4.58, 4.53
H-2^{II}	5.54	5.49	5.50	5.58	5.50	3.38	3.36	3.38	3.37
H-3^{II}	5.90	5.90	5.89	5.93	5.93	3.45	3.54	3.49	3.52
H-4^{II}	5.70	5.69	5.71	5.68	5.55	3.55	3.54	3.57	3.52
H-5^{II}	4.38	4.41	4.40	4.47	4.47	3.67	3.74	3.68	3.71
COOCH_3	3.62	3.67	3.63	3.65	3.68				
Coupling constants (J, in Hz)									
$J_{1^I,2^I}$	3.5	3.5	3.5	3.5	3.5	3.5	3.5	4.0, 8.0	4.0, 8.0
$J_{2^I,3^I}$	11.0	11.0	11.0	11.0	11.0	11.0	11.0	10.5	10.5
$J_{3^I,4^I}$	3.5	3.5	3.5	3.0	3.5	3.5	3.5	3.0	3.0
$J_{4^I,5^I}$	0.8	0.6	0.8	0.6	0.8	0.5	0.5	0.5	0.5
$J_{5^I,6^Ia}$	1.5	5.0	4.5	9.0	4.0	8.0			
$J_{5^I,6^Ib}$	2.0	4.0	8.0	8.0	9.0				
$J_{6^Ia,6^Ib}$	12.5	11.0	12.0	12.5	12.0	12.0			
$J_{2,\ NH}$	8.0	9.0	9.0						
$J_{1^{II},2^{II}}$	7.5	7.0	7.0	7.5	7.5	7.5	7.5	7.5, 7.5	7.5, 7.5
$J_{2^{II},3^{II}}$	9.0	9.0	9.0	9.5	9.5	9.0	9.5	9.5	9.5
$J_{3^{II},4^{II}}$	9.0	9.0	9.0	9.5	9.5	9.0	9.5	9.5	9.5
$J_{4^{II},5^{II}}$	9.0	9.0	9.0	9.5	9.5	9.0	9.5	9.5	9.5

[a] For solutions in $CDCl_3$, unless otherwise stated.
[b] CD_3OD.
[c] D_2O, equilibrium.

In conclusion, expeditious, stereocontrolled, and high-yielding preparations of chondroitin 4- and 6-sulfate disaccharides are reported. All intermediates were obtained in crystalline form, thus ensuring the purity of each compound. These molecules, readily obtained in gram amounts, are currently being evaluated in biological studies.

1. Experimental

General methods.—Melting points were determined in capillary tubes with a Büchi apparatus and are uncorrected. Optical rotations were measured at 20–25 °C with a Perkin–Elmer 241 polarimeter. ^1H and ^{13}C spectra were recorded at 25 °C with Bruker DPX-250 or AM-300 spectrometers at 250 or 300 MHz, and 63 or 75.4 MHz, respectively, with Me_4Si as internal standard, unless otherwise stated. Assignments were based on homonuclear decoupling experiments, and homo- and heteronuclear correlations. Chemical-ionization (ammonia) mass spectra (CIMS) were recorded with a Nermag R 10-10 spectrometer. The purity of the products was determined by TLC on Silica Gel F_{254} (E. Merck), with detection by charring with methanolic H_2SO_4. Flash-column chromatography was performed on Silica Gel (E. Merck, 40–63 μm). Elemental analyses were performed by the Service Central de Microanalyses du CNRS (Vernaison, France).

Benzyl methyl 2,3,4-tri-O-*benzoyl-β*-D-*glucopyranosyluronate - (1→3) - 2 - acetamido-4,6*-O - *benzylidene - 2 - deoxy-α*-D-*galactopyranoside* (**5**).—A mixture of benzyl 2-acetamido-4,6-O-benzylidene-2-deoxy-α-D-galactopyranoside **4** [10] (6.0 g, 15 mmol), methyl 2,3,-4-tri-O-benzoyl-1-bromo-1-deoxy-α-D-glucopyranuronate **3** [9] (12.26 g, 21 mmol), and 4 Å powdered molecular sieves (8 g) in dry CH_2Cl_2 (200 mL) was stirred for 1 h at rt under dry Ar. Silver triflate (9.8 g, 38 mmol) was added, and the mixture was stirred for 4 h at rt. Dry pyridine (4 mL) was added, and the mixture was diluted with CH_2Cl_2 (100 mL), filtered, washed with 5% aq $Na_2S_2O_3$, satd aq $NaHCO_3$, and water, dried ($MgSO_4$), and concentrated. The residue was eluted from a column (300 g) of silica gel with 2:1 EtOAc–heptane and crystallized from EtOAc–heptane to give **5** (9.47 g, 70%); mp 123–125 °C; $[\alpha]_D$ + 93° (*c* 1, $CHCl_3$); ^1H NMR ($CDCl_3$): see Table 1; MS: *m/z* 902, $[M + H]^+$. Anal. Calcd for $C_{50}H_{47}NO_{15}$: C, 66.58; H, 5.25; N, 1.55. Found: C, 66.46; H, 5.26; N, 1.50.

Benzyl methyl 2,3,4-tri-O-*benzoyl-β*-D-*glucopyranosyluronate - (1→3) - 2 - acetamido - 2-deoxy-α*-D-*galactopyranoside* (**6**).—A mixture of **5** (10 g) and AcOH (65 mL) was stirred at 100 °C. Water (35 mL) was added dropwise, and the mixture was stirred for 30 min at 100 °C, then cooled, concentrated, evaporated with water (3 × 30 mL), and dried. The solid residue was recrystallized from hot MeOH to give **6** (7.83 g, 87%); mp 200–202 °C; $[\alpha]_D$ + 78° (*c* 1, $CHCl_3$); ^1H NMR ($CDCl_3$): see Table 1; MS: *m/z* 814, $[M + H]^+$. Anal. Calcd for $C_{43}H_{43}NO_{15}$: C, 63.46; H, 5.32; N, 1.72. Found: C,63.39; H, 5.22; N, 1.61.

Benzyl methyl 2,3,4-tri-O-*benzoyl-β*-D-*glucopyranosyluronate - (1→3) - 2 - acetamido-6-*O-*benzoyl-2-deoxy-α*-D-*galactopyranoside* (**7**).—A solution of **6** (8.14 g, 10 mmol) and benzoyl cyanide (2.62 g, 20 mmol) in dry pyridine (100 mL) was stirred for 16 h at rt under dry Ar. Methanol (10 mL) was added, and the mixture was concentrated, then evaporated with toluene (3 × 30 mL). The residue was crystallized from MeOH–CH_2Cl_2 to give **7** (8.58 g, 93%); mp 266–268 °C; $[\alpha]_D$ + 64° (*c* 1, $CHCl_3$); ^1H NMR ($CDCl_3$): see Table 1; MS: *m/z* 918, $[M + H]^+$. Anal. Calcd for $C_{50}H_{47}NO_{16}$: C, 65.42; H, 4.51; N, 1.52. Found: C, 65.45; H, 4.47; N, 1.43.

Benzyl methyl 2,3,4-tri-O-*benzoyl-β*-D-*glucopyranosyluronate - (1→3) - 2 -acetamido-6-*O-*benzoyl-2-deoxy-4*-O-*sulfo-α*-D-*galactopyranoside*, *sodium salt* (**8**).—A mixture of **7** (4.59 g, 5 mmol) and sulfur trioxide–trimethylamine complex (5.57 g, 50 mmol) in dry DMF (70 mL) was stirred for 48 h at 50 °C under dry Ar, then cooled. MeOH (10 mL) was added, and the mixture was concentrated. The residue was eluted from a column (200 g) of silica gel with 11:1 CH_2Cl_2–MeOH, then from a column (1.5 × 20 cm) of Sephadex SP C25 (Na^+) with 5:9:1 CH_2Cl_2–MeOH–water, and crystallized from aq EtOH to give **8** (4.59 g, 90%); mp 187–190 °C (dec); $[\alpha]_D$ + 70° (*c* 1, MeOH); ^1H NMR (CD_3OD): see Table 1; Anal. Calcd for $C_{50}H_{46}NNaO_{19}S$: C, 58.88; H, 4.55; N, 1.37. Found: C, 58.62; H, 4.65; N, 1.31.

Benzyl methyl 2,3,4-tri-O-*benzoyl*-β-D-*glucopyranosyluronate* - *(1→3)* - *2* - *acetamido* - *2*-*deoxy*-*6*-O-*sulfo*-α-D-*galactopyranoside*, *sodium salt* (**9**).—A mixture of **6** (4.07 g, 5 mmol) and sulfur trioxide–trimethylamine complex (2.09 g, 15 mmol) in dry DMF (80 mL) was stirred for 4 h at 50 °C, then cooled. Methanol (20 mL) was added, and the mixture was concentrated. The residue was eluted from a column (150 g) of silica gel with 8:1 CH_2Cl_2–MeOH, then from a column (1.5 × 20 cm) of Sephadex SP C25 (Na^+) and crystallized as described for the preparation of **8** to give **9** (4.12 g, 90%); mp 178–181 °C (dec); $[\alpha]_D$ +66° (*c* 1, MeOH); ^{1}H NMR (CD_3OD): see Table 1. Anal. Calcd for $C_{43}H_{42}NNaO_{18}S$: C, 56.39; H, 4.62; N, 1.53. Found: C, 56.21; H, 4.68; N, 1.42.

Benzyl β-D-*glucopyranosyluronic acid-(1→3)* - *2* - *acetamido* - *2* - *deoxy* - *4* - O - *sulfo* - α - D-*galactopyranoside*, *disodium salt* (**10**).—A solution of **8** (5.1 g, 5 mmol) in 7:3 THF–water (50 mL) was treated at −5 °C with 30% H_2O_2 (12.5 mL) and lithium hydroxide (1 M, 25 mL), and the mixture was stirred for 2 h at this temperature and 15 h at rt, then cooled to 0 °C. Methanol (40 mL) and NaOH (4 M, 30 mL) were then added, and the mixture was stirred for 6 h at rt, then treated with Amberlite IR-120 (H^+) resin to pH 2 (pH meter control), filtered, and concentrated. The residue was stirred for 1 h at 0 °C with abs EtOH (50 mL), and the solids were filtered off, washed with cold abs EtOH (20 mL), and dissolved in water (100 mL). The pH of the solution was brought to 6.5 with M NaOH, and the mixture was concentrated. The residue was crystallized from 5:1 MeOH–water to give **10** (2.57 g, 83%); mp 254–258 °C (dec); $[\alpha]_D$ +71° (*c* 1, water); ^{1}H NMR (D_2O, internal H_2O, δ_H 4.754): see Table 1. Anal. Calcd for $C_{21}H_{27}NNa_2O_{15}S$: C, 41.25; H, 4.45; N, 2.29. Found: C, 41.08; H, 4.60; N, 2.10.

Benzyl β-D-*glucopyranosyluronic acid-(1→3)* - *2* - *acetamido* - *2* - *deoxy* - *6* - O - *sulfo* - α - D-*galactopyranoside*, *disodium salt* (**11**).—Compound **9** (4.58 g, 5 mmol) was treated as described for the preparation of **10** to give **11** (2.51 g, 82%); mp 275–278 °C (dec); $[\alpha]_D$ +73° (*c* 1, water); ^{1}H NMR (D_2O, internal H_2O): see Table 1. Anal. Calcd for $C_{21}H_{27}NNa_2O_{15}S$: C, 41.25; H, 4.46; N, 2.29. Found: C, 41.11; H, 4.59; N, 2.10.

β-D-*glucopyranosyluronic acid-(1→3)-2-acetamido-2-deoxy-4*-O-*sulfo*-D-*galactopyranose*, *disodium salt* (**1**).—A solution of **10** (3.06 g, 5 mmol) in 5:1 water–MeOH (60 mL) was hydrogenated in the presence of 10% Pd–C (1 g) for 24 h at rt, then filtered, and concentrated. The residue was eluted from a column (2 × 25 cm) of 1:1 charcoal–Celite with water and freeze-dried to give **1** as an amorphous powder (2.53 g, 97%); $[\alpha]_D$ +2° (*c* 1, equil., water); ^{1}H NMR (D_2O, internal H_2O): see Table 1; ^{13}C (D_2O, internal MeOH, δ_C 49.40): *δ* 178.34, 178.10, 174.60 (C=O), 103.40, 103.12 (C-1^{II}), 93.04 (C-1^Iβ), 89.12 (C-1^Iα), 79.20, 79.05 (C-3^I), 76.80, 76.54, 76.25 (C-4^I,5^{II}), 73.25, 73.04, 72.80, 72.34 (C-5^I,3^{II},4^{II}), 71.30, 71.05 (C-2^{II}), 65.48, 65.12 (C-6^I), 52.04, 51.60 (C-2^I), and 22.65, 22.18 (CH_3CO). Anal. Calcd for $C_{14}H_{21}NNa_2O_{15}S$: C, 32.25; H, 4.06; N, 2.68. Found: C, 32.08; H, 4.12; N, 2.51.

β-D-*glucopyranosyluronic acid-(1→3)-2-acetamido-2-deoxy-6*-O-*sulfo*-D-*galactopyranose*, *disodium salt* (**2**).—Compound **11** (3.06 g, 5 mmol) was treated as described for the preparation of **1** to give **2** (2.5 g, 96%); $[\alpha]_D$ +4° (*c* 1, equil., water); ^{1}H NMR (D_2O, internal H_2O): see Table 1; ^{13}C (D_2O, internal MeOH): *δ* 178.60, 177.82, 173.80 (C=O), 103.60, 103.10 (C-1^{II}), 93.25 (C-1^Iβ), 89.42 (C-1^Iα), 81.10, 80.60 (C-3^I), 76.50 (C-5^{II}), 74.20, 73.80, 73.12, 72.80 (C-5^I,3^{II},4^{II}), 71.24, 70.90, 70.52 (C-4^I,2^{II}), 69.04, 68.72 (C-6^I), 52.25, 51.95 (C-2^I), and 23.40, 22.85 (CH_3CO). Anal. Calcd for $C_{21}H_{27}NNa_2O_{15}S$: C, 32.25; H, 4.06; N, 2.68. Found: C, 32.11; H, 4.11; N, 2.51.

Acknowledgements

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