Synthesis of oligosaccharides related to the HNK-1 antigen. 5.* Synthesis of a sulfo-mimetic of the HNK-1 antigenic trisaccharide**

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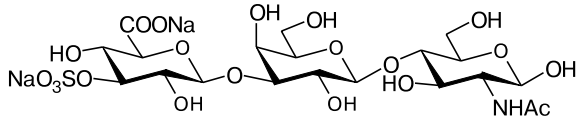
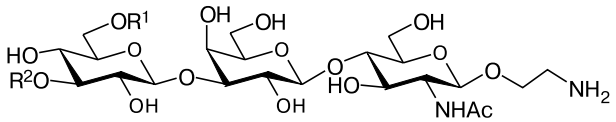
2-Aminoethyl 3,6-di-*O*-sulfo-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranoside, which is the sulfo-mimetic of the antigenic trisaccharide HNK-1, and the corresponding monosulfates, *viz.*, 2-aminoethyl 3-*O*-sulfo- and 2-aminoethyl 6-*O*-sulfo-β-D-glucopyranosyl-(1→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosides, were synthesized. 2-Azidoethyl 2,4-di-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-benzoyl-β-D-galactopyranosyl-(1→4)-2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside served as the common precursor for the sulfated trisaccharides. This compound was synthesized according to the [2+1] pattern from monosaccharidic precursors: 3,6-di-*O*-acetyl-2,4-di-*O*-benzoyl-D-glucopyranosyl trichloroacetimidate, allyl 2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galactopyranoside, and 2-azidoethyl 2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside. The structures of the glycosyl donors and glycosylation conditions were optimized for the efficient synthesis of the glucosyl-β-(1→3)-galactose disaccharide block and its subsequent transformation into the target trisaccharide sequence.

Key words: HNK-1 antigen, sulfo-mimetic, glycosylation, levoglucosan.

The HNK-1 carbohydrate antigens, parts of the carbohydrate chains of glycolipids and glycoproteins expressed on nervous tissue cells, include epitopes of the autoantibodies responsible for the development of serious diseases, *viz.*, peripheral neuropathies.[2] Although the role of the HNK-1 antigens has not been fully elucidated as yet, it was shown that they also determine the adhesion of nervous cells and the growth and development of nervous tissues[3—5] and participate in the nerve impulse transmission.[6] A common structural unit of the HNK-1 antigenic oligosaccharides is the trisaccharide $^{-}SO_3$-3GlcAβ-(1→3)-Galβ-(1→4)-GlcNAcβ (**1**) containing a sulfo group at the O(3) atom of the glucuronic acid residue.[7,8]



1



2a—c

$R^1 = R^2 = SO_3Na$ (**2a**); $R^1 = H$, $R^2 = SO_3Na$ (**2b**); $R^1 = SO_3Na$, $R^2 = H$ (**2c**)

This work continues our research dealing with the synthesis of HNK-1 antigenic oligosaccharides[1,9—11] and is devoted to the synthesis of a disulfated mimetic **2a** of the trisaccharide sequence **1** in which the sulfo group at the O(6) atom of the glucose residue mimics the carboxy group of glucuronic acid in structure **1**. Apart from compound **2a**, we also prepared the corresponding 3- and 6-monosulfates **2b** and **2c**. Sulfated oligosaccharides **2** were obtained as 2-aminoethyl glycosides for their subsequent transformation into molecular probes and neoglycoconjugates, which would be used to elucidate the possible role of anionic groups in positions 3 and 6 in the biological recognition of the HNK-1 antigens.

The retrosynthetic analysis (Scheme 1) has shown that diol **3** is the common precursor of trisaccharides **2a—c**;

* For Part 4, see Ref. 1.

** Dedicated to Academician V. A. Tartakovsky on the occasion of his 75th birthday.

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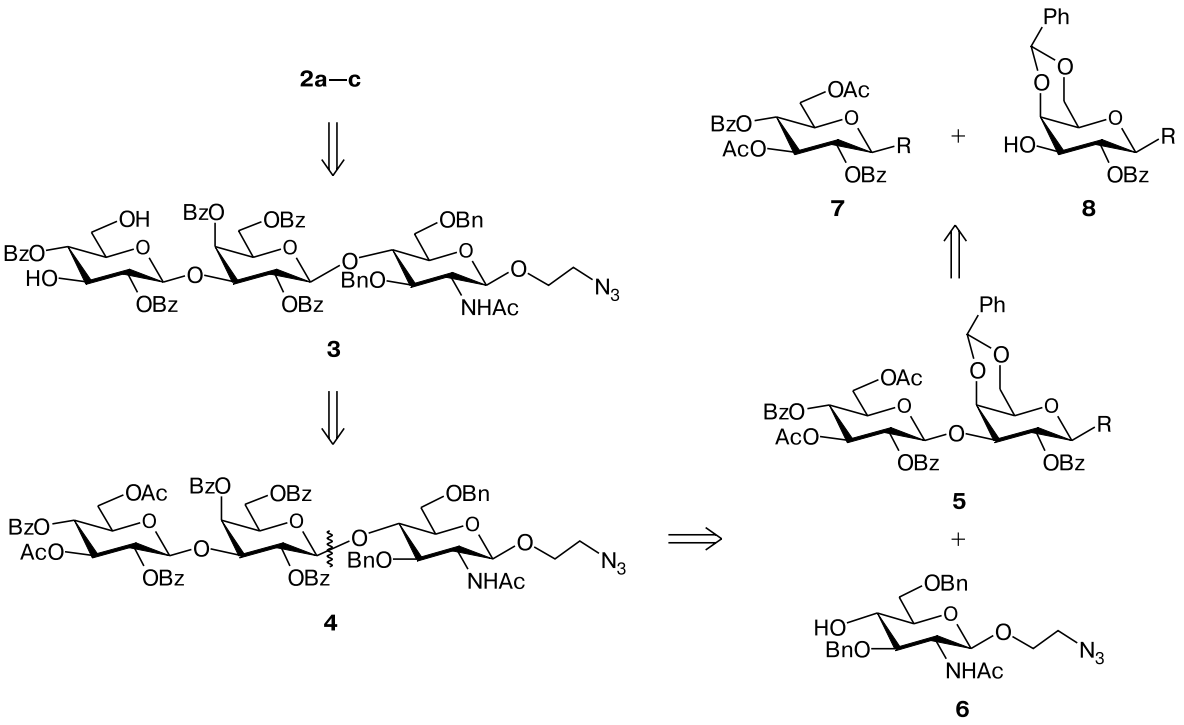
Scheme 1

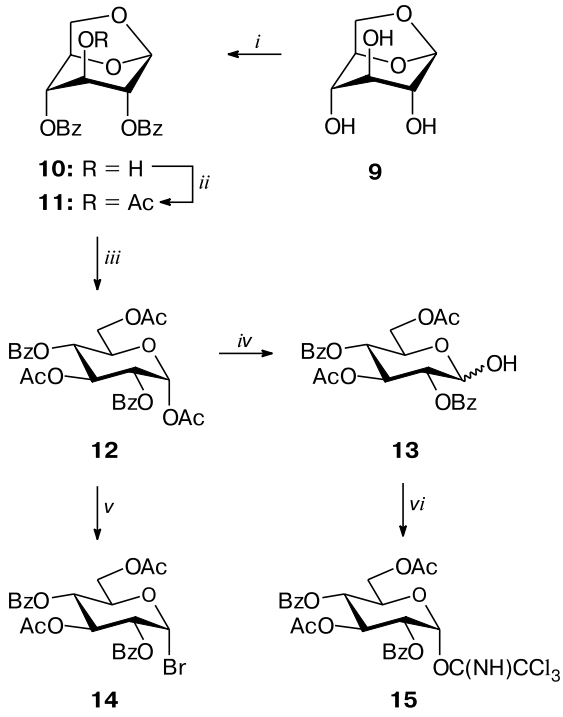


we intended to obtain **3** from trisaccharide **4** containing temporary protective groups at the O(3) and O(6) atoms of the glucose residue. In the synthesis of trisaccharide **4**, benzoyl and benzyl groups can be used as the permanent protective groups, while acetyl can serve as the temporary protective group. The latter can selectively be removed in the presence of benzoyl groups by mild acid-catalyzed methanolysis.[12] The synthesis of trisaccharide **4** was planned according to the [2+1] pattern using the disaccharide glucosyl-β-(1→3)-galactose **5** as the glycosyl donor and *N*-acetyl-D-glucosamine derivative **6** as the acceptor. The monosaccharide precursors of disaccharide **5**, namely, compounds **7** and **8**, can in turn be prepared from levoglucosan and D-galactose β-pentaacetate.

3,6-Di-*O*-acetylated derivatives, bromide **14** and trichloroacetimidate **15**, which correspond to the glucose residue **7**, were used as the glycosylating agents (Scheme 2).

The synthesis of 2,4-di-*O*-benzoylated glucopyranose derivatives from precursors with the $^4C_1$-conformation of the pyranose ring is a nontrivial task, whereas the use of levoglucosan **9** with the inverted ring conformation makes possible rather efficient one-step 2,4-dibenzoylation.[13] Acetylation of the resulting dibenzoate **10** afforded acetate **11**, which was then subjected to acetolysis to give 1,3,6-triacetate **12** in quantitative yield. This product reacted with HBr in AcOH affording glucosyl bromide **14** in quantitative yield. For the preparation of trichloroacetimidate **15**, compound **12** was first selectively

Scheme 2



Reagents and conditions: *i*. BzCl/pyridine (40%); *ii*. Ac_2O/pyridine (96%); *iii*. H_2SO_4(cat.)/Ac_2O (98%); *iv*. $N_2H_4 \cdot HOAc$/DMF (88%); *v*. 33% HBr in AcOH, Ac_2O/CH_2Cl_2 (99%); *vi*. CCl_3CN, DBU/CH_2Cl_2 (81%).

deacetylated by treatment with hydrazinium acetate[14] to give hemiacetal **13** in 88% yield. The reaction of the product with CCl_3CN in the presence of DBU[10] furnished trichloroacetimidate **15** in 81% yield.

The azidoethyl glycoside of glucosamine **6** was prepared as shown in Scheme 3. The reaction of chloride **16** (see Ref. 15) with 2-chloroetanol in the presence of mercuric cyanide afforded 2-chloroethyl glycoside **17** in 73% yield. The β-configuration of the glycosidic bond in product **17** was confirmed by the value of the coupling constant $J_{1,2}$ in the ^{1}H NMR spectrum (Table 1), equal to 8.3 Hz, while incorporation of the β-chloroethyl aglycone into the molecule is confirmed by the signal at δ 41.8 (Table 2) characteristic of the CH_2Cl group in the ^{13}C NMR spectrum. The reaction of chloro derivative **17** with NaN_3 in the presence of a phase-transfer catalyst

Table 1. ^{1}H NMR data for derivatives **2—4**, **5b**, **6**, **10—18**, **20—21**, **25—27**, **29**, **30**, **32—35**, and **36—40** ($CDCl_3$)

Compound	Residue	δ							*J*/Hz						
		H(1)	H(2)	H(3)	H(4)	H(5)	H(6_a)	H(6_b)	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6a}$	$J_{5,6b}$	$J_{6a,6b}$
2a[a]	Glc	4.77	3.58	4.32	3.65	3.99	4.33	4.19	7.9	9.2	9.1		5.8		
	Gal	4.52	3.69	3.83	4.22				7.9		3.1	<1			
	GlcNAc	4.56	3.78						8.2						
2b[a]	Glc	4.77	3.56	4.32	3.63				8.0	9.1	9.1				
	Gal	4.58	3.72	3.85	4.18				7.9		3.0	<1			
	GlcNAc	4.53	3.79						8.3						
2c[a]	Glc	4.67	3.40	3.52	3.46	3.66	4.33	4.18	7.9	8.7	9.1	9.4	<1	5.6	9.7
	Gal	4.52	3.69	3.82	4.22				7.9		3.0	<1			
	GlcNAc	4.56	3.77						7.9						
3	Glc	4.87	4.92	3.93	5.01	3.70	3.74	3.55	7.6	7.8	9.5	9.5			
	Gal	4.68	5.56	3.99	5.93	3.90	4.31	4.27	8.0	8.4	3.5	<1			
	GlcNAc	4.46	3.62	3.87	4.00	3.36	3.58	3.45	6.9	6.8	6.8		4.3		10.4
4	Glc	4.84	5.09	5.43	5.30	3.86	4.31	4.15	7.6	7.7	9.6	9.6	<1	4.1	11.4
	Gal	4.60	5.50	3.98	5.78	3.93	4.38	4.23	8.6	8.6	3.0	<1	4.9	4.7	11.4
	GlcNAc	4.52	3.55	3.86	3.98	3.32	3.55	3.45					3.2	3.6	10.4
5b	Glc	5.06	5.30	5.48	5.38	3.84	4.30	4.17	7.8	7.9	9.6	9.6		4.3	12.2
	Gal	4.60	5.54	4.07	4.35	4.37	4.34	4.07	7.9	8.0	<1	<1			10.9
6	GlcNAc	4.96	3.29	4.08	3.62	3.57	3.71—3.79		8.2	9.3	9.3	8.4	3.3		10.4
10	Glc	5.70	4.94	4.11	5.02	4.82	4.38	3.88	<1	<1	<1	<1	<1	5.3	7.5
11	Glc	5.64	4.90	5.19	4.94	4.80	4.24	3.87	<1	<1	<1	<1	<1	5.2	7.6
12	Glc	6.55	5.36	5.89	5.50	4.17—4.34		3.8	3.3	9.8	10.7	10.0			
13[b]	Glc	5.69	5.14	5.97	5.44	4.45	4.23	4.23	3.4	10.3	9.9	9.9			
14	Glc	5.71	5.19	5.98	5.44	4.48	4.25—4.29		3.2	7.3	9.9	10.0	3.5		
15	Glc	6.78	5.45	5.99	5.55	4.43	4.27	4.27	3.5	10.2	9.9	10.0			
17	GlcNAc	4.81	3.88	5.33	5.07	3.73	4.16	4.29	8.4	8.5	9.6	9.7	4.9	2.5	12.3
18	GlcNAc	4.82	3.79	5.33	5.06	3.71	4.14	4.23	8.3	8.5	10.4	9.7	4.8	2.4	12.3
20	GlcNAc	5.11	3.24	4.37	3.69	4.35	3.81	3.58	8.3	9.6	9.6		4.9	10.2	10.4
21	GlcNAc	4.67	3.51	3.88	3.48	3.39	4.23	3.62	8.3	10.0	10.0		4.1	10.1	10.1
25	Glc	4.73	5.39	5.65	5.43	3.95	4.24	4.29	10.0	9.7	9.5	9.8	5.2	2.9	12.3
26	Glc	4.90	5.38	5.61	5.46	3.92	4.31	4.05	7.8	9.5	9.8	9.7			
	Gal	4.51	5.29	4.47	4.30	4.25	3.96	4.21	9.6	9.5	6.3				
27	Glc	5.70	4.49	5.25	5.04	3.87	4.08	4.14	5.3	2.3	<1	9.1	3.1	5.5	12.2
	Gal	4.48	5.61	3.81	4.03	3.36	3.92	4.32			3.6	<1	<1	<1	11.4
29	Glc	4.73	4.92	5.01	5.03	3.61	4.13	4.25	7.8	9.1	9.2	9.2	2.4	4.2	12.2
	Gal	4.62	5.58	3.97	4.33	3.48	4.08	4.33	8.0	10.1	10.2	<1	<1	<1	
30[c]	Glc	4.90	5.33	5.52	5.31	3.91	4.32	4.17	7.9	9.7	9.6	8.0	2.9	5.5	12.3
	Gal	4.55	5.45	3.93	4.18	3.62	4.01	3.88	8.0	8.4	4.5	<1	6.7	5.0	11.4
32	Glc	4.88	5.12	5.40	5.30	3.81	4.26	4.14	7.7	7.8	9.6	9.7	3.1	4.6	12.3
	Gal	4.65	5.58	4.21	5.84	4.12	4.54	4.47	7.8	8.0	3.4	<1	5.1	7.3	11.6
33	Glc	5.03	5.13	5.45	5.33	3.89	4.34	4.19	7.8	7.8	9.6	9.7	3.0	4.7	12.2
	Gal	5.65	5.43	4.61	5.91	4.67	4.46	4.43	2.8	10.4	3.2	<1	6.0	6.0	11.6
34	Glc	5.02	5.15	5.46	5.32	3.94	4.30	4.20	7.7	7.8	9.6	9.7	3.0	4.9	12.2
	Gal	6.71	5.72	4.58	6.01	4.67	4.55	4.38	3.7	10.3	3.2	<1	4.3	7.6	11.8

(*to be continued*)

Table 1 (*continued*)

Compound	Residue	δ							*J*/Hz						
		H(1)	H(2)	H(3)	H(4)	H(5)	$H(6_a)$	$H(6_b)$	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6a}$	$J_{5,6b}$	$J_{6a,6b}$
35	Glc	4.90	5.12	5.41	5.31	3.84	4.31	4.16	7.7	7.7	9.6	9.7	3.1	4.6	12.1
	Gal	4.64	5.61	4.24	5.90	4.17	4.52	4.44	10.0	9.8	3.3	<1	5.1	7.2	11.8
36a[d]	Glc	4.95	5.07	4.86	5.24	4.19	4.29	4.18	7.7	8.3	9.1	9.1			
	Gal	4.73	5.51	4.31	5.92	4.09	4.41	4.08	8.1	8.3	3.1	<1	4.5		11.3
	GlcNAc	4.39	3.78	3.56	4.00	3.17	3.60	3.42	8.2	9.4				9.5	
36b[d]	Glc	5.10	5.12	4.95	5.36	4.21	4.47	4.47	7.9	8.0	9.6	9.6			
	Gal	4.71	5.55	4.19	5.88	3.96	4.29	3.87	8.0	9.8	3.3	<1	4.6		
	GlcNAc	4.38	3.80	3.55	3.98	3.11	3.59	3.40	8.4						
36c[c]	Glc	4.93	4.96	3.90	5.02	4.18	4.25	4.24	8.7		9.5	9.4	4.8		
	Gal	4.77	5.52	4.38	5.93	4.14	4.41	4.01	8.5	9.6	3.0	<1			
	GlcNAc	4.38	3.80	3.91	4.01	3.18	3.65	3.48			7.3	7.3	3.6		10.5
37	Glc	4.99	5.30	5.73	5.54	4.13	4.57	4.57	7.8	9.7	9.7	9.8			
	Gal	4.60	5.54	4.06	5.89	3.88	4.32	4.26	9.8	9.8	3.4	<1	8.2	7.8	11.5
	GlcNAc	4.50	3.60	3.84	3.98	3.46	3.56	3.48		7.5	6.6	6.6	4.4		10.3
38[c]	Glc	5.13	5.21	5.73	5.35	4.40	4.30	4.30	7.8	9.4	9.4	9.7			
	Gal	4.79	5.53	4.40	5.97	4.18	4.42	4.05	10.0	10.0	3.2	<1	5.0		10.0
	GlcNAc	4.38	3.76	3.56	4.03	3.18	3.67	3.49	8.5	8.6	10.0	10.0	3.5		
39a[c]	Glc	5.00	5.06	4.88	5.21	4.26	4.29	4.24	7.8	8.2	8.8				
	Gal	4.72	5.53	4.31	5.93	4.12	4.42	4.04	8.0	8.3	3.0	<1	4.4	7.0	11.3
	GlcNAc	4.30	3.78	3.50	4.00	3.12	3.61	3.41					3.0	10.3	10.6
39b[c]	Glc	5.11	5.12	4.96	5.36	4.20	4.48	4.43	8.0	7.9	9.5	9.6	3.6	9.9	
	Gal	4.68	5.56	4.18	5.88	3.96	4.28	3.86	8.1	8.2	3.3	<1			
	GlcNAc	4.24	3.77	3.48	3.96	3.10	3.56	3.37			9.2	9.2		9.4	
39c[c]	Glc	4.90	4.92	3.88	5.01	4.18	4.22	4.19	7.4	8.4	9.3	9.4			
	Gal	4.75	5.50	4.36	5.92	4.15	4.40	4.01	8.1	8.3	3.0	<1	3.7		11.4
	GlcNAc	4.29	3.76	3.52	3.99	3.19	3.63	3.47		9.6	9.6				10.2
40a[c]	Glc	5.01	5.04	4.81	5.19	4.16	4.21	4.15	7.9	7.9	9.2	9.3			
	Gal	5.00	5.57	4.64	6.00	4.50	4.68	4.29	7.9	8.4	3.0	<1	3.6	8.0	
	GlcNAc	4.28	3.75	3.12	3.18	3.20	3.43	3.43	8.3	8.3					
40b[c]	Glc	5.10	5.12	4.90	5.32	4.19	4.45	4.45	8.0	7.9	9.5	9.6			
	Gal	4.95	5.59	4.48	5.93	4.29	4.53	4.17	8.0	8.3	3.2	<1			
	GlcNAc	4.28	3.72	3.57	3.59	3.13	3.39	3.32		9.9	9.2				
40c[c]	Glc	4.93	4.94	3.83	5.01	4.07	4.21	4.21	7.8	8.8	9.6	9.6			
	Gal	4.98	5.59	4.62	6.00	4.49	4.69	4.30	8.3	8.4	3.0	<1	3.9	7.9	
	GlcNAc	4.30	3.72	3.62	3.66	3.18	3.45	3.39	9.4	9.4					

Note. Other signals: PhC$\underline{H}_2$ 4.25—4.97 ppm (for all compounds except for **40a—b**, **2a—c**), N$\underline{H}$Ac 5.77 ppm (for compounds **3** and **4**), O(O)CC$\underline{H}_3$ 1.88, 1.64 ppm (for compound **4**), NHCOC$\underline{H}_3$ 1.81—1.90 ppm (for all compounds except for **2a—c**), NHCOC$\underline{H}_3$ 2.02—2.08 ppm (for compounds **2a—c**), OC$\underline{H}_2$CH$_2$N 3.25—3.88 ppm (for all compounds except for **2a—c**), OCH$_2$C$\underline{H}_2$N 3.10—3.41 ppm (for all compounds except for **2a—c**), OC$\underline{H}_2$CH$_2$N 3.74—4.09 ppm (for compounds **2a—c**), OCH$_2$C$\underline{H}_2$N 2.94—3.28 ppm (for compounds **2a—c**).

[a] The spectrum was recorded in D_2O after preliminary deuterium exchange.

[b] Data for the α-anomer.

[c] The spectrum was recorded in CD_3OD.

[d] The spectrum was recorded in a $CDCl_3$—CD_3OD solvent mixture, 2 : 0.4.

gives 2-azidoethyl glycoside **18** in 89% yield. The formation of product **18** was accompanied by disappearance of the signal of the CH_2Cl group in the ^{13}C NMR spectrum, which was replaced by the signal for CH_2N_3 (δ 50.6).

Compound **18** was then deacetylated and the triol **19** thus formed was made to react with benzaldehyde dimethyl acetal in the presence of TsOH to be converted into 4,6-*O*-benzylidene derivative **20**; the free hydroxy group in **20** was benzylated by benzyl bromide in the presence of sodium hydride in DMF[16] to give benzyl ether **21** in 83% yield. Then compound **21** was converted into 3,6-di-*O*-benzyl derivative **6** (yield 84%) by means of $Me_3N \cdot BH_3/AlCl_3$-induced regioselective reductive cleavage of the benzylidene ring in the presence of 2 equiv. of water.[16] The position of the free hydroxy group in compound **6** was confirmed by NOESY correlation between

Table 2. ^{13}C NMR data for derivatives **2—4**, **5b**, **6**, **10—13**, **15**, **17—18**, **20—21**, **25—27**, **29**, **30**, **32—37**, and **39—40** ($CDCl_3$)

Compound	Residue	δ					
		C(1)	C(2)	C(3)	C(4)	C(5)	C(6)
2a[a]	Glc	104.7	73.5	85.3	69.7		68.7
	Gal	103.9		83.8	76.2		
	GlcNAc	102.5	56.4				
2b[a]	Glc	104.8		85.5			
	Gal	104.1		83.6	69.9		
	GlcNAc	102.4	56.3				
2c[a]	Glc	104.9	74.4	76.7	70.5	74.8	68.4
	Gal	103.7	71.2	83.5	69.5		
	GlcNAc	102.4	56.3				
3	Glc	101.7	74.7	73.7	71.4	75.1	61.3
	Gal	99.6	71.1	79.1	70.2	71.4	61.9
	GlcNAc	100.2	54.0	77.6	75.0	74.8	68.6
4	Glc	101.2	71.6	72.0	69.0	72.1	62.0
	Gal	99.6	71.4	77.2	69.9	71.8	62.5
	GlcNAc	100.2	54.2	77.7	75.0	74.7	68.4
5b	Glc	101.2	71.7	72.2	69.1	72.0	62.0
	Gal	100.0	70.1	78.1	76.1	66.7	68.9
6	GlcNAc	100.2	56.1	80.9	72.4	74.1	70.3
10	Glc	99.9	69.7	73.1	72.1	74.2	65.7
11	Glc	99.1	69.5	69.6	70.6	73.9	65.4
12	Glc	89.2					
13[b]	Glc	90.3					
15	Glc	93.3					
17	GlcNAc	101.0	54.7	72.2	68.7	72.0	62.1
18	GlcNAc	100.5	54.9	72.1	68.6	71.9	62.0
20	GlcNAc	100.9	57.5	70.8	81.5	66.2	68.5
21	GlcNAc	100.2	58.2	76.2	82.9	66.0	68.8
25	Glc	83.8	70.5	73.6	69.3	76.1	62.7
26	Glc	101.2	71.8	72.4	69.3	72.2	75.9
	Gal	82.7	72.7	76.6	75.8	62.4	68.9
27	Glc	97.4	72.7	68.7	68.3	67.2	63.3
	Gal	82.7	74.5	73.6	74.5	69.9	69.3
29	Glc	101.6	71.0	72.9	68.5	71.8	61.8
	Gal	99.8	70.5	78.3	75.9	66.8	69.0
30[c]	Glc	101.0	71.7	72.1	69.0	72.0	61.9
	Gal	99.8	71.2	77.4	69.9	71.8	63.0
32	Glc	101.0	71.7	72.1	69.0	72.0	61.9
	Gal	99.8	71.2	77.4	69.9	71.8	63.0
33	Glc	101.2	71.8	72.1	69.2	72.0	62.0
	Gal	90.6	71.0	73.8	71.2	67.4	63.1
34	Glc	101.2	71.7	72.1	69.0	72.1	62.1
	Gal	93.7	69.3	73.9	70.2	70.3	63.1
35	Glc	101.1	71.7	72.1	69.0	72.0	61.9
	Gal	83.9	69.6	78.5	70.4	75.7	63.2
36a[d]	Glc	102.5	74.0	79.3	71.3	74.3	68.0
	Gal	101.5	73.4	77.8	73.0	73.0	64.4
	GlcNAc	102.4	55.8	81.1	77.2	75.8	68.9
36b[d]	Glc	102.8	73.7	79.0	71.0	72.9	64.0
	Gal	101.5	72.8	79.8	71.9	73.1	64.1
	GlcNAc	102.5	55.9	81.2	77.2	75.7	68.8
36c[c]	Glc	102.7	75.7	73.8	73.3	74.5	68.5
	Gal	101.5	73.6	77.7	72.9	72.9	64.1
	GlcNAc	102.4	55.9	81.2	77.2	75.9	68.9
37	Glc	101.5	71.8	72.6	69.4	72.3	62.8
	Gal	99.6	71.5	77.6	69.8	71.8	62.3
	GlcNAc	100.2	53.9	77.6	75.0	74.7	68.5
39a[c]	Glc	102.5	73.9	79.2	71.3	74.2	68.0
	Gal	101.4	73.3	77.9	72.9	72.9	64.3
	GlcNAc	102.5	55.7	81.2	77.0	75.6	68.7
39b[c]	Glc	102.7	73.7	79.1	70.9	72.8	63.9
	Gal	101.5	73.0	79.8	71.9	72.9	64.1
	GlcNAc	102.5	55.8	81.2	77.1	75.6	68.7
39c[c]	Glc	102.6	75.1	73.8	73.4	74.5	68.7
	Gal	101.3	73.9	77.9	73.0	73.0	64.2
	GlcNAc	102.5	55.8	81.2	77.1	75.7	68.8
40a[c]	Glc	102.6	73.9	79.4	71.4	74.1	68.1
	Gal	102.6	72.7	77.6	73.2	73.5	64.7
	GlcNAc	102.5	56.4	73.7	81.4	76.0	61.1
40b[c]	Glc	102.6	73.6	79.3	70.9	73.0	64.0
	Gal	102.4	72.1	79.6	72.0	73.4	64.3
	GlcNAc	102.5	56.3	73.5	81.2	75.8	60.9
40c[c]	Glc	102.7	75.6	74.0	73.3	74.4	68.5
	Gal	102.7	72.9	77.2	73.2	73.7	64.7
	GlcNAc	102.7	56.3	73.6	81.7	76.0	61.1

Note. Other signals: $Ph\underline{C}H_2$ 73.2—75.1 ppm (for all compounds except for **40a—b**), $NH\underline{C}OCH_3$ 22.9—23.6 ppm, $O(O)C\underline{C}H_3$ 20.6, 20.4 ppm (for compound **4**), $O\underline{C}H_2CH_2N$ 67.8—69.3 ppm, $OCH_2\underline{C}H_2N$ 50.4—51.8 ppm (for compounds **3** and **4**, **36** and **37**), $OCH_2\underline{C}H_2N$ 40.8—41.0 ppm (for compounds **39** and **40**), $O\underline{C}H_2CH_2N$ 67.4—70.3 ppm (for compounds **2a—c**), $OCH_2\underline{C}H_2N$ 40.5—41.1 ppm (for compounds **2a—c**).

[a] The spectrum was recorded in D_2O after preliminary deuterium exchange.

[b] Data for the α-anomer.

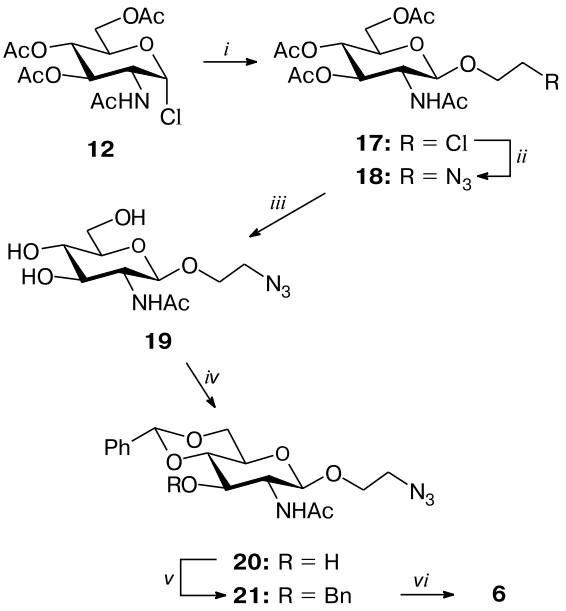
[c] The spectrum was recorded in CD_3OD.

[d] The spectrum was recorded in a $CDCl_3$—CD_3OD solvent mixture, 2 : 0.4.

the H(3) and H(6) protons of glucosamine and the benzylic methylene protons and the correlation between the H(4) and 4-OH protons.

Using the obtained monosaccharide derivatives, glucosyl donors **14**, **15**, benzobromoglucose (**22**, model compound), and known acceptors **23** [17] and **24**,[18] we started the synthesis of the disaccharide block Glcβ-(1→3)-Galβ **5** (Scheme 4). The 4,6-*O*-benzylidene group in galactosides **23** and **24** is expected to favor effective glycosylation at position 3 (see Refs 17 and 19) compared, for example, with the 4,6-di-*O*-benzoyl structure.[20,21] The presence of the benzoyl group at the O(2) atom in derivatives of the

Scheme 3



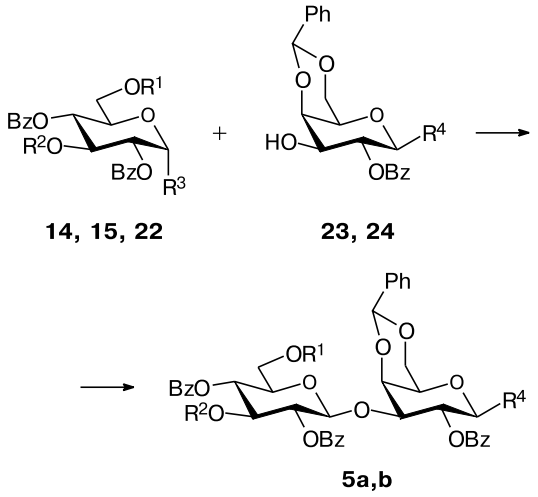
Reagents and conditions: *i*. $Hg(CN)_2$/2-chloroethanol (73%); *ii*. NaN_3, 18-crown-6/DMF (89%); *iii*. 1 *M* MeONa/MeOH; *iv*. $PhCH(OMe)_2$, $TsOH \cdot H_2O$/DMF (85% over two steps); *v*. BnBr, NaH/DMF (83%); *vi*. $Me_3N \cdot BH_3$, $AlCl_3$, H_2O/THF (84%).

type **8** is required for the control of the stereochemical outcome of glycosylation by disaccharide donors such as **5** obtained from monosaccharide derivatives **7** and **8**. The allyl protective group chosen for the anomeric center in galactoside **24** allows one to easily pass from allyl glycoside **5** (R = OAll) to the reducing derivative **5** (R = OH) and further to glycosyl donors of different types for subsequent glycosylation. The use of thiogalactoside **23** as the glycosyl acceptor leads directly to disaccharide glycosyl donor **5** (R = SEt) without any additional transformations.

Our attempts to obtain the target disaccharide structures by glycosylation of acceptors **23** and **24** with bromide **14** and benzobromoglucose **22** failed. Thus the Helferich condensation of bromide **22** with allyl glycoside **24** (both in the presence and in the absence of molecular sieves 3 Å) and the silver triflate-induced condensation in nitromethane yielded complex mixtures of unidentifiable products.

The reaction of bromide **22** with thioglycoside acceptor **23** in the presence of silver triflate and molecular sieves 4 Å also gave a complex mixture of products where unconsumed acceptor **23** was the major component (recovery ~40—60%). The largest yield of disaccharide **5a** was only ~15%; the β-configuration of the glycosidic bond was confirmed by the characteristic $J_{1,2}$ value of 7.5 Hz in the ^1H NMR spectrum.

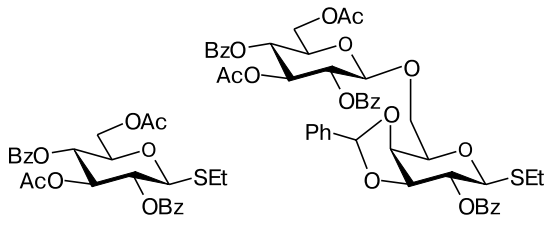
Scheme 4



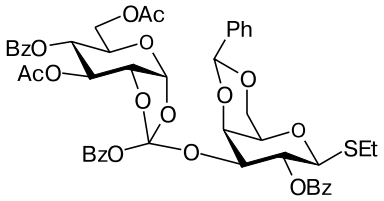
14: $R^1 = R^2$ = Ac, R^3 = Br
15: $R^1 = R^2$ = Ac, $R^3 = OC(NH)CCl_3$
22: $R^1 = R^2$ = Bz, R^3 = Br
5a: $R^1 = R^2$ = Bz, R^4 = SEt; **5b:** $R^1 = R^2$ = Ac, R^4 = OAll
23: R^4 = SEt
24: R^4 = OAll

The Helferich glycosylation of thiogalactoside **23** with bromide **14** in the presence of molecular sieves AW300 affords thioglycoside **25**, resulting from migration of the ethylthio group to the glucosyl donor, in 93% yield. When this reaction is promoted by silver triflate (in the presence of molecular sieves either 4 Å or AW300), the initial acceptor **23**, ethylthio group migration product **25**, and 1,6-linked disaccharide **26**, resulting from 4,6→3,4 migration of the benzylidene group in the acceptor followed by glycosylation at the 6-OH group liberated in the galactose residue, were isolated from the reaction mixture in approximately equal yields. The NMR spectra of disaccharide **26** (see Table 1 and 2) exhibited signals (δ_H 5.91, δ_C 105.3) nontypical of the Ph*CH* fragment of six-membered acetals of the 1,3-dioxane type (δ_H 5.5—5.6, δ_C 100—101) but coinciding with those for five-membered 1,3-dioxolane structures.[22] Glycosylation carried out in the presence of *sym*-collidine for decreasing the acidity and suppressing the migration of the benzylidene group furnished disaccharide orthoseter **27** in 46% yield.

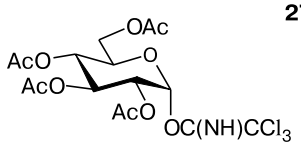
The structure of product **27** was confirmed by the ^1H NMR spectrum, which contained a low-field signal for H(1) of the α-glucose residue (δ 5.70, $J_{1,2}$ = 5.0 Hz), a high-field signal for H(2) of the glucose residue (δ 4.49), *i.e.*, in the region of ring protons for which the corresponding hydroxy group is not acylated. One more proof was provided by the unusual values of the spin-spin coupling constant ($J_{1,2}$ = 5.0 Hz, $J_{2,3}$ = 3.4 Hz, $J_{3,4}$ < 1 Hz), which is a consequence of distortion of the $^4C_1$ conformation in the orthoester structure of **27**. Note that in the ^{13}C NMR spectrum, the chemical shift for C(1) of the glucose residue (δ 97.4) attests to α-anomeric configura-



25 **26**



27



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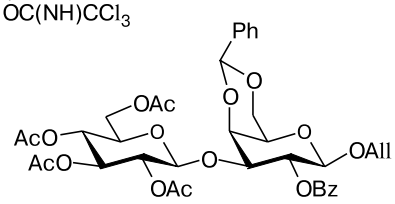

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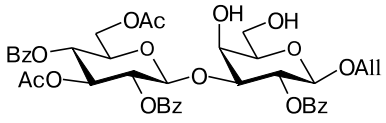
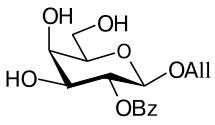


30



31

tion of this residue, whereas the corresponding signal for substituted disaccharide derivatives Glcβ-(1→3)-Galβ would have been located at δ ≈ 100—101.

Imidate **15** was used as the glycosyl donor for the synthesis of disaccharides of type **5**, or, in model experiments, this was its tetraacetyl analog **28** (see Ref. 23). In the reaction of trichloroacetimidate **28** with allyl glycoside **24** in the presence of TMSOTf and molecular sieves AW300 in CH_2Cl_2, the highest yield of disaccharide **29** was 36%. The β-configuration of the glycosidic bond in disaccharide **29** was confirmed by the value of the coupling constant $J_{1,2}$ in the ^{1}H NMR spectrum (7.8 Hz). Note that glycosylation with trichloroacetimidates was accompanied by fewer side processes than it was observed in experiments with glucosyl bromides. The isolation of reaction products **29** and **5b** was difficult in both cases, because disaccharides and the glycosyl acceptor **24** had similar chromatographic mobilities. In order to overcome this difficulty, we treated the reaction mixtures with acid to remove the 4,6-*O*-benzylidene groups; the products thus formed differed in chromatographic mobilities and could easily be separated by chromatography. Thus, after glycosylation of allyl glycoside **24** with donor **15** in the presence of TMSOTf and molecular sieves AW300 in CH_2Cl_2 and treatment of the reaction mixture with aqueous acetic acid, the disaccharide 4,6-diol **30** and 3,4,6-triol **31** were isolated in 28 and 40% yield, respectively.

The best results of glycosylation of allyl glycoside **24** with imidate **15** were obtained when $BF_3 \cdot Et_2O$ was used as the promoter and the reaction was performed in toluene. After removal of 4,6-*O*-benzylidene groups by treatment with pyridinium *p*-toluenesulfonate, disaccharide 4,6-diol **30** was isolated in 36% yield by chromatography.

The yield of disaccharide **5b** was increased to 48% when the product was isolated from the reaction mixture by direct crystallization. The β-configuration of the glycosidic bond was confirmed by characteristic spin-spin coupling constant $J_{1,2}$, equal to 7.8 Hz, in the ^{1}H NMR spectrum.

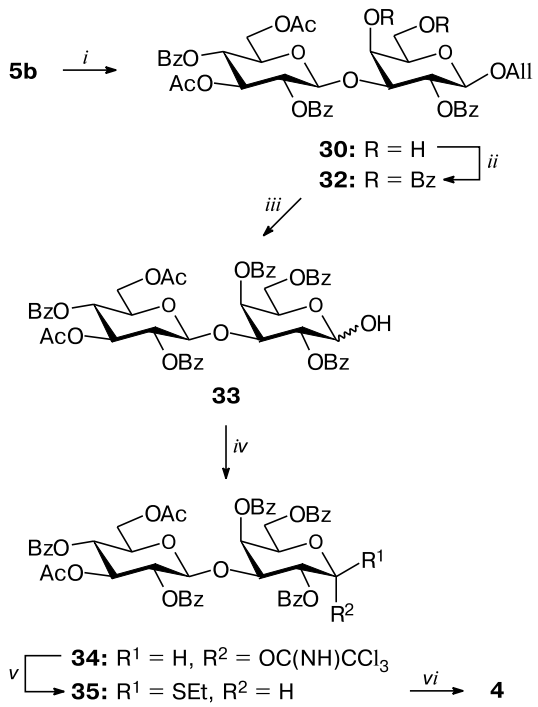
The 4,6-*O*-benzylidene group in disaccharide **5b** was replaced by acid-resistant benzoate; to this end, compound **5b** was treated with pyridinium *p*-toluenesulfonate in aqueous acetonitrile to give 4,6-diol **30** in 98% yield (Scheme 5). Subsequent benzoylation of disaccharide **30** provided 4,6-di-*O*-benzoyl derivative **32** in quantitative yield. Removal of the allyl group in glycoside **32** upon treatment with $PdCl_2$/AcONa in 95% acetic acid[24] furnished reducing disaccharide **33** (yield 67%), which was transformed into trichloroacetimidate **34** by the reaction with CCl_3CN in the presence of DBU[10] (yield 73%).

The attempt at glycosylation of acceptor **6** with donor **34** in the presence of TMSOTf was unsuccessful; only gradual destruction of the donor was observed, while acceptor **6** was recovered almost quantitatively from the reaction mixture. Therefore, we tested thioglycoside **35**, which was prepared by reaction of imidate **34** with ethanethiol in the presence of TMSOTf in 98% yield.

Glycosylation of acceptor **6** with thioglycoside **35** in the presence of NIS/TfOH and molecular sieves AW300 in CH_2Cl_2 afforded the target trisaccharide **4** in 50% yield. The presence of the β-bond between the galactopyranose and glucosamine residues in trisaccharide **4** was confirmed by the corresponding spin-spin coupling constant $J_{1,2}$ = 8.6 Hz in the ^{1}H NMR spectrum.

On treatment with HCl in methanol,[12] 3″,6″-diacetate **4** was converted into 3″,6″-diol **3** in 81% yield (Scheme 6). The structure of diol **3** was confirmed by the fact that the signals for the two acetyl groups disappeared from the ^{1}H and ^{13}C NMR spectra and by the upfield shifts of the ^{1}H NMR signals for the protons H(3) and H(6) of the glucopyranose ring (by 1.5 and ~0.6 ppm, respectively).

Scheme 5

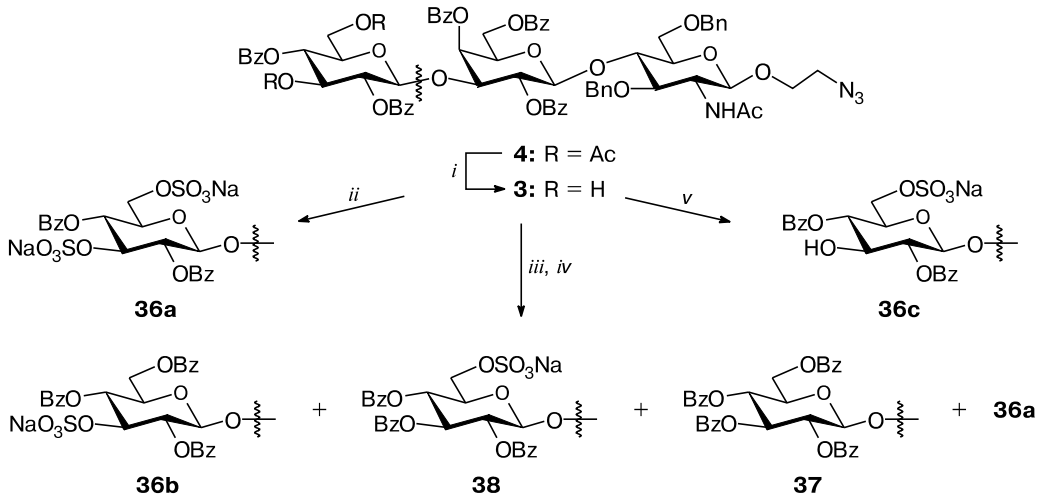


Reagents and conditions: *i*. PPTS/90% aq. CH_3CN (98%); *ii*. BzCl/pyridine (99%); *iii*. $PdCl_2$, AcONa/95% aq. AcOH (67%); *iv*. CCl_3CN,DBU/CH_2Cl_2 (73%); *v*. EtSH, TMSOTf/CH_2Cl_2, MS 4 Å (98%); *vi*. **6**, NIS, TfOH/CH_2Cl_2, MS AW300 (50%).

Diol **3** served as the starting compound in the synthesis of three target sulfated trisaccharides, *viz.*, 3″,6″-disulfate **2a**, 3″-sulfate **2b**, and 6″-sulfate **2c**. Compound **36c** was prepared in 79% yield by selective 6-sulfation of 3″,6″-diol **3** with complex $SO_3 \cdot Py$ at reduced temperature.[25] The position of the sulfate group in product **36c** followed from the downfield shifts observed in the ^1H and ^{13}C NMR spectra for H(6) (by ~0.5 ppm) and C(6) (by 7 ppm) of the glucose residue with respect to those in the starting diol **3**. Meanwhile, the chemical shifts of the H(3) signals in ^1H NMR spectrum and the C(3) signals in the ^{13}C NMR spectrum have remained almost unchanged. This indicates that the OH group at C(3) was not involved in the reaction. Complete sulfation of diol **3** with $SO_3 \cdot Py$ (see Ref. 26) resulted in disulfate **36a** in 86% yield. The structure of disulfated trisaccharide **36a** was confirmed by characteristic downfield shift of the signals for the H(3) and H(6) protons of the glucose residue (see Table 1). The ^{13}C NMR signals for C(3) and C(6) atoms of the glucopyranose residue also shifted downfield by 6 and 7 ppm, respectively.

For the synthesis of 3″-sulfated trisaccharide derivative **3**, it was necessary first to protect the more reactive primary hydroxy group (see Scheme 6). For this purpose, diol **3** was monobenzoylated with benzoyl cyanide (1.2 equiv.) in the presence of Et_3N at room temperature.[27] The reaction was moderately regioselective and resulted in a mixture containing mono- and dibenzoylated products along with the starting compound **3**. Due to similar chromatographic mobilities of these compounds, they were not subjected to product separation. Instead, the reaction mixture obtained upon benzoylation was subjected to complete sulfation with an excess of $SO_3 \cdot Py$. As a result, fully benzoylated trisaccharide **37**, disulfate **36a**, and the products of monobenzoylation–monosulfation of diol **3**, namely, compounds **36b** and **38**, were isolated.

Scheme 6



Reagents and conditions: *i*. AcCl/MeOH (81%; *ii*. $SO_3 \cdot Py$/DMF (86%); *iii*. BzCN, Et_3N/CH_3CN; *iv*. $SO_3 \cdot Py$/DMF (45% over two steps); *v*. $SO_3 \cdot Py$/pyridine (80%).

The presence of polar sulfate groups in products **36a,b** and **38** increased essentially the difference between their chromatographic mobilities both compared with 3,6-dibenzoate **37** and between each other, which facilitated the separation. Thus, product **37** was isolated in 10% yield, disulfate **36a**, in 32% yield, and 3-sulfated trisaccharide **36b**, in 45% yield (see Scheme 6).

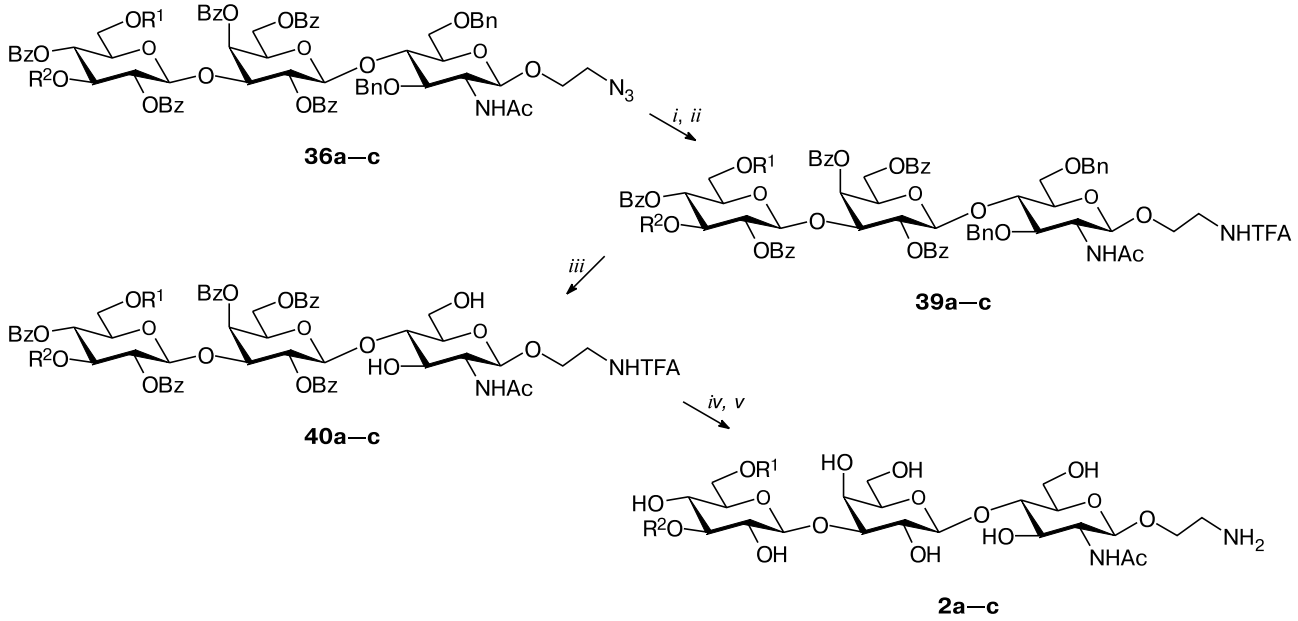
The position of the sulfate group in isomeric monosulfates—monobenzoates **36b** and **38** was established based on the combination of ^{1}H and ^{13}C NMR data. Benzoylation and sulfation induce similar downfield shifts of the corresponding proton signals of the glucose residue in the ^{1}H NMR spectra with respect to those in unsubstituted derivatives. At the same time, a comparison of the data for diol **3**, 3,6-dibenzoate **37**, and 3,6-disulfate **36a** (see Table 1) shows that benzoylation induces a greater shift than sulfation. A comparison of the shifts of the signals for H(3) and H(6a,b) for monosulfates **36b** and **38** suggests that **36b** is sulfated at position 3, and **38**, at position 6. However, a more reliable proof for the structure of monosulfate **36b** comes from ^{13}C NMR data, because the sulfate group, unlike the benzoyl group, has a pronounced α-effect (5—7 ppm) (see Table 2).

The azide group in compounds **36a—c** was converted into the amino group by catalytic hydrogenation (Scheme 7). Since the presence of free amino groups prevents effective hydrogenolysis of benzyl groups,[11] the reduction products were treated with ethyl trifluoroacetate to give trifluoroacetamides **39a—c** in 62—83% yield. The ^{13}C NMR spectra of compounds **39a—c** displayed a characteristic change in the chemical shift of the signal for the methylene group of the spacer (δ 50—52 → 40—41), which corresponds to the transformation $CH_2N_3 \rightarrow CH_2NHCOCF_3$.

Subsequent removal of the benzyl groups in derivatives **39a—c** by hydrogenolysis was accompanied by partial desulfation. The optimization of the reaction conditions for each substrate allowed us to obtain debenzylation products **40a—c** in 44—83% yields. In the final step of the preparation of the target compounds, the benzoyl and *N*-trifluoroacetyl groups were removed by treatment with an alkali, and the target sulfated trisaccharides **2a—c** were isolated by gel chromatography on Sephadex G-15. The presence and the positions of the sulfate groups in compounds **2a—c** were confirmed by characteristic downfield shifts of the corresponding proton and carbon signals in the ^{1}H and ^{13}C NMR spectra (see Tables 1 and 2).

Thus, we carried out the first synthesis of 2-aminoethyl glycosides of 6-sulfo-mimetic of the natural HNK-1 antigenic trisaccharide and the corresponding monosulfated derivatives.

Scheme 7



$R^1 = R^2 = SO_3Na$ (**36a**, **39a**, **40a**); R^1 = Bz, $R^2 = SO_3Na$ (**36b**, **39b**, **40b**); $R^1 = SO_3Na$, R^2 = H (**36c**, **39c**, **40c**)

Reagents and conditions: *i*. H_2, 10% yield $Pd(OH)_2/C$, AcOH/MeOH; *ii*. CF_3CO_2Et, Et_3N/MeOH (62—83% yield over two steps); *iii*. H_2, 10% yield PdO/C, AcOH/MeOH (44—83% yield); *iv*. 1 *M* MeONa/MeOH; *v*. 1*M* NaOH/H_2O (94—99% yield over two steps).

Experimental

Commercial Fluka, Acros, and Merck chemicals were used. The methods for solvent and reagent purification, conditions for recording the NMR spectra and determination of physicochemical parameters were described previously.[28,29] All 2D correlation NMR experiments were carried out by standard Bruker procedures. The MALDI-TOF mass spectra were recorded on a Microflex Bruker Daltonics instrument. The optical rotation of solutions of the compounds obtained was measured in chloroform (c = 1) on a PU-07 digital polarimeter (Russia) at 19—21 °C. Thin layer chromatography was carried out on plates with silica gel Kieselgel-60 (Merck), the compounds were detected by spraying with a 10% (v/v) solution of orthophosphoric acid in ethyl alcohol with subsequent heating at ~150 °C. Column chromatography was carried out on silica gel Kiesegel 60 (Merck, 230—400 mesh). Melting points were determined of a Koffler hot stage. Gel chromatography was carried out on a 38×3 cm column with Sephadex G-15 gel using water as the eluent (flow rate 1.5 mL min^{-1}). Hydrogenolysis was performed under atmospheric pressure and 20 °C.

^1H and ^{13}C NMR data for the pyranose ring signals in the synthesized compounds are summarized in Tables 1 and 2.

1,6-Anhydro-2,4-di-*O*-benzoyl-β-D-glucopyranose (10). Benzoyl chloride (7.5 mL, 65.12 mmol) was added dropwise at 4 °C to a solution of 1,6-anhydro-β-D-glucopyranose **9** (5.25 g, 32.38 mmol) in pyridine (25 mL) and the reaction mixture was kept for 2 h at the same temperature, diluted with $CHCl_3$ (100 mL), and washed with 1*M* H_2SO_4 (3×50 mL), water (3×50 mL), and saturated solution of $NaHCO_3$ (3×50 mL). The organic layer was separated and concentrated. Column chromatography (ethyl acetate—light petroleum, 12 : 5) gave dibenzoate **10**. Yield 4.89 g (40%), white crystals, $[\alpha]_D$ −34 (lit.[13]: $[\alpha]_D$ −34), R_f 0.10 (toluene—ethyl acetate, 10 : 1), m.p. 130 °C (lit.[13]: m.p. 128—129 °C). Found (%): C, 64.60; H, 4.76. $C_{20}H_{18}O_7$. Calculated (%): C, 64.86; H, 4.90. ^1H NMR, δ: 8.10—7.10 (m, 10 H, 2Ph); 3.33 (d, 1 H, 3-OH, $J_{3,OH}$ = 5.3 Hz).

1,6-Anhydro-3-*O*-acetyl-2,4-di-*O*-benzoyl-β-D-glucopyranose (11). Dibenzoyl derivative **10** (3.8 g, 10.26 mmol) was acetylated with acetic anhydride (4.9 mL, 52 mmol) in pyridine (8.5 mL) at room temperature for 24 h. The mixture was concentrated, the residue was dissolved in toluene, and the solvent was evaporated (3×5 mL). The residue was crystallized from an ethyl acetate—light petroleum mixture; subsequent column chromatography of the mother liquor (toluene—ethyl acetate, 25 : 1) gave additional amount of acetate **11**. Overall yield 4.06 g (96% yield), m.p. 125 °C, $[\alpha]_D$ −35, R_f 0.35 (toluene—ethyl acetate, 10 : 1). Found (%): C, 64.18; H, 4.60. $C_{22}H_{20}O_8$. Calculated (%): C, 64.07; H, 4.89. ^1H NMR, δ: 8.12—7.48 (m, 10 H, 2 Ph); 2.12 (s, 3 H, $CH_3C(O)O$).

1,3,6-Tri-*O*-acetyl-2,4-di-*O*-benzoyl-α-D-glucopyranose (12). Concentrated H_2SO_4 (0.25 mL, 4.69 mmol) was added dropwise at 4 °C to a solution of derivative **11** (4.0 g, 9.70 mmol) in Ac_2O (35 mL). The reaction mixture was kept for 18 h at the same temperature and poured onto ice (200 mL). The mixture was stirred for 2 h and extracted with chloroform (2×100 mL). The extract was washed with water (2×100 mL) and a cold saturated solution of $NaHCO_3$ (2×100 mL) and concentrated, the residue was dissolved in toluene, the solvent was evaporated (4×20 mL), and the residue was dried *in vacuo* to give triacetate **12**. Yield 4.97 g (98%), amorphous, $[\alpha]_D$ +57, R_f 0.33 (light petroleum—ethyl acetate, 2 : 1). Found (%): C, 60.56; H, 5.16. $C_{26}H_{26}O_{11}$. Calculated (%): C, 60.70; H, 5.09. ^1H NMR (δ: 8.10—7.12 (m, 10 H, 2Ph); 2.21, 2.08, 1.89 (three s, 9 H, 3 $CH_3C(O)O$). ^{13}C NMR, δ: 21—20 (three signals, 3 $CH_3C(O)O$).

3,6-Di-*O*-acetyl-2,4-di-*O*-benzoyl-D-glucopyranose (13). The salt $N_2H_4 \cdot HOAc$ (225 mg, 2.44 mmol) was added at 4 °C to a solution of triacetate **12** (505 mg, 0.98 mmol) in DMF (7 mL). The mixture was kept for 2 h at room temperature, diluted with EtOAc (60 mL), and washed with water (3×50 mL). The organic layer was separated, dried with $MgSO_4$, and concentrated. Column chromatography of the residue (toluene—ethyl acetate, 3 : 1) gave hemiacetal **13** as a mixture of α,β-anomers in ~1 : 1 ratio. Yield 409 mg (88%), amorphous, $[\alpha]_D$ +36, R_f 0.23; 0.29 (toluene—ethyl acetate, 4 : 1). Found (%): C, 60.82; H, 5.28. $C_{24}H_{24}O_{10}$. Calculated (%): C, 61.01; H, 5.12. ^1H NMR, δ: 8.10—7.40 (m, 10 H, 2 Ph); 3.95, 3.19 (both d, 2 H, 1-OH for β and α anomers, respectively); 2.05, 1.87 (both s, 6 H, 2 $CH_3C(O)O$).

3,6-Di-*O*-acetyl-2,4-di-*O*-benzoyl-α-D-glucopyranosyl bromide (14). A 33% solution of HBr in AcOH (3.0 mL) and acetic anhydride (0.15 mL) were added at 4 °C to a solution of triacetate **12** (334 mg, 0.65 mmol) in CH_2Cl_2 (2.5 mL). The mixture was kept for 18 h at 4 °C, diluted with $CHCl_3$ (50 mL), and washed with ice water (3×30 mL) and a saturated solution of $NaHCO_3$ (3×30 mL). The organic layer was separated, the solvent was evaporated, and the residue was dried *in vacuo* to give bromide **14**. Yield 344 mg (99%), foam, $[\alpha]_D$ +212 (c 0.5, $CHCl_3$), R_f 0.52 (toluene—ethyl acetate, 8 : 1). ^1H NMR, δ: 8.10—7.45 (m, 10 H, 2 Ph); 2.05, 1.85 (both s, 6 H, 2 CH_3COO).

3,6-Di-*O*-acetyl-2,4-di-*O*-benzoyl-α-D-glucopyranosyl trichloroacetimidate (15). Trichloroacetonitrile (7.62 mL, 75.99 mmol) was added under dry argon to a solution of hemiacetal (3.6 g, 7.63 mmol) **13** in CH_2Cl_2 (68 mL). Then 1,8-diazabicyclo[5.4.0]undec-7-ene (1.45 mL, 9.54 mmol) was added at 4 °C. After the reaction mixture has warmed to room temperature (2 h), chromatography in the toluene—ethyl acetate system (9 : 1) containing 1% (v/v) Et_3N was carried out to give trichloroacetimidate **15**. Yield 3.81 g (81%), foam, $[\alpha]_D$ +60, R_f 0.32 (toluene—ethyl acetate, 9 : 1). ^1H NMR, δ: 8.75 (s, 1 H, $OC(NH)CCl_3$); 8.12—7.12 (m, 10 H, 2 Ph); 2.12, 1.75 (both s, 6 H, 2 $CH_3C(O)O$).

2-Chloroethyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside (17). A suspension of chloride **16** (see Ref. 20) (5.0 g, 13.70 mmol) and $Hg(CN)_2$ (6.93 g, 27.43 mmol) in 2-chloroethanol (14 mL) was heated at 60 °C until the promoter completely dissolved (3 h). The reaction mixture was concentrated, the residue was dissolved in chloroform (100 mL), the precipitated mercury salts were filtered off through a celite bed, the filtrate was washed successively with a 1 *M* solution of KBr, a saturated aqueous solution of $NaHCO_3$, and water, the organic layer was separated, and the solvent was evaporated. The residue was recrystallized from isopropyl alcohol to give chloroethyl glycoside **17**. Yield 4.14 g (73% yield), m.p. 143 °C, $[\alpha]_D$ −16 (c 0.5, CH_3OH), R_f 0.28 (toluene—acetone, 7 : 4). Found (%): C, 46.76; H, 5.72; N, 3.68. $C_{16}H_{24}ClNO_9$. Calculated (%): C, 46.89; H, 5.90; N, 3.42. ^1H NMR, δ: 5.77 (d, 1 H, NHAs, $J_{2,NHAc}$ = 8.7 Hz); 4.19—3.60 (m, 4 H, OCH_2CH_2Cl); 2.11—1.92 (four s, 12 H, 4 $CH_3C(O)$). ^{13}C NMR, δ: 69.7 (OCH_2CH_2Cl); 42.9 (OCH_2CH_2Cl); 23.4 ($CH_3C(O)N$); 20.7—20.8 (three signals, 3 $CH_3C(O)O$).

2-Azidoethyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside (18). 2-Chloroethyl derivative **17** (4.1 g, 10.00 mmol) was dissolved in anhydrous DMF (65 mL), then NaN_3 (13.2 g, 0.20 mol) and 18-crown-6 (264 mg, 1.00 mmol) were added. The mixture was stirred for 36 h at 70 °C, diluted with EtOAc (200 mL), and washed with water (3×200 mL). The organic layer was concentrated and the residue was dried in a water-jet pump vacuum to give 2-azidoethyl glycoside **18**, yield 3.70 g (89%), m.p. 149 °C, $[\alpha]_D$ −30, R_f 0.29 (toluene—acetone, 7 : 4). Found (%): C, 45.87; H, 5.65; N, 13.68. $C_{16}H_{24}N_4O_9$. Calculated (%): C, 46.15; H, 5.81; N, 13.46. ^{1}H NMR, δ: 5.60 (d, 1 H, NHAs, $J_{2,NHAc}$ = 8.6 Hz); 4.08—3.64 (m, 2 H, $OCH_2CH_2N_3$); 3.51—3.22 (m, 2 H, $OCH_2CH_2N_3$); 2.08—1.92 (four s, 12 H, 4 $CH_3C(O)$). ^{13}C NMR, δ: 68.4 ($OCH_2CH_2N_3$); 50.6 ($OCH_2CH_2N_3$); 23.4 ($CH_3C(O)N$); 20.8—20.6 (three signals, 3 $CH_3C(O)O$).

2-Azidoethyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (20). A 1 *M* solution of sodium methoxide in methanol (0.9 mL) was added to a solution of 2-azidoethyl glycoside **18** (3.7 g, 8.89 mmol) in anhydrous MeOH (12 mL). After 3 h, the mixture was deionized by the cation exchange resin KU-2 (H^+), the resin was filtered off and washed with methanol, and the filtrate was concentrated to give 2.47 g of triol **19**. α,α-Dimethoxytoluene (2.56 mL, 17 mmol) was added to a solution of triol **19** (2.47 g, 8.51 mmol) and $TsOH \cdot H_2O$ (81 mg, 0.43 mmol) in anhydrous DMF (14 mL), and the mixture was stirred for 5 h at 60 °C and neutralized with Et_3N (120 μL, 0.86 mmol). The reaction mixture was diluted with CH_2Cl_2 (150 mL) and washed with water (3×100 mL), and the organic layer was concentrated. Column chromatography of the residue (chloroform—methanol, 40 : 1.2) gave 4,6-*O*-benzylidene derivative **20**. Yield 2.86 g (85% yield), m.p. 239 °C, $[\alpha]_D$ −92 (*c* 0.5, CH_3OH), R_f 0.48 (chloroform—methanol, 40 : 1.2). Found (%): C, 53.94; H, 5.91; N, 14.68. $C_{17}H_{22}N_4O_6$. Calculated (%): C, 53.96; H, 5.86; N, 14.81. ^{1}H NMR, δ: 7.48—7.26 (m, 5 H, Ph); 5.49 (s, 1 H, PhCH<O); 3.98—3.58 (m, 2 H, $OCH_2CH_2N_3$); 3.47—3.19 (m, 2 H, $OCH_2CH_2N_3$); 1.93 (s, 3 H, $CH_3C(O)N$). ^{13}C NMR, δ: 101.7 (PhCH < O); 68.3 ($OCH_2CH_2N_3$); 50.6 ($OCH_2CH_2N_3$); 22.9 ($CH_3C(O)N$).

2-Azidoethyl 2-acetamido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (21). A mixture of 4,6-*O*-benzylidene derivative **20** (2.75 g, 7.28 mmol) and a 60% mineral oil suspension of NaH (814 mg, 20.30 mmol) in anhydrous DMF (35 mL) was cooled to −20 °C, and benzyl bromide (0.96 mL, 8.03 mmol) was added with stirring. The cooling bath was removed and, after warming-up to room temperature, the reaction mixture was stirred for 1 h. Then the mixture was cooled to −40 °C and acetic acid (1.95 mL) was added. After warming-up to room temperature, the reaction mixture was diluted with CH_2Cl_2 (150 mL) and washed with water and saturated aqueous solution of $NaHCO_3$, and the organic layer was dried and concentrated. Crystallization of the residue from an ethyl acetate—light petroleum mixture gave 3-*O*-benzyl derivative **21**. Yield 2.84 g (83%), m.p. 242 °C, $[\alpha]_D$ −71 (*c* 0.5, CH_3OH), R_f 0.20 (toluene—ethyl acetate, 3 : 2). Found (%): C, 61.32; H, 5.81; N, 11.81. $C_{24}H_{28}N_4O_6$. Calculated (%): C, 61.53; H, 6.02; N, 11.96. ^{1}H NMR, δ: 7.51—7.23 (m, 10 H, 2 Ph); 5.63 (d, 1 H, NHAs, $J_{2,NHAc}$ = 7.3 Hz); 5.57 (s, 1 H, PhCH<O); 4.88—4.63 (2d, 2 H, CH_2Ph, J_{gem} = 11.7 Hz); 4.04—3.68 (m, 2 H, $OCH_2CH_2N_3$); 3.48—3.23 (m, 2 H, $OCH_2CH_2N_3$); 1.89 (s, 3 H, $CH_3C(O)N$). ^{13}C NMR, δ: 101.3 (PhCH < O); 74.7 (OCH_2Ph); 68.8 ($OCH_2CH_2N_3$); 50.7 ($OCH_2CH_2N_3$); 23.7 ($CH_3C(O)N$).

2-Azidoethyl-2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside (6). Anhydrous $AlCl_3$ (350 mg, 2.62 mmol) was added at 4 °C under dry argon to a solution of 4,6-*O*-benzylidene derivative **21** (205 mg, 0.44 mmol) and $Me_3N \cdot BH_3$ (127 mg, 1.74 mmol) in anhydrous THF (7 mL). After complete dissolution of aluminum chloride, water (15.8 μL, 0.88 mmol) was added. The mixture was stirred for 12 h at 20 °C, diluted with EtOAc (50 mL), and washed successively with 1 *M* HCl (40 mL), brine (40 mL), and water (40 mL), and the organic layer was dried and concentrated. The residue was recrystallized from isopropyl alcohol to give 3,6-di-*O*-benzyl derivative **6**. Yield 173 mg (84%), m.p. 243 °C, $[\alpha]_D$ −17 (*c* 1, CH_3OH), R_f 0.25 (toluene—acetone, 20 : 6). Found (%): C, 60.97; H, 6.23; N, 11.74. $C_{24}H_{30}N_4O_6$. Calculated (%): C, 61.26; H, 6.43; N, 11.91. ^{1}H NMR, δ: 7.45—7.20 (m, 10 H, 2 Ph); 5.73 (d, 1 H, NHAs, $J_{2,NHAc}$ = 7.6 Hz); 4.84—4.78 (both d, 2 H, CH_2Ph, J_{gem} = 11.7 Hz); 4.65—4.53 (both d, 2 H, CH_2Ph, J_{gem} = 12.1 Hz); 4.11—3.63 (m, 2 H, $OCH_2CH_2N_3$); 3.53—3.19 (m, 2 H, $OCH_2CH_2N_3$); 2.80 (d, 1 H, 4-OH, $J_{4,OH}$ < 1 Hz); 1.85 (s, 3 H, $CH_3C(O)N$). 13C NMR (δ: 74.6, 73.6 (2 OCH_2Ph); 68.1 ($OCH_2CH_2N_3$); 50.6 ($OCH_2CH_2N_3$); 23.6 ($CH_3C(O)N$).

Glycosylation of ethyl thiogalactoside 23 with glucosyl bromide 22. A mixture of ethylthio derivative **23** (29 mg, 69 μmol), glucosyl bromide **22** (70 mg, 97 μmol), and molecular sieves MS 4 Å (170 mg) in anhydrous CH_2Cl_2 (2 mL) was stirred for 2 h under dry argon and cooled to −22 °C. A solution of AgOTf (37 mg, 0.14 mmol) in anhydrous toluene (0.5 mL) was added. The reaction mixture was heated to 0 °C over a period of 2 h. Then pyridine (0.1 mL) was added and the mixture was diluted with chloroform (80 mL), filtered through a celite bed, and washed successively with a saturated aqueous solution of $Na_2S_2O_3$ (80 mL) and water (80 mL). The organic layer was concentrated, the residue was dissolved in toluene, and the solvent was evaporated. The residue was chromatographed in a toluene—ethyl acetate system (8 : 1) to give 16 mg (55%) of the starting glycosyl acceptor **23** and 10 mg (15%) of disaccharide **5a**, amorphous, R_f 0.28 (toluene—acetone, 15 : 1).

Glycosylation of ethyl thiogalactoside 23 with glucosyl bromide 14. *A* (*in the presence of molecular sieves 4 Å and AgOTf*). Under the conditions of glycosylation of ethyl thiogalactoside **23** with glucosyl bromide **22**, derivative **23** (15 mg, 36 μmol) was made to react with glucosyl bromide **14** (25 mg (47 μmol) in anhydrous CH_2Cl_2 (2 mL) in the presence of molecular sieves MS 4 Å (220 mg) and AgOTf (20.5 mg, 80 μmol) in anhydrous toluene (0.5 mL). Chromatography in a toluene—ethyl acetate system (8 : 1) gave 5 mg (33%) of the starting acceptor **23** (amorphous, R_f 0.21 (toluene—acetone, 7 : 1)), 6 mg (32%) of the ethylthio group migration product **25** (amorphous, R_f 0.50 (toluene—acetone, 7 : 1)), and 8 mg (26%) of 1,6-bound disaccharide **26** (amorphous, R_f 0.42 (toluene—acetone, 7 : 1)). ^{1}H NMR (**25**), δ: 8.09—7.42 (m, 10 H, 2 Ph); 2.76 (m, 2 H, SCH_2CH_3); 2.02, 1.81 (both s, 6 H, 2 $CH_3C(O)O$); 1.29 (t, 3 H, SCH_2CH_3). ^{13}C NMR, δ: 29.6 (SCH_2CH_3); 20.6, 20.4 (two signals, 2 $CH_3C(O)O$); 14.8 (SCH_2CH_3). ^{1}H NMR (**26**), δ: 8.15—7.10 (m, 20 H, 4 Ph); 5.91 (s, 1 H, PhCH<O); 2.45 (m, 2 H, SCH_2CH_3); 2.01, 1.79 (both s, 6 H, 2 $CH_3C(O)O$); 1.05 (t, 3 H, SCH_2CH_3). ^{13}C NMR, δ: 105.2 (PhCH<O); 24.0 (SCH_2CH_3); 20.6, 20.4 (two signals, 2 $CH_3C(O)O$); 14.7 (SCH_2CH_3).

***B* (*in the presence of molecular sieves AW300 and AgOTf*).** Glycosylation of derivative **23** (28 mg, 67 μmol) with glucosyl bromide **14** (50 mg, 93 μmol) in anhydrous CH_2Cl_2 (2 mL) in the presence of molecular sieves AW300 (200 mg) and AgOTf (35 mg, 136 μmol) in anhydrous toluene (0.5 mL) under above-described conditions gave, after chromatography, 12 mg (42%) of the starting acceptor **23**, 8 mg (23%) of ethylthio group transfer product **25**, and 15 mg (25%) of 1,6-bound disaccharide **26**.

***C* (*in the presence of molecular sieves 4 Å, AgOTf, and sym-collidine*).** A mixture of ethylthio derivative **23** (28.7 mg, 68.9 μmol), glucosyl bromide **14** (51.6 mg, 96.5 μmol), and molecular sieves MS 4 Å (170 mg) in anhydrous CH_2Cl_2 (2 mL) was stirred for 2 h under dry argon and cooled to −22 °C. sym-Collidine (15 μL, 0.11 mmol) and, 5 min later, a solution of AgOTf (37.1 mg, 0.14 mmol) in anhydrous toluene (0.5 mL) were added. The reaction mixture was heated to 0 °C over a period of 2 h and worked up as described above. Chromatography in a toluene—acetone system (15 : 1) gave orthoester **27**. Yield 27.7 mg (46% yield), amorphous. R_f 0.19 (toluene—acetone, 15 : 1). ^{1}H NMR, δ: 8.03—7.24 (m, 20 H, 4 Ph); 5.36 (s, 1 H, PhC<u>H</u><O); 2.90—2.71 (m, 2 H, SC<u>H</u>$_2$CH$_3$); 1.99, 1.91 (both s, 6 H, 2 C<u>H</u>$_3$C(O)O); 1.37 (t, 3 H, SCH$_2$C<u>H</u>$_3$). ^{13}C NMR, δ: 101.1 (Ph<u>C</u>H<O); 22.7 (S<u>C</u>H$_2$CH$_3$); 20.6, 20.6 (two signals, 2 <u>C</u>H$_3$C(O)O); 14.8 (SCH$_2$<u>C</u>H$_3$).

***D* (*in the presence of molecular sieves AW300, Hg(CN)$_2$, and HgBr$_2$*).** A mixture of ethylthio derivative **23** (31 mg, 75 μmol), glucosyl bromide **14** (59 mg, 110 μmol), and molecular sieves AW 300 (200 mg) in anhydrous CH_2Cl_2 (4 mL) was stirred for 2 h under dry argon, and $Hg(CN)_2$ (37 mg, 0.14 mmol) and $HgBr_2$ (37 mg, 0.14 mmol) were added. The reaction mixture was stirred for 12 h, diluted with chloroform (80 mL), and filtered through a celite bed. The filtrate was washed successively with a saturated aqueous solution of NaBr + $NaHCO_3$ (1 : 1) (80 mL) and water (80 mL). The organic layer was concentrated, the residue was dissolved in toluene, and the solvent was evaporated. Chromatography in a toluene—acetone system (15 : 1) gave the product of ethylthio group migration to glycosyl acceptor **25**. Yield 36 mg (93%).

Allyl (2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→3)-4,6-*O*-benzylidene-2-*O*-benzoyl-β-D-galactopyranoside (29). Anhydrous CH_2Cl_2 (2 mL) was added under dry argon to a mixture of allyl galactoside **24** (62 mg, 0.15 mmol), trichloroacetimidate **28** (74 mg, 0.15 mmol), and molecular sieves AW300 (210 mg), the mixture was stirred for 1 h at 20 °C and cooled to −20 °C, and TMSOTf (3 μL, 17 μmol) was added. The reaction mixture was stirred for 1 h at −20 °C and heated to 10 °C over a period of 1.5 h, Et_3N (50 μL) was added, and the mixture was stirred for 10 min, filtered through a celite bed, and washed with dichloromethane (80 mL). The filtrate was washed with a saturated aqueous solution of $NaHCO_3$ (80 mL) and water (80 mL). The organic layer was filtered through a cotton wool bed and concentrated. The residue was chromatographed in an ethyl acetate—light petroleum system (1 : 1) to give disaccharide **29**. Yield 40 mg (36%), amorphous, R_f 0.30 (ethyl acetate—light petroleum, 3 : 1). ^{1}H NMR, δ: 8.05—7.30 (m, 10 H, 2 Ph); 5.28—5.18 (m, 1 H, OCH$_2$C<u>H</u>=CH$_2$); 5.55 (s, 1 H, PhC<u>H</u><O); 5.15—5.01 (both dd, 2 H, OCH$_2$CH=C<u>H</u>$_2$); 4.33—4.10 (both d, 2 H, OC<u>H</u>$_2$CH=CH$_2$); 2.01, 1.98, 1.89, 1.52 (four s, 12 H, 4 C<u>H</u>$_3$C(O)O). ^{13}C NMR, δ: 100.8 (Ph<u>C</u>H<O).

Glycosylation of allyl galactoside 24 with trichloroacetimidate 15. Anhydrous CH_2Cl_2 (1 mL) was added under dry argon to a mixture of allyl galactoside **24** (18 mg, 44 μmol), trichloroacetimidate **15** (33 mg, 53 μmol), and molecular sieves AW300 (100 mg), the mixture was stirred for 1 h at 20 °C and cooled to −20 °C, and TMSOTf (1 μL, 6 μmol) was added. The reaction mixture was stirred for 2 h at −20 °C and for 12 h at −10 °C, and heated to 10 °C over a period of 1.5 h. Triethylamine (50 μL) was added, and the mixture was stirred for 10 min, filtered through a celite bed, and washed with dichloromethane (80 mL). The filtrate was washed with a saturated aqueous solution of $NaHCO_3$ (80 mL) and water (80 mL). The organic layer was filtered through a cotton wool layer and concentrated to a volume of ~5 mL, 75% aqueous AcOH (4 mL) was added, and the mixture was stirred for 4 h at 80 °C. The organic layer was concentrated, the residue was dissolved in toluene, and the solvent was evaporated. The residue was chromatographed in an ethyl acetate—light petroleum system (7 : 3) to give 9.5 mg of disaccharide 4,6-diol **30** (28%, amorphous, R_f 0.30 (ethyl acetate—light petroleum, 7 : 3)) and 5.7 mg of 3,4,6-triol **31** (40%, amorphous, R_f 0.08 (ethyl acetate—light petroleum, 7 : 3)).

Glycosylation of allyl galactoside 24 with trichloroacetimidate 28. Anhydrous toluene (5 mL) was added under dry argon to a mixture of allyl galactoside **24** (40 mg, 97 μmol), trichloroacetimidate **28** (84 mg, 136 μmol), and molecular sieves AW300 (500 mg), the mixture was stirred for 1 h at 20 °C and cooled to 0 °C, and $BF_3 \cdot Et_2O$ (10 μL, 80 μmol) was added. The reaction mixture was stirred for 2 h at 0 °C and for 48 h at −10 °C. The temperature was raised to 10 °C over a period of 2.5 h, and the mixture was diluted with CH_2Cl_2 (5 mL), stirred for 10 min, filtered through a celite bed, and washed with a dichloromethane—ethyl acetate mixture (3 : 1) (2×50 mL). The filtrate was concentrated without heating, and the residue was diluted with chloroform (50 mL) and washed with a saturated aqueous solution of $NaHCO_3$ (2×50 mL) and water (50 mL). The organic layer was concentrated and the residue was dried *in vacuo*. The residue was dissolved in 90% aq. CH_3CN (3 mL), and Py·TsOH (20 mg, 80 μmol) was added. The mixture was stirred for 4 h at 80 °C, concentrated without heating, diluted with chloroform (50 mL), and washed with a saturated aqueous solution of $NaHCO_3$ (2×50 mL) and water (50 mL). The organic layer was concentrated. The residue was chromatographed in a toluene—ethyl acetate system (10 : 3) to give 27.2 mg of disaccharide 4,6-diol **30** (36%).

Allyl (3,6-di-*O*-acetyl-2,4-di-*O*-benzoyl-β-D-glucopyranosyl)-(1→3)-4,6-*O*-benzylidene-2-*O*-benzoyl-β-D-galactopyranoside (5b). Molecular sieves AW300 (800 mg) were added under dry argon to a solution of allyl galactoside **24** (116 mg, 0.28 mmol) and trichloroacetimidate **15** (174 mg, 0.28 mmol) in anhydrous toluene (8 mL), the mixture was stirred for 1 h at 20 °C and cooled to 0 °C, and $BF_3 \cdot Et_2O$ (21.3 μL, 0.17 mmol) was added. The reaction mixture was stirred for 48 h at 4 °C. The temperature was raised to 10 °C over a period of 2.5 h, and the mixture was diluted with dichloromethane (5 mL), stirred for 10 min, filtered through a celite bed, and washed with a dichloromethane—ethyl acetate mixture (3 : 1) (2×80 mL). The filtrate was concentrated without heating, diluted with chloroform (100 mL), and washed with a saturated aqueous solution of $NaHCO_3$ (2×80 mL) and water (80 mL). The organic layer was concentrated. Crystallization of the residue from an ethyl acetate—light petroleum mixture gave disaccharide **5b**. Yield 121 mg (48%), m.p. 251 °C, $[\alpha]_D$ +10, R_f 0.38 (toluene—acetone, 20 : 6). Found (%): C, 65.12; H, 5.48. $C_{47}H_{46}O_{16}$. Calcu-

lated (%): C, 65.12; H, 5.35. ^{1}H NMR, δ: 7.95—7.13 (m, 20 H, 4 Ph); 5.71—5.62 (m, 1 H, $OCH_2C\underline{H}=CH_2$); 5.51 (s, 1 H, $PhC\underline{H}<O$); 5.14—4.97 (two dd, 2 H, $OCH_2CH=C\underline{H}_2$); 4.28—4.13 (both d, 2 H, $OC\underline{H}_2CH=CH_2$); 1.92, 1.70 (both s, 6 H, 2 $C\underline{H}_3C(O)O$). ^{13}C NMR, δ: 129.7 ($OCH_2\underline{C}H=CH_2$); 117.0 ($OCH_2CH=\underline{C}H_2$); 100.8 ($Ph\underline{C}H<O$); 68.9 ($O\underline{C}H_2CH=CH_2$); 20.6, 20.3 (two signals, 2 $\underline{C}H_3C(O)O$).

Allyl (3,6-di-*O*-acetyl-2,4-di-*O*-benzoyl-β-D-glucopyranosyl)-(1→3)-2-*O*-benzoyl-β-D-galactopyranoside (30). Salt Py·TsOH (946 mg, 3.77 mmol) was added to a solution of 4,6-*O*-benzylidene derivative **5b** (1.75 g, 1.98 mmol) in 90% aq. acetonitrile (170 mL) and the reaction mixture was stirred at 80 °C for 36 h and concentrated. The diol derivative was extracted from the aqueous phase with dichloromethane (3×80 mL). The extract was concentrated and the residue was dried in an oil pump vacuum. The yield of disaccharide **30** was 1.51 g (98%), syrup, $[\alpha]_D$ +3, R_f 0.27 (toluene—acetone, 2 : 1). Found (%): C, 61.53; H, 5.42. $C_{40}H_{42}O_{16}$. Calculated (%): C, 61.69; H, 5.44. ^{1}H NMR, δ: 7.95—7.13 (m, 20 H, 4 Ph); 5.71—5.62 (m, 1 H, $OCH_2C\underline{H}=CH_2$); 5.51 (s, 1 H, $PhC\underline{H}<O$); 5.14—4.97 (two dd, 2 H, $OCH_2CH=C\underline{H}_2$); 4.28—4.13 (both d, 2 H, $OC\underline{H}_2CH=CH_2$); 1.92, 1.70 (both s, 6 H, 2 $C\underline{H}_3C(O)O$). ^{13}C NMR, δ: 129.7 ($OCH_2\underline{C}H=CH_2$); 117.0 ($OCH_2CH=\underline{C}H_2$); 100.8 ($Ph\underline{C}H<O$); 68.9 ($O\underline{C}H_2CH=CH_2$); 20.6, 20.3 (two signals, 2$\underline{C}H_3C(O)O$).

Allyl (3,6-di-*O*-acetyl-2,4-di-*O*-benzoyl-β-D-glucopyranosyl)-(1→3)-2,4,6-tri-*O*-benzoyl-β-D-galactopyranoside (32). Benzoyl chloride (1.38 mL, 11.90 mmol) was added at −10 °C to a solution of diol **30** (1.54 g, 1.98 mmol) in pyridine (15 mL), the mixture was stirred for 3 h at room temperature, diluted with dichloromethane (100 mL), washed successively with 1 *M* HCl (80 mL), water (80 mL), and a saturated aqueous solution of $NaHCO_3$ (80 mL), and the solvent was evaporated. Column chromatography (gradient elution with light petroleum—ethyl acetate (2 : 1) → ethyl acetate) gave benzoylated product **32**. Yield 1.95 g (99%), amorphous, $[\alpha]_D$ +16, R_f 0.33 (light petroleum—ethyl acetate, 1 : 0.8). Found (%): C, 65.74; H, 5.08. $C_{54}H_{50}O_{18}$. Calculated (%): C, 65.71; H, 5.11. ^{1}H NMR, δ: 8.13—7.13 (m, 25 H, 5 Ph); 5.70—5.61 (m, 1 H, $OCH_2C\underline{H}=CH_2$); 5.09—4.96 (both dd, 2 H, $OCH_2CH=C\underline{H}_2$); 4.27—4.03 (both d, 2 H, $OC\underline{H}_2CH=CH_2$); 1.91, 1.63 (both s, 6 H, 2 $C\underline{H}_3C(O)O$). ^{13}C NMR, δ: 132.7 ($OCH_2\underline{C}H=CH_2$); 117.6 ($OCH_2CH=\underline{C}H_2$); 69.7 ($O\underline{C}H_2CH=CH_2$); 20.5, 20.2 (two signals, 2 $\underline{C}H_3C(O)O$).

(3,6-Di-*O*-acetyl-2,4-di-*O*-benzoyl-β-D-glucopyranosyl)-(1→3)-2,4,6-tri-*O*-benzoyl-β-D-galactopyranose (33). A suspension of allyl glycoside **32** (2.06 g, 2.09 mmol), palladium chloride (422 mg, 2.38 mmol), and sodium acetate (414 mg, 5.05 mmol) in 95% aq. acetic acid (40 mL) was heated for 3 h at 70 °C. The reaction mixture was diluted with chloroform (70 mL) and filtered through celite, and the filtrate was concentrated. The residue was dissolved in toluene and the solvent was evaporated. Column chromatography (light petroleum—ethyl acetate, 2 : 1) gave hemiacetal **33**. Yield 1.33 g (67%), amorphous, $[\alpha]_D$ +33, R_f 0.30 (light petroleum—ethyl acetate, 2 : 1.5). Found (%): C, 64.42; H, 5.08. $C_{51}H_{46}O_{18}$. Calculated (%): C, 64.69; H, 4.90. ^{1}H NMR, δ: 8.10—6.99 (m, 25 H, 5 Ph); 1.92, 1.62 (both s, 6 H, 2 $C\underline{H}_3C(O)O$). 13C NMR (δ: 20.7, 20.3 (two signals, 2 $\underline{C}H_3C(O)O$).

(3,6-Di-*O*-acetyl-2,4-di-*O*-benzoyl-β-D-glucopyranosyl)-(1→3)-2,4,6-tri-*O*-benzoyl-D-galactopyranosyl trichloroacetimidate (34). Trichloroacetonitrile (1.16 mL, 11.62 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (0.22 mL, 1.45 mmol) were added at 4 °C under dry argon to a solution of hemiacetal **33** (1.10 g, 1.16 mmol) in anhydrous dichloromethane (6 mL). Over a period of 2 h, the temperature of the reaction mixture was raised to 20 °C. Chromatography in the ethyl acetate—light petroleum system (2 : 1.5) containing 1% (v/v) of triethylamine gave trichloroacetimidate **34**. Yield 931 mg (73%), foam, $[\alpha]_D$ +50, R_f 0.42 (ethyl acetate—light petroleum, 1 : 1). ^{1}H NMR, δ: 8.49 (s, 1 H, $OC(N\underline{H})CCl_3$); 8.11—7.06 (m, 25 H, 5 Ph); 1.99, 1.68 (both s, 6 H, 2 $C\underline{H}_3C(O)O$). ^{13}C NMR, δ: 20.6, 20.2 (two signals, 2 $\underline{C}H_3C(O)O$).

Ethyl (3,6-di-*O*-acetyl-2,4-di-*O*-benzoyl-β-D-glucopyranosyl)-(1→3)-2,4,6-tri-*O*-benzoyl-1-thio-β-D-galactopyranoside (35). Molecular sieves 4 Å (500 mg) and ethanethiol (105 μL, 1.42 mmol) were added under dry argon to a solution of trichloroacetimidate **34** (913 mg, 0.84 mmol) in anhydrous CH_2Cl_2 (5 mL). The mixture was stirred for 40 min and cooled to 4 °C, and TMSOTf (53 μL, 0.29 mmol) was added. The reaction mixture was stirred for 2 h, filtered through a celite bed, and washed with CH_2Cl_2 (80 mL). The filtrate was washed with a saturated aqueous solution of $NaHCO_3$ and water and the solvent was evaporated. Column chromatography in a light petroleum—ethyl acetate system (2 : 1.3) gave thioglycoside **35**. Yield 815 mg (98%), m.p. 84 °C, $[\alpha]_D$ +12, R_f 0.33 (light petroleum—ethyl acetate, 2 : 1.5). Found (%): C, 64.00; H, 5.30. $C_{53}H_{50}O_{17}S$. Calculated (%): C, 64.23; H, 5.09. ^{1}H NMR, δ: 8.12—7.13 (m, 25 H, 5 Ph); 2.76—2.61 (m, 2 H, $SC\underline{H}_2CH_3$); 1.91, 1.64 (both s, 6 H, 2 $C\underline{H}_3C(O)O$); 1.18 (t, 3 H, $SCH_2C\underline{H}_3$). ^{13}C NMR, δ: 24.1 ($S\underline{C}H_2CH_3$); 20.5, 20.2 (two signals, 2 $\underline{C}H_3C(O)O$); 14.8 ($SCH_2\underline{C}H_3$).

2-Azidoethyl (3,6-di-*O*-acetyl-2,4-di-*O*-benzoyl-β-D-glucopyranosyl)-(1→3)-(2,4,6-tri-*O*-benzoyl-β-D-galactopyranosyl)-(1→4)-2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside (4). A mixture of thioglycoside **35** (50 mg, 0.05 mmol), acceptor **6** (15 mg, 0.03 mmol), and molecular sieves AW300 (300 mg) in anhydrous CH_2Cl_2 (3 mL) was stirred under dry argon for 40 min and cooled to −25 °C. *N*-Iodosuccinimide (16 mg, 0.06 mmol) and, 5 min later, trifluoromethanesulfonic acid (7 μL, 0.08 mmol) were added. The reaction mixture was stirred for 2.5 h with gradual temperature rise to −10 °C, and then pyridine (0.8 mL) was added. The mixture was diluted with dichloromethane (80 mL) and filtered through a celite bed, the filtrate was washed successively with a 1 *M* solution of $Na_2S_2O_3$ (80 mL) and a saturated aqueous solution of $NaHCO_3$ (80 mL). The organic layer was concentrated and the residue was chromatographed in a light petroleum—ethyl acetate system (1 : 2) to give trisaccharide **4**. Yield 22 mg (50%), m.p. 77 °C, $[\alpha]_D$ −14, R_f 0.23 (light petroleum—ethyl acetate, 1 : 2). Found (%): C, 64.32; H, 5.16; N, 4.22. $C_{75}H_{74}N_4O_{23}$. Calculated (%): C, 64.37; H, 5.33; N, 4.00.

2-Azidoethyl (2,4-di-*O*-benzoyl-β-D-glucopyranosyl)-(1→3)-(2,4,6-tri-*O*-benzoyl-β-D-galactopyranosyl)-(1→4)-2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside (3). A solution of HCl in MeOH (5.2 mL, prepared by adding 0.2 mL of acetyl chloride to 5 mL of anhydrous MeOH at 0—5 °C) was added to trisaccharide **4** (747 mg, 0.53 mmol). The mixture was stirred for 16 h at 4 °C, diluted with CH_2Cl_2 (100 mL), and washed with a saturated aqueous solution of NaCl + $NaHCO_3$ (1 : 1) (100 mL). The organic layer was concentrated. Chromatography of the residue in a chloroform—methanol system

(20 : 1) gave diol **3**. Yield 571 mg (81%), amorphous, $[\alpha]_D$ −15, R_f 0.19 (ethyl acetate—light petroleum, 2 : 1). Found (%): C, 64.96; H, 5.62; N, 4.31. $C_{71}H_{70}N_4O_{21}$. Calculated (%): C, 64.83; H, 5.36; N, 4.26.

Disodium salt of 2-azidoethyl (2,4-di-*O*-benzoyl-3,6-di-*O*-sulfo-β-D-glucopyranosyl)-(1→3)-(2,4,6-tri-*O*-benzoyl-β-D-galactopyranosyl)-(1→4)-2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside (36a). The complex $SO_3 \cdot Py$ (60 mg, 0.38 mmol) was added to a solution of 3,6-diol **3** (50 mg, 38 μmol) in DMF (1 mL), the reaction mixture was stirred for 1.5 h at 20 °C, then $NaHCO_3$ (54 mg, 0.64 mmol) was added, and the mixture was stirred for 1 h and filtered. The precipitate was washed on the filter with methanol (10 mL) and the filtrate was concentrated. The residue was dissolved in aq. MeOH (10 : 1) (5 mL) and the cation exchange resin Amberlite IR-120 (Na^+) (2 mL) was added. The mixture was stirred for 20 min and filtered, the resin was washed with methanol (10 mL), and the filtrate was concentrated. Chromatography of the residue in a chloroform—methanol system (10 : 1) gave disulfate **36a**. Yield 49 mg (86%), amorphous, $[\alpha]_D$ +5 (*c* 1, CH_3OH), R_f 0.28 (chloroform—methanol, 20 : 1.8). MALDI-TOF-MS, calculated for $[C_{71}H_{68}N_4Na_2O_{27}S_2 + Na]^+$: 1542.4. Found: 1542.2. Calculated for $[C_{71}H_{68}N_4Na_2O_{27}S_2 + K]^+$: 1558.4. Found: 1558.2.

Sodium salt of 2-azidoethyl (2,4,6-tri-*O*-benzoyl-3-*O*-sulfo-β-D-glucopyranosyl)-(1→3)-(2,4,6-tri-*O*-benzoyl-β-D-galactopyranosyl)-(1→4)-2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside (36b). Benzoyl cyanide (17 mg, 0.13 mmol) and triethylamine (15 μL, 0.11 mmol) were added to a solution of 3,6-diol **3** (141 mg, 0.11 mmol) in anhydrous CH_3CN (4 mL). The mixture was stirred for 12 h at 20 °C, methanol (7 mL) was added, and 15 min later, the solvent was evaporated to dryness. The residue was dissolved in DMF (3 mL) and the complex $SO_3 \cdot Py$ (119 mg, 0.75 mmol) was added. The reaction mixture was stirred for 3 h at 20 °C, $NaHCO_3$ (128 mg, 1.78 mmol) was added, and the mixture was stirred for 1 h and filtered. The precipitate was washed with methanol (10 mL) and the filtrate was concentrated. The residue was dissolved in a MeOH—H_2O mixture (10 : 1) (5.5 mL) and the cation exchange resin Amberlite IR-120 (Na^+) (2 mL) was added. The mixture was stirred for 20 min and filtered, the resin was washed with methanol (10 mL), and the filtrate was concentrated. Chromatography of the residue in a chloroform—methanol system (20 : 1) gave 73 mg (45%) of 3-sulfated product **36b**; the other isolated products included 16 mg (10%) of fully benzoylated product **37**, 13 mg of a mixture of 3-sulfate **36b** and 6-sulfate **38**, and 54 mg (32%) of disulfated product **36a**. Data for 3-sulfate **36b**: amorphous, $[\alpha]_D$ +4 (*c* 1, CH_3OH), R_f 0.49 (chloroform—methanol, 5 : 1). MALDI-TOF-MS, calculated for $[C_{78}H_{73}N_4NaO_{25}S + Na]^+$: 1544.5. Found: 1544.4. Calculated for $[C_{78}H_{73}N_4NaO_{25}S + K]^+$: 1560.5. Found: 1560.4.

Sodium salt of 2-azidoethyl (2,4-di-*O*-benzoyl-6-*O*-sulfo-β-D-glucopyranosyl)-(1→3)-(2,4,6-tri-*O*-benzoyl-β-D-galactopyranosyl)-(1→4)-2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside (36c). The complex $SO_3 \cdot Py$ (7.6 mg, 48 μmol) was added with ice cooling to a solution of 3,6-diol **3** (21 mg, 16 μmol) in pyridine (1.5 mL). The reaction mixture was stirred for 12 h at 4 °C, $NaHCO_3$ (6.8 mg, 94 μmol) was added, and the mixture was stirred for 1 h and filtered. The precipitate was washed with methanol (10 mL) and the filtrate was evaporated. The residue was dissolved in a MeOH—H_2O mixture (10 : 1) (5.5 mL) and the cation exchange resin Amberlite IR-120 (Na^+) (2 mL) was added. The mixture was stirred for 20 min and filtered, the resin was washed with methanol (10 mL), and the filtrate was concentrated. Chromatography of the residue in a chloroform—methanol system (10 : 1) gave 6-sulfated product **36c**. Yield 18 mg (79%), amorphous, $[\alpha]_D$ −14 (*c* 1, CH_3OH), R_f 0.19 (chloroform—methanol, 10 : 1). MALDI-TOF-MS, calculated for $[C_{71}H_{69}N_4NaO_{24}S + Na]^+$: 1440.4. Found: 1440.1. Calculated for $[C_{71}H_{69}N_4NaO_{24}S + K]^+$: 1456.4. Found: 1456.1.

Disodium salt of 2-trifluoroacetamidoethyl (2,4-di-*O*-benzoyl-3,6-di-*O*-sulfo-β-D-glucopyranosyl)-(1→3)-(2,4,6-tri-*O*-benzoyl-β-D-galactopyranosyl)-(1→4)-2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside (39a). 3,6-Disulfate **36a** (54 mg, 35 μmol) in anhydrous MeOH (2 mL) was hydrogenated for 1 h in a hydrogen atmosphere in the presence of acetic acid (10 μL) and 10% $Pd(OH)_2/C$ (30 mg). The reaction mixture was filtered through a celite bed, which was then washed with methanol (30 mL) and the combined filtrates were concentrated. The residue was dissolved in anhydrous methanol (3.8 mL), and ethyl trifluoroacetate (25 μL, 0.21 mmol) and triethylamine (20 μL, 0.14 mmol) were added. After 3 h, a MeOH—H_2O mixture (3 : 1) (2 mL) and cation exchange resin Amberlite IR-120 (Na^+) (2 mL) were added. The reaction mixture was stirred for 20 min and filtered, the resin was washed with methanol (10 mL), and the filtrate was concentrated. Chromatography of the residue in a chloroform—methanol system (5 : 1) gave *N*-trifluoroacetylated product **39a**. Yield 47 mg (83%), amorphous, $[\alpha]_D$ −9 (*c* 1, CH_3OH), R_f 0.32 (chloroform—methanol, 10 : 3). MALDI-TOF-MS, calculated for $[C_{73}H_{69}F_3N_2Na_2O_{28}S_2 + Na]^+$: 1612.4. Found: 1611.7. Calculated for $[C_{73}H_{69}F_3N_2Na_2O_{28}S_2 + K]^+$: 1628.4. Found: 1627.7.

Sodium salt of 2-trifluoroacetamidoethyl (2,4,6-tri-*O*-benzoyl-3-*O*-sulfo-β-D-glucopyranosyl)-(1→3)-(2,4,6-tri-*O*-benzoyl-β-D-galactopyranosyl)-(1→4)-2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside (39b). 3-Sulfate **36b** (42 mg, 28 μmol) was hydrogenated in a similar way. The product was converted into *N*-trifluoroacetate **39b**, which was isolated in a chloroform—methanol system (10 : 1), yield 36 mg (81%), amorphous, $[\alpha]_D$ +4 (*c* 1, CH_3OH), R_f 0.40 (chloroform—methanol, 5 : 1). MALDI-TOF-MS, calculated for $[C_{80}H_{74}F_3N_2NaO_{26}S + Na]^+$: 1614.5. Found: 1614.4. Calculated for $[C_{80}H_{74}F_3N_2NaO_{26}S + K]^+$: 1630.5. Found: 1630.4.

Sodium salt of 2-trifluoroacetamidoethyl (2,4-di-*O*-benzoyl-6-*O*-sulfo-β-D-glucopyranosyl)-(1→3)-(2,4,6-tri-*O*-benzoyl-β-D-galactopyranosyl)-(1→4)-2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside (39c). A similar procedure for 6-sulfate **36c** (24 mg, 17 μmol) gave *N*-trifluoroacetate **39s,** yield 16 mg (63%), amorphous, $[\alpha]_D$ −12 (*c* 0.5, CH_3OH), R_f 0.21 (chloroform—methanol, 5 : 3). MALDI-TOF-MS, calculated for $[C_{59}H_{58}F_3N_2NaO_{25}S + Na]^+$: 1510.4. Found: 1510.1. Calculated for $[C_{59}H_{58}F_3N_2NaO_{25}S + K]^+$: 1526.4. Found: 1526.1.

Disodium salt of 2-trifluoroacetamidoethyl (2,4-di-*O*-benzoyl-3,6-di-*O*-sulfo-β-D-glucopyranosyl)-(1→3)-(2,4,6-tri-*O*-benzoyl-β-D-galactopyranosyl)-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranoside (40a). 3,6-Disulfate **39a** (21 mg, 13 μmol) was hydrogenated in anhydrous MeOH (2 mL) for 40 h in the presence of acetic acid (10 μL) and 10% PdO/C (15 mg). The reaction mixture was filtered through a celite bed, which was then washed with methanol (30 mL). The filtrate was concentrated, chromatography of the residue in a chloroform—methanol system (5 : 1) gave debenzylated product **40a**. Yield 15 mg (83%), amorphous, $[\alpha]_D$ +5 (*c* 1, CH_3OH), R_f 0.32

(chloroform—methanol, 10 : 3). MALDI-TOF-MS, calculated for $[C_{59}H_{57}F_3N_2Na_2O_{28}S_2 + Na]^+$: 1432.2. Found: 1432.2. Calculated for $[C_{59}H_{57}F_3N_2Na_2O_{28}S_2 + K]^+$: 1448.2. Found: 1448.1.

Sodium salt of 2-trifluoroacetamidoethyl (2,4,6-tri-*O*-benzoyl-3-*O*-sulfo-β-D-glucopyranosyl)-(1→3)-(2,4,6-tri-*O*-benzoyl-β-D-galactopyranosyl)-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranoside (40b). 3-Sulfate **39b** (13 mg, 8 μmol) was hydrogenated in anhydrous methanol (1 mL) for 5 h in the presence of acetic acid (5 μL) and 10% PdO/C (26 mg). The reaction mixture was filtered through a celite bed, which was then washed with methanol (30 mL). The filtrate was concentrated, chromatography of the residue in a chloroform—methanol system (10 : 1) gave debenzylated product **40b**. Yield 5 mg (44%), amorphous, $[\alpha]_D$ +18 (*c* 0.5, CH_3OH), R_f 0.37 (chloroform—methanol, 5 : 1). MALDI-TOF-MS, calculated for $[C_{66}H_{62}F_3N_2NaO_{26}S + Na]^+$: 1434.3. Found: 1434.0. Calculated for $[C_{66}H_{62}F_3N_2NaO_{26}S + K]^+$: 1450.3. Found: 1450.0.

Sodium salt of 2-trifluoroacetamidoethyl (2,4-di-*O*-benzoyl-6-*O*-sulfo-β-D-glucopyranosyl)-(1→3)-(2,4,6-tri-*O*-benzoyl-β-D-galactopyranosyl)-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranoside (40c). 6-Sulfate **39c** (16 mg, 11 μmol) was hydrogenated in anhydrous methanol (2 mL) for 12 h in the presence of acetic acid (10 μL) and 10% PdO/C (16 mg). The reaction mixture was filtered through a celite bed, which was then washed with methanol (30 mL).The filtrate was concentrated, chromatography of the residue in a chloroform—methanol system (10 : 1) gave debenzylated product **40c**. Yield 8 mg (56%), amorphous, $[\alpha]_D$ +4 (*c* 0.5, CH_3OH), R_f 0.40 (chloroform—methanol, 10 : 1).

Disodium salt of 2-aminoethyl (3,6-di-*O*-sulfo-β-D-glucopyranosyl)-(1→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranoside (2a). A 1 *M* solution of sodium methoxide in methanol (0.16 mL) was added to a solution of trisaccharide **40a** (22 mg, 15 μmol) in methanol (1.5 mL) and the mixture was stirred for 18 h. A 1 *M* aqueous solution of NaOH (100 μL) was added and the mixture was stirred for 24 h, neutralized by acetic acid (15 μL, 0.25 mmol), and concentrated. Gel chromatography on a column with Sephadex G-15 in water followed by freeze drying gave 12 mg (96%) of 3,6-disulfated trisaccharide **2a**, amorphous, $[\alpha]_D$ −5 (*c* 0.5, water), R_f 0.43 (acetonitrile—water—methanol—butanol—propanol—0.1 *N* HCl, 1 : 1 : 1 : 1 : 2 : 1). MALDI-TOF-MS, calculated for $[C_{22}H_{38}N_2Na_2O_{22}S_2 + Na]^+$: 815.6. Found: 815.1. Calculated for $[C_{22}H_{38}N_2Na_2O_{22}S_2 + K]^+$: 831.6. Found: 831.1.

Sodium salt of 2-aminoethyl (3-*O*-sulfo-β-D-glucopyranosyl)-(1→3)-β-D-galactopyranosyl)-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranoside (2b). Trisaccharide **40b** (19 mg, 13 μmol) was N,O-deacetylated as described for derivative **40a**. Gel chromatography on a column with Sephadex G-15 in water followed by freeze drying gave 9 mg (99%) of 3-sulfated trisaccharide **2b**, amorphous, $[\alpha]_D$ −5 (*c* 0.5, water), R_f 0.43 (acetonitrile—water—methanol—butanol—propanol—0.1 *M* HCl, 1 : 1 : 1 : 1 : 2 : 1). MALDI-TOF-MS, calculated for $[C_{22}H_{39}N_2NaO_{19}S + Na]^+$: 713.6. Found: 714.3. Calculated for $[C_{22}H_{39}N_2NaO_{19}S + K]^+$: 729.6. Found: 730.2.

Sodium salt of 2-aminoethyl (6-*O*-sulfo-β-D-glucopyranosyl)-(1→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranoside (2c). Trisaccharide **40c** (32 mg, 25 μmol) was N,O-deacetylated as described for derivative **40a**. Gel chromatography on a column with Sephadex G-15 in water followed by freeze drying gave 6-sulfated trisaccharide **2c**. Yield 16 mg (94%), amorphous, $[\alpha]_D$ −10 (*c* 1, water), R_f 0.52 (acetonitrile—water—methanol—butanol—propanol—0.1 *N* HCl, 1 : 1 : 1 : 1 : 2 : 1). MALDI-TOF-MS, calculated for $[C_{22}H_{39}N_2NaO_{19}S + Na]^+$: 713.6. Found: 713.3. Calculated for $[C_{22}H_{39}N_2NaO_{19}S + K]^+$: 729.6. Found: 729.3.

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