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Synthesis of Aminoethyl Glycosides of the Carbohydrate Chains of Glycolipids Gb3, Gb4, and Gb5

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Abstract—4-*O*-Glycosylation of 2-azidoethyl 2,3,6-tri-*O*-benzoyl-4-*O*-(2,3,6-tri-*O*-benzoyl-β-*D*-galactopyranosyl)-β-*D*-glucopyranoside with ethyl 2,3,4,6-tetra-*O*-benzyl- and ethyl 3-*O*-acetyl-2,4,6-tri-*O*-benzyl-1-thio-α-*D*-galactopyranoside in the presence of methyl trifluoromethanesulfonate led to trisaccharide 2-azidoethyl (2,3,4,6-tetra-*O*-benzyl-α-*D*-galactopyranosyl)-(1→4)-(2,3,6-tri-*O*-benzoyl-β-*D*-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzoyl-β-*D*-glucopyranoside and its 3''-*O*-acetylated analogue, 2-azidoethyl (3-*O*-acetyl-2,4,6-tri-*O*-benzyl-α-*D*-galactopyranosyl)-(1→4)-(2,3,6-tri-*O*-benzoyl-β-*D*-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzoyl-β-*D*-glucopyranoside in yields of 85 and 83%, respectively. Deacetylation of the latter compound and subsequent glycosylation with 4-trichloroacetamidophenyl 3,4,6-tri-*O*-acetyl-2-deoxy-1-thio-2-trichloroacetamido-β-*D*-galactopyranoside and 4-trichloroacetamidophenyl 4,6-di-*O*-acetyl-2-deoxy-3-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl)-1-thio-2-trichloroacetamido-β-*D*-galactopyranoside in dichloromethane in the presence of *N*-iodosuccinimide and trifluoromethanesulfonic acid resulted in the corresponding selectively protected derivatives of the tetrasaccharide GalNAc(β1→3)Gal(α1→4)Gal(β1→4)Glcβ-$OCH_2CH_2N_3$ and the pentasaccharide Gal(β1→3)GalNAc(β1→3)Gal(α1→4)Gal(β1→4)Glcβ-$OCH_2CH_2N_3$ in 88 and 73% yields, respectively. Removal of *O*-protecting groups, substitution of acetyl group for the *N*-trichloroacetyl group, and reduction of the aglycone azide group resulted in the target 2-aminoethyl *globo*-tri-, -tetra-, and -pentasaccharide, respectively.

Key words: *aminoethyl glycosides, glycosylation; glycolipids Gb3, Gb4, and Gb5; globosides*

INTRODUCTION

Glycolipids of the *globo* series (Gb) refer to membrane-associated antigens and are characterized by the presence of galabiose fragment α-*D*-Gal-(1→4)-β-*D*-Gal in their carbohydrate backbones, which is responsible for their specific role in the processes of biological recognition.[2] For example, *globo*-oligosaccharide chains serve as oncomarkers [1, 2], are parts of P-group-specific blood antigens [3], and are recognized by various bacterial adhesins [4].

Natural glycolipids of the *globo*-series [5–8] and also their other glycoside derivatives [6–12] have been synthesized in several laboratories. A spacered derivative, 3-aminopropyl glycoside of galactosyl globoside (Gb5-chain) [13], has also been synthesized. However, the suggested synthetic scheme had a low stereoselectivity and, therefore, resulted in unsatisfactory yield of the target product.

We herein report the synthesis of aminoethyl glycosides of *globo*-tri-, -tetra-, and -pentasaccharides from selectively protected derivatives of lactose, *D*-galactose, *D*-galactosamine, and disaccharide β-*D*-Gal-(1→3)-*D*-GalNAc. The target oligosaccharides have been obtained in the spacered form for their subsequent conjugation with carriers and labels.

RESULTS AND DISCUSSION

The target oligosaccharide structures (**I**), (**II**), and (**III**) (Scheme 1) contain common lactose and α-galactose fragments, to which the β-*D*-GalNAc residue [Gb4-chain, structure (**II**)] or a β-*D*-Gal-(1→3)-β-*D*-GalNAc moiety [Gb5-chain, structure (**III**)] is attached.

The synthesis of the target *globo*-oligosaccharides was performed using selectively protected lactose derivative (**XII**) containing the azidoethyl prespacer and free OH group at C4' for subsequent introduction of α-galactosyl residue. For the synthesis of block (**XII**), which was the precursor of (**VIII**), we had examined two routes based on 3',4'- or 4',6'-isopropylidenation of lactose (**IV**) (Scheme 2).

3'4'-Acetonation according to the method [14] we used led to (**V**) only in 43% yield and was accompanied by the formation of other isopropylidene derivatives of lactose, whose separation required column chromatography. The directed 4',6'-*O*-isopropylidenation of lac-

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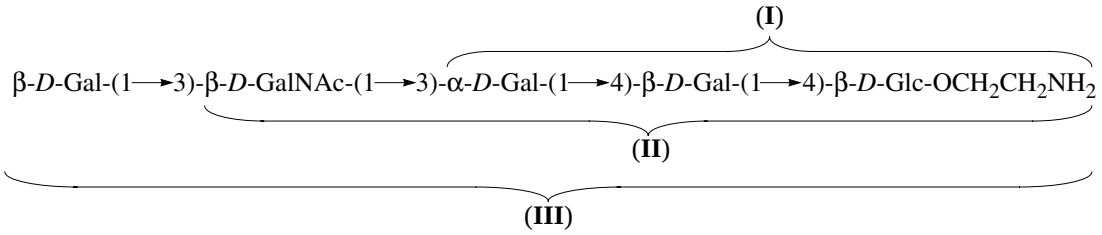
[2] Abbreviations: Bn, benzyl; Boc, *tert*-butyloxycarbonyl; Bz, benzoyl; NIS, *N*-iodosuccinimide; and Tf, trifluoromethanesulfonyl.



Scheme 1. Target aminoethyl glycosides of *globo*-tri-, -tetra-, and -pentasaccharide (**I**)–(**III**) containing oligosaccharide chains of glycolipids Gb3, Gb4, and Gb5, respectively.

tose by the method [15] resulted, according to TLC, in practically quantitative yield of acetonide (**VI**) and, therefore, was used for the preparative synthesis of (**VIII**). The preparation of (**VIII**) included exhaustive benzoylation of hexaol (**VI**), removal of isopropylidene protecting group, and regioselective 6'-*O*-benzoylation of diol (**VII**). This reaction sequence led to (**VIII**) in total yield of 70% from lactose. The presence of benzoyl group at O6' in (**VIII**) was confirmed by a low-field chemical shift of the signals of $H6_a$ (3.53–3.63 ppm) and $H6_b$ (3.96 ppm) protons of the Gal unit as compared to those in the starting diol (**VII**), where they resonate at 3.02–3.19 ppm. The presence of free OH group was confirmed by the up-field chemical shift of the signal of H4 in Gal (4.02 ppm, see Table 1).

Compound (**VIII**) was then acetylated and converted to lactosyl bromide (**IX**), which was used for glycosylation of chloroethanol in dichloromethane in the presence of silver triflate to yield chloroethyl glycoside (**X**). The chlorine atom in the aglycone moiety of (**X**) was replaced with azide group to give (**XI**), which was selectively de-*O*-acetylated by acidic methanolysis [16] to monohydroxy derivative (**XII**) in 40% yield from the starting (**VIII**).

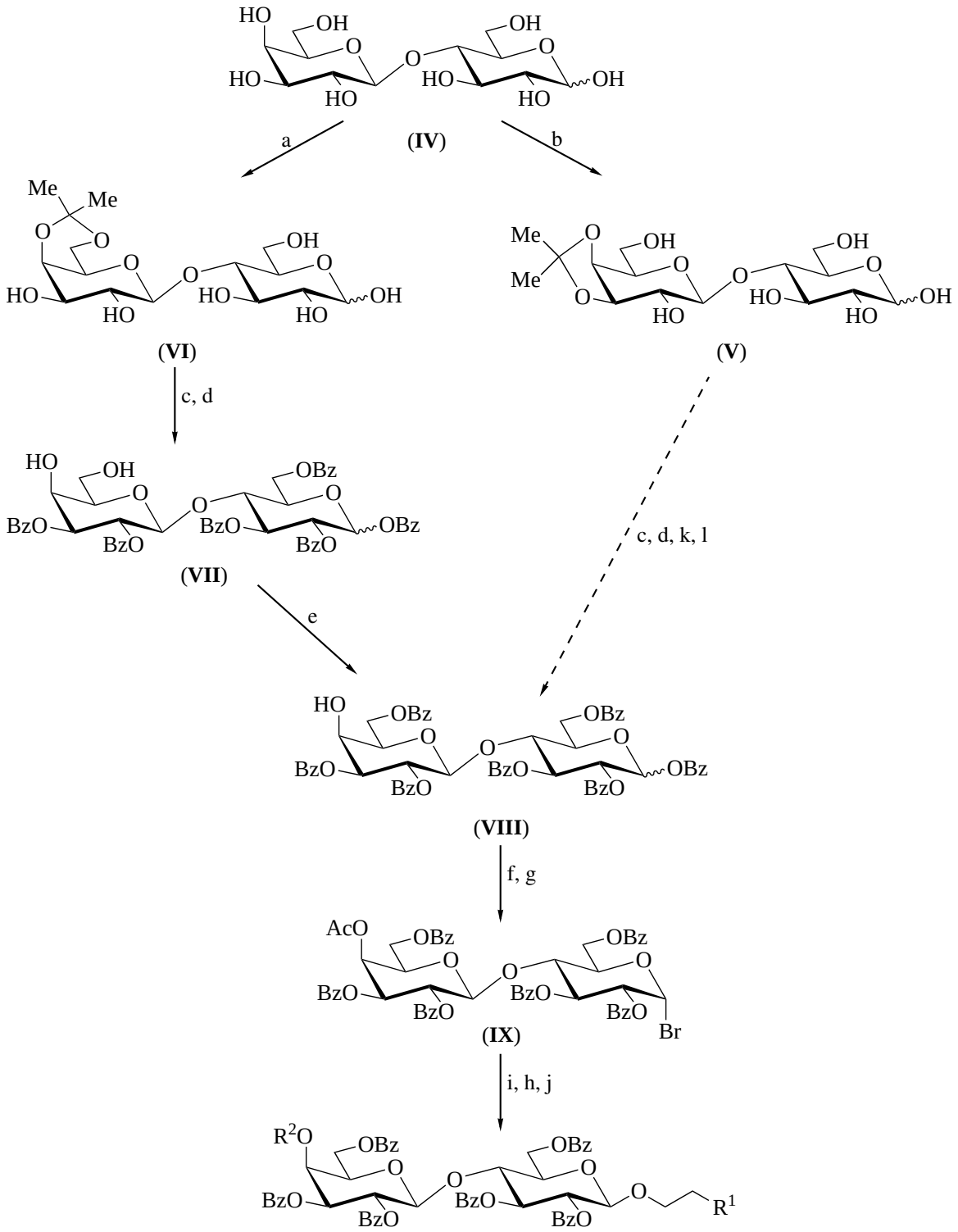
The structure of compound (**XII**) was confirmed by ^{1}H and ^{13}C NMR spectroscopy. In particular, the characteristic value of coupling constant $J_{1,2}$ = 7.7 Hz pointed out to the β-configuration of the anomeric center of glucose unit, and the presence of azide group at C2 of the aglycone was confirmed by the low-field position of the signal of the carbon atom of the methylene group of $\underline{C}H_2N_3$ (51.0 ppm). The presence of free OH group at C4 of Gal residue was corroborated by the upfield value of the chemical shift of H4 signal in Gal (4.19 ppm) in the ^{1}H NMR spectrum (see Table 1). This signal was additionally split due to spin–spin coupling with the proton of OH group.

Previously, various types of glycosyl donors with nonparticipating groups at C2 were used in the syntheses of globoside carbohydrate chains for the creation of 1,2-*cis*-glycoside bond. The use of glycosyl bromides [9, 10], fluorides [5], chlorides [7, 8], and trichloroacetimidates [6, 12] proceeded with low stereoselectivity and did not give high yields of target compounds. The use of thioglycosides [7, 11, 13] appeared to be the most effective; therefore, we selected totally benzylated thiogalactoside (**XIII**) [17] and its 3-*O*-acetylated analogue (**XV**) for α-galactosylation of the lactose block (**XII**) (Scheme 3); (**XV**) was obtained by acetylation of the corresponding monohydroxy derivative (**XIV**) [18].

Galactosylation of lactose acceptor (**XII**) with thioglycoside (**XIII**) in the presence of methyl trifluoromethanesulfonate in dichloromethane proceeded stereoselectively and led to protected derivative (**XVI**) in 85% yield. The α-configuration of the terminal galactose unit in (**XVI**) followed from the characteristic value of the coupling constant $J_{1,2}$ (3.8 Hz, Table 1) for H1 of the Galα unit of trisaccharide (**I**), which was obtained directly from trisaccharide (**XVI**). The presence of namely (1→4)-coupling was confirmed by the low-field resonance of C4 of Galα (76.4 ppm) in its ^{13}C NMR spectrum (Table 2).

Trisaccharide (**XVI**) was deacetylated with sodium methylate in methanol. The simultaneous hydrogenolysis of benzyl groups and the reduction of azide group over Pd/C in the presence of HCl gave, after gel chromatography, the target aminoethyl globotrioside (**I**) in total yield of 88%. The structure of trisaccharide (**I**) was established by ^{1}H and ^{13}C NMR spectroscopy. In particular, the values of coupling constants of the signals of anomeric protons H1 of Glc (δ 4.53 ppm, $J_{1,2}$ = 8.0 Hz), H1 of Galβ (δ 4.49 ppm, $J_{1,2}$ = 7.8 Hz), and H1 of Galα (δ 4.93 ppm, $J_{1,2}$ = 3.8 Hz) (Table 1) confirmed the α-configuration of the terminal galactose unit and the β-configuration of the other two monosaccharide residues. The chemical shift of the signal of the carbon atom in $-\underline{C}H_2N$ of the aglycone of (**I**) (38.4 ppm) as compared to that of (**XVI**) (51.0 ppm, Table 2) indicated the transformation of azide to amino group.

As in the case of galactosylation of acceptor (**XII**) with thioglycoside (**XIII**), the coupling of (**XII**) and (**XV**) in the presence of methyl trifluoromethanesulfonate in dichloromethane proceeded stereoselectively and resulted in selectively 3''-*O*-acetylated derivative (**XVII**) in 83% yield. The presence of α-(1→4)-bond in this compound was proved by the characteristic value of coupling constant $J_{1,2}$ (2.9 Hz) (Table 1) and the low-field position of the signal of C4 (75.4 ppm) in the Galα unit.



Scheme 2. Reagents: a, $Me_2C(OMe)_2$, TosOH; b, $Me_2C(OMe)_2$, TosOH, DMF; c, BzCl, Py; d, CF_3COOH, CH_2Cl_2; e, BzCl, CH_2Cl_2/Py; f, Ac_2O, Py; g, HBr/AcOH; h, $ClCH_2CH_2OH$, AgOTf, CH_2Cl_2; i, NaN_3, DMF, 18-crown-6; j, HCl/MeOH; k, Bu_2SnO/toluene; and l, BzCl/Py.

Table 1. Spectra ^{1}H NMR for (**I**)–(**III**) (D_2O) and (**VII**), (**VIII**), (**X**)–(**XII**), (**XV**)–(**XVIII**), (**XX**), and (**XXII**) ($CDCl_3$)

Compound	Residue	Chemical shifts (δ), ppm							Coupling constants (*J*), Hz						
		H1	H2	H3	H4	H5	$H6_a$	$H6_b$	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6a}$	$J_{5,6b}$	$J_{6a,6b}$
(**I**)	Glcβ	4.53	3.36	3.66		3.62	3.82	3.98	8.0	ND*	ND	ND	6.3	<1	12.3
	Galβ	4.49	3.56	3.74	4.03	3.77	3.82	3.92	7.8	10.1	3.0	<1	ND	8.0	11.6
	Galα	4.93	3.83	3.88	4.01	4.33	3.69		3.8	ND	3.1	<1	ND	ND	ND
(**II**)	Glcβ	4.54	3.37	3.66	3.62	3.84	3.85	4.00	8.0	ND	ND	ND	ND	ND	ND
	Galβ	4.51	3.58	3.75	4.92		3.70	3.91	7.8	10.2	ND	ND	ND	ND	ND
	Galα	4.91	3.85	3.96	4.24	4.37	3.73–3.82		3.8	ND	2.4	ND	ND	6.4	
	GalN	4.64	3.93	3.73	4.04	3.95	3.86	3.90	8.4	ND	3.0	ND	ND	ND	ND
(**III**)	Glcβ	4.48	3.31	3.59		3.57	3.77	3.93	8.0	8.4	ND	ND	4.6	1.9	11.2
	Galβ	4.44	3.52	3.68	3.97	3.83	ND	ND	7.8	10.1	3.3	ND	ND	ND	ND
	Galα	4.85	3.83	3.90	4.18	4.32	3.62		3.9	ND	2.6	<1	ND	ND	ND
	GalN	4.63	3.99	3.84	4.12	3.75	ND	ND	8.5	8.6	3.0	ND	ND	ND	ND
	Galβ**	4.38	3.46	3.55	3.84	ND	ND	ND	7.7	9.9	3.4	ND	ND	ND	ND
(**VIIα**)	Glcα	6.58	5.48	6.04	4.25	3.99	4.34–4.49		3.75	9.3		ND	ND	ND	ND
	Galβ	4.77	5.70	5.01	4.09	3.27	3.02–3.19		7.9	10.4	3.2	ND	ND	ND	ND
(**VIIβ**)	Glcβ	6.07	5.62	5.78	4.24	4.22	4.34–4.49		7.8	8.8	8.8	ND	ND	ND	ND
	Galβ	4.71	5.68	5.01	4.07	3.27	3.02–3.19		7.9	10.4	3.2	ND	ND	ND	ND
(**VIIIα**)	Glcα	6.62	5.48	6.04	4.24	4.00	4.37–4.46		3.4	10.2		ND	ND	ND	ND
	Galβ	4.75	5.73	5.03	4.02	3.53–3.63		3.96	7.9	9.3	3.1	ND	ND	ND	ND
(**VIIIβ**)	Glcα	6.03	5.65	5.81	4.22	4.40–4.45			9.2	9.2	9.2	ND	ND	ND	ND
	Galβ	4.69	5.71	5.03	4.02	3.53–3.63		3.96	7.9	9.3	3.1	ND	ND	ND	ND
(**X**)	Glcβ	4.77	5.44	5.78	4.24	3.86	4.44	4.63	7.8	9.5	9.5	9.5	4.2	<1	12.0
	Galβ	4.83	5.62	5.27	5.45	3.73–3.80 3.3–4.0			7.8	10.3	3.3	<1	ND	ND	ND
(**XI**)	Glcβ	4.77	5.47	5.80	4.26	3.85	4.45	4.63	7.7	9.4	9.4	9.4	4.3	1.1	12.3
	Galβ	4.83	5.63	5.27	5.49	3.65–3.80 3.3–4.0			7.9	10.4	3.5	<1	ND	ND	ND
(**XII**)	Glcβ	4.79	5.47	5.80	4.24	3.89	4.50	4.62	8.0	8.0	8.1	8.1	4.4	<1	11.6
	Galβ	4.82	5.79	5.19	4.19	3.67	3.36	4.15	8.0	10.5	3.0	<1	ND	ND	ND
(**XV**)	Galβ	4.60	3.84	4.97	4.05	3.63	3.73	3.74	9.3	9.3	2.4	<1	ND	ND	ND
(**XVI**)	Glcβ	4.66	5.30	5.72	4.18	3.81	4.66	4.41	7.8	9.2	9.2	ND	4.4	ND	12.0
	Galβ	4.82	5.66	4.98	4.23	3.63	4.48	4.10	7.8	10.8	2.7	<1	ND	ND	ND
	Galα	4.64	3.85		3.99	4.15	3.30	2.94	ND	ND	ND	<1	4.9	ND	8.4
(**XVII**)	Glcβ	4.75	5.41	5.83	4.26	3.93	4.48	4.70	7.5	9.0	9.0	9.0	ND	<1	12.3
	Galβ	4.89	5.74	5.09	4.30	3.62	4.03	4.48	7.7	10.5	2.8	<1	5.6	ND	11.0
	Galα	4.78	3.91	5.21	4.18	3.36	3.13	4.37	2.9	10.7	2.7	<1	5.2	ND	8.8
(**XVIII**)	Glcβ	4.76	5.44	5.81	4.29	3.88	4.48	4.68	8.0	8.0	8.0	8.0	ND	ND	ND
	Galβ	4.88	5.68	5.07	4.24	3.73	4.10	4.45	7.8	10.7	2.5	<1	6.5	ND	11.1
	Galα	4.74	3.63	3.84	3.98	3.47	3.24	4.27	3.2	7.0	2.9	<1	ND	ND	ND
(**XX**)	Glcβ	4.72	5.40	5.88	4.27	4.07	4.63	4.74	7.5	9.3	9.3	ND	ND	ND	ND
	Galβ	5.06	5.77	5.17	4.12	3.89	4.46	4.58	7.9	10.5	ND	ND	ND	ND	11.2
	Galα	4.61	3.95	4.33	4.20	4.26	2.94	3.35	2.9	10.4	3.4	<1	ND	ND	8.3
	GalN	5.17	4.55	5.38	5.49	4.23	4.24	4.33	8.5	8.0	2.9	<1	ND	ND	ND
(**XXII**)	Glcβ	4.79	5.22	5.72	4.18	ND	ND	ND	7.9	9.1	ND	ND	ND	ND	ND
	Galβ	4.88	5.60	4.96	4.17	ND	ND	ND	7.8	10.6	ND	ND	ND	ND	ND
	Galα	4.74	3.91	4.63	ND	ND	ND	ND	3.3	ND	ND	ND	ND	ND	ND
	GalN	5.20	3.78	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Galβ**	4.05	5.10	4.90	5.27	ND	ND	ND	8.0	10.4	3.5	ND	ND	ND	ND

*ND, not determined.

**Terminal Galβ unit.

Other signals: $C\underline{H}_3COO$, 1.9–2.1 ppm; $C_6\underline{H}_5COO$, 7.7–8.0 ppm; $C\underline{H}_2$-Ph, 4.56 ppm; $C_6\underline{H}_5CH_2$, 6.8–7.5 ppm; $OCH_2C\underline{H}_2Cl$, 3.15–3.40 ppm; $OC\underline{H}_2CH_2Cl$, 3.50–4.00 ppm; $OCH_2C\underline{H}_2N_3$, 3.13–3.52 ppm; $OC\underline{H}_2CH_2N_3$, 3.50–3.82 ppm; $SC\underline{H}_2CH_3$, 3.67 ppm; $SCH_2C\underline{H}_3$, 1.28 ppm; $N\underline{H}C(O)CCl_3$, 6.8 ppm ($J_{NH,2}$ 10 Hz); $OCH_2C\underline{H}_2NH_2$, 3.26 ppm; $OC\underline{H}_2CH_2NH_2$, 3.94 and 4.12 ppm.

Table 2. Spectra ^{13}C NMR for (**I**)–(**III**) (D_2O) and (**XVI**), (**XVII**), (**XX**), and (**XXII**) ($CDCl_3$)

Compound	Residue	Chemical shifts (δ), ppm					
		C1	C2	C3	C4	C5	C6
(**I**)	Glcβ	100.9	71.8	73.3	77.6	73.8	58.9
	Galβ	102.3	69.9	71.2	76.4	74.4	59.5
	Galα	99.3	67.5	68.1	68.0	69.9	59.4
(**II**)	Glcβ	103.1	74.0	75.5	79.9	76.1	61.1
	Galβ	104.5	72.1	72.0	79.9	76.6	61.6
	Galα	101.6	67.0	79.9	70.1	71.5	62.2
	GalN	104.4	53.8	73.4	78.5	69.0	61.6
(**III**)	Glcβ	102.2	73.2	74.6	79.0	75.1	60.2
	Galβ	103.6	71.2	72.5	77.6	75.8	60.7
	Galα	100.7	67.9	79.0	69.3	70.6	60.7
	GalN	103.2	51.8	79.9	68.3	74.9	61.3
	Galβ**	105.1	70.9	72.8	68.9	75.3	61.3
(**XVI**)	Glcβ	100.8	72.2	73.0	76.3	73.3	62.5
	Galβ	101.1	69.9	74.4	75.8	73.4	62.4
	Galα	101.2	75.6		74.9	69.8	67.5
(**XVII**)	Glcβ	100.4	ND*	ND	75.9	ND	62.3
	Galβ	100.8	ND	ND	75.4	ND	62.1
	Galα	101.2	ND	ND	75.1	ND	67.2
(**XX**)	Glcβ	100.9	ND	ND	76.1	ND	62.7
	Galβ	100.0	64.9	ND	ND	ND	62.4
	Galα	100.4	ND	80.8	70.9	70.1	67.4
	GalN	103.0	52.8	71.2	66.8	77.3	61.4
(**XXII**)	Glcβ	100.4	ND	ND	ND	ND	62.2
	Galβ	101.0	ND	ND	ND	ND	61.2
	Galα	100.4	ND	79.9	ND	ND	66.7
	GalN	101.0	53.0	ND	ND	ND	60.7
	Galβ**	101.2	ND	ND	ND	ND	60.0

*ND, not determined.

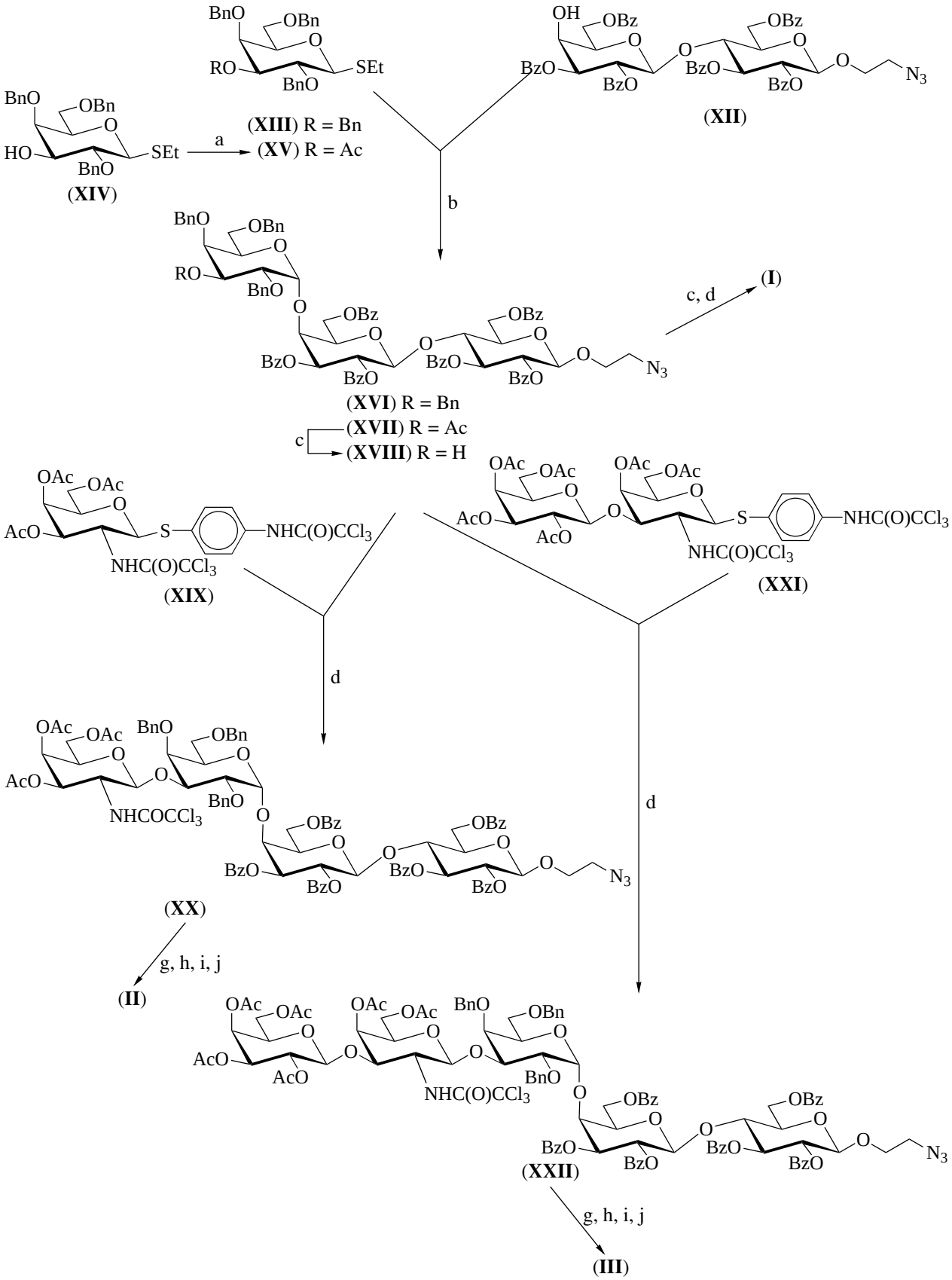
**Terminal Galβ unit.

Other signals: $O\underline{C}H_2CH_2NH_2$, 64.8 ppm; $OCH_2\underline{C}H_2NH_2$, 38.4 ppm; $\underline{C}H_3CONH$, 22.6 ppm; $CH_3\underline{C}ONH$, 175.5 ppm; $\underline{C}H_2N_3$, 51.0 ppm; $O\underline{C}H_2CH_2N_3$, 68.1–68.2 ppm; $\underline{C}OCCl_3$, 159.5–161.6 ppm.

Acetate (**XVII**) was converted into monohydroxy derivative (**XVIII**) under the conditions of acidic methanolysis [16] in 81% yield (Scheme 3). The position of free OH group at C3 of the terminal galactose unit in (**XVIII**) followed from the upfield shift of the signal of H3 of Galα by 1.374 ppm (δ 5.21→3.84 ppm) in the ^1H NMR spectrum of (**XVIII**) as compared to that of (**XVII**) (Table 1).

Trisaccharide (**XVIII**) was glycosylated with thioglycoside (**XIX**) [19] in dichloromethane in the presence of NIS and trifluoromethanesulfonic acid to give tetrasaccharide (**XX**) in 88% yield (Scheme 3). The β-configuration of the galactosamine residue in (**XX**) was confirmed by the characteristic value of the corresponding coupling constant $J_{1,2}$ (8.5 Hz) in the ^1H NMR spectrum (Table 1), and the presence of the GalN-(1→3)-Gal bond, by the low-field shift of the C3 signal in GalN (80.8 ppm) in the ^{13}C NMR spectrum (Table 2).

In order to transform (**XX**) to the target tetrasaccharide (**II**), all acyl groups were removed by the treatment with 0.5 M NaOH in aqueous methanol. Then the resulting free amino group in the galactosamine residue was *N*-acetylated with acetic anhydride. The hydrogenolysis of benzyl ethers and the reduction of azide group were performed in 10% aqueous ethanol upon the catalysis by Pd/C in the presence of Boc_2O to fix the amine generated in the reaction. Upon the hydrogenol-



Scheme 3. a, Ac_2O, Py; b, MeOTf, CH_2Cl_2, MS-4 Å; c, HCl/MeOH; d, NIS/TfOH, CH_2Cl_2; e, MeONa, MeOH; f, H_2, Pd/C, HCl; g, NaOH, MeOH/H_2O; h, Ac_2O, NaOH; i, H_2, Pd/C, Boc_2O; and j, CF_3COOH, H_2O/MeOH.

ysis in the presence of HCl (without addition of Boc_2O), i.e., under the conditions used in the synthesis of trisaccharide (**I**), we failed to completely remove benzyl groups, which was likely due to a partial poisoning of the catalyst with the generated amine. After the removal of Boc protecting group by the treatment with trifluoroacetic acid in aqueous methanol, aminoethyl globotetraoside (**II**) was obtained in 54% yield from the starting (**XX**). The structure of (**II**), in particular, the configurations of its anomeric centers, directions of interunit bonds, and the presence of the aminoethyl aglycone ($\delta\underline{C}H_2NH_2$ 38.4 ppm) were proven by ^1H (Table 1) and ^{13}C (Table 2) NMR spectra.

To obtain the target pentasaccharide (**III**), we glycosylated trisaccharide (**XXI**) with disaccharide thioglycoside (**XVIII**) [19] under the conditions used for the synthesis of tetrasaccharide (**XX**) to give pentasaccharide (**XXII**) in 73% yield (Scheme 3). The β-configuration of the galactosamine residue in (**XXII**) was proved by the characteristic value of coupling constant $J_{1,2}$ (8.5 Hz), and the presence of the Gal-(1→3)Gal bond, by the low-field shift of the signal of C3 in Galα at 79.9 ppm in the ^{13}C NMR spectrum.

Note that trichloroacetimidate glycosyl donors based on *N*-phthaloylated disaccharide β-*D*-Gal-(1→3)-*D*-GalN [8, 13] were previously used in the syntheses of pentasaccharide Gb5. However, the glycosylation of the derivatives of trisaccharide Gb3 with these glycosyl donors proceeded much less effectively, than in the case of the synthesis of pentasaccharide (**XXII**). This was connected with a low stereoselectivity of the reaction [13] and the side rearrangement of glycosylimidate to the corresponding glycosyl amide [8]. We have recently demonstrated a high effectiveness of glycosyl donor (**XXI**) by the example of successful synthesis of the derivative of tetrasaccharide asialo-GM1 [19].

The saponification of ester groups in pentasaccharide (**XXII**) was performed in 1 M NaOH solution in aqueous methanol (10% of water). *N*-Acetylation, hydrogenolysis, and isolation by gel filtration were carried out under the conditions similar to those used for the transformation of protected tetrasaccharide (**XX**) to the target (**II**). The deprotected aminoethyl pentaoside (**III**) resulted in total yield of 86% from (**XXII**). The structure of (**III**) was proved by ^1H and ^{13}C NMR spectroscopy (Tables 1 and 2) as described above for (**I**) and (**II**).

Thus, oligosaccharide chains of glycolipids Gb3, Gb4, and Gb5 were synthesized in the form of aminoethyl glycosides. The effectiveness of the synthetic scheme using the division of the target structures into β-*D*-Gal-(1→4)-*D*-Glc, α-*D*-Gal, β-*D*-GalNAc, and β-*D*-Gal-(1→3)-*D*-GalNAc blocks and also the effectiveness of the use of thioglycoside glycosyl donors like (**XIX**) and (**XXI**) for the obtaining of the globoside oligosaccharide chains was demonstrated.

EXPERIMENTAL

The procedures for purification of solvents and reagents and the conditions for registration of NMR spectra and for determination of physicochemical constants are the same as in [20]. ^1H NMR spectra were registered on Bruker DRX-500 and Bruker AM-300 spectrometers at 25°C. Optical rotation values were measured on a Jasco DIP-360 digital polarimeter at 18–25°C. TLC was performed on Silica gel 60 (Merck) precoated plates. The spots were visualized by the treatment with 10 vol % solution of orthophosphoric acid in ethanol or with ninhydrin solution (3 g/l in 30 : 1 butanol–acetic acid for amines) and subsequent heating at ~150°C. Column chromatography was carried out on 0.063–0.2 mm Silica gel 60 (Fluka); MPLC on Silasorb 600 (200 μm, Chemapol) columns, and gel chromatography on Sephadex LH-20 (2 × 40 cm) columns (elution with methanol, 1 ml/min), Sephadex G-10 (1.5 × 20 cm) columns (elution with water, 2 ml/min), and TSK-HW40s (1.5 × 90 cm) columns (elution with 0.1 M aqueous acetic acid, 1 ml/min). Hydrogenolysis was performed over 10% Pd/C (Merck) at atmospheric pressure. TLC of the deprotected aminoethyl glycosides was performed in (BPH) 1 : 2 : 1 butanol–propanol—0.1 M hydrochloric acid and (AMW) 1 : 1 : 1 acetonitrile–methanol–water developing systems.

4-*O*-(3,4-*O*-Isopropylidene-β-*D*-galactopyranosyl)-α,β-*D*-glucopyranose (V). A suspension of lactose (18 g, 52.7 mmol) and TsOH · H_2O (180 mg, 0.915 mmol) in 2,2-dimethoxypropane (10 ml) and DMF (50 ml) was stirred for 1 h at 70°C. Triethylamine (3 ml) was added, and the mixture was concentrated in a vacuum. Acetonide (**V**) was isolated by column chromatography (elution with 1 : 2 methanol–chloroform); yield 9.6 g (43%); R_f 0.25 (1 : 2 methanol–chloroform).

1,2,3,6-Tetra-*O*-benzoyl-4-*O*-(2,3-di-*O*-benzoyl-β-*D*-galactopyranosyl)-α,β-*D*-glucopyranose (VII). A suspension of lactose (3.2 g, 9.36 mmol) and TsOH · H_2O (210 mg, 1.1 mmol) in 2,2-dimethoxypropane (3 ml) was stirred for 2 h at 20°C until is was completely dissolved and form acetonide (**VI**). Triethylamine (3 ml) was then added, and the reaction mixture was evaporated in a vacuum. The residue was suspended in anhydrous pyridine (30 ml, 370 mmol), and benzoyl chloride (20 ml, 172 mmol) was added at intensive stirring and cooling to 0°C. The reaction mixture was stirred for 3 h at 20°C, poured on ice, and diluted with dichloromethane (500 ml). The organic layer was separated; washed with 1 M H_2SO_4 (400 ml), water (2 × 400 ml), and saturated $NaHCO_3$ solution (200 ml); filtered through a layer of cotton; and evaporated in a vacuum. The residue was dissolved in a mixture of dichloromethane (80 ml) and 90% trifluoroacetic acid (10 ml), kept for 30 min at 20°C, concentrated, and coevaporated with toluene (5 × 50 ml). The residue was chromatographed on a column eluted with 3 : 1 toluene–ethyl acetate to isolate 5.67 g (63%) of diol (**VII**),

R_f 0.21 (3 : 1 toluene–ethyl acetate). For ^{1}H NMR spectrum, see Table 1.

1,2,3,6-Tetra-*O*-benzoyl-4-*O*-(2,3,6-tri-*O*-benzoyl-β-*D*-galactopyranosyl)-α,β-*D*-glucopyranose (VIII). Benzoyl chloride (750 μl, 6.5 mmol) was added for 10 min to intensively stirred and cooled to 0°C solution of diol (**VII**) (5.67 g, 5.9 mmol) in a mixture of anhydrous dichloromethane (66 ml) and anhydrous pyridine (1.4 ml, 17.3 mmol). The reaction mixture was stirred for 2 h at 0°C and diluted with dichloromethane (500 ml) and water (10 ml). Then the reaction mixture was treated as described for (**VII**). Product (**VIII**) (4.24 g, 70%) was isolated by column chromatography (elution with 10 : 1 toluene–ethyl acetate), R_f 0.31 (10 : 1 toluene–ethyl acetate). Found, %: C 68.54, H 4.68. $C_{61}H_{50}O_{18}$. Calculated, %: C 68.41, H 4.67. For ^{1}H NMR spectrum, see Table 1.

4-*O*-(4-*O*-Acetyl-2,3,6-tri-*O*-benzoyl-β-*D*-galactopyranosyl)-2,3,6-tri-*O*-benzoyl-α-*D*-glucopyranosyl bromide (IX). Compound (**VIII**) (4.24 g, 4.13 mmol) was acetylated with acetic anhydride (6 ml, 64 mmol) in anhydrous pyridine (9 ml, 110 mmol) for 18 h at 20°C, evaporated, coevaporated with toluene (3 × 50 ml), and dissolved in anhydrous dichloromethane (9.5 ml). A 40% solution of HBr in AcOH (18.5 ml) was added at –10°C and intensive stirring. The reaction mixture was kept without stirring for 40 min at –10°C, poured on ice, and diluted with dichloromethane (400 ml). The organic layer was separated; washed with ice-cold water (300 ml), cold saturated $NaHCO_3$ solution (2 × 150 ml), and ice-cold water (150 ml); filtered through a layer of cotton; and evaporated. The residue was dried in a vacuum of oil pump to give 4.21 g (99%) of bromide (**IX**) as a white foam, R_f 0.42 (10 : 1 toluene–ethyl acetate).

2-Chloroethyl 4-*O*-(4-*O*-acetyl-2,3,6-tri-*O*-benzoyl-β-*D*-galactopyranosyl)-(2,3,6-tri-*O*-benzoyl-β-*D*-glucopyranoside (X). A solution of lactosyl bromide (**IX**) (6.53 g, 6.1 mmol) in a mixture of anhydrous 2-chloroethanol (6.4 ml, 95 mmol) and anhydrous dichloromethane (64 ml) was stirred under argon for 30 min at 20°C with the preliminarily heated molecular sieves MS-4 Å (200 mg); silver triflate (1.87 g, 7.3 mmol) was added; and the mixture was stirred for 1 h at 20°C. Triethylamine (3 ml) was added; the mixture was diluted with dichloromethane (350 ml); the organic layer was washed with 1 M $Na_2S_2O_3$ solution (2 × 50 ml), saturated $NaHCO_3$ solution (2 × 150 ml), and water (200 ml), and evaporated. The residue was chromatographed on a silica gel column in 30 : 1 toluene–acetone to give 6.35 g (91%) of glycoside (**X**) as a white foam, R_f 0.4 (8 : 1 toluene–ethyl acetate), $[\alpha]_D$ +36.5° (*c* 1, ethyl acetate). Found, %: 64.85, H 4.79. $C_{58}H_{50}O_{18}Cl$. Calculated, %: C 65.02, H 4.77. For ^{1}H NMR spectrum, see Table 1.

2-Azidoethyl 4-*O*-(4-*O*-acetyl-2,3,6-tri-*O*-benzoyl-β-*D*-galactopyranosyl)-2,3,6-tri-*O*-benzoyl-β-*D*-glucopyranoside (XI). A suspension of NaN_3 (297 mg, 4.57 mmol) in a solution of chloroethyl glycoside (**X**) (490 mg, 0.457 mmol) and 18-crown-6 (120 mg, 0.45 mmol) in DMF (2.5 ml) was stirred for 22 h at 65°C. The mixture was diluted with ethyl acetate (150 ml), washed with water (4 × 50 ml), filtered through a layer of cotton, and evaporated. The residue was chromatographed on a column eluted with 15 : 1 toluene–ethyl acetate to isolate 427 mg (86%) of azide (**XI**) as a white foam; R_f 0.27 (8 : 1 toluene–ethyl acetate); $[\alpha]_D$ +34° (*c* 1, ethyl acetate). Found, %: C 64.63, H 4.77, N 3.90. $C_{58}H_{51}O_{18}N_3$. Calculated, %: C 64.62, H 4.77, N 3.90. For ^{1}H NMR spectrum, see Table 1.

2-Azidoethyl 4-*O*-(2,3,6-tri-*O*-benzoyl-β-*D*-galactopyranosyl)-2,3,6-tri-*O*-benzoyl-β-*D*-glucopyranoside (XII). Acetyl chloride (165 μl, 2.3 mmol) was added to absolute methanol (4.14 ml) at 0°C and kept for 10 min. A solution of acetate (**XI**) (402 mg, 0.373 mmol) in anhydrous dichloromethane (2.4 ml) was added to the resulting solution. The mixture was kept for 60 h at 20°C, poured on ice, and diluted with dichloromethane (150 ml). The organic layer was separated, washed with saturated $NaHCO_3$ solution (50 ml) and water (50 ml), and evaporated. The residue was separated by column chromatography in 20 : 1 toluene–acetone to get 197 mg (51%) of alcohol (**XII**) as a white foam, R_f 0.15 (8 : 1 toluene–ethyl acetate), $[\alpha]_D$ +58° (*c* 1, ethyl acetate). Found, %: C 64.86, H 4.68, N 4.05. $C_{56}H_{48}O_{17}N_3$. Calculated, %: C 64.98, H 4.67, N 4.06. For ^{1}H NMR spectrum, see Table 1.

Ethyl 3-*O*-acetyl-2,4,6-tri-*O*-benzyl-1-thio-β-*D*-galactopyranoside (XV). Acetic anhydride (3 ml, 31 mmol) was added to a solution of (**XIV**) [18] (0.5 g, 1.01 mmol) in anhydrous pyridine (5 ml), the mixture was kept for 12 h at 20°C, and the excess of Ac_2O was quenched with methanol (10 ml). The mixture was evaporated and coevaporated with toluene (3 × 20 ml). The residue was filtered through a silica gel layer in 12 : 1 toluene–ethyl acetate, evaporated, and dried in a vacuum of oil pump to isolate 0.5 g (92%) of acetate (**XV**) as a white foam, R_f 0.3 (12 : 1 toluene–ethyl acetate), $[\alpha]_D$ +25.7° (*c* 0.63, $CHCl_3$).

2-Azidoethyl 4-*O*-[4-*O*-(2,3,4,6-tetra-*O*-benzyl-α-*D*-galactopyranosyl)-2,3,6-tri-*O*-benzoyl-β-*D*-galactopyranosyl]-2,3,6-tri-*O*-benzoyl-β-*D*-glucopyranoside (XVI). A solution of glycosyl acceptor (**XII**) (405 mg, 0.388 mmol) and thiogalactoside (**XIII**) (575.7 mg, 0.985 mmol) in anhydrous dichloromethane (35 ml) was stirred with heated molecular sieves MS-4 Å (6.6 g) under argon for 30 min at 20°C, methyl triflate (540 μl, 4.78 mmol) was added, and the mixture was stirred for addional 30 min. Triethylamine (2 ml) was added; the reaction mixture was filtered, the filtrate was diluted with dichloromethane (150 ml) and washed with saturated $NaHCO_3$ solution (2 × 50 ml) and water (100 ml). The organic layer was separated and evaporated. The residue was chromatographed on a column

eluted with 12 : 1 toluene–ethyl acetate to isolate 517 mg (85%) of trisaccharide (**XVI**) as a white foam, R_f 0.48 (8 : 1 toluene–ethyl acetate), $[\alpha]_D$ +55.5° (*c* 1, ethyl acetate). Found, %: C 69.51, H 5.36, N 2.69. $C_{90}H_{83}O_{22}N_3$. Calculated, %: C 69.35, H 5.36, N 2.69. For ^{1}H NMR spectrum, see Table 1.

2-Azidoethyl 4-*O*-[4-*O*-(4-*O*-acetyl-2,3,6-tri-*O*-benzyl-α-*D*-galactopyranosyl)-2,3,6-tri-*O*-benzoyl-β-*D*-galactopyranosyl]-2,3,6-tri-*O*-benzoyl-β-*D*-glucopyranoside (XVII). The reaction of glycosyl acceptor (**XII**) (360 mg, 0.347 mmol) and thioglycoside (**XV**) (466 mg, 0.868 mmol) was carried out and treated as described for (**XVI**). Glycoside (**XVII**) (580 mg, 83%) was isolated by column chromatography in 3 : 1 petroleum ether–ethyl acetate as a white foam, R_f 0.28 (2 : 1 petroleum ether–ethyl acetate). Found, %: C 67.58, H 5.32, N 2.78. $C_{85}H_{80}O_{23}N_3$. Calculated, %: C 67.60, H 5.33, N 2.78. For ^{1}H NMR spectrum, see Table 1.

2-Azidoethyl 4-*O*-[4-*O*-(2,3,6-tri-*O*-benzyl-α-*D*-galactopyranosyl)-2,3,6-tri-*O*-benzoyl-β-*D*-galactopyranosyl]-2,3,6-tri-*O*-benzoyl-β-*D*-glucopyranoside (XVIII). A solution of acetate (**XVII**) (101 mg, 0.069 mmol) in anhydrous dichloromethane (0.5 ml) was added to a solution of HCl in methanol obtained by addition of acetyl chloride (40 μl, 0.56 mmol) to absolute methanol (1.0 ml). Then the reaction mixture was treated as described for (**XII**). Alcohol (**XVIII**) (82 mg, 81%) was isolated by column chromatography in 20 : 1 toluene–acetone as a white foam, R_f 0.33 (3 : 1 petroleum ether–ethyl acetate), $[\alpha]_D$ +55° (*c* 1, ethyl acetate). Found, %: C 67.92, H 5.29, N 2.86. $C_{83}H_{77}O_{22}N_3$. Calculated, %: C 67.89, H 5.28, N 2.86. For ^{1}H NMR spectrum, see Table 1.

2-Azidoethyl (3,4,6-tri-*O*-acetyl-2-deoxy-2-trichloroacetamido-β-*D*-galactopyranosyl)-(1→3)-(2,4,6-tri-*O*-benzyl-α-*D*-galactopyranosyl)-(1→4)-(2,3,6-tri-*O*-benzoyl-β-*D*-galactopyranosyl)-(1→4)-(2,3,6-tri-*O*-benzoyl-β-*D*-glucopyranoside (XX). A solution of trisaccharide (**XVIII**) (50 mg, 0.034 mmol) and glycosyl donor (**XIX**) [19] (29 mg, 0.041 mmol) in anhydrous dichloromethane (2.5 ml) was stirred with preliminarily heated molecular sieves MS-4 Å (200 mg) for 2 h at 20°C. Then NIS (10 mg, 0.044 mmol) was added; the mixture was stirred for additional 20 min at 20°C, cooled to –30°C; and dropwise treated with 5% TfOH in CH_2Cl_2 (100 μl) at the same temperature. The mixture was stirred for 1.5 h at a temperatures from –30 to 20°C, treated with saturated $NaHCO_3$ solution (1 ml) and 1 M $Na_2S_2O_3$ solution (1 ml), stirred for 10 min, and filtered through a layer of Celite. The filtrate was diluted with dichloromethane (75 ml), washed with saturated $NaHCO_3$ solution (50 ml), and the organic layer was separated and evaporated. The residue was chromatographed on a column eluted with the dichloromethane–ethyl acetate (10 : 1→5 : 1) gradient to isolate 57 mg (88%) of tetrasaccharide (**XX**) as a white foam, R_f 0.5 (5 : 1 toluene–ethyl acetate). For ^{1}H NMR spectrum, see Table 1.

2-Azidoethyl (2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl)-(1→3)-(4,6-di-*O*-acetyl-2-deoxy-2-trichloroacetamido-β-*D*-galactopyranosyl)-(1→3)-(2,4,6-tri-*O*-benzyl-α-*D*-galactopyranosyl)-(1→4)-(2,3,6-tri-*O*-benzoyl-β-*D*-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzoyl-β-*D*-glucopyranoside (XXII). A solution of trisaccharide (**XVIII**) (60 mg, 0.041 mmol) and glycosyl donor (**XXI**) (44 mg, 0.044 mmol) in anhydrous dichloromethane (3 ml) was stirred under dry argon for 2 h at 20°C with preliminarily heated molecular sieves MS-4 Å (200 mg). Then NIS (13 mg, 0.058 mmol) was added; the mixture was stirred for additional 20 min at 20°C, cooled to –30°C; and treated dropwise at the same temperature with 5% TfOH in CH_2Cl_2 (200 μl). The reaction mixture was stirred for 2 h at –30 to –20°C. The product was isolated and purified as described for (**XX**) to give 65 mg (73%) of pentasaccharide (**XXII**) as a white foam, R_f 0.43 (5 : 1 dichloromethane–ethyl acetate), $[\alpha]_D$ + 75.7° (*c* 0.5, $CHCl_3$). For ^{1}H NMR spectrum, see Table 1.

2-Aminoethyl α-*D*-galactopyranosyl-(1→4)-β-*D*-galactopyranosyl-(1→4)-α-*D*-glucopyranoside (I). Trisaccharide (**XVI**) (180.4 mg, 0.116 mmol) was dissolved in absolute methanol (3 ml) and treated with 1 M sodium methylate in methanol (0.3 ml). After 20 min, the solution was neutralized with cation exchange resin KU-2 (H^+) and filtered. The resin was washed with methanol (2 × 5 ml), the combined filtrate was evaporated in a vacuum, and the residue was chromatographed on a column eluted with ethyl acetate to isolate 88.5 g of hexaol, the product of *O*-debenzoylation of trisaccharide (**XV**). The resulting hexaol was dissolved in absolute methanol (2 ml), the solution of HCl in methanol [obtained by addition of acetyl chloride (0.12 ml, 1.7 mmol) to absolute methanol (3 ml) and subsequent keeping at 20°C for 20 min] and Pd/C (115 mg) were added, and the mixture was stirred for 1 h under hydrogen. Then triethylamine (2 ml) was added, the reaction mixture was filtered through a layer of Celite, the filtrate was evaporated, and the residue was dissolved in water (5 ml) and treated with anion exchange resin A-26 (OH^-) (Serva). The resin was filtered off and washed with water (1 ml), the combined filtrate was evaporated in a vacuum, and the residue was chromatographed on TSK-HW40s gel to isolate 58 mg (87%) of trisaccharide (**I**), R_f 0.32 (3 : 2 BPH–AMW), $[\alpha]_D$ + 76° (*c* 2, water). For ^{1}H and ^{13}C NMR spectra, see Tables 1, 2.

2-Aminoethyl (2-acetamido-2-deoxy-β-*D*-galactopyranosyl)-(1→3)-α-*D*-galactopyranosyl-(1→4)-β-*D*-galactopyranosyl-(1→4)-β-*D*-glucopyranoside (II). Tetrasaccharide (**XX**) (53 mg, 0.028 mmol) was dissolved in 5% aqueous methanol (4 ml), NaOH (80 mg) was added, and the mixture was stirred until complete dissolution and kept for 17 h at 20°C. Then

Ac_2O was added dropwise to pH 6 upon cooling to 0°C (monitoring by universal pH-indicator, Merck), the reaction mixture was deionized with cation exchange resin KU-2 (H^+), the resin was filtered off and washed with methanol (2 × 3 ml), and the combined filtrate was evaporated. The residue was chromatographed on a Sephadex LH-20 column. The carbohydrate-containing fractions were evaporated and dried in a vacuum of oil pump. The dry residue was dissolved in 10% aqueous ethanol (3 ml), Boc_2O (60 mg) and the catalytic amount of Pd/C were added, and the reaction mixture was stirred for 14 h under hydrogen at 20°C up to complete removal of benzyl protective groups (TLC monitoring). The reaction mixture was filtered through a layer of Celite, the filtrate was washed with aqueous methanol in the 100–0% methanol–water gradient (30 ml), and 90% aqueous CF_3COOH (2 ml) was added. The reaction mixture was kept for 30 min, evaporated, and co-evaporated with water to remove the acid. The residue was chromatographed on TSK-HW-40s gel column to isolate 13 mg (54%) of aminoethyl glycoside (**II**) (in the form of trifluoroacetate), R_f 0.21 (1 : 1 BPH–AMW). For ^1H and ^{13}C NMR spectra, see Tables 1 and 2.

2-Aminoiethyl β-*D*galactopyranosyl-1→3)-(2-acetamido-2-deoxy-β-*D*-galactopyranosyl)-(1→3)-α-*D*-galactopyranosyl-(1→4)-β-*D*-galactopyranosyl-(1→4)-β-*D*-glucopyranoside (III). Sodium hydroxide (170 mg) was added to a solution of pentasaccharide (**XXII**) (42 mg, 0.019 mmol) in 10% aqueous methanol (4.4 ml); the mixture was stirred up to complete dissolution and kept for 2 h at 40°C and then for 14 h at 20°C. Then the *N*-acetylation, hydrogenolysis, and reduction (including the intermediate protection of amino group with Boc_2O) were performed. The purification as described for tetrasaccharide (**II**) resulted in 15 mg (86%) of aminoethyl glycoside (**III**) (in the form of trifluoroacetate), R_f 0.23 (1 : 1 BPH–AMW). For ^1H and ^{13}C NMR spectra, see Tables 1, 2.

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