Russian Journal of Bioorganic Chemistry, Vol. 28, No. 5, 2002, pp. 419–429. Translated from Bioorganicheskaya Khimiya, Vol. 28, No. 5, 2002, pp. 462–473.

Syntheses of α- and β-Glycosyl Donors with a Disaccharide β-*D*-Gal-(1→3)-*D*-GalNAc Backbone

P. E. Cheshev, L. O. Kononov, Yu. E. Tsvetkov, A. S. Shashkov, and N. E. Nifantiev[1]

Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Leninskii pr. 47, Moscow, 119991 Russia

Received August 17, 2001; in final form, September 6, 2001

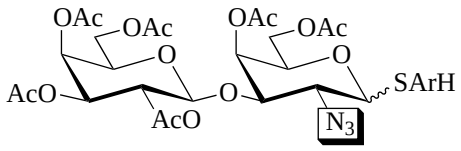
Abstract—The synthesis of thioglycoside glycosyl donors with a disaccharide β-*D*-Gal-(1 ⟶ 3)-*D*-GalNAc backbone was studied using the glycosylation of a series of suitably protected 3-monohydroxy- and 3,4-dihydroxyderivatives of phenyl 2-azido-2-deoxy-1-thio-α- and 1-thio-β-*D*-galactopyranosides by galactosyl bromide, fluoride, and trichloroacetimidate. In the reaction with the monohydroxylated glycosyl acceptor, the process of intermolecular transfer of thiophenyl group from the glycosyl acceptor onto the cation formed from the molecule of glycosyl donor dominated. When glycosylating 3,4-diol under the same conditions, the product of the thiophenyl group transfer dominated or the undesired (1 ⟶ 4), rather than (1 ⟶ 3)-linked, disaccharide product formed. The aglycon transfer was excluded when 4-nitrophenylthio group was substituted for phenylthio group in the galactosyl acceptor molecule. This led to the target disaccharide, 4-nitrophenyl 2-azido-4,6-*O*-benzylidene-2-deoxy-3-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl)-1-thio-β-*D*-galactopyranoside, in 57% yield. This disaccharide product bears nonparticipating azido group in position 2 of galactosamine and can hence be used to form α-glycoside bond. Azido group and the aglycon nitro group were simultaneously reduced in this product and then trichloroacetylated, which led to the β-glycosyl donor, 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 62% yield. The resulting glycosyl donor was used in the synthesis of tetrasaccharide asialo-GM_1.

Key words: *aglycon transfer, asialo-GM_1, galactosamine, 4-nitrophenyl thiogalactosides, phenyl thiogalactosides*

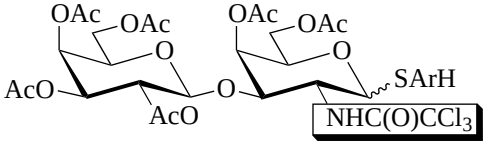
INTRODUCTION

Disaccharide β-*D*-Gal-(1 ⟶ 3)-*D*-GalNAc is a structural block of many natural glycoconjugates.[2] In particular, this block is a fragment of the structures of the group A specific oligosaccharides and of glycolipids of globo and ganglio series when being linked through α- and β-glycoside bonds, respectively. In the majority of previous studies devoted to the obtaining of various oligosaccharides bearing chains of the mentioned types [1–3], the synthetic block on the basis of β-*D*-Gal-(1 ⟶ 3)-*D*-GalNAc was not used; instead, galactosamination followed by glycosylation with various oligosaccharides with the galactose residue on the reducing end was used.

In this work, we consider a possibility of a preparative synthesis of the selectively protected thioglycoside α- and β-glycosyl donors (**I**) and (**II**) with the β-*D*-Gal-(1 ⟶ 3)-*D*-GalNAc backbone for their subsequent use in the synthesis of oligosaccharide chains of natural glycoconjugates. The type (**I**) disaccharide has a nonparticipating azido group in position 2 of galactosamine residue, which allows its use as an α-glycosyl donor. The type (**II**) glycosyl donor bearing 2-participating group necessary for the efficient β-glycosylation can be obtained from (**I**) by the reduction of the azido group and the subsequent acylation of the resulting amine.



(I)

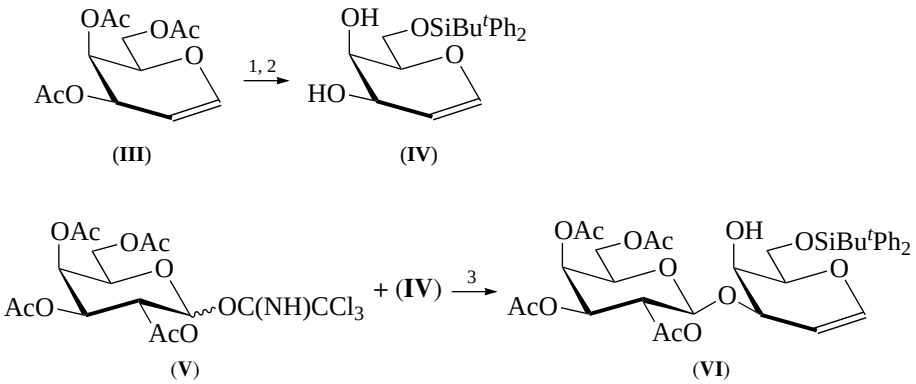


(II)

[1] Please send correspondence to phone/fax: +7 (095) 135-8784; e-mail: nen@ioc.ac.ru.

[2] Abbreviations: All, allyl; Bn, benzyl; CSA, (±)-camphor-10-sulfonic acid; DMAP, 4-dimethylaminopyridine; NIS, *N*-iodosuccinimide; Np, *p*-nitrophenyl; and Tf, trifluorometanesulfonyl.

1068-1620/02/2805-0419$27.00 © 2002 MAIK "Nauka / Interperiodica"



1, MeONa + MeOH; 2, Bu^{t}Ph$_2$SiCl, Et$_3$N, DMF; 3, $BF_3 \cdot Et_2O$, CH_2Cl_2.

Scheme 1.

RESULTS AND DISCUSSION

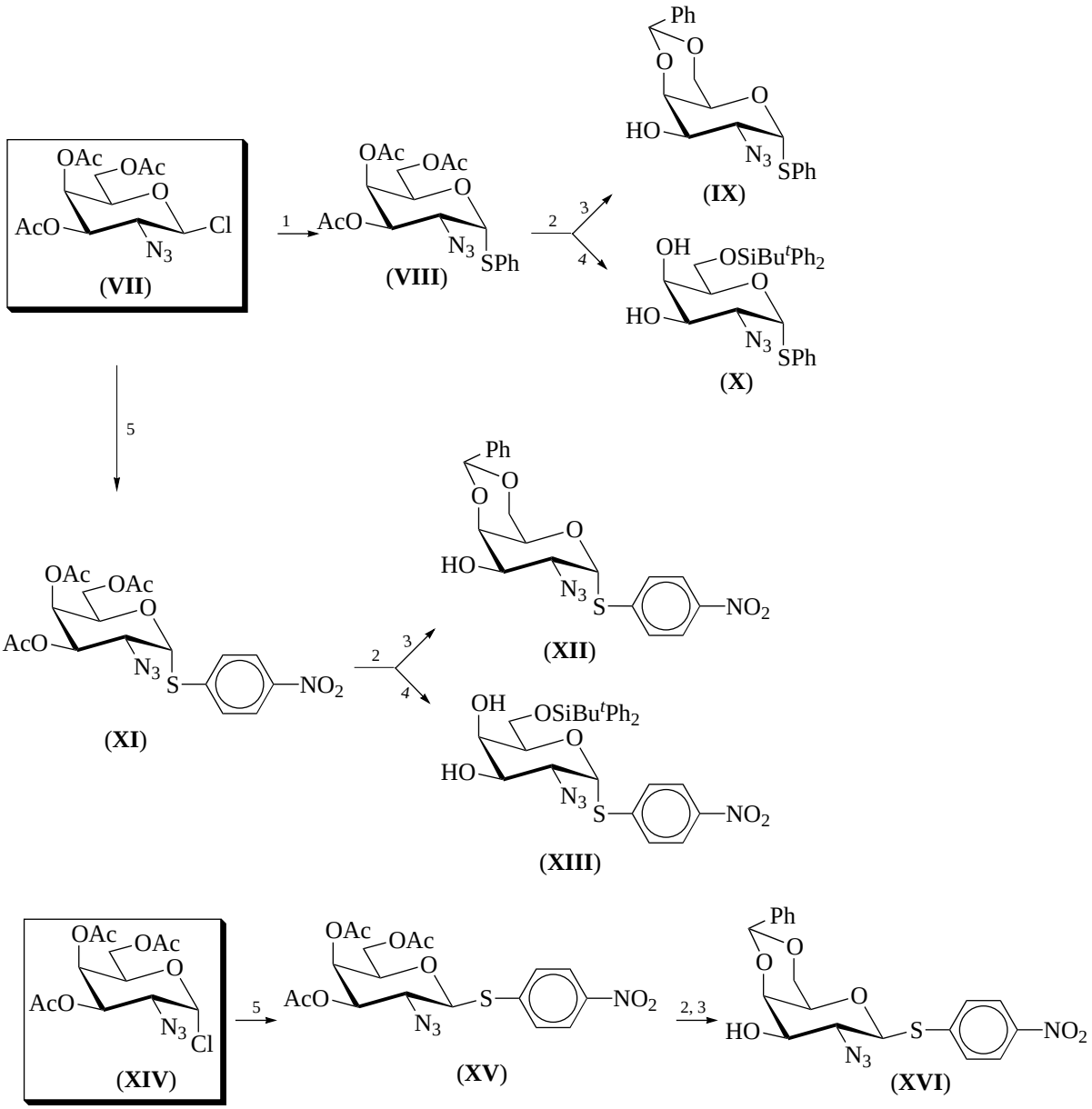
At present, the most useful and often applied preparative method for the synthesis of *D*-galactosamine derivatives is based on the reaction of azidonitration of galactal or its derivatives [4]. Two variants of the use of this method for the obtaining of (1–3)-linked galactosylgalactosamine are possible. The first of them is based on the azidonitration of galactal and the subsequent galactosylation of the azido derivative, and the second, on the azidonitration of galactosylgalactal [5]. The efficiency of the use of the second approach particularly depends on the yield in which the stage of obtaining of the target derivative of galactosylgalactal proceeds.

In the synthesis of galactosylgalactal, we applied 3,4,5-tri-*O*-acetyl-*D*-galactal (**III**) as the starting compound. Its deacetylation with sodium methylate in methanol and selective silylation at O6 with *tert*-butyldiphenylsilyl chloride led to the known 3,4-diol (**IV**) [6] (yield 80%, Scheme 1). The allyl hydroxyl group at C3 of galactal is known to be particularly active, and the glycosylation of 3,4-diols proceed at O3 with a high regioselectivity. It is also known that, due to the presence of double bond, the glycosylation of glycals is very sensitive to the type of the donor and the promotion conditions used and often proceeds in rather low yields [7]. In our case, the $BF_3 \cdot Et_2O$-catalyzed glycosylation of acceptor (**IV**) with a mixture of α- and β-2,3,4,6-tetra-*O*-acetyl-*D*-galactopyranosyl trichloroacetamidates (**V**) [8] in dichloromethane (Scheme 1) led to the target disaccharide (**VI**) in yield 35%, which does not allow to consider the approach with the use of this disaccharide as preparative. The double bond in the acceptor molecule substantially restricts the possibilities of the further optimization of the disaccharide (**VI**) synthesis. The presence of just (1–3)-bond in the disaccharide (**VI**) molecule unequivocally followed from a comparison of ^{1}H NMR spectra of (**VI**) and its *O*-acetyl derivative, in which the resonance of H4 shifted to low field by 1.35 ppm (δ 4.15 ⟶ 5.50 ppm), whereas the chemical shift value of H3 was practically unchanged. The β-configuration of glycoside bond in (**VI**) was confirmed by the characteristic value of spin-spin coupling constant $J_{1,2}$ 8.3 Hz.

Next, we studied the approach based on the galactosylation of the 2-azido-2-deoxy-*D*-galactose derivatives. As the first group of acceptors, we used phenyl thioglycosides (**IX**) and (**X**), which were obtained by the interaction of azido chloride (**VII**) with thiophenol (Scheme 2).

By the action of sodium thiophenolate in anhydrous THF, β-chloride (**VII**) [4] was converted into the corresponding phenyl α-thioglycoside (**VIII**) in 62% yield; the displacement reaction proceeded stereoselectively with the inversion of configuration, which was confirmed by the characteristic value of spin–spin coupling constant ($J_{1,2}$ = 5.2 Hz) of (**VIII**). The relatively low yield could be explained by the concomitant side reaction of the azido group reduction to amino group, which proceeded under the thiophenol action. The resulting thioglycoside (**VIII**) was deacetylated and converted quantitatively into the benzylidene derivative (**IX**) and, then, into 6-*O*-silylated diol (**X**) in 91% yield.

An attempt of glycosylating monohydroxyderivative (**IX**) with acetobromogalactose (**XVII**) under the conditions of Helferich reaction [activation by $HgBr_2/Hg(CN)_2$ salts] in dry acetonitrile led to the complete degradation of all the reagents without the formation of the glycosylation product (Table 1, experiment 1). The reaction in dichloromethane in the presence of silver triflate (experiment 2) resulted in a complex mixture of substances, which lacked the target glycosylation product and contained phenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-*D*-galactopyranoside (**XIX**) as the major product (yield 24%); the latter is the product of the thiophenyl aglycon transfer from the glycosyl acceptor to the cation formed from the glycosyl donor molecule. The structure of (**XIX**) was elucidated by means of NMR spectroscopy. In particular, the charac-



1, PhSH/NaH, THF; 2, MeONa, MeOH; 3, $PhCH(OMe)_2$, CSA, CH_3CN; 4, Bu^tPh_2SiCl, DMAP, Py; 5, Np-SH, Bu_4NHSO_4, $NaHCO_3$, $EtOAc/H_2O$.

Scheme 2.

teristic spin–spin coupling constant $J_{1,2}$ of 10.5 Hz confirms its β-configuration.

We could presume that the process of aglycon transfer was brought about by the predominant attack of the glycosyl cation formed from bromide (**XVII**) on the sulfur atom in aglycon rather than on hydroxy group at C3 [9]. Probably, azido group at C2 decreases the reactivity of hydroxyl at C3, and this becomes lower than that of the sulfur atom in aglycon.

A similar pattern with the predominance of (**XIX**) rather than the glycosylation products in the reaction mixture was observed when glycosylating acceptor (**IX**) in other solvents, under different temperature conditions, or with the use of other glycosylating agents, including trichloroacetimidate (**V**) in dichloromethane under promotion by $BF_3 \cdot Et_2O$ (Table 1, experiment 3) and fluoride (**XVIII**) in toluene under promotion by $AgOTf/SnCl_2$ (Table 1, experiment 4).

Our result of glycosylation with galactosyl fluoride (**XVIII**) differed from that obtained in [10] where the authors specially claimed that no products of aglycon transfer arise at the glycosylation of thioglycosides by

Table 1. Results of glycosylation reactions

Experiment no.	Reagents	Promoter	Solvent	Temperature, °C	Product	Yield, %
1	(**IX**) + (**XVII**)	$Hg(CN)_2/HgBr_2$	CH_3CN	20	–	–
2	(**IX**) + (**XVII**)	AgOTf	CH_2Cl_2	–40…–30	(**XIX**)	24
3	(**IX**) + (**V**)	$BF_3 \cdot Et_2O$	CH_2Cl_2	–30…–20	(**XIX**)	40*
4	(**IX**) + (**XVIII**)	$AgOTf/SnCl_2$	Toluene	10…15	(**XIX**)	30*
5	(**X**) + (**XVII**)	AgOTf	CH_2Cl_2	–40…–30	(**XXIII**)	48**
6	(**X**) + (**XVII**)	AgOTf	Toluene	–40…–30	(**XXIII**)	56
7	(**X**) + (**V**)	$BF_3 \cdot Et_2O$	CH_2Cl_2	–30…–20	(**XIX**)	30*
8	(**X**) + (**XVIII**)	$AgOTf/SnCl_2$	Toluene	0…10	(**XIX**)	20*
9	(**XVI**) + (**XVII**)	AgOTf	CH_2Cl_2	–30…–20	(**XX**)	57
10	(**XII**) + (**XVII**)	AgOTf	CH_2Cl_2	–30…–20	(**XXI**)	48
11	(**XIII**) + (**XVII**)	AgOTf	Toluene	–30…–20	(**XXIV**)	37

* An approximate estimate of yield by TLC data.

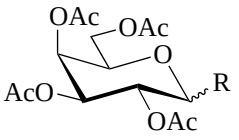
** Incomplete acceptor conversion; yield is calculated from the reacted acceptor.

glycosyl fluorides. The transfer of thiophenyl aglycon was previously observed when using 4,6-*O*-isopropylidene-*N*-trichloroacetylated derivatives of galactosamine; and it was shown [11] that the transfer process is characteristic of just glycosyl acceptors with *galacto*- rather than *gluco*-configuration.

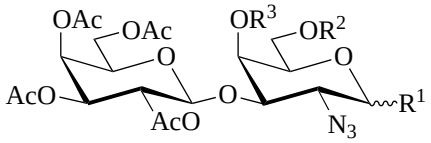
We could hope that the reactivity of hydroxy group at C3 would be higher in the case of diol (**X**) in comparison with monohydroxy derivative (**IX**); for example, it would be due to the absence of conformational rigidity provided with the fused dioxane ring in the benzylidene derivative (**IX**). In this case, the use of the more reactive acceptor (**X**) might help decrease the yield of the transfer product and provide for efficient glycosylation.

However, the glycosylation of diol (**X**) with acetobromogalactose (**XVII**) (Table 1, experiments 5, 6) resulted in the formation of one disaccharide product, namely β-(1–4)-linked (**XXIII**), which is a derivative of the structural unit of isoganglioligosaccharide chains. The presence of just (1–4)-bond in (**XXIII**) unequivocally followed from a comparison of the ^1H NMR spectra of disaccharide (**XXIII**) and its *O*-acetyl derivative (the spectrum not shown). The resonance of H3 is shifted to a low field by 1.1 ppm (δ 3.94 ⟶ 4.04 ppm) when going from (**XXIII**) to its *O*-acetyl derivative, whereas the chemical shift of H4 was practically unchanged. The (1–4)-linking was also confirmed by a low-field signal from C4 (77.5 ppm) of the galactosamine residue in the ^{13}C NMR spectrum of disaccharide (**XXIII**) (Table 3).

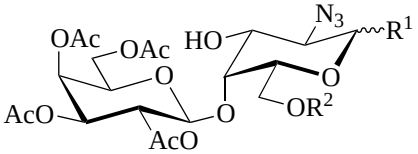
The variation of temperature conditions of the reaction (from –30 to –10°C) and the use of toluene as the solvent led only to changes in the conversion degree of the starting acceptor (**X**) and in the increased yield of the isomeric product (**XXIII**) rather than to the formation of the target product with the β-(1–3)-bond. At the same time, the use of the mixture of galactosyl trichloroacetimidates (**V**) and galactosyl fluoride (**XVIII**) as glycosylating agents (Table 1, experiments 7, 8) led only to the aglycon transfer product (**XIX**). These results were difficult to predict, because the equatorial hydroxy group at C3 is usually more reactive in the galactosamine derivatives than the axial hydroxy group at C4.



	R
(**V**)	α/β-OC(NH)CCl_3
(**XVII**)	α-Br
(**XVIII**)	α-F
(**XIX**)	β-SPh



	R^1	R^2	R^3
(**XX**)	β-$SC_6H_4NO_2$	–PhCH–	
(**XXI**)	α-$SC_6H_4NO_2$	–PhCH–	
(**XXII**)	β-$SC_6H_4NO_2$	Ac	Ac



	R^1	R^2
(**XXIII**)	α-SPh	TBDPS
(**XXIV**)	α-$SC_6H_4NO_2$	TBDPS

Table 2. Parameters of ^{1}H NMR spectra of (**IV**), (**VI**), (**IX**), (**X**), (**XII**), (**XIII**), (**XVI**), (**XX**)–(**XXVI**), and (**XXVIII**) ($CDCl_3$; δ, ppm; *J*, Hz)

Compound	Residue	H1	H2	H3	H4	H5	$H6_a$ | $H6_b$	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6a}$	$J_{5,6b}$	$J_{6a,6b}$
(**IV**)	*	6.37	4.73	4.39	4.15	3.94	3.90–4.08	6.2		4.6		7.7	7.8	11.7
(**VI**)	*	6.38	4.58	4.46	4.17	4.00	3.90–4.05	6.3		3.6				
	Gal	4.65	5.22	5.05	5.42	3.95	4.10–4.20	8.7	10.8	3.4				
(**IX**)	GalN	5.78	3.90–4.30					5.5						
(**X**)	GalN	5.72	4.28	3.92	4.27	4.43	4.02	5.4	10.4	2.9	0.9	4.5	4.7	11.0
(**XII**)**	GalN	5.87	4.30	4.11	4.28	3.92	3.98–4.11	5.2		2.4		9.3	10.0	
(**XIII**)	GalN	5.90	4.31	3.87	4.23	4.20	3.95	5.5	10.3	3.2		3.2	4.3	
(**XVI**)***	GalN	4.74	3.95	3.92	4.51	3.93	4.38	8.9		4.2				12.4
(**XX**)	GalN	4.58	3.85	3.57	4.34	4.37	3.55 | 4.05	9.9	10.0	2.9				
	Gal	4.78	5.24	5.02	5.38	3.92	4.15	7.9	10.3	3.4		6.6	6.7	11.4
(**XXI**)	GalN	6.06	4.68	3.95	4.49	4.05–4.32		5.4	10.7	3.1				
	Gal	4.88	5.36	5.10	5.47	4.02	4.05–4.32	7.9	10.4	3.5		6.4	6.5	
(**XXII**)	GalN	4.58	3.70	3.67	5.42	3.87	4.09 | 4.11	9.2	11.0	3.6		7.4	8.1	
	Gal	4.70	5.15	4.97	5.34	3.90	3.98–4.22	7.8	10.8	3.1		6.6	7.3	
(**XXIII**)	GalN	5.67	4.03	3.94	4.09	4.53	3.98	5.3	10.6	2.6		5.7	5.9	
	Gal	4.78	5.19	5.04	5.34	3.78	3.71 | 3.96	7.9	10.4	3.4		6.5	6.9	10.9
(**XXIV**)	GalN	5.86	4.05	3.88	3.99	4.31	3.84–3.96	5.4	10.4	2.3	1.5	6.5	6.7	
	Gal	4.68	5.15	3.98	5.28	3.64	3.64 | 3.81	7.8	10.3	3.4		6.1	6.7	10.4
(**XXV**)	GalN	4.94	4.20	5.30	5.40	3.96	4.10–4.24	10.3	10.8	2.8		6.4	6.6	11.7
(**XXVI**)	GalN	5.26	3.83	4.42	5.48	3.88	4.05–4.20	10.1	11.7	1.6				
	Gal	4.65	5.07	4.89	5.23	3.85	4.05–4.20	7.5	10.5	3.0				
(**XXVIII**)	Glc	4.46	3.45	3.60	4.03	3.42	3.45 | 3.67	7.4	9.6	10.2	3.3			
	Gal	4.48	3.62	3.45	4.08	3.40	3.70–3.86	7.8	8.8	2.6				
	GalN	5.10	3.86	4.27	5.45	3.82	4.18–4.29	8.3		3.1				
	Gal	4.55	5.08	4.90	5.37	3.87	4.05 | 4.25	7.8	10.6	3.4				

Other signals: C*H*-Ph 5.58–5.78; S*Ph* 7.20–7.60; S*Ph*-NO_2 7.50–8.15; C*H*=CH_2 5.9–6.1; C*H*=CH_2 5.3–5.5; SPhN*H*$COCl_3$ 8.4; N*H*$COCl_3$ 6.8 ($J_{NH,2}$ 10 Hz).

* Galactal residue. ** The spectrum was measured in acetone-d_6. *** The spectrum was measured in $CDCl_3$ + ~10 vol % of acetone-d_6.

To avoid the undesired process of the aglycon transfer, we tried to use 4-nitrophenyl analogues (**XII**), (**XIII**), and (**XVI**) instead of the phenyl thioglycosides. We might expect that the introduction of electron-withdrawing nitro group into aglycon could substantially decrease the nucleophilicity of its sulfur atom and, thereby, would inhibit the aglycon transfer process [12].

The 4-nitrophenyl thioglycoside acceptors were obtained from chlorides (**VII**) and (**XIV**) [4] (Scheme 1) according to the procedure [13]. Under the conditions of phase-transfer catalysis in the two-phase system ethyl acetate–1 M Na_2CO_3, chlorides (**VII**) and (**XIV**) reacted with *p*-nitrophenol with the formation of the corresponding glycosides (**XI**) and (**XV**) and the complete inversion of configuration of the anomeric center, which was confirmed by the characteristic spin-spin coupling constants $J_{1,2}$ 5.4 and 10 Hz in the ^{1}H NMR spectra of (**XI**) and (**XV**), respectively (Table 2).

4-Nitrophenyl thioglycosides (**XI**) and (**XV**) were deacetylated and converted into benzylidene derivatives (**XII**) and (**XVI**) in the total yields of 72 and 66%, respectively. In addition, 6-*O*-silyl derivative (**XIII**) was obtained from (**XI**) in total yield of 90% (Scheme 2).

The target β-(1–3)-linked disaccharide (**XX**) was obtained by the glycosylation of *p*-nitrophenyl β-thioglycoside (**XVI**) with acetobromogalactose (**XVII**) in dichloromethane in the presence of silver triflate in yield of 57% (Table 1, experiment 9). The β-configuration of galactose residue was confirmed by the characteristic value of spin–spin coupling constant ($J_{1,2}$ 7.9 Hz) in the ^{1}H NMR spectrum of (**XX**) (Table 2). The presence of (1–3)-glycoside bond was confirmed by the low-field chemical shift of C3 in the galactosamine res-

Table 3. Parameters of ^{13}C NMR spectra of (**IV**), (**VI**), (**IX**), (**X**), (**XII**), (**XIII**), (**XVI**), (**XX**)–(**XXVI**), and (**XXVIII**) ($CDCl_3$; δ, ppm)

Compound	Residue	C1	C2	C3	C4	C5	C6
(**IV**)	*	144.4	103.3	64.5	65.6	76.4	63.6
(**VI**)	*	145.5	100.3	68.8	63.8	76.6	62.4
	Gal	98.1	71.0	70.7	66.9	73.3	61.1
(**IX**)	GalN	87.1	61.0	68.9	74.9	69.2	63.5
(**X**)	GalN	87.5	61.2	70.3	69.9	70.4	64.2
(**XII**)**	GalN	85.5	60.5	68.8	75.2	69.4	64.4
(**XIII**)	GalN	85.5	60.8	70.7	69.8	70.8	64.4
(**XVI**)***	GalN	84.6	61.9	70.2	74.4	70.2	69.1
(**XX**)	GalN	85.1	60.1	80.3	74.7	70.2	69.0
	Gal	102.3	68.8	71.0	67.1	71.0	61.5
(**XXI**)	GalN	85.8	58.6	77.2	75.4	69.1	68.7
	Gal	102.3	67.1	71.2	64.7	71.2	61.5
(**XXII**)	GalN	85.6	61.6	79.3	68.1	75.6	62.7
	Gal	101.4	68.1	70.6	66.7	70.9	61.0
(**XXIII**)	GalN	87.6	61.9	70.6	77.5	72.1	63.6
	Gal	102.0	69.6	70.8	66.6	70.4	60.7
(**XXIV**)	GalN	85.9	61.8	71.0	77.8	73.2	64.1
	Gal	102.5	69.8	71.0	66.8	70.7	61.0
(**XXV**)	GalN	86.5	51.3	70.6	66.9	74.8	61.7
(**XXVI**)	GalN	85.0	53.6	74.8	68.9	75.5	62.6
	Gal	100.6	68.9	70.8	66.8	71.0	61.1
(**XXVIII**)	Glc	102.7	81.7	82.9	76.1	75.0	68.9
	Gal	102.3	80.5	81.5	72.5	73.2	68.3
	GalN	99.3	55.4	73.5	69.0	71.2	61.0
	Gal	100.5	68.6	70.5	66.8	70.8	62.0

Other signals: *C*H-Ph 100.4–101.2; S*Ph* 127.2–132.3; S*Ph*-NO_2 123.8–141.5; *C*$OCCl_3$ 159.5–161.6.
For footnotes *,**, and ***, see Table 2.

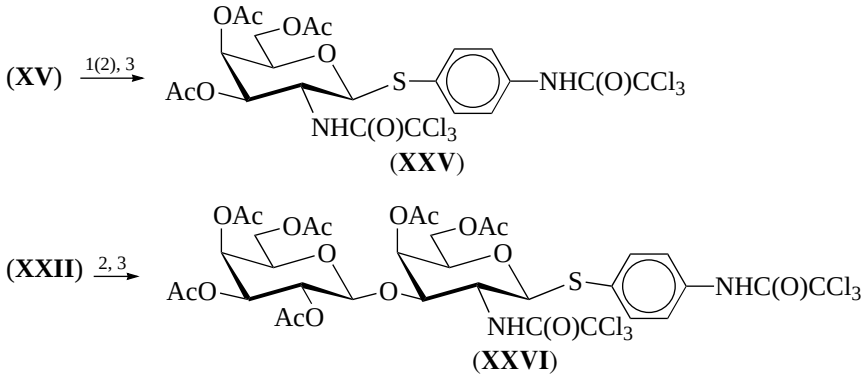
idue (80.3 ppm) in the ^{13}C NMR spectrum of (**XX**) (Table 3). The use of toluene instead of dichloromethane resulted in a substantial reduction of the glycosylation product yield.

The galactosylation of *p*-nitrophenyl α-thioglycoside (**XII**) with bromide (**XVII**) (experiment 10) led to 48% yield of the corresponding disaccharide (**XXI**). The β-configuration of its galactose residue was deduced from the characteristic spin–spin coupling constant ($J_{1,2}$ 7.9 Hz) in the ^1H NMR spectrum of (**XXI**) (Table 2). The presence of (1–3)-glycoside bond was confirmed by the low-field chemical shift of C3 in the galactosamine residue (77.2 ppm) in the ^{13}C NMR spectrum of (**XXI**) (Table 3).

The regioselectivity of the glycosylation at O3 and O4 was comparatively studied in the cases of nitrophenyl thioglycosides of 2-deoxy-2-azidogalactose and phenyl thioglycoside (**X**). To this end, diol (**XIII**), an analogue of (**X**), was galactosylated with bromide (**XVII**) in toluene under the conditions similar to those used for (**X**). Only the isomeric product of β-(1–4)-linking (**XXIV**) was obtained in this case in yield of 37% (Table 1, experiment 11). The characteristic $J_{1,2}$ value (7.8 Hz) in the ^1H NMR spectrum (Table 2) confirmed the β-configuration of galactose residue in (**XXIV**), whereas (1–4)-bond followed from the low-field position of the C4 resonance of galactosamine residue (77.7 ppm) in its ^{13}C NMR spectrum (Table 3).

Therefore, among the studied ways of synthesis of the type (**I**) disaccharides, the scheme based on the reaction (**XVI**) + (**XVII**) (Table 1, experiment 9) seems to be optimal. After the debenzylidenation of disaccharide (**XX**) and subsequent acetylation, the complete acetate (**XXII**) was obtained in the quantitative yield. This can be used as the α-glycosyl donor for, e.g., obtaining the structures related to group-A-specific oligosaccharides.

Next, for the obtaining of the type (**II**) β-glycosyl donor, it was necessary to convert the azido group in disaccharide (**XXII**) into the participating amide group.



1, $SnCl_2$, EtOH; 2, Zn, HOAc; 3, CCl_3COCl, Et_3N, CH_2Cl_2.

Scheme 3.

The nitro group of the aglycon should also be reduced in order to increase the nucleophilicity of the sulfur atom and, in this manner, enhance the reactivity of the type (**II**) glycosyl donor. With this end in view, we studied various methods of simultaneous reduction of the aromatic nitro group in aglycon and azido group at C2 in sugar moiety followed by the trichloroacetylation of the two resulting amine groups. The conditions of these reactions were chosen when applying monosaccharide (**XV**) as the substrate (Scheme 3). The presence of a sulfur atom in (**XV**) and (**XXII**) precludes the use of catalytic hydrogenation for the reduction of the aromatic nitro and aliphatic azido groups. Of the other available approaches to the reduction of these groups, we chose and studied the following systems: a saturated solution of hydrogen sulfide in aqueous pyridine [14], a solution of sodium sulfide in methanol [15], a suspension of nickel boride in a borate buffer [16], tin(II) chloride [12, 17], tin(II) chloride/sodium borohydride [18], and zinc in acetic acid [19].

According to TLC data, the reduction by hydrogen or sodium sulfide, as well as with a nickel boride suspension resulted in complex mixtures, which were not studied further. The use of tin(II) chloride and the subsequent trichloroacetylation of intermediate diamine resulted in the target product (**XXV**) in 44% yield. The reduction of the azido and nitro groups to amines was confirmed by the presence in the ^{1}H NMR spectrum of amide (**XXV**) of the resonances of NH of aliphatic (6.8 ppm, d, $J_{NH,2}$ 10 Hz) and aromatic (8.4 ppm, s) amide groups (Table 2). The use of the tin(II) chloride/sodium borohydride system did not result in any substantial changes in the reaction pattern (TLC data). The most successful was the reduction by zinc in acetic acid: in this case, the yield of the target product was 62%.

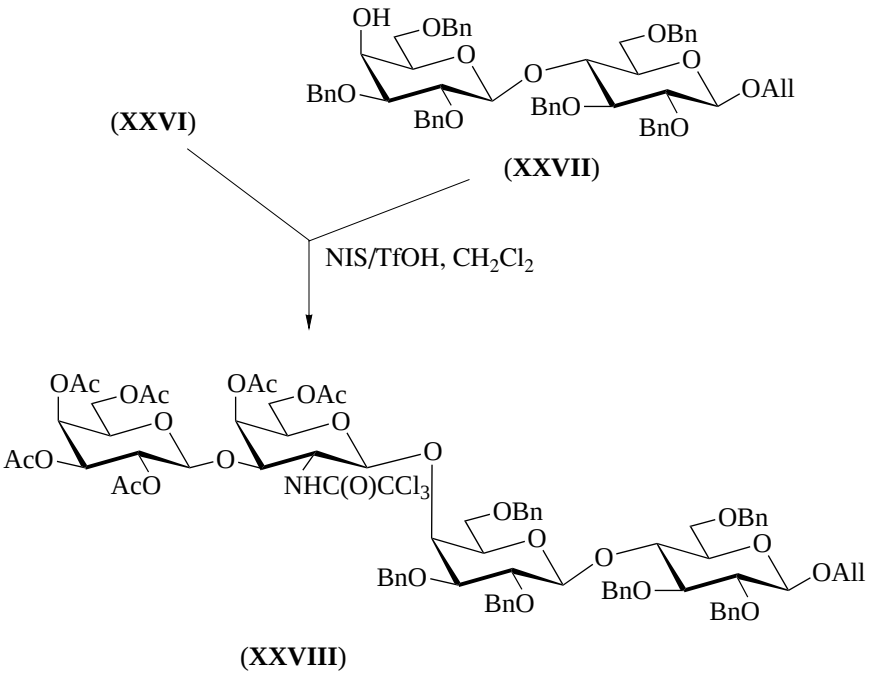
The required β-glycosyl donor (**XXVI**) was obtained in a total yield of 61% when using the reduction of disaccharide (**XXII**) with zinc in acetic acid, followed by *N*-acylation (Scheme 3). The reduction of the azide and nitro groups to amines was confirmed by the presence in the ^{1}H NMR spectrum of disaccharide (**XXVI**) of the resonances of NH of aliphatic (6.8 ppm, d, $J_{NH,2}$ 10 Hz) and aromatic (8.4 ppm, s) amide groups (Table 2).

An efficient use of the disaccharide donor (**XXVI**) was demonstrated by the example of glycosylation of the known [20] acceptor (**XXVII**): an asialo-GM_1 tetrasaccharide derivative (**XXVIII**), was obtained in 67% yield (Scheme 4). The β-configuration of galactosamine residue in (**XXVIII**) was confirmed by a characteristic spin–spin coupling constant ($J_{1,2}$ = 8.3 Hz) for H1 of GalN residue in ^{1}H NMR spectrum (Table 2). The presence of (1–3)-glycoside bond between the galactosamine residue and the galactose residue in the acceptor lactose block followed from the low-field shift of the C3 resonance (81.5 ppm) of the galactose residue in the ^{13}C NMR spectrum of tetrasaccharide (**XXVIII**) (Table 3).

Thus, a preparative method of the synthesis of α- and β-glycosyl donors on the basis of disaccharide β-*D*-Gal-(1 ⟶ 3)-*D*-GalNAc was developed. The efficiency of using the β-glycosyl donor in the preparation of oligosaccharide chains of natural glycoconjugates was demonstrated by the example of the synthesis of the carbohydrate chain of the asialo-GM_1 ganglioside derivative.

EXPERIMENTAL

The purification procedures for solvents and reagents and the measurement conditions of the NMR spectra and physicochemical constants are given in [21]. The ^{1}H and ^{13}C NMR spectra were registered on a Bruker DRX-500 or a Bruker AM-300 instrument at 25°C. The optical rotation was measured on a digital polarimeter Jasco DIP-360 at 18–25°C. For TLC, the precoated plates with Kieselgel-60 (Merck) were used; the substances were detected by spraying with 10 vol %



Scheme 4.

of orthophosphoric acid in ethanol or, for amines, by a ninhydrin solution (3 g/l in a 30 : 1 butanol–acetic acid mixture, followed by heating at ~150°C. For column chromatography, Silica gel 60 (0.063–0.2 mm, Fluka) or Silasorb 600 (20 μm, Chemapol) was used.

1,5-Anhydro-6-*O*-(*tert*-butyl)diphenylsilyl-2-deoxy-*D*-*lyxo*-hex-1-enitol (IV). DMAP (5 mg) was added to a stirred and cooled to 0°C solution of galactal (**III**) [4] (420 mg, 2.9 mmol), Bu^tPh_2SiCl (Fluka, 736 μl, 2.9 mmol), and triethylamine (808 μl, 5.8 mmol) in dry DMF. The reaction mixture was stirred for 16 h at 20°C, diluted with ethyl acetate (150 ml), washed with water (200 ml), and evaporated. A flash chromatography of the residue (10 : 1 dichloromethane–diethyl ether) afforded diol (**IV**); yield 883 mg (80%), white foam; R_f 0.52 (10 : 1 dichloromethane–diethyl ether); $[\alpha]_D$ +50.9° (*c* 2.2, $CHCl_3$).

1,5-Anhydro-6-*O*-(*tert*-butyl)diphenylsilyl-2-deoxy-3-*O*-2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl)-*D*-*lyxo*-hex-1-enitol (VI). A solution of glycosyl acceptor (**IV**) (150 mg, 0.39 mmol) and trichloroacetimidate (**V**) [8] (202 mg, (0.41 mmol) in anhydrous dichloromethane (3 ml) was stirred under argon with the preliminarily heated molecular sieves MS-4 Å (200 mg) for 1 h at 20°C. The reaction mixture was then cooled to –80°C, treated with $BF_3 \cdot Et_2O$ (3 μl, and, after 30 min, with a saturated solution of $NaHCO_3$ (2 ml). The mixture was diluted with dichloromethane (50 ml) and washed with a solution of $NaHCO_3$ (100 ml). The organic phase was evaporated, chromatographed in a dichloromethane–diethyl ether gradient (from 20 : 1 to 10 : 1), and disaccharide (**VI**) was isolated; white foam; yield 97 mg (35%); R_f 0.31 (10 : 1 dichloromethane–diethyl ether); $[\alpha]_D$ +57.5° (*c* 2, $CHCl_3$).

Phenyl 2-azido-3,4,6-tri-*O*-acetyl-2-deoxy-1-thio-α-*D*-galactopyranoside (VIII). Thiophenol (968 μl, 23.74 mmol) was slowly added dropwise to a intensively stirred cooled to –10°C suspension of sodium hydride (343 mg, 8.58 mmol of 60% suspension in an oil) in dry THF (15 ml) under argon. After a gas evolution ceased, the reaction mixture was a white suspension. It was heated to +5°C, and (**VII**) [4] (1 g, 2.86 mmol) was then added to it. The mixture was stirred for 16 h at this temperature, diluted with dichloromethane (200 ml), and washed with a saturated $NaHCO_3$ solution (2 × 250 ml). The organic phase was evaporated and filtered through a silica gel layer. The unreacted thiophenol was eluted with dichloromethane, and the reaction products, with a 10 : 1 dichloromethane–diethyl ether mixture. Thioglycoside (**VIII**) was obtained as white foam; yield 750 mg (62%); R_f 0.62 (10 : 1 dichloromethane–diethyl ether); it was further used without any additional purification.

Phenyl 2-azido-4,6-*O*-benzylidene-2-deoxy-1-thio-α-*D*-galactopyranoside (IX). A solution of (**VIII**) (180 mg, 0.46 mmol) in absolute methanol (4 ml) was deacetylated with 0.1 ml of 1 M MeONa solution in methanol. After 20 min, the solution was neutralized with cation-exchange resin KU-2 (H^+), the resin was filtered off, washed with methanol, and filtrate was evaporated. The resulting crystalline deacetylated product was coevaporated with toluene (to remove methanol), dried in a vacuum of an oil pump,

and used in the reaction of benzylidenation with α,α-dimethoxytoluene (105 μl) and CSA (5 mg) in dry acetonitrile (5 ml) without additional treatment. The reaction mixture was kept for 16 h at 20°C, neutralized with triethylamine, and evaporated. After a chromatography (3 : 1 toluene–ethyl acetate mixture), (**IX**) was obtained as a white foam; yield 170 mg (quantitative); R_f 0.54 (3 : 1 toluene–ethyl acetate); $[\alpha]_D$ +134.9° (*c* 0.5, $CHCl_3$).

Phenyl 2-azido-5-*O*-(*tert*-butyl)diphenylsilyl-2-deoxy-1-thio-α-*D*-galactopyranoside (X). A solution of (**VIII**) (750 mg, 1.92 mmol) in absolute methanol (10 ml) was deacetylated with 0.2 ml of 1 M solution of MeONa in methanol and then treated as described above. Without any additional treatment, the resulting product of deacetylation was dissolved in dry pyridine (10 ml) and treated with Bu^tPh_2SiCl (748 μl, 2.9 mmol, Fluka) and then with DMAP (5 mg). The reaction mixture was kept for 18 h at 20°C, evaporated, and coevaporated several times with toluene to remove pyridine traces (odor). After the flash chromatography (10 : 1 dichloromethane–diethyl ether), diol (**X**) was obtained as a white foam; yield 867 mg (91%); R_f 0.50 (3 : 1 toluene–ethyl acetate); $[\alpha]_D$ +127.8° (*c* 2, $CHCl_3$).

4-Nitrophenyl 2-azido-4,6-*O*-benzylidene-2-deoxy-1-thio-α-*D*-galactopyranoside (XII). Two ml of 1 M Na_2CO_3 were added to a solution of (**VII**) (100 mg, 0.29 mmol), *p*-nitrothiophenol (133 mg, 0.86 mmol), and Bu_4NHSO_4 (97 mg, 0.29 mmol) in ethyl acetate (2 ml). The reaction mixture was stirred at 40°C for 5 h (until the disappearance of the starting chloride monitored by TLC in a 10 : 1 dichloromethane–diethyl ether mixture). The reaction mixture was then diluted with ethyl acetate (100 ml), washed with a saturated solution of $NaHCO_3$ (2 × 100 ml), filtered through a layer of cotton wool, and evaporated. The residue was filtered through a layer of silica gel, unreacted *p*-nitrophenol was eluted with 10 : 1 toluene–ethyl acetate mixture, and the product with 3 : 1 toluene–ethyl acetate mixture. Crude glycoside (**XI**) (123 mg) was obtained; it was deacetylated and treated as described above for (**IX**). The resulting triol was benzylidenated without any additional purification with α,α-dimethoxytoluene (60 μl) and CSA (5mg) in dry acetonitrile (3 ml), and the reaction mixture was treated as described above for (**IX**). After chromatography (3 : 1 toluene–ethyl acetate), (**XII**) was obtained; white foam; yield 88 mg (72%); R_f 0.44 (10 : 1 dichloromethane–diethyl ether); $[\alpha]_D$ +134.9° (*c* 2, $CHCl_3$).

4-Nitrophenyl 2-azido-6-*O*-(*tert*-butyl)diphenylsilyl-2-deoxy-1-thio-α-*D*-galactopyranoside (XIII). Thioglycoside (**XI**) (50 mg, 0.15 mmol) in absolute methanol (2 ml) was deacetylated with 0.05 ml of 1 M solution of MeONa in methanol and then, without additional purification, silylated in 2 ml of dry pyridine with Bu^tPh_2SiCl (62 μl, 0.22 mmol) and DMAP (1 mg) for 16 h at 20°C as described above. Diol (**XIII**) was isolated by flash chromatography (10 : 1 dichloromethane–diethyl ether); white foam; yield 76 mg (90%); R_f 0.37 (3 : 1 toluene–ethyl acetate); $[\alpha]_D$ +149.8° (*c* 2, $CHCl_3$).

4-Nitrophenyl 2-azido-4,6-*O*-benzylidene-2-deoxy-1-thio-β-*D*-galactopyranoside (XVI). Under the conditions similar to those used for the synthesis of (**XII**), crude (**XIV**) (105 mg) was obtained from (**XIV**) [4] (86 mg, 0.25 mmol), *p*-nitrothiophenol (114 mg, 0.74 mmol), and Bu_4NHSO_4 (70 mg, 0.25 mmol) in 2 ml of ethyl acetate and 2 ml of 1 M Na_2CO_3. (**XV**) was then deacetylated and benzylidenated as described above to give (**XVI**); white foam; yield 70 mg (66%); R_f 0.37 (10 : 1 dichloromethane–diethyl ether); $[\alpha]_D$ –24.2° (*c* 2, $CHCl_3$).

General glycosylation procedure for obtaining disaccharides (XX), (XXI), (XXIII), and (XXIV). A mixture of acetobromogalactose and glycosyl acceptor was trice coevaporated with toluene to remove water traces, dissolved in freshly distilled dry dichloromethane or toluene (see Table 1) under argon, and transferred by argon pressure to the reaction flask containing the preliminarily heated molecular sieves MS-4 Å. The reaction mixture was stirred for 2–14 h at 20°C, cooled to –40°C, and treated with silver triflate. The glycosylation was carried out within the temperature range from –40 to –20°C in dependence on the type of glycosyl donor and glycosyl acceptor (see Table 1), monitoring the reaction course by TLC. When glycosyl acceptor was completely consumed, a saturated solution of sodium bicarbonate (1–2 ml) and 2 M sodium thiosulfate (1–2 ml) were added, the reaction mixture was heated to 20°C, diluted with dichloromethane, and filtered through a layer of Celite. The filtrate was washed with a saturated solution of sodium bicarbonate, the aqueous phase was extracted with dichloromethane, and the organic layers were combined and evaporated. The reaction products were isolated by column chromatography.

4-Nitrophenyl 2-azido-4,6-*O*-benzylidene-2-deoxy-3-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl)-1-thio-β-*D*-galactopyranoside (XX). The reaction of glycosyl acceptor (**XVI**) (200 mg, 0.47 mmol) and acetobromogalactose (**XVII**) (230 mg, 0.56 mmol) was promoted by silver triflate (173 mg, 0.67 mmol). Upon completion of the reaction (2.5 h), the mixture was subjected to the standard treatment and chromatography in 20 : 1 to 10 : 1 gradient of dichloromethane in diethyl ether to give (**XX**); white foam; yield 201 mg (57%), R_f 0.33 (10 : 1 dichloromethane–diethyl ether); $[\alpha]_D$ –48.0° (*c* 2, $CHCl_3$).

4-Nitrophenyl 2-azido-4,6-*O*-benzylidene-2-deoxy-3-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl)-1-thio-α-*D*-galactopyranoside (XXI). The reaction of glycosyl acceptor (**XII**) (100 mg, 0.23 mmol) and acetobromogalactose (**XVII**) (115 mg, 0.28 mmol) was promoted by silver triflate (86 mg, 0.34 mmol). Upon completion of the reaction (2 h), the mixture was subjected to the standard treatment and

chromatography in 20 : 1 to 10 : 1 gradient of dichloromethane in diethyl ether to give (**XXI**); white foam; yield 85 mg (48%), R_f 0.57 (10 : 1 dichloromethane–diethyl ether); $[\alpha]_D$ +57.9° (*c* 0.5, $CHCl_3$).

Phenyl 2-azido-6-*O*-(*tert*-butyl)diphenylsilyl-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl)-1-thio-α-*D*-galactopyranoside (XXIII). The reaction of glycosyl acceptor (**X**) (150 mg, 0.3 mmol) and acetobromogalactose (**XVII**) (140 mg, 0.34 mmol) was promoted by silver triflate (105 mg, 0.4 mmol). Upon completion of the reaction (1.5 h), the mixture was subjected to the standard treatment and chromatography in 3 : 1 toluene–ethyl acetate system to give (**XXIII**); white foam; yield 138 mg (56%), R_f 0.40 (3 : 1 toluene–ethyl acetate); $[\alpha]_D$ +99.8° (*c* 2, $CHCl_3$).

4-Nitrophenyl 2-azido-6-*O*-(*tert*-butyl)diphenylsilyl-2-deoxy-3-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl)-1-thio-α-*D*-galactopyranoside (XXIV). The reaction of glycosyl acceptor (**XIII**) (76 mg, 0.13 mmol) and acetobromogalactose (**XVII**) (65 mg, 0.16 mmol) was promoted by silver triflate (49 mg, 0.19 mmol). Upon completion of the reaction (2 h), the mixture was subjected to the standard treatment and chromatography in 7 : 1 to 5 : 1 toluene–ethyl acetate gradient to give (**XXIV**); white foam; yield 44 mg (37%), R_f 0.40 (9 : 4 toluene–ethyl acetate); $[\alpha]_D$ +108.4° (*c* 2, $CHCl_3$).

4-Nitrophenyl 2-azido-4,6-di-*O*-acetyl-2-deoxy-3-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl)-1-thio-β-*D*-galactopyranoside (XXII). A solution of (**XX**) (100 mg, 0.13 mmol) in 90% acetic acid (3 ml) was kept for 3 h at 80°C. The reaction mixture was cooled to 20°C, evaporated, and coevaporated with toluene to remove the acetic acid odor. The residue was dissolved in dry pyridine (2 ml) and treated dropwise with acetic anhydride (1 ml). The reaction mixture was kept for 18 h at 20°C, treated with methanol, evaporated, and many times coevaporated with toluene to remove the pyridine odor. After flash chromatography (5 : 1 dichloromethane–diethyl ether), per-*O*-acetyl derivative (**XXII**) was obtained; white foam; yield 99 mg (100%), R_f 0.38 (5 : 1 dichloromethane–diethyl ether); $[\alpha]_D$ +10.9° (*c* 2, $CHCl_3$).

4-Trichloroacetamidophenyl 2-deoxy-3,4,6-tri-*O*-acetyl-1-thio-2-trichloroacetamido-β-*D*-galactopyranoside (XXV). Method a. Tin(II) chloride dihydrate (463 mg, 2.05 mmol) was gradually added under intensive stirring to a solution of (**XV**) (160 mg, 0.34 mmol) in ethanol preliminarily dried by azeotropic distillation with benzene. The reaction mixture was heated to 40°C, stirred for 2 h at this temperature, diluted with dichloromethane (100 ml), and washed with a saturated solution of soda (100 ml). The organic phase was separated, and the aqueous phase was extracted with dichloromethane (2 × 30 ml). The organic phase and extracts were combined, evaporated, trice coevaporated with toluene, and dried in a vacuum of an oil pump. The residue dissolved in dry dichloromethane (3 ml), and the solution was dropwise treated with trichloroacetic anhydride (380 μl, 2.07 mmol) under stirring on an ice–water bath. After 20 min, methanol (1 ml) was added to the reaction mixture; it was diluted with dichloromethane (100 ml) and washed with a saturated soda solution (100 ml). The aqueous phase was extracted with dichloromethane (2 × 30 ml) and the extracts were combined and evaporated. The residue was separated with column chromatography in 3 : 1 toluene–ethyl acetate system to give (**XXV**); while foam; yield 106 mg (44%); R_f 0.40 (2 : 1 toluene–ethyl acetate).

Method b. A solution of (**XV**) (190 mg, 0.41 mmol) in THF (4 ml) was successively treated under intensive stirring with drops of acetic acid (1.2 ml) and with zinc dust (2.6 g). The reaction mixture was stirred 16 h at 20°C and filtered through Celite. Filtrate was diluted with dichloromethane (75 ml) and washed with a saturated solution of sodium bicarbonate (100 ml) until gas evolution ceased. The aqueous layer was extracted with dichloromethane (2 × 20 ml), and the organic layers were combined and evaporated. The residue was twice coevaporated with toluene, dried in an oil pump vacuum, dissolved in dry dichloromethane (3 ml), and treated with triethylamine (290 μl) and, under stirring on an ice bath and dropwise, with trichloroacetyl chloride (115 μl). After 20 min, methanol (1 ml) was added to the reaction mixture; it was diluted with dichloromethane (70 ml), washed with a saturated solution of sodium bicarbonate (100 ml), and evaporated. (**XXV**) was isolated from the residue by column chromatography in 10 : 1 dichloromethane–diethyl ether system; white foam; yield 177 mg (62%); R_f 0.54 (10 : 1 dichloromethane–diethyl ether); $[\alpha]_D$ –15.5° (*c* 1, $CHCl_3$).

4-Trichloroacetamidophenyl 2-deoxy-4,6-di-*O*-acetyl-3-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl)-1-thio-2-trichloroacetamido-β-*D*-galactopyranoside (XXVI). Acetic acid (0.75 ml) and, gradually, zinc dust (1.7 g) were added under intensive stirring to a solution of (**XXII**) (198 mg, 0.26 mmol) in THF (4 ml). The reaction mixture was stirred overnight at 20°C and filtered through a layer of Celite. The filtrate was diluted with dichloromethane (150 ml) and washed with a saturated soda solution (200 ml) until gas evolution ceased. The aqueous layer was reextracted with dichloromethane (2 × 50 ml), and extracts were combined and evaporated. The residue was twice coevaporated with toluene, dried in an oil pump vacuum, and dissolved in dry dichloromethane (4 ml). Triethylamine (220 μl) and, under stirring on an ice bath and dropwise, trichloroacetyl chloride (88 μl) were added. After 20 min, methanol (1 ml) was added to the reaction mixture; it was diluted with dichloromethane (150 ml), washed with a saturated solution of sodium bicarbonate (200 ml), and evaporated. The aqueous layer was extracted with dichloromethane (2 × 50 ml), and extracts were combined and evaporated. (**XXVI**) was isolated from the residue by column chromatography in

10 : 3 dichloromethane–diethyl ether system; white foam; yield 160 mg (62%); R_f 0.37 (10 : 3 dichloromethane–diethyl ether); $[\alpha]_D$ +11.3° (*c* 2, $CHCl_3$).

Allyl *O*-(2,3,4,6-tetra-*O*-acetyl–β-*D*-galactopyranosyl)-(1–3)-*O*-(4,6-di-*O*-acetyl-2-deoxy-2-trichloroacetamido-β-*D*-galactopyranosyl)-(1–4)-*O*-(2,3,6-tri-*O*-benzyl-β-*D*-galactopyranosyl)-(1–4)- 2,3,6-tri-*O*-benzyl-β-*D*-galactopyranoside (XXVIII). A solution of (**XXVII**) [17] (100 mg, 0.108 mmol) and (**XXVI**) (79 mg, 0.08 mmol) in anhydrous dichloromethane (3 ml) was stirred under argon with the preliminarily heated molecular sieves MS-4 Å (200 mg) for 2 h at 20°C. *N*-Iodosuccinimide (27 mg) was then added, and the mixture was stirred for additional 15 min at 20°C. The reaction mixture was cooled to –30°C, treated with 5% solution of TfOH in dichloromethane (50 μl and, after 30 min, 150 μl), and stirred for 1.5 h at –30 to –20°C. A saturated solution of sodium bicarbonate (1 ml) was added, the mixture was filtered through a Celite layer, and the filtrate was diluted with dichloromethane (100 ml) and washed with $NaHCO_3$ solution (100 ml). The organic phase was evaporated, and the residue was separated by column chromatography in 10 : 1 to 5: 1 gradient of dichloromethane in diethyl ether to give white foam of (**XXVIII**); yield 90 mg (67%); R_f 0.34 (5 : 1 dichloromethane–diethyl ether); $[\alpha]_D$ +10.6° (*c* 2, $CHCl_3$).

ACKNOWLEDGMENTS

This work was supported by Russian Foundation for Basic Research, project nos. 99-03-33047a and 00-03-32815a.

REFERENCES

1. Ito, H., Ishida, H., Waki, H., Ando, S., and Kiso, M., *Glycoconjugate J.*, 1999, vol. 16, pp. 585–596.
2. Ishida, H.-K., Ishida, H., Kiso, M., and Hasegawa, A., *Tetrahedron Asymmetry*, 1994, vol. 5, pp. 2493–2512.
3. Lassaletta, J.M., Carlsson, K., Garegg, P.J., and Schmidt, R.R., *J. Org. Chem.*, 1996, vol. 61, pp. 6873–6880.
4. Lemieux, R.U. and Ratcliffe, R.M., *Can. J. Chem.*, 1979, vol. 57, pp. 1244–1251.
5. Look, G.C., Ichijawa, Y., Shen, G.-J., Cheng, P.-W., and Wong, C.-H., *J. Org. Chem.*, 1993, vol. 58, pp. 4326–4330.
6. Koseki, K., Griffith, D.A., and Danishefsky, S.J., *J. Am. Chem. Soc.*, 1992, vol. 114, pp. 8331–8333.
7. Danishefsky, S.J., Gervay, J., Peterson, J.M., McDonald, F.E., Koseki, K., Griffith, D.A., Oriyama, T., and Marsden, S.P., *J. Am. Chem. Soc.*, 1995, vol. 117, pp. 1940–1953.
8. Schmidt, R.R. and Stumpp, M., *Liebigs Ann. Chem.*, 1983, pp. 1249–1256.
9. Nilsson, S., Lohn, H., and Norberg, T., *Glycoconjugate J.*, 1991, vol. 8, p. 9.
10. Nicolaou, K.C. and Ueno, H., *Preparative Carbohydrate Chemistry*, Hanessian, S., Ed., Marcel Dekker Inc., 1997, pp. 313–338.
11. Belot, F. and Jaquinet, J.-C., *Carbohydr. Res.*, 1996, vol. 290, pp. 79–86.
12. Cao, S., Hernandes-Mateo, F., and Roy, R., *Carbohydr. Chem.*, 1998, vol. 17, pp. 609–631.
13. Kim, J.M. and Roy, R., *Carbohydr. Chem.*, 1997, vol. 16, pp. 1281–1292.
14. Adachi, T., Yoshihisa, Y., and Ichizo, I., *Synthesis*, 1977, pp. 45–46.
15. Belinka, B.A. and Hassner, A., *J. Org. Chem.*, 1979, vol. 44, pp. 4712–4713.
16. Nilsson, U., Ray, A.K., and Magnusson, G., *J. Am. Chem. Soc.*, 1992, vol. 114, pp. 2256–2257.
17. Bellamy, F.D. and Ou, K., *Tetrahedron Lett.*, 1984, vol. 25, pp. 839–842.
18. Satoh, T., Mitsuo, N., Nishiki, M., Inoue, Y., and Ooi, Y., *Chem. Pharm. Bull.*, 1981, vol. 29, pp. 1443–1445.
19. Weygan, D.F., Ziemann, H., and Bestmann, H.J., *Chem. Ber.*, 1958, vol. 91, p. 2524.
20. Youssef, R.H., Silwanis, B.A., El-Sokkary, R.I., Nematalla, A.S., and Nashed, M.A., *Carbohydr. Res.*, 1993, vol. 240, pp. 287–293.
21. Nifant'ev, N.E., Bakinovskii, L.V., Lipkind, G.M., Shashkov, A.S., and Kochetkov, N.K., *Bioorg. Khim.*, 1991, vol. 17, pp. 517–530.