ELSEVIER

Carbohydrate Research 272 (1995) 149–157

CARBOHYDRATE RESEARCH

Stereoselective glycosylation using fully benzylated pyrimidin-2-yl 1-thio-β-D-glycopyranosides

Qian Chen, Fanzuo Kong *

Research Center for Eco-Environmental Sciences, Academia Sinica, P.O. Box 2871, Beijing 100085, China

Received 15 July 1994; accepted 11 November 1994

Abstract

Pyrimidin-2-yl 2,3,4,6-tetra-*O*-benzyl-1-thio-β-D-gluco- (**5**) and -β-D-galacto-pyranoside (**6**), and pyrimidin-2-yl 2,3,4-tri-*O*-benzyl-1-thio-β-D-xylo- (**7**), and -α-D-arabino-pyranoside (**8**) were readily prepared from the corresponding per-*O*-acetylated 1-thioglycopyranosides, which were in turn obtained from the relevant acetobromosugars and 2-mercaptopyrimidine under phase-transfer conditions. Glycosidic coupling reactions using **5** (or **6**, **7**, or **8**) as the donor and methyl 2,4,6-tri-*O*-benzyl-α-D-mannopyranoside as the acceptor in the presence of trimethylsilyl triflate afforded 1,2-*cis*-configured, 1 → 3-linked disaccharides (α from **5**, **6**, and **7**, β from **8**) as the sole products in moderate to excellent yields. The coupling reaction of **6** (or **7** or **8**) with 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose in the presence of silver triflate furnished 1 → 6-linked disaccharides in high yield, with the 1,2-*cis* isomers predominant.

Keywords: Stereoselective; Glycosylation; 1-Thio-β-D-galactopyranosides; Pyrimidin-2-yl

1. Introduction

The synthesis of 1,2-*cis*-(usually α)linked disaccharides and oligosaccharides is important because these structures are constituents of many biologically active glycoconjugates [1–5]. Thus, much effort has been spent on attempts to devise efficient and stereocontrolled 1,2-*cis*-glycoside syntheses. At the same time, thioglycosides have received considerable attention in recent years, not only because of their ability to induce or competitively inhibit the activity of enzymes but also because of the excellent qualities of alkylthio and arylthio groups as both protecting and activating groups for C-1 [6–17]. Hanessian et al. [16] studied the activity of basic, heterocyclic thioglyco-

* Corresponding author.

Elsevier Science Ltd.
SSDI 0008-6215(95)00031-3

Table 1
Physical data for thioglycosides **1–8**

Datum	Values							
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Yield (%)	95	97	73.4	81.8	87	71.4	81.8	80
Mp (°C)	103	syrup	137	syrup	syrup	96	syrup	syrup
$[\alpha]_D^{20}$ (deg)	+8.3	+66.2	−26.2	−2.8	+18.2	+21.7	+23.4	+56.1
c (%) in $CHCl_3$	0.4	0.4	0.3	0.3	1.6	0.9	3.2	0.7
	Analysis							
	$C_{18}H_{22}N_2O_9$		$C_{15}H_{18}N_2O_7S$		$C_{38}H_{38}N_2O_5S$		$C_{30}H_{30}N_2O_4S$	
Calcd C	48.87		48.65		71.90		70.02	
H	5.01		4.90		6.03		5.88	
Found C	48.77	48.99	48.61	48.46	71.63	71.67	69.74	70.00
H	4.95	4.85	4.90	5.07	6.01	6.15	5.70	6.09

sides and reported that with suitable catalysis unprotected pyrimidin-2-yl 1-thio-β-D-glucopyranoside could effectively glycosylate simple alcohols. However, no data were given on the specific cases examined. We now report the glycosylation of methyl 2,4,6-tri-*O*-benzyl-α-D-mannopyranoside and 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose using pyrimidin-2-yl 1-thio-β-D-gluco-, -β-D-galacto-, -β-D-xylo-, and -α-D-arabino-pyranose benzyl ethers as the glycosyl donors.

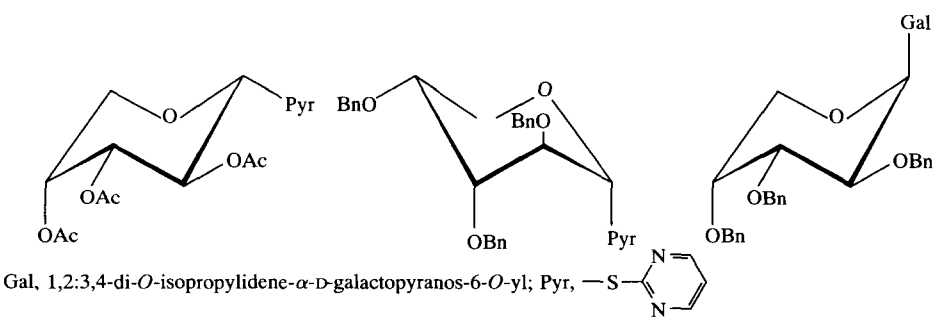
2. Results and discussion

Fully benzylated pyrimidin-2-yl 1-thio-β-D-gluco- (**5**), -β-D-galacto- (**6**), -β-D-xylo- (**7**), and -α-D-arabino-pyranoside (**8**) were synthesized via the coupling of the corresponding acetobromosugars with 2-mercaptopyrimidine, followed by benzylation. Thus treatment of the acetobromosugars, prepared by a standard method [18], with 2-mercaptopyrimidine, tetrabutylammonium hydrogensulfate, and sodium carbonate in a mixture of dichloromethane and water under phase-transfer conditions [19] at room temperature afforded the fully acetylated pyrimidin-2-yl 1-thio-D-glycopyranosides **1–4**. When 3 equiv of 2-mercaptopyrimidine were used, the yields of thioglycoside were almost quantitative (compounds **1** and **2**, Table 1). Deacetylation of **1–4** with catalytic amounts of sodium methoxide in methanol followed by benzylation with benzyl bromide and sodium hydride in *N,N*-dimethylformamide gave **5–8** in good yield. It was found that the acetylated pyrimidin-2-yl 1-thio-β-D-gluco- (**1**), -β-D-galacto- (**2**), and -β-D-xylo- (**3**) pyranosides assumed a conformation close to $^4C_1$, and the corresponding 1-thio-α-D-arabinopyranoside (**4**) a conformation close to $^1C_4$, as indicated by the relatively large values of the coupling constants $J_{1,2}$ and $J_{2,3}$ in all four cases (Table 2). After benzylation compounds **5**, **6**, and **7** still took the $^4C_1$ form but a conformational inversion to a form close to $^4C_1$ occurred for pyrimidin-2-yl 2,3,4-tri-*O*-benzyl-1-thio-α-D-arabinopyranoside (**8**), as indicated by the small value (3.1 Hz) of $J_{1,2}$ and the downfield chemical shift of H-1 (δ 6.31, equatorial). A large coupling constant $J_{4,5'}$ (8.5

Table 2
^{1}H NMR data for thioglycosides **1–8**

Datum	Values (δ in ppm, J in Hz)							
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
H-1δ	5.78 d	5.83 d	6.04 d	6.14 d	5.68 d	5.69 d	5.69 d	6.31 d
$J_{1,2}$	10.3	6.0	7.0	6.0	9.8	10.3	9.3	3.1
H-2δ	5.18 [a] t	5.45 t	5.14 [a] t	5.35 t	3.64	3.98	3.57	3.89
$J_{2,3}$	10.3	6.0	7.0	6.0				—
H-3δ	5.25 [a] t	5.19 dd	5.24 [a] t	5.26 dd				4.00
$J_{3,4}$	10.3	3.4	7.0	3.4				3.6
H-4δ	5.34 [a] t	5.47 d	4.93 m	3.82 dd		4.17	3.80	3.83 m
H-5δ	3.90 m	4.10	4.32 dd	4.18 m		3.58	4.06 dd	4.23 dd
$J_{4,5}$			4.2				4.5	3.6
$J_{5,5'}$			12.7				11.5	11.2
H-5'δ			3.66 dd				3.44 dd	3.65 dd
$J_{4,5'}$			7.1				9.2	8.5
$J_{5,5'}$			12.7				11.5	11.2
H-6δ	4.28 dd		—	—			—	—
$J_{5,6}$	4.3							
$J_{6,6'}$	12.9							
H-6'δ	4.10 dd	4.15	—	—	3.82	3.80	—	—
$J_{5,6'}$	1.8							
$J_{6,6'}$	12.9							
CH_3CO	2.03 s	2.00 s	2.10 s	2.13 s				
	2.04 s	2.02 s	2.11 s	2.13 s				
	2.06 s	2.07 s	2.14 s	2.17 s				
	2.07 s	2.20 s						
CH_2Ph					4.44–4.98 m	4.34–5.02 m	4.60–4.95 m	4.49–4.78 m
Ph					7.14–7.35 m	7.20–7.39 m	7.23–7.37 m	7.25–7.37 m
pyr H-4,6	8.55 d	8.58 d	8.58 d	8.60 d	8.51 d	8.50 d	8.55 d	8.55d
pyr H-5	7.06 t	7.07 t	7.07 t	7.07 t	6.98 t	6.96 t	7.00 t	6.99 t

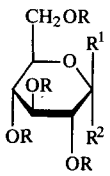
[a] Assignments may be interchanged.



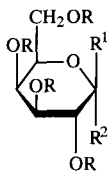
Gal, 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranos-6-*O*-yl; Pyr, —S—

Fig. 1. Conformations of the arabinose derivatives.

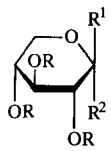
Hz) representing a *trans*-relationship between H-4 and H-5′ also confirmed the $^4C_1$ conformation. The advantages of using 2-mercaptopyrimidine as the thiol in these preparations are that the reagent is simple and odorless, and all of the acetylated and benzylated thioglycosides **1–8** are quite stable, being capable of a long term storage at room temperature (Fig. 1).



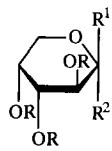
	R	R^1	R^2
1	Ac	Pyr	H
5	Bn	Pyr	H
9	Bn	H	Man



	R	R^1	R^2
2	Ac	Pyr	H
6	Bn	Pyr	H
10	Bn	H	Man
13α	Bn	H	Gal
13β	Bn	Gal	H



	R	R^1	R^2
3	Ac	Pyr	H
7	Bn	Pyr	H
11	Bn	H	Man
14α	Bn	H	Gal
14β	Bn	Gal	H



	R	R^1	R^2
4	Ac	H	Pyr
8	Bn	H	Pyr
12	Bn	Man	H
15α	Bn	H	Gal
15β	Bn	Gal	H

Gal, see Fig. 1; Man, methyl 2,4,6-tri-*O*-benzyl-α-D-mannopyranosid-3-*O*-yl

It was gratifying to find that the condensation of **5–8** with a secondary alcohol, methyl 2,4,6-tri-*O*-benzyl-α-D-mannopyranoside [20], in dichloromethane at room temperature in the presence of trimethylsilyl triflate afforded the 1,2-*cis* disaccharides

Table 3
Reaction conditions for the preparation of disaccharides **9–15**

Datum	Values						
	9	**10**	**11**	**12**	**13**	**14**	**15**
Reaction time	6 h	6.5 h	7.5 h	8 h	40 min	50 min	40 min
Cat.	Me_3SiOTf	Me_3SiOTf	Me_3SiOTf	Me_3SiOTf	AgOTf	AgOTf	AgOTf
Yield (%)	80	93	64	92	93	93	93
$\alpha:\beta$	1:0	1:0	1:0	0:1	1.6:1	1.2:1	1:2.3
$[\alpha]_D^{20}$ (deg)	+49.6	+32.0	+43.8	−59.0	+51 [a][22]	+9.8 [a]	−39.6 [b]
c (%) $CHCl_3$	0.3	0.4	0.4	0.3	0.9	1.6	2.4
	Analysis						
	$C_{62}H_{66}O_{11}$		$C_{54}H_{58}O_{10}$			$C_{38}H_{46}O_{10}$	
Calcd C	75.43		74.80			68.86	
H	6.74		6.74			7.00	
Found C	75.34	75.50	74.89	74.78		68.91	68.79
H	6.39	6.79	6.81	6.59		6.87	6.99

[a] For the α isomer. [b] For the β isomer.

Table 4
^{1}H NMR data for disaccharides **9–12**

Datum [a]	Values (δ in ppm, J in Hz)				
	9	**10**	**10A** [b]	**11**	**12**
H-1b δ	5.18 d	5.22 d	5.18 d	5.07 d	5.12 d
$J_{1,2}$	2.9	2.7	3.3	3.6	3.3
H-1a δ	4.79 s	4.75 d	4.70 d	4.81 d	4.68 d
$J_{1,2}$		1.3	1.3	1.8	1.7
OCH_3	3.33 s	3.12 s	3.32 s	3.35 s	3.31 s
H-2a–6a, 6′a;	3.51–3.63 m	3.38 d	3.42 dd	3.43 dd	3.48–3.78 m
H-2b–6b, 6′b δ	3.67–3.80 m	3.44 dd	3.50 dd	3.50–3.58 m	3.83 m
(5b, 5′b)	3.88 m	3.50 dd	3.57–3.71 m	3.69–3.79 m	3.87–3.92 m
	3.98–4.34 m	3.62–3.77 m	3.82 m	3.83 dd	3.95–4.02 m
		3.83 m	3.88–3.95 m	3.95–4.03 m	4.05 dd
		3.90 dd	4.00–4.07 m	4.07 dd	4.10 dd
		3.96 t			
		3.94–4.04 m			
		4.10 d			
PhCH_2	4.41 d	4.42 d	4.29 d	4.44 d	4.46 d
	4.43 d	4.43 d	4.30 d	5.07 d	4.51 d
	4.59 s	4.44 d	4.30 d	4.84 d	4.53 d
	4.47 d	4.45 d	4.32 d	4.85 d	4.58 d
	4.51 d	4.49 d	4.37 d	4.50–4.74 m	4.63 d
	4.53 d	4.53 d	4.43 d		4.64 d
	4.57 d	4.59 d	4.46 d		4.65 d
	4.62 d	4.60 d	4.47 d		4.68 d
	4.69 d	4.60 d	4.52 d		4.71 d
	4.79 d	4.68 d	4.54 d		4.72 d
	4.83 d	4.72 d	4.58 d		4.77 d
	4.92 d	4.79 d	4.71 d		4.81 d
	5.08 d	4.91 d	4.93 d		
		5.05 d	4.98 d		
Ph	7.10–7.36 m	7.07–7.40 m	6.85–7.40 m	7.13–7.47 m	7.00–7.35 m

[a] Designation of protons: a, acceptor residue; b, donor residue.
[b] The acceptor was methyl 2,4,6-tri-*O*-*p*-bromobenzyl-α-D-mannopyranoside.

(α-linked **9–11,** β-linked **12**) as the sole products in good to excellent yields (Table 3). The use of silver triflate as the catalyst also gave exclusive 1,2-*cis* selectivity, but caused the yields to drop substantially (data not shown). However, if methyl 2,4,6-tri-*O*-*p*-bromobenzyl-α-D-mannopyranoside [20] was used as the acceptor for the glycosidic coupling reaction of **6** under similar conditions, the reaction was complete within 1 h and gave a 96% conversion to the α-linked disaccharide.

Condensation of thioglycosides **6–8** with 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose was also investigated. It was found that the condensation was best achieved with high yield and good selectivity by the use of 2 equiv of silver triflate as promoter, reacting in dichloromethane at room temperature for 40 min (Table 3). A longer reaction time (16 h) led to poorer selectivity, and a very short time (5 min) did not change the

Table 5
^{1}H NMR data for disaccharides **13–15**

Datum [a]	Values (δ in ppm, J in Hz)					
	13α	**13β**	**14α**	**14β**	**15β**	**15α**
H-1b δ	5.00 d	4.40 d	4.88 d	4.40 d	4.98 d	4.37 d
$J_{1,2}$	3.5	7.6	4.0	7.7	3.3	7.0
H-1a δ	5.51 d	5.56 d	5.53 d	5.55 d	5.54 d	5.33 d
$J_{1,2}$	5.1	4.9	5.0	5.0	5.1	5.0
H-2a δ	4.31 m	4.30 dd	4.32 dd	4.32 dd	4.30 dd	4.30 dd
$J_{2,3}$		2.6	2.0	2.9	2.4	2.0
H-3a δ	4.57 m	4.56 dd	4.60 m	4.58 m	4.56 dd	4.57 dd
H-4a δ	4.31 m	4.20 dd	4.37 dd	4.22 dd	4.23 dd	4.34 dd
$J_{3,4}$		8.0	8.0	7.7	7.9	8.0
$J_{4,5}$		1.0	1.4	1.8	2.0	1.0
H-2b–6b, 6'b	3.56–3.61 m	3.48–3.90 m	3.46 dd	3.19 dd	3.66 dd	3.49 dd
(5b, 5'b); δ	3.67–3.83 m	4.03–4.15 m	3.52–3.63 m	3.38 t	3.73–3.82 m	3.67–3.70 m
H-5a–6a, 6'a	3.92–4.08 m		3.68–3.79 m	3.54–3.63 m	3.88 dd	3.74–3.88 m
			3.89 t	3.75 dd	3.99 dd	3.97–4.15 m
		4.03 t	3.91 dd	4.07–4.15 m		
			4.03–4.08 m	4.23 dd		
				4.30 dd		
PhCH_2	4.40 d	4.40 d	4.61 d	4.61 d	4.63 d	4.63 d
	4.48 d	4.41 d	4.64 d	4.69 d	4.68 s	4.64 d
	4.57 d	4.60 d	4.71 d	4.73 d	4.73 d	4.69 d
	4.72 d	4.70 d	4.73 d	4.83 d	4.75 d	4.73 d
	4.75 s	4.73 d	4.85 d	4.89 d	4.80 d	4.78 d
	4.84 d	4.80 d	4.92 d	5.00 d		4.92 d
	4.94 d	4.93 d				
		5.05 d				
Ph	7.22-7.40 m	7.23-7.48 m	7.25-7.45 m	7.30-7.45 m	7.20-7.47 m	7.25-7.40 m
C(CH_3)$_2$	1.27, 1.31	1.30, 1.30	1.33, 1.35	1.30, 1.30	1.05, 1.06	1.25, 1.33
	1.42, 1.50	1.44, 1.50	1.48, 1.58	1.47, 1.50	1.08, 1.09	1.41, 1.52

[a] Designation of protons: a, acceptor residue; b, donor residue.

selectivity appreciably, but decreased the yield (data not shown). The use of trimethylsilyl triflate as the promoter gave similar results. When mercuric chloride was used, similar stereoselectivity was obtained but the yields were low ($\sim$ 60%).

The anomeric configurations of the disaccharides **9–15** were established from their ^{1}H NMR spectra (Tables 4 and 5). For the α-linked disaccharides **9, 10, 11, 13α,** and **14α** the signal for H-1 of the donor residue had a downfield position and a small coupling constant, while the donor H-1 signal of the β-linked disaccharides **13β** and **14β** had an upfield position and a large coupling constant as expected. A conformational inversion from $^4C_1$ to $^1C_4$ took place during the glycosidation of **8** with the diisopropylidenegalactose as indicated from the ^{1}H NMR spectrum of **15β**, which showed the signal for H-1 of the donor residue in a downfield position (δ 4.98), a small coupling constant $J_{1,2}$ of 3.3 Hz, and a large coupling constant $J_{2,3}$ of 9.2 Hz.

Conversely the spectrum of **15α** showed an upfield position for the donor-residue H-1 signal (δ 4.37), and large values of $J_{1,2}$ (7.0 Hz) and $J_{2,3}$ (7.0 Hz). The higher *cis–trans* ratio in the reaction of the arabinosyl donor (**15β:15α** = 2.3:1) indicated that the anomeric effect and the thermodynamic stability of the conformation controlled the stereochemical outcome. We deduced from the preceding observation that the anomeric configuration of the arabinosyl unit in **12** was β and the conformation nearly $^1C_4$, as shown from the downfield position of the signal of H-1 (δ 5.12) and the small value of $J_{1,2}$ (3.3 Hz). The coupling constant $J_{2,3}$ could not be determined because of overlapped signals. The fact that the optical rotation of **12** has the same sign as that of **15β** may be further evidence that the two compounds have similar conformations ($^1C_4$). The basis for the high stereoselectivity observed in the synthesis of the 1 → 3-linked disaccharides remains to be elucidated.

3. Experimental

General methods.—Optical rotations were determined at 20°C with a Perkin–Elmer Model 241-MC automatic polarimeter for solutions in a 1-dm, jacketed cell. Melting points were determined with a Mel-Temp apparatus and are uncorrected. ^{1}H NMR spectra were recorded with Varian XL-400 and Varian XL-200 spectrometers for solutions in $CDCl_3$. Chemical shifts are given in ppm downfield from internal Me_4Si. Analytical LC was carried out in stainless-steel columns packed with silica gel (10 × 150 mm or 4.6 × 250 mm) or Lichrosorb-NH_2 (4.6 × 250 mm), with peak detection by a differential refractometer (Perkin–Elmer LC-25 RI detector). Ethyl acetate–petroleum ether (bp 60–90°C) was used as the eluent, at a flow rate of 1–4 mL min^{-1}. TLC was performed on Silica gels G and HF, with detection either by charring with 30% (v/v) H_2SO_4 in MeOH or by UV light. Preparative chromatography was performed on columns (16 × 240, 18 × 300, and 35 × 400 mm) of silica gel (120–200 mesh).

*Per-*O*-acetylated pyrimidin-2-yl 1-thio-*D*-glycopyranosides* **1–4**.—To a stirred solution of acetobromosugar [18] (10 mmol) in dichloromethane (35 mL) was added a solution of 2-mercaptopyrimidine (purchased from Aldrich, 30 mmol for **1** and **2**, and 12 mmol for **3** and **4**) and tetrabutylammonium hydrogensulfate (10 mmol) in M sodium carbonate (35 mL). The mixture was stirred at room temperature for 1 h. TLC (1:2 ethyl acetate–petroleum ether) indicated that the reaction was complete. The mixture was partitioned between dichloromethane and water, and the organic layer was concentrated to a syrup. Column chromatography with 1:2 ethyl acetate–petroleum ether as the eluent gave chloro(pyrimidin-2-ylthio)methane as the first fraction (mp 78°C, ^{1}H NMR: δ 8.60, d, 2 H; 7.06, t, 1 H; and 5.30, s, 2 H), di(pyrimidin-2-ylthio)methane as the second fraction (mp 89°C, ^{1}H NMR: δ 8.55, d, 4 H; 6.98, t, 2 H; and 4.90, s, 2 H), and the per-*O*-acetylated thioglycoside as the third fraction. Compounds **1** and **3** were obtained as crystals.

*Per-*O*-benzylated pyrimidin-2-yl 1-thio-*D*-glycopyranosides* **5–8**.—To a solution of **1** (or **2, 3,** or **4**) (10 mmol) in anhydrous methanol (15 mL) was added sodium methoxide (11 mg, 0.2 mmol), and the solution was stirred at room temperature for 3 h, at the end

of which time TLC (1:2 ethyl acetate–petroleum ether) indicated that the reaction was complete. The solution was concentrated, and the resulting solid, residual pyrimidin-2-yl thioglycoside was dissolved in *N,N*-dimethylformamide (15 mL). To the stirred solution was added sodium hydride (2 g, 80% in oil, 66 mmol) and then benzyl bromide (8.0 mL, 64 mmol). The mixture was stirred at room temperature for 5 h, at the end of which time TLC (1:2 ethyl acetate–petroleum ether) indicated that the reaction was complete. The mixture was poured into water, the solution was extracted repeatedly with dichloromethane, and the combined extract was concentrated to a syrup. Purification by column chromatography with 1:3 ethyl acetate–petroleum ether as the eluent afforded compound **5** (or **6, 7,** or **8**). Only compound **6** was obtained as crystals.

1 → 3-Linked disaccharides **9–12**.—To a solution of methyl 2,4,6-tri-*O*-benzyl-(or -*p*-bromobenzyl-)α-D-mannopyranoside [20] (1.2 mmol) and the pyrimidin-2-yl 1-thioglycoside **5** (or **6, 7,** or **8**) (1.0 mmol) in dichloromethane (5 mL) was added 4 Å molecular sieves (200 mg). The mixture was stirred under a nitrogen atmosphere at room temperature, Me_3SiOTf (2.0 mmol) was added, and stirring was continued until TLC indicated that the thioglycoside had disappeared completely. Neutralization of the mixture with triethylamine, dilution with dichloromethane, filtration, and concentration gave a syrup. Column chromatography with 1:3 ethyl acetate–petroleum ether as the eluent afforded the 1 → 3-linked disaccharide **9** (or **10, 11,** or **12**).

1 → 6-Linked disaccharides **13–15**.—To a solution of 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose [21] (1.2 mmol) and the pyrimidin-2-yl 1-thioglycoside **6** (or **7,** or **8**) (1 mmol) in dichloromethane (5 mL) was added 4 Å molecular sieves (200 mg), and the mixture was stirred at room temperature. To the mixture was added AgOTf (2.0 mmol), and the reaction was monitored by TLC. When the reaction was complete dichloromethane (15 mL) was added. The mixture was neutralized with 0.1 N sodium hydroxide, and the organic layer was separated and concentrated. Separation and purification by analytical LC with 1:3 ethyl acetate–petroleum ether as the eluent gave **13α** and **13β** (or **14α** and **14β**, or **15α** and **15β**).

References

[1] A.F. Bochkov and C.E. Zaikov, *Chemistry of the O-Glycosidic Bond: Formation and Cleavage*, Pergamon Press, Oxford, 1979.
[2] K. Toshima and K. Tatsuta, *Chem. Rev.*, 93 (1993) 1503–1531.
[3] P. Fügedi, P.J. Garegg, H. Lönn, and T. Norberg, *Glycoconjugate J.*, 4 (1987) 97–108.
[4] R.R. Schmidt, *Angew. Chem. Int. Ed. Engl.*, 25 (1986) 212–235.
[5] H. Paulsen, *Chem. Soc. Rev.*, 13 (1984) 15–45.
[6] H.B. Mereyala and V.R. Gurijala, *Carbohydr. Res.*, 242 (1993) 277–280.
[7] T. Terada, M. Kiso, and A. Hasegawa, *J. Carbohydr. Chem.*, 12 (1993) 425–440.
[8] K. Takeo, Y. Teramoto, Y. Shimono, and Y. Nitta, *Carbohydr. Res.*, 209 (1991) 167–179.
[9] S. Sato, M. Mori, Y. Ito, and T. Ogawa, *Carbohydr. Res.*, 155 (1986) C6–C10.
[10] K.C. Nicolaou, S.P. Seitz, and D.P. Papahatjis, *J. Am. Chem. Soc.*, 105 (1983) 2430–2434.
[11] K.C. Nicolaou, R.E. Dolle, D.P. Papahatjis, and J.L. Randall, *J. Am. Chem. Soc.*, 106 (1984) 4189–4192.
[12] G.H. Veeneman and J.H. van Boom, *Tetrahedron Lett.*, 31 (1990) 275–278.
[13] F. Anderson, P. Fügedi, P.J. Garegg, and M. Nashed, *Tetrahedron Lett.*, 27 (1986) 3919–3922.
[14] P. Fügedi and P.J. Garegg, *Carbohydr. Res.*, 149 (1986) C9–C12.

[15] F. Dasgupta and P.J. Garegg, *Carbohydr. Res.*, 177 (1988) C13–C17.
[16] S. Hanessian, C. Bacquet, and N. Lehong, *Carbohydr. Res.*, 80 (1980) C17–C22.
[17] M. Kiso and L. Anderson, *Carbohydr. Res.*, 72 (1979) C12–C14.
[18] M. Bárczai-Martos and F. Kőrösy, *Nature*, 165 (1950) 369.
[19] F.D. Tropper, F.O. Andersson, C.G. Maitre, and R. Roy, *Synthesis*, (1991) 734–736.
[20] F. Kong and C. Schuerch, *Carbohydr. Res.*, 112 (1983) 141–147.
[21] O.T. Schmidt, *Methods Carbohydr. Chem.*, 2 (1963) 318–325.
[22] H.B. Mereyala and G.V. Reddy, *Tetrahedron*, 47 (1991) 6435–6448.