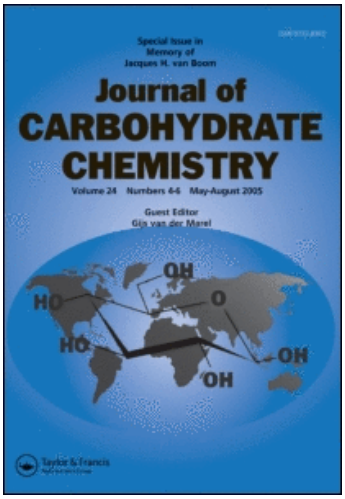

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COMMUNICATION

SYNTHESIS OF GLYCOSYL ESTERS AND GLYCOSYL HEMIACETALS FROM METHYLTHIOGLYCOSIDES‡

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Glycosyl esters constitute a widespread family of natural products such as anti-tumor agents,[1] antibiotics,[2] terpenoid glycosides,[3] plant pigments[4] and other substances.[5] It has been shown that aromatic carboxylic acids are metabolized by humans as glycosyl esters,[6] and D-glucopyranosyl fatty acid esters were found to inhibit the growth of leukemia cells[7] and plant growth.[8] The synthesis of a prodrug in the form of a glycosyl ester has been reported.[9] In synthetic chemistry glycosyl acetates are frequently used glycosyl donors in Lewis-acid catalyzed glycosylation reactions[10] and other transformations.[11]

Because of their biological and synthetic importance, numerous protocols have been developed for the synthesis of glycosyl esters. These include the regioselective esterification of the anomeric hydroxyl group of free sugars with N-acylimidazoles,[12a] N-acyltriazoles,[12a] p-nitrophenyl esters[12b] and N-acyl thiazolidine thiones[12b], and the esterification of protected glycosyl hemiacetals with carboxylic acids activated by triphenylphosphine diethylazodicarboxylate[1] or by dicyclohexylcarbodiimide[13], and with acyl chloride and pyridine,[14] BuLi[15] or

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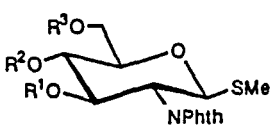
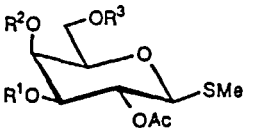
CsF.[16] A number of glycosyl ester syntheses utilize glycose derivatives having activating groups at the anomeric center. Such approaches include reaction of 1-thioaldoses with silver[17a] or mercuric[17b] carboxylates, reaction of 1-O-stannyl aldoses with acyl chlorides,[18] and reaction of glycosyl halides with tributylstannyl,[18] silver[19] and potassium[19] carboxylates. Furthermore, glycosyl esters were prepared by reaction of glycosyl fluorides,[20] glycosyl imidates[21] and O-glycosylpseudoureas[22] with carboxylic acids, by acidolytic ring opening of 1,2-orthoacetates[11b,23] and by acyl-exchange between 1-O-trifluoroacetyl glycoses and free carboxylic acids.[23,24] In a unique approach, 1-O-benzoyl-β-D-glucopyranose was prepared by CrO_3-oxidation of the corresponding benzyl glycoside.[25] Frequently, glycosyl acetates are obtained by acetolysis of O-glycosides.[10c]

Recently, 2-trimethylsilylethyl glycosides have been used as starting compounds for stereoselective synthesis of glycosyl acetates and other glycosyl esters,[26] giving excellent yields and a high degree of stereoselectivity. However, the scope of these transformations appears to be limited by the fact that neither O-benzyl nor O-isopropylidene or other acetal protecting groups survive the reaction conditions.[26]

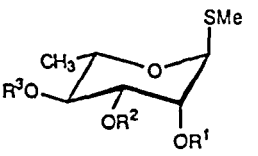
In connection with our interest in synthesis[27] and transformation[28] of thioglycosides we developed a new procedure for the preparation of 1-O-acyl derivatives of sugars. It was found that protected methyl 1-thioglycosides[27] in the presence of an equimolar quantity of nitrosyl tetrafluoroborate, in dichloromethane or acetonitrile, react with carboxylic anhydrides at temperatures between 0-25 °C to give the corresponding 1-O-acyl derivatives in good to excellent yields. The scope of the new reaction is illustrated by the examples given in Table I. Common functional groups such as O-acetyl (entries 1-13), O-benzyl (entries 2,9,14), O-isopropylidene (entries 8,10,11, 13), O-benzylidene (entry 12), 4,6-O-(4-methoxybenzylidene) (entry 14) and N-phthalyl groups (entries 1, 3) were found to be compatible with the reaction condition. The yields were generally high and the reaction fast (< 1h) except for the 1-O-benzoate formation (entry 5) which indicates a decreased reactivity for benzoic anhydride under the conditions used. Entries 6 and 7 appear to indicate that the configuration of the anomeric center in the precursor thioglycosides is



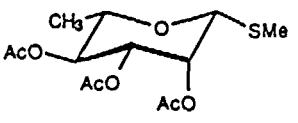
1 R^1=R^2=R^3=Ac
2 R^1=Bn, R^2,R^3=MBn



3 R^1=R^2=Ac, R^3=Bn
4 R^1=R^2=R^3=Ac
5 R^1,R^2=C(Me)$_2$, R^3=Ac
6 R^1=Ac, R^2,R^3=C(Me)$_2$
7 R^1=Ac, R^2,R^3=C(H)Ph



8 R^1=R^2=R^3=Ac
9 R^1=R^2=C(Me)$_2$, R^3=Ac
10 R^1=Ac, R^2=R^3=Bn
11 R^1=R^2=R^3=Bz



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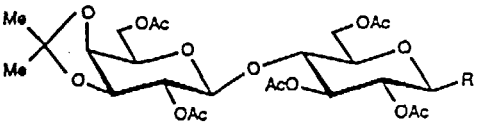
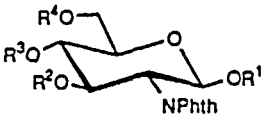
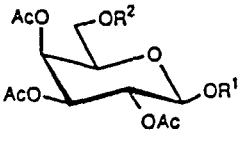


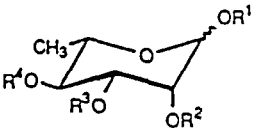
13 R=SMe
14 R=OAc



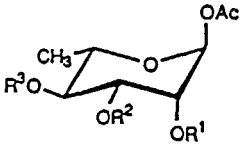
15 R^1= R^2=R^3=R^4=Ac
16 R^1=COC_5H_{11}, R^2=R^3=R^4=Ac
17 R^1=Ac, R^2=Bn, R^3,R^4=MBn



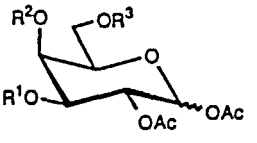
18 R^1=Ac, R^2=Bn
19 R^1=R^2=Ac
20 R^1=Bz, R^2=Ac



21 R^1=R^2=R^3=R^4=Ac
22 R^1=H, R^2=Ac, R^3=R^4=Bn
23 R^1=H, R^2=R^3=R^4=Bz
24 R^1=H, R^2=R^3=R^4=Ac



25 R^1,R^2= C(Me)$_2$, R^3=Ac
26 R^1=Ac, R^2=R^3=Bn



27 R^1,R^2=C(Me)$_2$, R^3=Ac
28 R^1=Ac, R^2,R^3=C(Me)$_2$
29 R^1=Ac, R^2,R^3=C(H)Ph

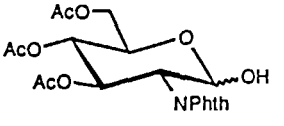


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TABLE I.

Transformation of methylthio glycosides into 1-O-acyl glycoses under $NOBF_4$-activation of the anomeric carbon atom

Entry	Precursor	Reagent	Product[a]	Ratio (1,2-*trans*/1,2-*cis*)	Yield[b] (%)
1	**1**[28b]	Ac_2O	**15**[55]	*c*	90
2	**3**[54]	Ac_2O	**18**	100:2.5	82
3	**1**[28b]	$(C_5H_{11}CO)_2O$	**16**[d]	*c*	96
4	**4**[28b]	Ac_2O	**19**	*c,e*	80
5	**4**[28b]	Bz_2O	**20**[f]	*c*	64
6	**8**[28c]	Ac_2O	**21**[56]	100:7	83
7	**12**[28c]	Ac_2O	**21**[56]	100:10	86
8	**9**[54]	Ac_2O	**25**[g]	*c*	73
9	**10**[28c]	Ac_2O	**26**[10c,56]	*c*	72
10	**5**[28b]	Ac_2O	**27**	100:66	91
11	**6**[29]	Ac_2O	**28**	66:100	86
12	**7**[30]	Ac_2O	**29**	100:30	85
13	**13**[54]	Ac_2O	**14**	100:5	69
14	**2**[54]	Ac_2O	**17**[h]	*c*	57

[a]The structures of the products have been verified of ^1H and ^{13}C NMR spectroscopy. Satisfactory elemental analytical data were obtained for all crystalline products. [b]Yields refer to chromatographically homogeneous products. [c]1,2-*Trans* isomer only was isolated in pure form. [d]$[\alpha]_D$ +35°. [e]Chromatography of the mother liquor gave 13 % of a 1:2 mixture of 1,2-*trans*/1,2-*cis* isomers. [f]Mp 124-125 °C, $[\alpha]_D$ -10°. [g]Mp 106-108 °C, $[\alpha]_D$ -14°. [h]Mp 177-179 °C, $[\alpha]_D$ +64°.

TABLE II.

Hydrolysis of methylthio glycosides under $NOBF_4$-activation of the anomeric carbon atom

Entry	Precursor	Product[a]	Yield[b] (%)
1	**1**[28b]	**30**[26c]	93
2	**10**[28c]	**22**[56]	94
3	**11**[28c]	**23**[c]	89
4	**12**[28c]	**24**[56]	88

[a]The structures of the products were verified by ^1H and ^{13}C NMR spectroscopy. [b]Yields refer to chromatographically homogeneous products. [c]Mp 126-129 °C, $[\alpha]_D$ +205°.

relatively unimportant for the final stereochemical outcome, which for entry 8 is probably dictated by the anomeric effect. The degree of participation by the acetoxy substituent at C-2 in galactopyranosides having either 3,4-O- or 4,6-O-acetal functions (entries 10-12) is decreased, relative to the peracetyl-substituted derivative (entry 4) as indicated by the anomeric product mixture (Table I). ^{1}H NMR data[28b] clearly indicate that the conformation of methyl 2,6-di-O-acetyl-3,4-O-isopropylidene-1-thio-β-D-galactopyranoside is distorted from the chair conformation of methyl 2,3,4,6-tetra-O-acetyl-1-thio-β-D-galactopyranoside[28b] thus helping explain the difference in the anomeric composition of the products (entry 10 vs. entry 4). No such differences are found between the ^{1}H NMR data for the 4,6-O-acetylated thiogalactosides (compounds 6[29] and 7[30]) and the corresponding tetraacetate (compound 3[28b]). In these cases it is probable that the 4,6-O-acetal function merely decreases the ability of the acetoxy group at C-2 to interact with the anomeric center in the transition state, making the anomeric effect the determinant factor in case of the 4,6-O-isopropylidene derivative (entry 11), and an efficiently competing one in the 4,6-O-benzylidene derivative (entry 12).

Glycosyl hemiacetals are equally important intermediates, among others in the synthesis of glycosyl donors (halides,[31] imidates[32]), trehalose-type compounds,[33] 1-O-trimethylsilyl glycoses,[34] and other sugar derivatives.[13-16,35] Preparation of this class of compound involves acid-hydrolysis of O-[36a] and N-glycosides,[36b] hydrolysis of thioglycosides with silver[37] or mercury(II)[38] salts, hydrolysis of glycosyl halides with silver salts,[39] regioselective deacetylation of sugar acetates with benzylamine,[40] piperidine,[41] hydrazine,[42] ammonia,[43] magnesium oxide,[44] and tin alkoxides,[45] potassium cyanide,[45c] potassium hydroxide,[45c] sodium methoxide,[46] tin tetrachloride,[47] ammonium carbonate[48] and hydrolysis of trimethylsilylethyl glycosides with $LiBF_4$[49] and $BF_3.Et_2O$.[26b,c,50] Recently reported, modern approaches include lipase-catalyzed, regioselective hydrolysis of the anomeric acetyl group in hexopyranoses,[51] hydrolysis of n-pentenyl glycosides by N-bromosuccinimide under neutral conditions,[52] and hydrolysis of thioglycosides under the agency of methyl trifluoromethanesulfonate.[53] In the present study we found that treatment of methyl 1-thioglycosides in acetonitrile with $NOBF_4$ in the presence of 1.1-1.5

TABLE III. Selected ^{1}H NMR spectral data for glycosyl esters and hemiacetals[a]

Compound		Chemical shift[b]							Coupling constants[c]						
		H-1	H-2	H-3	H-4	H-5	H-6	H-6'	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{5,6'}$	$J_{6,6'}$
14[d]	α	6.254							3.7						
	β	5.673							8.3						
16		6.519	4.478	5.910	5.220	4.042	4.376	4.144	8.8	10.7	9.0		4.4	1.9	12.4
17		6.344	4.341	4.544		4.400	3.75 - 3.85		8.8	10.3	8.7				
18	α	6.365							3.2						
	β	5.715	5.305	5.1	5.505	4.007	3.553	3.466	8.3	10.4	3.4		5.8	7.3	9.5
20	α	6.539							2.5						
	β	5.929	5.552	5.198	5.496	4.1	———	4.25	8.2	10.4	3.4				
22[e]	α	5.051	5.342						1.9	3.3					
	β		5.480						1.2	3.3					
23		5.462	5.776	5.925	5.693	4.459	1.367		1.7	3.2	10.0	10.0	6.6		
25		6.310	4.119	4.221	4.903	3.818	1.18		0.8	5.4	7.9	10.0	6.2		
27	α	6.238							3.4						
	β	5.606	5.1			4.1			7.8						
28	α	6.433	5.490	5.236	4.469	3.784	4.037	3.892	3.5	10.9	3.5	0.8	2.0	1.6	13.0
	β	5.648	5.458	4.918	4.389	3.549	4.050	3.949	8.3	10.3	3.5		2.0	1.8	13.0
29	α	6.484	5.540	5.322	4.515	3.929	4.280	4.048	3.5	10.9	3.4		1.5	1.7	12.7
	β	5.715	5.524	5.012	4.428	3.675	4.324	4.059	8.3	10.3	3.6	0.6	1.5	1.6	12.7
30	α	5.416		6.190					3.4	11.3	8.9				
	β	5.638		5.839	5.178	3.94			8.4	10.7	8.9				

[a]At 500 MHz, in $CDCl_3$ at 300 K. [b]In ppm (δ), $(CH_3)_4Si$=0.00 ppm. [c]In Hz. [d]Additional data: 2.13, 2.11, 2.10, 2.08, 2.06, 2.03 ppm (6 CH_3CO); 1.53, 1.32 ppm [$(CH_3)_2C$]. ^{13}C NMR data (125 MHz, $CDCl_3$, δ, $CDCl_3$=77.0 ppm): 110.7 [$C(CH_3)_2$]; 100.1 (C-1'), 91.5 (C-1); 63.0, 61.8 (C-6,6'); 27.2, 26.0 [$(CH_3)_2C$]; 20.7, 20.6 20.5 (6 CH_3CO). [e]^{13}C NMR data: 92.3 (C-1(β), $^1J_{C\text{-}1,H\text{-}1}$ =159 Hz), 91.7 (C-1(α), $^1J_{C\text{-}1,H\text{-}1}$=171 Hz).

equivalents of water quickly removes the methylthio group and gives sugar hemiacetals in excellent yields (Table II). The molar ratio of water to thioglycoside is crucial in the hydrolytic reaction: amounts of water in excess of those given above were found to promote side reactions, especially in case of polyacetylated thioglycosides. Again, the reaction conditions are compatible with commonly used protecting groups, such as O-acetyl, O-benzoyl, O-benzyl, and N-phthalyl groups.

EXPERIMENTAL

For general methods see Ref. 28b. MBn stands for 4-methoxybenzylidene group. Selected NMR spectral data of the new compounds are given in Table III.

General procedure for the preparaton of glycosyl esters

A stirred solution of methyl 1-thioglycoside (0.3-1 mmol) in dichloromethane (5-15 mL), containing 1.5-2 equimolar amounts of acetic anhydride, was treated at 0 °C with $NOBF_4$ (1 equivalent). The solution was then allowed to reach room temperature. The initially colorless solution gradually turned into violet then yellow, intensity of which decreased at completion of the reaction. Ice-cold, aqueous $NaHCO_3$ was added, the organic phase separated, dried (Na_2SO_4) and concentrated. The product (Table I) was isolated either by direct crystallization or by silica gel chromatography.

In case of highly reactive thioglycosides, containing O-benzyl protective groups, the reaction was conducted at 0 °C, and the transformation of acid-sensitive thioglycosides (entries 8, 10-14) was performed in the presence of an approximately equal amount of powdered, 4Å molecular sieves, activated in vacuo prior to reaction.

General procedure for hydrolysis of thioglycosides

A stirred solution of methyl 1-thioglycoside (∿ 1 mmol) in acetonitrile (10-30 mL) containing 1.1-1.5 equivalents of water was treated with an equimolar amount of $NOBF_4$ at 0 °C. The solution was allowed to reach room temperature. The color of the reaction changed to violet, yellow, then light yellow. Ice-cold, aqueous $NaHCO_3$ was added, the organic layer separated, dried (Na_2SO_4) and concentrated. The hemiacetal products (Table II) were isolated by chromatography.

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29. Compound 6 was obtained by acetylation (Ac_2O/Py) of methyl 4,6-O-isopropylidene-1-thio-β-D-galactopyranoside[28b]. ^1H NMR ($CDCl_3$, δ): 5.441 (t, 1H, $J_{1,2} = J_{2,3}$ = 9.9 Hz, H-2), 4.913 (dd, 1H, $J_{3,4}$ = 3.4 Hz, H-3), 4.371 (dd, 1H, $J_{4,5}$ = 1.3 Hz, H-4), 4.320 (d, 1H, H-1), 4.017 (dd, 1H, $J_{5,6}$ = 2.3 Hz, $J_{6,6'}$ = 12.9 Hz, H-6),

3.968 (dd, 1H, $J_{5,6'}$ = 1.9 Hz, H-6'), 3.473 (m, 1H, H-5), 2.214, 2.089, 2.078 (3s, 3 x 3 H , 2 CH_3CO, SCH_3), 1.447, 1.394 [2s, 2 x 3H, $(CH_3)_2C$].

30. Compound 7 was obtained from methyl 1-thio-β-D-galacto-pyranoside[28b] by successive benzylidination ($C_6H_5CH(OMe)_2$, PTS, DMF) followed by acetylation (Ac_2O/Py). 1H NMR ($CDCl_3$, δ): 7.55-7.35 (m, 5H, aromatic protons), 5.478 [s, 1H, CH (benzylidene)], 5.474 (t, 1H, $J_{1,2} = J_{2,3}$ = 9.9 Hz, H-2), 4.993 (dd, 1H, $J_{3,4}$ = 3.5 Hz, H-3), 4.383 (dd, 1H, H-4), 4.369 (d, 1H, H-1), 4.300 (dd, 1H $J_{5,6}$ = 1.6 Hz, $J_{6,6'}$ = 12.6 Hz, H-6), 3.985 (dd, 1H, $J_{5,6'}$ = 1.6 Hz, H-6'), 3.547 (m, 1H, H-5), 2.229, 2.066, 2.046 (3s, 3 x 3H, 2 CH_3CO, SCH_3).

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