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Efficient synthesis of ω-mercaptoalkyl 1,2-*trans*-glycosides from sugar peracetates

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Abstract—Lewis acid-promoted reactions of peracetylated sugars (glucose, galactose, maltose, lactose) with ω-bromo-1-alkanols (C_8, C_{12}) were investigated. $ZnCl_2$ was found to promote the 1,2-*trans*-glycosylation of the alcohols in toluene at about 60 °C in a stereocontrolled manner with better yields than commonly employed promoters such as $SnCl_4$. The ω-bromoalkyl acetylated glycosides were readily converted to ω-mercaptoalkyl glycosides, which are useful for the preparation of glycoclusters.

Keywords: Glycosylation; Glycolipids; Sugar peracetates; Lewis acids; Alkanethiols

1. Introduction

Recent studies in molecular biology have revealed that carbohydrate–protein interactions on cell surfaces are involved in essential biological processes such as cell growth, cellular adhesion, immune response, and inflammation.[1] Carbohydrate–protein binding events usually involve several simultaneous contacts between carbohydrates that are clustered on cell surfaces and protein receptors that contain multiple binding sites.[2] Such aggregated structures enhance the low binding affinity of the monomeric interaction, an observation referred to as the cluster glycoside effect.[3] Because of the complexity of cell surfaces, it would be difficult to evaluate carbohydrate–protein binding events in their native state. Simplified model systems such as self-assembled glycolipid monolayers[4] and gold glyconanoparticles[5] have been usually used to study polyvalent interactions.

We planned to study specific carbohydrate–lectin interactions using multivalent carbohydrate model systems. To prepare the assembled systems, we required substantial quantities of glycolipids having a thiol group at the terminal position of the hydrocarbon chain. Although such glycolipids have been prepared, the synthetic methods suffer from some drawbacks. For example, Penádes and co-workers have prepared 11-mercaptoundecyl-β-lactoside and -β-maltoside (each dimeric form as the disulfide).[5c] They employed *O*-benzoyl protected sugar 1-*O*-trichloroacetimidates as glycosyl donors whose preparation can be laborious. Lin et al. have prepared 5-mercaptopentyl α-D-mannoside (dimer),[5b] whose synthesis is rather straightforward, but with the drawback that they used toxic $Hg(CN)_2$ as glycosylation promoter. Therefore, a relatively simple and safe procedure is needed to enable a rapid synthesis in good yields. Herein we report a general and convenient route to the lipids.

2. Results and discussion

2.1. Glycosylation studies

Glycosylation of alcohols (O-glycosylation)[6] is an essential process for the synthesis of oligosaccharides and glycoconjugates. Simple *n*-alkyl 1,2-*trans*-glycosides such as octyl β-glucoside, a nonionic detergent, have been traditionally prepared from *O*-acetyl-protected glycosyl

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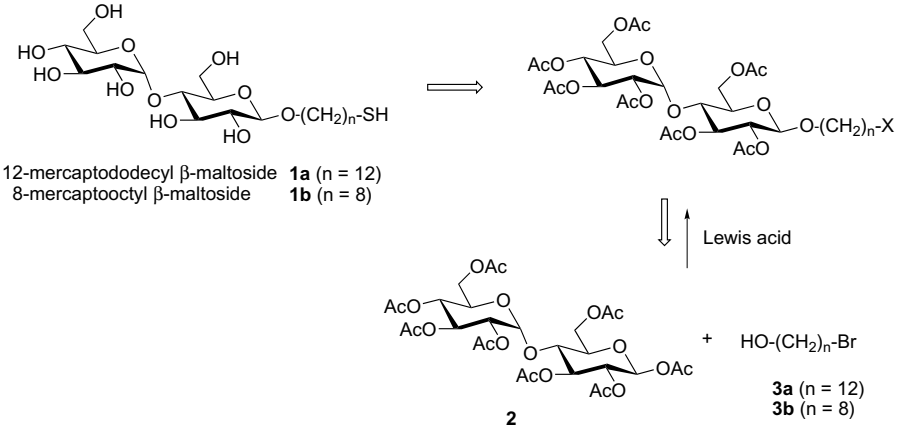
bromides with *n*-alkanols in the presence of promoter(s). Typical promoters employed in this type of glycosylation are silver salts (Ag_2CO_3,[7a] Ag_2CO_3 with a catalytic amount of I_2,[7c,d] AgOTf,[7b] $AgClO_4$[7e]) (Koenigs–Knorr method) and mercury salts ($Hg(CN)_2$–$HgBr_2$,[8a,c] $Hg(CN)_2$,[5b] $HgBr_2$[8b]). To avoid the use of these heavy metal salts, some Lewis acids ($Sn(OTf)_2$,[9a] $InCl_3$,[9b] $FeCl_3$[9c]) or iodonium reagents[10] have occasionally been employed.

Another effective method is Lewis acid-catalyzed glycosylation using sugar peracetates. Typical acid catalysts employed are $SnCl_4$,[11] $BF_3{\cdot}OEt_2$,[12] Me_3SiOTf,[13] and $FeCl_3$.[14] Peracetylated sugars would be preferable glycosyl donors in view of their ready accessibility (available by only one-step acetylation of the parent sugar) and stability. In addition, peracetylated sugars are versatile precursors of other donors such as anomeric halides,[15] 1-thio-sugars,[16] and 1-*O*-trichloroacetimidates.[17] It has been known that, as for glucose and galactose derivatives, the anomeric β-acetate is much more reactive than the corresponding α-acetate.[18] In general, reactions of *O*-acetyl-protected sugars with alcohols preferentially give 1,2-*trans*-glycosides due to the neighboring C-2 acetoxy group participation.[6] However, recent reports have indicated that thermodynamically more stable 1,2-*cis*-α-glycosides (glucosides or galactosides at the reducing end) are preferentially formed via anomerization under acidic conditions.[11b,e,14,19] Penta-*O*-acetylmannose should give 1,2-*trans*-α-mannoside exclusively as dictated by both the neighboring group participation and the anomeric effect.

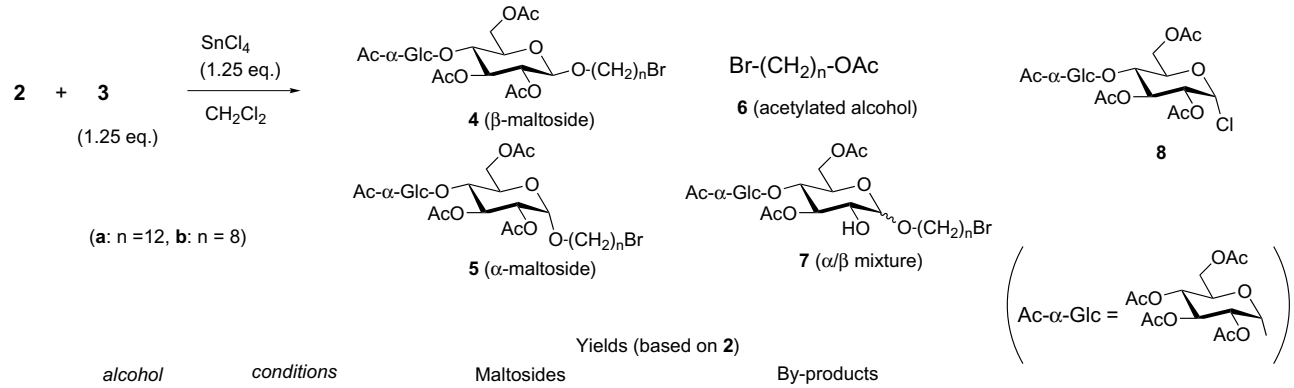
Concanavalin A, a readily available lectin,[20] can specifically recognize a 1,2-*trans*-α-mannoside and a 1,2-*cis*-α-glucoside residue at the nonreducing end of the glycosides. In mammalian glycolipids, glucose is a major component, whereas mannose is a minor one. We planned to prepare ω-mercaptoalkyl β-maltosides **1**, which have an α-glucoside residue as shown in Scheme 1. For the synthesis of **1**, we first examined the reaction of β-maltose octaacetate **2** and commercially available ω-bromo-1-alkanols **3** under Lewis acid conditions.[21]

According to a literature precedent,[11a] β-maltose octaacetate (**2**) was treated with 12-bromo-1-dodecanol (**3a**, 1.25 equiv) using $SnCl_4$ (1.25 equiv) as a promoter at 0 to 5 °C for 5 h. The reaction gave the expected bromododecyl β-maltoside **4a** in 46% yield along with several byproducts: 12-bromododecyl acetate **6a** (32% based on **2**), 2-O-deacetylated bromododecyl maltoside **7a** (α/β-mixture, 3%), and hepta-*O*-acetyl-α-maltosyl chloride **8** (14%) (Scheme 2). Partially anomerized octaacetate **2** (12%, $\beta/\alpha = 2$) and more polar, hepta-*O*-acetyl maltose (15%) were also formed. Prolonged reaction at rt for 10 h reduced the amounts of **2** and the chloride **8** (3%). However, **6a** and **7a** increased, and the major product was an inseparable mixture of **4a** and the α-anomer **5a** (2:1, 50% yield). The α/β ratio of the mixture was determined by ^1H NMR spectroscopy. $SnCl_4$-promoted reaction of **2** with 8-bromo-1-octanol **3b** was also examined. The reaction at 0 to 5 °C for 5 h gave the 8-bromooctyl β-maltoside **4b** in 40% yield containing a trace amount of the α-anomer **5b** (1%), whereas prolonged reaction at rt for 16 h gave an inseparable mixture of **4b** and **5b** (2:3) in 42% yield. These results indicate that initially formed β-anomer was epimerized to more stable α-maltoside by $SnCl_4$ at rt. Banoub and Bundle reported[11b] the almost complete β to α anomerization of 8-ethoxycarbonyloctyl maltoside by $SnCl_4$ at rt for 4 h. In our cases, however, the equilibrium would not lie close to the α-anomer.

It proved very difficult to separate the α and β anomers of bromoalkyl acetylated maltosides. Although concanavalin A would recognize both α- and β-maltosides, stereochemically pure compounds are desirable for proper evaluation. Thus formation of the α anomers should be minimized. It has been reported that the two anomers of disaccharides could be separated after deacetylation.[9c] However, for our purpose, it would be preferable to separate the anomers before deacetylation.

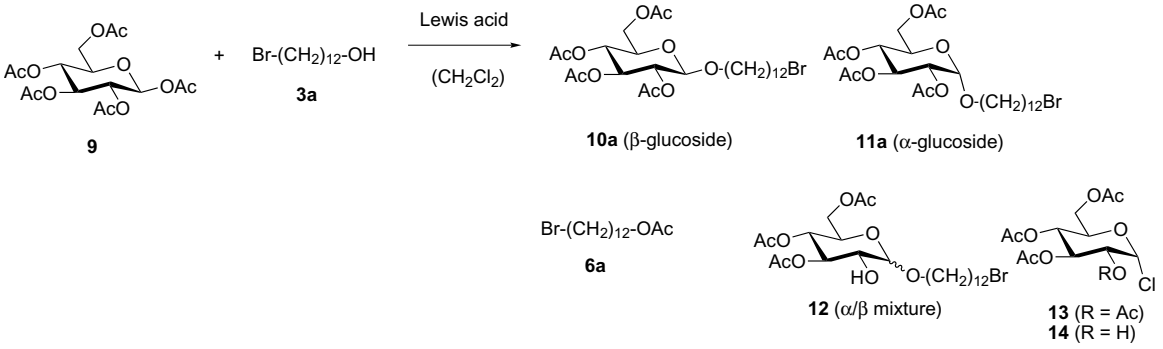


Scheme 1.



alcohol	conditions	Yields (based on **2**) Maltosides	By-products
3a	5 °C, 5 h	**4a** (46%) + **5a** (<1%)	**6a** (32%), **7a** (3%), **8** (14%)
3a	5 °C to rt, 10 h	**4a** + **5a** (50%, 2:1 mixture)	**6a** (55%), **7a** (15%), **8** (3%)
3b	5 °C, 5 h	**4b** (40%) + **5b** (1%)	**6b** (34%), **7b** (2%), **8** (18%)
3b	5 °C to rt, 16 h	**4b** + **5b** (42%, 2:3 mixture)	**6b** (56%), **7b** (20%), **8** (3%)

Scheme 2. Maltosylation of bromo-alkanols **3a**,**b** promoted by $SnCl_4$.



Scheme 3. Lewis acid-promoted reaction of β-D-glucose pentaacetate (**9**) with 12-bromo-1-dodecanol (**3a**).

Table 1. Lewis acid-promoted reaction of β-D-glucose pentaacetate (**9**) with 12-bromo-1-dodecanol (**3a**)[a]

Entry	Lewis acid	Additive (equiv)	Conditions[b]	Yield[c] (%)			
				10a (β)	**11a** (α)	**12**	**6a**
1	$SnCl_4$		5 °C, 5 h	43	3	4	33
2	$SnCl_4$		5 °C to rt, 20 h	3	54	6	50
3	$SnCl_4$	$AgClO_4$ (0.6)[d]	−10 to 0 °C, 15 h	24	0	6	37
4	$SnCl_4$	Ag_2CO_3 (1.0)	5 °C, 3 h	44	1	8	31
5	$SnCl_4$	$CaCO_3$ (1.2)	5 °C, 5 h	47	4	4	38
6	$SnCl_4$	TMU[e] (0.5)	5–15 °C, 5 h	40	1	7	36
7	$BF_3{\cdot}OEt_2$		5 °C to rt, 3 h	42	2	5	34
8	Me_3SiOTf	MS4A	−20 to 0 °C, 3 h	25	0	5	92
9	$FeCl_3$		5 °C, 1 h	27	4	26	63
10	$ZrCl_4$		5 °C, 5 h	19	0	4	61
11	$InBr_3$		5–15 °C, 4 h	27	1	25	56
12	$CeCl_3$		rt to 40 °C, 1 h		No reaction		
13	$BiCl_3$		rt, 2 h	12	2	42	70
14	$ZnCl_2$		5 °C to rt, 2 h		No reaction		
15	$ZnCl_2$		rt to 65 °C,[f] 1 h	58	3	16	28
16	$Zn(OTf)_2$		rt to 75 °C,[f] 3 h	4	1	13	52

[a] Lewis acid and **3a** used were 1.25–1.50 equiv to **9**.
[b] Reaction was carried out in CH_2Cl_2 unless otherwise noted.
[c] Isolated yield after chromatography, based on sugar **9**, not on alcohol **3a**.
[d] 4 Å Molecular sieves were also added.
[e] Tetramethylurea.
[f] The reaction was carried out in toluene.

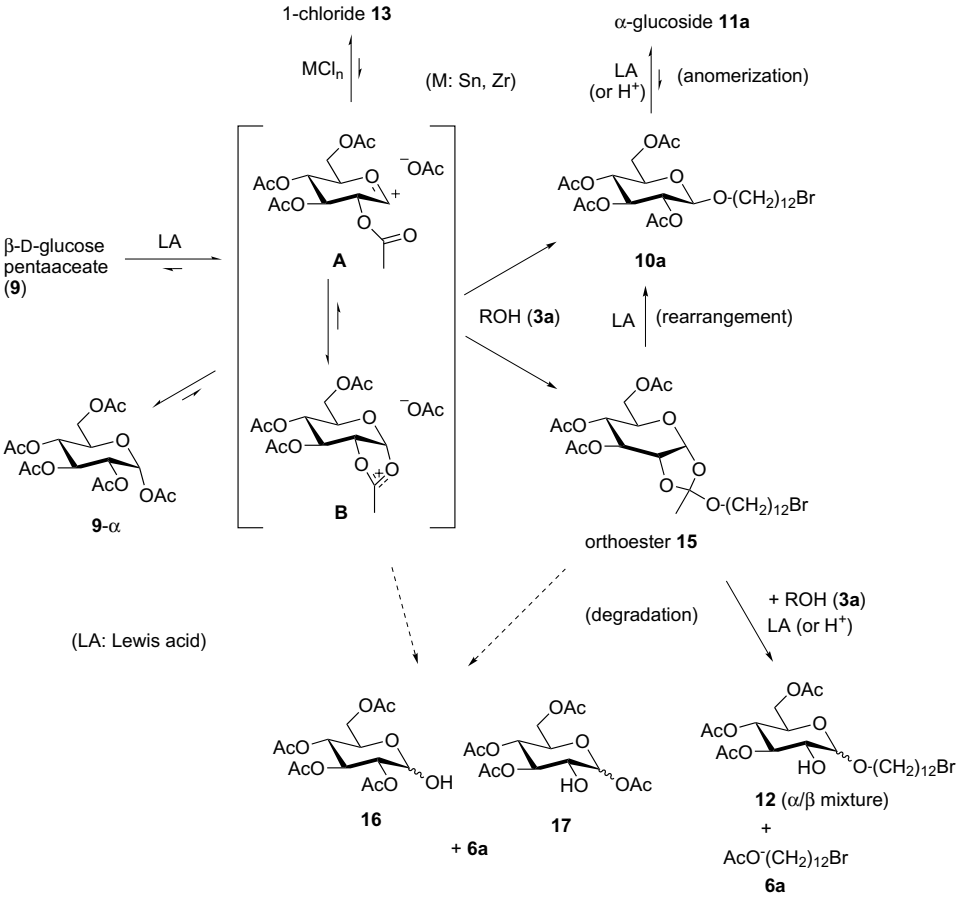
In order to improve the yield of 1,2-*trans*-glycosides, we investigated the reaction of β-D-glucopyranose pentaacetate (**9**) with 12-bromododecanol (**3a**, 1.2–1.5 equiv) under various Lewis acid conditions (Scheme 3). Penta-*O*-acetyl-β-D-glucose (**9**) is cheap, and the products, alkyl α- and β-glucosides (**10a** and **11a**) can be separated by silica gel chromatography. The results are summarized in Table 1. Molecular sieves were not used in principle because they sometimes considerably retard this type of glycosylation. The reaction was quenched when most of the β-peracetate **9** was consumed, though the end point was not clear because of the similarity in its mobility on TLC with the much less reactive, α-anomerized **9**.

With $SnCl_4$, similar to the maltosylation, β-glucoside **10a** was selectively formed at 5 to 10 °C. Above 10 °C, the anomerization was observed, and α-glucoside **11a**, less polar anomer, was predominantly obtained in 54% yield at rt for 16 h. Below 10 °C, a significant amount of anomeric chloride **13** (10–20%) was formed by $SnCl_4$,[11a] and separation from the glucoside **10a** was difficult in this case. For the reaction of the chloride **13** with **3a**, addition of silver salt was attempted: addition of $AgClO_4$ decreased the yield, whereas Ag_2CO_3 had little effect. To suppress the anomerization and by-product formation, addition of proton scavengers was examined. However, both $CaCO_3$ and tetramethylurea did not have much effect on the yield of **10a**.

Next, other commonly employed Lewis acids ($BF_3{\cdot}OEt_2$, Me_3SiOTf, $FeCl_3$) were examined. Glucosylation using $BF_3{\cdot}OEt_2$ at rt gave **10a** in 42% yield with a small amount of α-anomer **11a**. This yield is consistent with that reported for the reaction of **9** and 2-bromoethanol with 5 equiv of $BF_3{\cdot}OEt_2$ (42%).[12b] Me_3SiOTf and $FeCl_3$ gave lower yields of **10a** and higher yields of bromododecyl acetate **6a**.

Less common Lewis acids ($ZrCl_4$, $InBr_3$, $CeCl_3$, $BiCl_3$) were also examined. These salts except $CeCl_3$ promoted the reaction at 5 °C to rt, but the yields of **10a** were low (12–27%). With $ZrCl_4$, the anomeric chloride **13** was formed at the early stage, and then gradually decreased, and 3,4,6-tri-*O*-acetyl-α-D-glucopyranosyl chloride (**14**) was obtained in 30% yield as a major product. The product distribution by $InBr_3$ was similar to that by $FeCl_3$. $BiCl_3$ gave 2-O-deacetylated glucoside **12** ($\alpha/\beta = 2{:}3$) as a major product.

No reaction took place by using $ZnCl_2$ at rt. However, the glucoside **10a** was formed above 50 °C, and the best

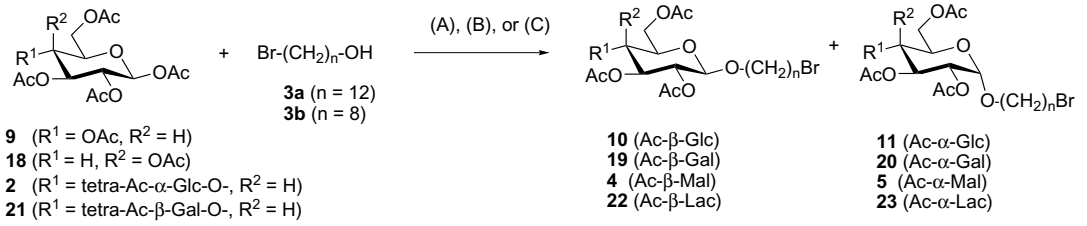


Scheme 4. Plausible reaction pathways.

yield (58%) was obtained in toluene at 65 °C for 1 h. In contrast to $ZnCl_2$, zinc triflate gave **10a** in very low yield.

The plausible reaction pathways of the glycosylation are depicted in Scheme 4.[22] The initial step of the reaction is a Lewis acid-promoted dissociation of **9**, involving the participation of the C-2 acetoxy group, to give an oxocarbenium–acetate ion pair (**A**) or a more stabilized dioxolenium ion (**B**). The carbenium ion would react with the alcohol **3a** to give the desired 1,2-*trans*-glucoside **10a** and 1,2-orthoester **15**. Under acidic reaction conditions, the orthoester **15** would rearrange[23] to **10a** or would react with **3a** to give the acetylated alcohol **6a** and 2-O-deacetylated glucoside **12**. However, in most entries in Table 1, the yield of **6a** was much higher than that of **12**. In the $SnCl_4$- and BF_3-promoted glucosylations, the yields of **10a** were modest (40–50%), but it would be acceptable in view of the precedents.[11,12,21] Other byproducts were tetra-*O*-acetyl-glucoses **16** (major) and **17** (minor) (total 15–30% based on **9**), a mixture of **9** and **9**-α (3–10%), and the glucosyl chlorides (**13**, **14**) (10–20% using $SnCl_4$). The combined yields of the coupled products (**10a**, **11a**, **12**) and the byproducts derived from **9** were 85–95% in all, and the total yield of the deacetylated products (**12**, **16**, **17**) was comparable to the yield of the acetylated alcohol **6a**. These results would suggest a degradation pathway(s) to both **6a** and **16**/**17**. Further studies will be necessary to elucidate the mechanism of the formation of these byproducts under essentially anhydrous conditions.

We next examined the $ZnCl_2$-promoted glycosylation of **3a**,**b** with β-peracetylated sugars (glucose **9**, galactose **18**, maltose **2**, and lactose **21**), and compared to $SnCl_4$-promoted glycosylation (Scheme 5). The results are summarized in Table 2. It was observed that initially dispersed zinc halide, which is almost insoluble in toluene, began to deposit and finally attached to the flask with the progress of the reaction. 8-Bromooctyl-



Scheme 5. Glycosylation of **3a**,**b** with peracetylated β-D-sugars. Reagents and conditions: (A) $SnCl_4$, CH_2Cl_2, 5–10 °C, 3–5 h. (B) $ZnCl_2$, toluene, 60–65 °C, 0.5–1 h. (C) $ZnBr_2$ ($CaCO_3$), toluene, 60–65 °C, 0.5–1 h.

Table 2. Glycosylation of **3a**,**b** with peracetylated β-D-sugars[a] promoted by $SnCl_4$, $ZnCl_2$, or $ZnBr_2$

Sugar	Alcohol	Yield[b] (β:α ratio)[c]					
		By $SnCl_4$		By $ZnCl_2$		By $ZnBr_2$	
		β	α	β	α	β	α
9 (Glc)	**3a**	43	3	58	3	57	6
9	**3b**	40	7	50	3	39	14
16 (Gal)	**3a**	60	2	64	4	63	7
16	**3b**	53	<1	54	5	39[d]	17[d]
2 (Mal)	**3a**	46 (100:<1)		57 (100:2)		67 (100:6)[e]	
2	**3b**	40 (100:1)		57 (100:3)		60 (100:13)[d,f]	
19 (Lac)	**3a**	40 (100:2)		51 (100:2)		55 (100:6)[e]	
19	**3b**	42 (100:<1)		45 (100:4)		46 (100:14)[g]	

[a] Alcohol and Lewis acid used were 1.2–1.5 equiv to sugar peracetate.
[b] Isolated yield (%) after chromatography.
[c] The ratio in parenthesis was determined by ^1H NMR spectroscopy.
[d] The reaction was carried out at 50 °C for 0.5 h.
[e] $CaCO_3$ (1.5 equiv) was added.
[f] In the absence of $CaCO_3$, a 1:1 mixture was obtained in 60% yield.
[g] $CaCO_3$ (3 equiv) was added.

and 12-bromododecyl glycosides were obtained in 45–68% yields by $ZnCl_2$ in toluene at 60–65 °C (bath temperature) within 1 h. Bromoalkyl acetate **6a**,**b** and 2-O-deacetylated glycosides such as **7** were obtained in 18–36% and 13–25% yields, respectively (individual data not shown), but glycosyl chlorides were not obtained. The glucosylation of **3a** with $ZnCl_2$ proceeded in dichloroethane at 60 °C with lower stereoselectivity (β: 47%, α: 7%). No reaction took place in acetonitrile even at 80 °C, presumably due to the Lewis base character of the solvent.

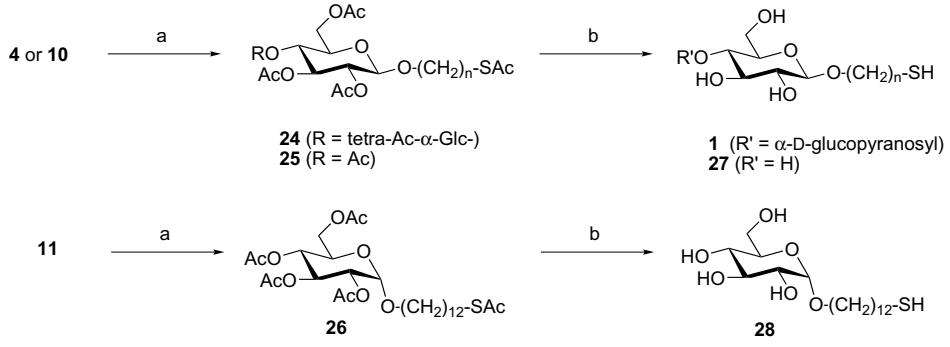
The following trends on the yield and stereoselectivity were observed.

(1) In most cases, the yield of β-glycoside by using $ZnCl_2$ is ca. 5–15% higher than that by using $SnCl_4$. However, the β selectivity is slightly lower, probably due to the higher reaction temperature.
(2) $ZnBr_2$ gave the glycosides in slightly better yields, but with lower β selectivity than $ZnCl_2$. The anomerization was suppressed to some extent by adding $CaCO_3$.
(3) The yields and β selectivities of bromooctyl glycosides are lower than those of bromododecyl glycosides, though bromooctanol **3b** appears to be more reactive than bromododecanol **3a**.
(4) Among four sugars, the yields of galactosides are generally higher, whereas those of lactosides are lower.

Zinc chloride has been employed as a glycosylation promoter in the following cases: (1) phenols with glycosyl peracetates at high temperatures (>100 °C) without solvent;[24] (2) alcohols with 1,2-anhydro sugars;[25] (3) alcohols with 'armed' glycosyl phosphites.[26] However, it has rarely been used for the reaction of alcohols with per-*O*-acetyl sugars, presumably due to the lower activity compared to $SnCl_4$ or $BF_3{\cdot}OEt_2$. Indeed as shown in Table 1, $ZnCl_2$ showed little or no activity at rt, but it gave the β-glucoside **10a** on heating with the best yield among the Lewis acids examined. This type of glycosylation should involve various factors that would affect the product distribution as shown in Scheme 4. When a reactive primary alcohol and/or an active catalyst are employed, side reactions such as orthoester formation and the degradation, anomerization, and anomeric halogenation would also proceed rapidly, resulting in the decrease of β-glycoside.

2.2. Synthesis of ω-mercaptoalkyl glycosides

Synthesis of ω-mercaptoalkyl glycosides from protected ω-bromoalkyl glycosides is straightforward as shown in Scheme 6. Besides β-maltosides **4a**,**b**, β-glucosides **10a**,**b**, and α-glucoside **11a** were used for comparison. These ω-bromoalkyl glycosides were treated with potassium thioacetate in DMF to give the thioacetates (**24a**,**b**, **25a**,**b**, **26**) in high yields. Deacetylation with NaOMe (ca. 1 equiv) in MeOH and CH_2Cl_2 afforded ω-mercaptoalkyl glycosides (**1a**,**b**, **27a**,**b**, **28**) as major products (82–85% yields) and the disulfides as minor ones (10–15% yields). The disulfides were much more polar than the corresponding thiols on TLC, for example, R_f 0.36 for **27a** and 0.05 for the disulfide (8:1, CH_2Cl_2–MeOH). In the ^{13}C NMR spectra of the thiols in $CDCl_3$ with CD_3OD (10:1), the terminal carbon signal appeared to split ($\Delta\delta$ 0.1–0.2 ppm) as shown in Table 8. The signal of the carbon next to the terminal was slightly split as well ($\Delta\delta$ ca. 0.03 ppm). In their ^1H NMR spectra, small but sharp triplets ($J = 7.8$ Hz) were observed at δ ca. 1.35 ppm as shoulders of huge methylene signals (δ 1.25–1.40 ppm). These observations indicate that both the thiol (RSH) and the deuterated thiol (RSD) would exist as an equilibrium mixture with excess CD_3OD, in which all sugar hydroxy groups have been deuterated. Dodecanethiol derivatives (**1a**, **27a**, **28**) solidified, whereas octanethiol derivatives (**1b**, **27b**) were syrupy. The thiol group was gradually oxidized in the air to the disulfide, which can also be used for the preparation of gold glyconanoparticles.[5] Similarly, mercaptoalkyl β-galactosides and β-lactosides should be prepared from **19** and **22**.



Scheme 6. Reagents and conditions: (a) KSAc, DMF, rt, 2 h; (b) NaOMe, MeOH–CH_2Cl_2, 5 °C, 2 h.

3. Conclusions

To prepare glycolipid clusters, the synthesis of ω-mercaptoalkyl glycosides was investigated. It was found that $ZnCl_2$ promotes the 1,2-*trans*-glycosylation of ω-bromo-1-alkanols (C_8, C_{12}) with per-O-acetylated sugars in toluene at about 60 °C in a stereocontrolled manner with better yields than commonly employed promoters such as $SnCl_4$. These results would be advantageous from an ecological and economical point of view because of the low toxicity and cost of $ZnCl_2$. We have developed an efficient synthetic route to ω-mercaptoalkyl glycosides, which can be used to prepare assembled carbohydrate model systems.

4. Experimental

4.1. General methods

Melting points were determined with a Yanaco melting point apparatus MP-500D. Optical rotations were measured with a JASCO DIP-1000 polarimeter, and $[\alpha]_D$ values are given in 10^{-1} deg cm^2 g^{-1}. ^{1}H NMR spectra were recorded at 270 MHz on a JEOL JNM-GSX-270 spectrometer, and chemical shifts (δ) are reported in ppm relative to internal tetramethylsilane (δ 0.00). ^{13}C NMR spectra were recorded at 67.8 MHz and chemical shifts (δ) are reported in ppm relative to $CDCl_3$ (δ 77.0). Most of the NMR data are summarized in Tables 3–8. Elemental analyses were performed in the analytical section in this Institute (AIST). High-resolution mass (HRMS) and fast-atom bombardment mass (FABMS) spectra were obtained on Hitachi M80B and a JEOL MS600H mass spectrometers, respectively. Routine monitoring of reactions was carried out using E. Merck Silica Gel 60F_{254} TLC plates, and compounds were detected by dipping the plates in 10% aq H_2SO_4, followed by heating. Column chromatography was performed with indicated solvents on silica gel (Kanto Chemicals, neutral, 100–210 μm, or Wakogel C-300, 45–75 μm). Commercially available sugar peracetates (**2**, **9**, **18**, **21**) were used without further purification. $SnCl_4$ (1.0 M solution in heptane) was purchased from Aldrich and used as received. Sugar peracetates and solid Lewis acids were dried in vacuo for over 1 h before use.

4.1.1. General glycosylation procedure (A) using $SnCl_4$ as promoter. To a cooled solution of sugar peracetate (0.30 mmol) and bromo-1-alkanol (**3**, 0.40 mmol) with or without additive in CH_2Cl_2 (3 mL) was added dropwise a 1.0 M solution of $SnCl_4$ in heptane (0.4 mL, 0.4 mmol), and the mixture was stirred at 0–5 °C until most of the peracetate was consumed. (For the synthesis of the α-glucoside, the mixture was stirred at rt for more than 5 h.) The resulting mixture was diluted with EtOAc (20 mL) and aq $NaHCO_3$ (20 mL), and the mixture was stirred for 10 min, filtered through Celite, and washed thoroughly with EtOAc (10 mL). The combined filtrate and washings were successively washed with H_2O and brine. The aqueous phase was extracted with EtOAc (2×20 mL), and the combined organic layers were dried over Na_2SO_4. Removal of the solvent gave a residue that was purified by silica gel column chromatography. For maltose derivatives, the column was eluted with 2:1→1.5:1 hexane–EtOAc to give acetylated alcohol **6**,

Table 3. ^{1}H NMR chemical shifts (δ in ppm) of acetylated monosaccharides in $CDCl_3$

	Glucoside						Galactoside	
	10a	**10b**	**11a**	**25a**	**25b**	**26**	**19a**	**19b**
H-1′	4.49	4.49	5.07	4.49	4.49	5.06	4.46	4.46
H-2′	4.99	4.98	4.85	4.98	4.98	4.85	5.20	5.20
H-3′	5.21	5.21	5.49	5.21	5.20	5.48	5.02	5.02
H-4′	5.09	5.09	5.05	5.08	5.08	5.05	5.39	5.38
H-5′	3.69	3.69	4.01	3.69	3.69	4.02	3.90	3.90
H-6′a	4.14	4.14	4.09	4.13	4.13	4.09	4.13	4.13
H-6′b	4.27	4.27	4.26	4.27	4.27	4.26	4.19	4.19
H-1a	3.47	3.47	3.42	3.47	3.47	3.42	3.47	3.48
H-1b	3.87	3.87	3.68	3.86	3.86	3.68	3.88	3.88
2-H_2	1.85	1.85	1.86	1.56	1.56	1.57	1.85	1.85
3-H_2	1.42	1.42	1.43	1.33	1.42	1.35	1.42	1.43
CH_2–C–X[a]	1.56	1.56	1.59	1.56	1.56	1.55	1.57	1.57
CH_2–X[a]	3.41	3.41	3.41	2.86	2.85	2.86	3.41	3.40
Other CH_2	1.26	1.30	1.28	1.25	1.29	1.27	1.27	1.30
AcO	2.01	2.01	2.02	2.00	2.00	2.01	1.98	1.98
	2.03	2.03	2.03	2.02	2.02	2.03	2.05	2.04
	2.04	2.04	2.06	2.04	2.04	2.06	2.05	2.05
	2.09	2.09	2.09	2.06	2.08	2.09	2.15	2.15
Ac–S				2.32	2.32	2.32		

[a] X = Br or S.

Table 4. ^{13}C NMR chemical shifts (δ in ppm) of acetylated monosaccharides in $CDCl_3$

	Glucoside						Galactoside	
	10a	**10b**	**11a**	**25a**	**25b**	**26**	**19a**	**19b**
C-1′	100.8	100.8	95.5	100.8	100.8	95.5	101.3	101.3
C-2′	71.4	71.3	70.2	71.3	71.3	70.2	70.3	70.0
C-3′	72.9	72.8	70.9	72.8	72.8	70.9	70.5	70.5
C-4′	70.2	70.1	67.1	70.1	70.1	67.0	67.0	67.0
C-5′	71.7	71.7	68.6	71.7	71.7	68.6	70.9	70.9
C-6′	62.0	62.0	61.9	61.9	62.0	61.9	61.2	61.2
C-1	68.5	68.5	68.7	68.5	68.5	68.7	68.9	68.9
CH_2–X[a]	34.0	33.9	34.0	30.5	30.5	30.6	34.0	33.8
CH_2–C–Br	32.8	32.7	32.7				32.8	32.6
C-3	25.8	25.7	25.9	25.7	25.7	25.9	25.8	25.6
Other CH_2	28.1	28.0	28.1	28.7	28.6	28.7	28.1	27.9
	28.7	28.6	28.7	29.0	28.9	29.03	28.7	28.5
	29.27	29.0	29.17	29.1	29.01	29.07	29.27	29.0
	29.36	29.3	29.25	29.2	29.02	29.17	29.36	29.3
	29.37		29.34	29.31	29.3	29.25	29.37	
	29.47		29.43	29.36	29.4	29.37	29.46	
	29.49		29.48	29.41		29.42	29.48	
	29.52		29.49	29.45[b]		29.46	29.51	
				29.48		29.48		
CH_3CO	20.56	20.55	20.56	20.50	20.50	20.55	20.57	20.45
	20.59	20.58	20.61	20.53	20.53	20.60	20.64[b]	20.53[b]
	20.61	20.61	20.65[b]	20.55	20.56	20.64[b]	20.71	20.62
	20.70	20.69		20.63	20.64			
O–C=O	169.2	169.2	169.6	169.2	169.2	169.6	169.3	169.2
	169.4	169.4	170.07	169.3	169.3	170.06	170.1	170.0
	170.3	170.3	170.11	170.2	170.2	170.10	170.2	170.1
	170.7	170.6	170.6	170.6	170.6	170.6	170.3	170.2
S–C=O				195.9	195.9	195.9		

[a] X = Br or S.
[b] Two carbons would overlap.

unreacted **3**, maltoside **4/5** (α/β mixture), maltosyl chloride **8** (if formed), and a mixture of **2** and **7** in that order. For glucose derivatives, elution with 3:1→2:1 hexane–EtOAc gave acetylated alcohol **6**, unreacted **3**, α-glucoside **11**, β-glucoside **10**, glucosyl chloride **13** (if formed), **12**, and **9** (α/β mixture) in that order. When the separation was incomplete, the product ratio in fractions of the mixture was determined by ^1H NMR spectroscopy. This procedure was also applied to the glycosylation with liquid Lewis acids ($BF_3{\cdot}OEt_2$, Me_3SiOTf). When solid acids were used (except zinc salts), bromo-alkanol in CH_2Cl_2 was added to a cooled mixture of sugar acetate and a Lewis acid in CH_2Cl_2.

4.1.2. General glycosylation procedure (B) using $ZnCl_2$ as promoter. To a mixture of sugar peracetate (0.30 mmol), bromo-1-alkanol (**3**, 0.4 mmol), and $ZnCl_2$ (56 mg, 0.4 mmol, dried in vacuo at 110 °C for 1 h prior to use) with or without additive was added toluene (4 mL), and the suspension was stirred at 60–65 °C for 0.5–1 h. The reaction was quenched by dilution with EtOAc (20 mL) and aq $NaHCO_3$ (20 mL), and the mixture was worked up as described in procedure (A).

4.1.3. 12-Bromododecyl 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (4a). Compound **4a** was prepared from **2** and **3a** either using general procedure (A) in 46% yield or (B) in 57% yield as a colorless solid: mp 82–85 °C; $[\alpha]_D^{24}$ +37.5 (*c* 1.6, $CHCl_3$); R_f 0.44 (3:2 hexane–EtOAc). Anal. Calcd for $C_{38}H_{59}BrO_{18}$: C, 51.64; H, 6.73. Found: C, 51.80; H, 6.93.

4.1.4. 8-Bromooctyl 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (4b). Compound **4b** was prepared from **2** and **3b** either using (A) in 40% yield or (B) in 57% yield as a colorless oil: $[\alpha]_D^{23}$ +51.7 (*c* 1.2, $CHCl_3$); R_f 0.38 (3:2 hexane–EtOAc); FABMS (positive-ion, NBA) *m/z* (%) 851.2 ($[M+Na]^+$, 6), 619.3 (14), 559.1 (7), 331.2 (20).

4.1.5. 12-Bromododecyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (10a). Compound **10a** was prepared from **9** and **3a** either using (A) in 43% yield or (B) in 58% yield as a colorless solid: mp 50–52 °C; $[\alpha]_D^{24}$ −12.7 (*c* 2.2, $CHCl_3$); R_f 0.31 (3:1 hexane–EtOAc). Anal. Calcd for $C_{26}H_{43}BrO_{10}$: C, 52.44; H, 7.28. Found: C, 52.48; H, 7.17.

Table 5. ^{1}H NMR chemical shifts (δ in ppm) of acetylated disaccharides[a] in $CDCl_3$

	Maltoside				Lactoside	
	4a	**4b**	**24a**	**24b**	**22a**	**22b**
H-1′	4.51	4.51	4.51	4.51	4.49	4.49
H-2′	4.81	4.81	4.81	4.81	4.88	4.87
H-3′	5.25	5.25	5.25	5.25	5.19	5.19
H-4′	4.00	4.00	4.00	4.00	3.79	3.79
H-5′	3.67	3.67	3.67	3.68	3.59	3.59
H-6′a	4.23	4.23	4.23	4.24	4.11	4.11
H-6′b	4.47	4.47	4.47	4.47	4.47	4.47
H-1″	5.42	5.41	5.42	5.41	4.45	4.45
H-2″	4.86	4.86	4.86	4.86	5.11	5.10
H-3″	5.36	5.36	5.36	5.36	4.95	4.96
H-4″	5.05	5.05	5.05	5.05	5.34	5.34
H-5″	3.98	3.98	3.98	3.98	3.87	3.87
H-6″a	4.03	4.04	4.03	4.04	4.08	4.08
H-6″b	4.26	4.26	4.23	4.24	4.14	4.14
H-1a	3.47	3.47	3.47	3.46	3.45	3.45
H-1b	3.84	3.84	3.85	3.84	3.82	3.82
2-H_2	1.85	1.84	1.55	1.55	1.85	1.85
3-H_2	1.41	1.42	1.33	1.33	1.42	1.42
CH_2–C–X[b]	1.55	1.55	1.55	1.55	1.54	1.55
CH_2–X[b]	3.41	3.40	2.86	2.85	3.41	3.40
Other CH_2	1.26	1.30	1.25	1.28	1.26	1.30
Ac–S			2.32	2.32		

[a] Acetoxy proton signals (1.95–2.15 ppm) are not shown.
[b] X = Br or S.

Table 6. ^{13}C NMR chemical shifts (δ in ppm) of acetylated disaccharides[a] in $CDCl_3$

	Maltoside				Lactoside	
	4a	**4b**	**24a**	**24b**	**22a**	**22b**
C-1′	100.2	100.2	100.2	100.2	100.5	100.5
C-2′	72.2	72.2	72.2	72.2	71.7	71.7
C-3′	75.4	75.4	75.4	75.4	72.8	72.8
C-4′	72.7	72.7	72.7	72.7	76.3	76.3
C-5′	72.0	72.0	72.0	72.0	72.5	72.6
C-6′	62.8	62.8	62.8	62.8	62.0	62.0
C-1″	95.4	95.5	95.4	95.5	101.0	101.0
C-2″	70.1	70.1	70.2	70.1	70.2	70.0
C-3″	69.9	69.9	69.9	69.9	70.9	71.0
C-4″	68.0	68.0	68.0	68.0	66.6	66.6
C-5″	69.3	69.3	69.3	69.3	70.6	70.7
C-6″	61.5	61.5	61.4	61.5	60.7	60.8
C-1	68.4	68.4	68.4	68.4	69.1	69.1
CH_2–X[b]	34.0	33.9	30.6	30.6	34.0	33.8
CH_2–C–Br	32.8	32.7			32.8	32.7
C-3	25.7	25.6	25.7	25.7	25.7	25.6
Other CH_2	28.1	28.0	28.7	28.6	28.1	28.0
	28.7	28.6	29.0	28.96	28.7	28.6
	29.2	29.0	29.1	29.04[c]	29.23	29.0
	29.30	29.3	29.2	29.3	29.35[c]	29.3
	29.34		29.3	29.4	29.44[c]	
	29.42		29.38		29.49	
	29.45		29.43			
	29.48		29.48			
O–C=O	169.3	169.4	169.4	169.4	169.0	169.0
	169.5	169.5	169.5	169.5	169.5	169.5
	169.9	169.9	169.9	169.9	169.8	169.7
	170.2	170.2	170.2	170.2	170.0	169.9
	170.4	170.4	170.4	170.4	170.1	170.0
	170.5[c]	170.5[c]	170.5[c]	170.5[c]	170.28	170.22
					170.32	170.25
S–C=O			196.0	196.0		

[a] The methyl signal of acetyl group (20.4–21.0 ppm) is not shown.
[b] X = Br or S.
[c] Two carbons would overlap.

4.1.6. 8-Bromooctyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (10b). Compound **10b** was prepared from **9** and **3b** either using (A) in 40% yield or (B) in 50% yield as a colorless oil: $[\alpha]_D^{24}$ −14.2 (*c* 1.1, $CHCl_3$); R_f 0.23 (3:1 hexane–EtOAc); FABMS (positive-ion, NBA) *m/z* 563 ([M (for ^{81}Br)+Na]$^+$, 3), 561 ([M (for ^{79}Br)+Na]$^+$, 3), 331 (100).

4.1.7. 12-Bromododecyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranoside (19a). Compound **19a** was prepared from **18** and **3a** either using (A) in 53% yield or (B) in 54% yield as a colorless oil: $[\alpha]_D^{24}$ −9.1 (*c* 2.75, $CHCl_3$); R_f 0.31 (3:1 hexane–EtOAc); FABMS (positive-ion, NBA) *m/z* (%) 619 ([M (for ^{81}Br)+Na]$^+$, 16), 617 ([M (for ^{79}Br)+Na]$^+$, 16), 331 (100).

4.1.8. 8-Bromooctyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranoside (19b). Compound **19b** was prepared from **18** and **3b** either using (A) in 60% yield or (B) in 64% yield as a colorless oil: $[\alpha]_D^{24}$ −9.0 (*c* 2.1, $CHCl_3$); R_f 0.27 (3:1 hexane–EtOAc); CIHRMS *m/z* calcd for $C_{20}H_{31}BrO_8$ [M−AcOH]$^+$: 478.1202 for ^{79}Br and 480.1182 for ^{81}Br. Found: 478.1076 and 480.1069. (M$^+$ was not observed.)

4.1.9. 12-Bromododecyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (22a). Compound **22a** was prepared from **21** and **3a** either using (A) in 40% yield or (B) in 51% yield as a colorless oil: $[\alpha]_D^{24}$ −10.3 (*c* 2.7, $CHCl_3$); R_f 0.35 (3:2 hexane–EtOAc); FABMS (positive-ion, NBA) *m/z* (%) 907.5 ([M+Na]$^+$, 36), 619.3 (53), 559.2 (28), 331.0 (100).

4.1.10. 8-Bromooctyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (22b). Compound **22b** was prepared from **21** and **3b** either using (A) in 42% yield or (B) in 45% yield as a colorless oil: $[\alpha]_D^{24}$ −10.8 (*c* 1.2, $CHCl_3$); R_f 0.30 (3:2 hexane–EtOAc); FABMS (positive-ion, NBA) *m/z* (%) 851.4 ([M+Na]$^+$, 18), 619.1 (33), 559.2 (34), 475.3 (35), 331.0 (100).

4.1.11. 12-Bromododecyl 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranoside (11a). Compound **11a** was prepared from **9** and **3a** by using (A) (at rt for 20 h) in 54% yield as a colorless oil: $[\alpha]_D^{24}$ +81.2 (*c* 2.4, $CHCl_3$); R_f 0.37 (3:1

Table 7. ^{1}H–^{1}H coupling constant (J)[a] data for 12-bromododecyl per-*O*-acetylglycosides[b]

	10a (β-Glc)	**11a** (α-Glc)	**19a** (β-Gal)	**4a** (β-Mal)	**22a** (β-Lac)
$J_{1',2'}$	8.1	3.9	7.8	8.1	8.1
$J_{2',3'}$	9.5	10.3	10.5	9.5	9.5
$J_{3',4'}$	9.5	9.5	3.4	9.2	9.1
$J_{4',5'}$	9.8	10.3	<1	9.2	9.9
$J_{5',6'a}$	2.4	2.2	6.8	5.6	2.1
$J_{5',6'b}$	4.6	4.4	6.6	2.7	5.0
$J_{6'a,b}$	12.2	12.3	11.2	12.2	12.2
$J_{1'',2''}$				3.9	8.1
$J_{2'',3''}$				10.5	10.5
$J_{3'',4''}$				9.8	3.4
$J_{4'',5''}$				10.0	<1
$J_{5'',6''a}$				2.0	6.8
$J_{5'',6''b}$				5.4	6.6
$J_{6''a,b}$				12.2	11.2
$J_{1a,1b}$	9.8	9.8	9.8	9.8	9.8
$J_{1a,2}$	6.7	6.7	6.7	6.6	6.8
$J_{1b,2}$	6.3	6.6	6.3	6.3	6.1
$J_{11,12}$	7.0	6.8	7.0	6.8	6.8

[a] J Values are given in hertz in $CDCl_3$.
[b] Coupling constants for the sugar protons of 8-bromooctyl, 12-acetylthiododecyl, and 8-acetylthiooctyl per-*O*-acetylglycosides are almost the same as these values.

Table 8. ^{13}C NMR chemical shift (δ)[a] data for ω-mercaptoalkyl glycosides

	1a	**1b**	**27a**	**27b**	**28**
C-1′	102.6	102.6	102.7	102.8	98.5
C-2′	72.9	72.9	73.4	73.4	71.4
C-3′	76.0	76.0	76.2	76.3	74.0
C-4′	79.4	79.3	70.2	70.4	69.3
C-5′	74.8	74.7	75.6	75.6	71.8
C-6′	61.1	61.0	61.7	61.5	61.1
C-1″	101.3	101.3			
C-2″	72.3	72.2			
C-3″	73.5	73.4			
C-4″	70.3	70.2			
C-5″	73.1	73.0			
C-6″	60.8	60.8			
C-1	69.5	69.4	70.0	69.4	68.4
C-3	25.8	25.7	25.7	25.8	26.0
CH_2–SH	24.5	24.4	24.4	24.6	24.6
CH_2–SD	24.3	24.3	24.3	24.5	24.4
CH_2–C–SH	33.89	33.80	33.85	33.99	33.95
CH_2–C–SD	33.86	33.77	33.82	33.96	33.92
Other CH_2	28.2	28.1	28.2	28.3	28.3
	28.9	28.9	28.9	29.1	29.0
	29.40[b]	29.2	29.28	29.4	29.36
	29.46	29.4	29.32	29.6	29.40
	29.50[c]		29.39[c]		29.44
			29.47		29.50
					29.52
					29.54

[a] δ Values are reported in ppm for solution in 10:1 $CDCl_3$–CD_3OD.
[b] Two carbons would overlap.
[c] Three carbons would overlap.

hexane–EtOAc); FABMS (positive-ion, NBA) calcd for $C_{26}H_{43}BrO_{10}$: 595.52. Found 618.5 $[M+Na]^+$.

4.2. General procedure for the synthesis of ω-acetylthioalkyl per-*O*-acetylglycosides

A solution of ω-bromoalkyl per-*O*-acetylglycoside (0.20 mmol) and potassium thioacetate (0.60 mmol) in *N*,*N*-dimethylformamide (1.5 mL) was stirred at rt for 2 h. The reaction mixture was diluted with 1:1 hexane–EtOAc (10 mL) and H_2O (10 mL), and the layers were separated. The aqueous phase was extracted with 1:1 hexane–EtOAc (2 × 20 mL), and the combined organic layers were dried over Na_2SO_4. Removal of the solvent gave a residue that was purified by chromatography eluting with 2:1→1.5:1 hexane–EtOAc to give the ω-acetylthioalkyl glycoside in high yield.

4.2.1. 12-Acetylthiododecyl 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (24a). Compound **24a** was prepared from **4a** in 95% yield as a colorless solid: mp 84–85 °C; $[\alpha]_D^{25}$ +38.5 (*c* 1.4, $CHCl_3$); R_f 0.41 (3:2 hexane–EtOAc). Anal. Calcd for $C_{40}H_{62}O_{19}S$: C, 54.73; H, 7.00; S, 3.56. Found: C, 54.66; H, 7.11; S, 3.65.

4.2.2. 8-Acetylthiooctyl 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (24b). Compound **24b** was prepared from **4b** in 96% yield as a colorless solid: mp 56–58 °C; $[\alpha]_D^{25}$ +51.4 (*c* 2.0, $CHCl_3$); R_f 0.35 (3:2 hexane–EtOAc); FABMS (positive-ion, NBA) *m*/*z* (%) 845.3 ($[M+Na]^+$, 70), 619.2 (44), 559.1 (29), 331.2 (100).

4.2.3. 12-Acetylthiododecyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (25a). Compound **25a** was prepared from **10a** in 97% yield as a colorless solid: mp 56–58 °C; $[\alpha]_D^{25}$ −12.7 (*c* 2.2, $CHCl_3$); R_f 0.27 (3:1 hexane–EtOAc). Anal. Calcd for $C_{28}H_{46}O_{11}S$: C, 56.93; H, 7.85; S, 5.43. Found: C, 57.28; H, 7.77; S, 5.39.

4.2.4. 8-Acetylthiooctyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (25b). Compound **25b** was prepared from **10b** in 95% yield as a colorless oil: $[\alpha]_D^{25}$ −13.0 (*c* 1.8, $CHCl_3$); R_f 0.20 (3:1 hexane–EtOAc); CIHRMS *m*/*z* calcd for $C_{28}H_{46}O_{11}S$ (M^+): 534.2135. Found: 534.2122.

4.2.5. 12-Acetylthiododecyl 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranoside (26). Compound **26** was prepared from **11a** in 94% yield as a colorless oil: $[\alpha]_D^{25}$ +91.4 (*c* 3.5, $CHCl_3$); R_f 0.34 (3:1 hexane–EtOAc); CIHRMS *m*/*z* calcd for $C_{28}H_{46}O_{11}S$ (M^+): 590.2761. Found: 590.2848.

4.3. General procedure for the synthesis of ω-mercaptoalkyl glycosides

To a stirred solution of the thioacetate (0.20 mmol) in MeOH (1 mL) and CH_2Cl_2 (2 mL) was added 3.0% solution of NaOMe in MeOH (0.5 mL, 0.25 mmol),

and the mixture was stirred for 2 h at 5–10 °C. HOAc (50 mg) was added and the solvent was removed. The residue was purified by silica gel column chromatography, eluting with 5:1→4:1 CH_2Cl_2–MeOH for maltoside derivatives, or with 9:1→8:1 CH_2Cl_2–MeOH for glucoside derivatives, to afford the glycolipid.

4.3.1. 12-Mercaptododecyl α-D-glucopyranosyl-(1→4)-β-D-glucopyranoside (1a). From **24a** (142 mg, 0.16 mmol) the title compound was obtained (73 mg, 84%) as a colorless solid: mp ca. 100 °C; $[\alpha]_D^{23}$ +44.5 (*c* 1.30, $CHCl_3$–MeOH); R_f 0.32 (4:1 CH_2Cl_2–MeOH); ^{1}H NMR ($CDCl_3$–CD_3OD): δ 1.27 (s, 14H), 1.37 (m, 2H), 1.61 (m, 4H), 2.51 (t, 2H, *J* 7.2 Hz, CH_2S), 3.36 (m, 4H), 3.48–3.75 (m, 6H), 3.85 (m, 4H), 4.29 (d, 1H, $J_{1',2'}$ 7.6 Hz, H-1′), 5.20 (d, 1H, $J_{1'',2''}$ 3.2 Hz, H-1″); CIHRMS *m*/*z* calcd for $C_{24}H_{46}O_{11}S$ (M^+): 542.2761. Found: 542.2774.

4.3.2. 8-Mercaptooctyl α-D-glucopyranosyl-(1→4)-β-D-glucopyranoside (1b). From **24b** (74 mg, 0.09 mmol) the title compound was obtained (36 mg, 82%) as a colorless syrup: $[\alpha]_D^{24}$ +60.8 (*c* 0.72, $CHCl_3$–MeOH); R_f 0.28 (4:1 CH_2Cl_2–MeOH); ^{1}H NMR ($CDCl_3$–CD_3OD): δ 1.32 (m, 8H), 1.60 (m, 4H), 2.51 (t, 2H, *J* 7.1 Hz, CH_2S), 3.25–3.95 (m, 14H), 4.29 (d, 1H, $J_{1',2'}$ 7.3 Hz, H-1′), 5.20 (d, 1H, $J_{1'',2''}$ 3.2 Hz, H-1″); FABMS (positive-ion, NBA) *m*/*z* (%) 509.1 ([M+Na]$^+$, 74), 325.2 ([maltose−OH]$^+$, 12), 307.1 (35).

4.3.3. 12-Mercaptododecyl β-D-glucopyranoside (27a). From **25a** (178 mg, 0.30 mmol) the title compound was obtained (96 mg, 84%) as a colorless solid: mp 82–85 °C; $[\alpha]_D^{24}$ −25.0 (*c* 1.45, $CHCl_3$); R_f 0.36 (8:1 CH_2Cl_2–MeOH); ^{1}H NMR ($CDCl_3$–CD_3OD): δ 1.27 (14H, s), 1.33 (t, 0.3H, *J* 7.7 Hz), 1.37 (m, 2H), 1.61 (m, 4H), 2.51 (t, 2H, *J* 7.1 Hz, CH_2S), 3.28 (m, 2H), 3.46 (m, 2H), 3.54 (dt, 1H, $J_{1a,1b}$ 9.3, $J_{1a,2}$ 7.1 Hz, H-1a), 3.80 (m, 2H, H-6′a, 6′b), 3.87 (dt, 1H, $J_{1a,1b}$ 9.5, $J_{1b,2}$ 6.8 Hz, H-1b), 4.29 (d, 1H, $J_{1',2'}$ 7.8 Hz, H-1′). Anal. Calcd for $C_{18}H_{36}O_6S$: C, 56.81; H, 9.54; S, 8.43. Found: C, 57.24; H, 9.62; S, 8.37.

4.3.4. 8-Mercaptooctyl β-D-glucopyranoside (27b). From **25b** (70 mg, 0.13 mmol), the title compound was obtained (35 mg, 83%) as a colorless syrup: $[\alpha]_D^{24}$ −31.5 (*c* 1.3, $CHCl_3$); R_f 0.32 (8:1 CH_2Cl_2–MeOH); ^{1}H NMR ($CDCl_3$–CD_3OD): δ 1.32 (m, 8H), 1.61 (m, 4H), 2.51 (t, 2H, *J* 7.1 Hz, CH_2S), 3.31 (m, 2H), 3.52 (m, 3H), 3.84 (m, 3H), 4.29 (d, 1H, $J_{1',2'}$ 7.6 Hz, H-1′); CIHRMS *m*/*z* calcd for $C_{14}H_{28}O_6S$ (M^+): 324.1607. Found: 324.1634.

4.3.5. 12-Mercaptododecyl α-D-glucopyranoside (28). From **26** (200 mg, 0.34 mmol), the title compound was obtained (110 mg, 85%) as a colorless solid: mp 77–79 °C; $[\alpha]_D^{24}$ +77.4 (*c* 0.64, $CHCl_3$); R_f 0.36 (8:1 CH_2Cl_2–MeOH); ^{1}H NMR ($CDCl_3$–CD_3OD): δ 1.27 (s-like, 14H), 1.36 (m, 2H), 1.61 (m, 4H), 2.51 (t, 2H, *J* 7.2 Hz, CH_2S), 3.44 (dt, 1H, $J_{1a,1b}$ 9.8, $J_{1a,2}$ 6.8 Hz, H-1a), 3.52 (m, 3H, H-2′,3′,4′), 3.66 (dt, 1H, $J_{1a,1b}$ 9.8, $J_{1b,2}$ 7.0 Hz, H-1b), 3.72 (m, 1H, H-5′), 3.75 (dd, 1H, $J_{5',6'a}$ 2.0, $J_{6'a,6'b}$ 12.0 Hz, H-6′a), 3.87 (dd, 1H, $J_{5',6'b}$ 2.8, $J_{6'a,6'b}$ 12.1 Hz, H-6′b), 4.84 (d, 1H, $J_{1',2'}$ 3.7 Hz, H-1′). Anal. Calcd for $C_{18}H_{36}O_6S$: C, 56.81; H, 9.54; S, 8.43. Found: C, 56.95; H, 9.48; S, 8.35.

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