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Stereoselective synthesis of 2-*S*-ethyl(phenyl)-2-thio-β-glucopyranosides via 1,2-migration and concurrent glycosidation of ethyl(phenyl) 2,3-orthoester-1-thio-α-mannopyranosides

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Abstract

1,2-Migration and concurrent glycosidation of ethyl(phenyl) 2,3-orthoester-1-thio-α-D- and L-mannopyranosides under the action of TMSOTf readily afforded the corresponding 2-*S*-ethyl(phenyl)-2-thio-β-glucopyranosides, ready precursors to 2-deoxy-*arabino*-hexopyranosides (2-deoxy-β-glucopyranosides). © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

1,2-Migration of 1-thioglycosides to give 2-thioglycosides is well known in carbohydrate chemistry, which is facilitated by a 'pull' from the C-2 initiated by the departure of a leaving group and a 'push' from the ring oxygen's lone pair of electrons, providing the groups involved are in trans configuration.[1–8] As outlined in Scheme 1, the migration has been believed to be mainly involved in the formation of a 1,2-episulfonium (A), therefore resulting in the stereoselective formation of 1,2-*trans* glycosides; however, calculations using both MNDO semiempirical and high-level ab initio methods argued the oxacarbenium ions (B) were likely to be of the lower energy,[1,2] and indeed, experimental results of producing the anomeric isomers have also been reported.[3a] The 'pull' has been installed by means of a mesyl group,[3] a hydroxyl group (under the action of Mitsunobu conditions[4] or by means of the DAST reagent[5]), or a phenoxythiocarbonyl group[6] (upon subjection to NIS–TfOH). Incidentally, Bundle and Auzanneau have observed 1,2-migration during the
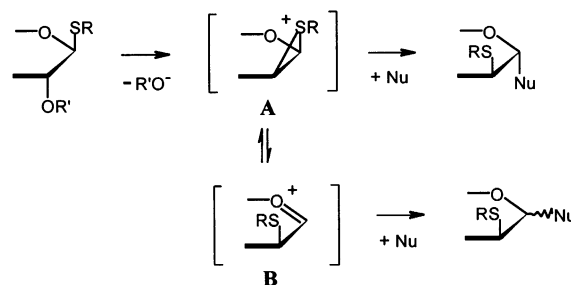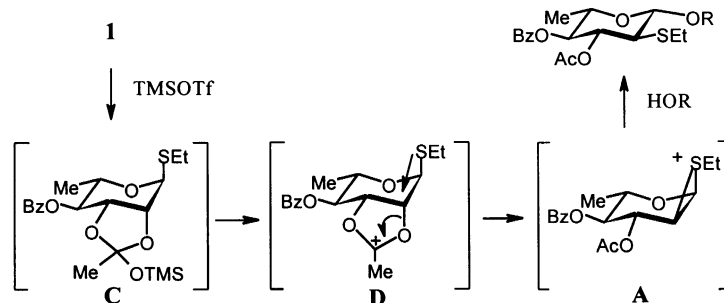

Scheme 1.

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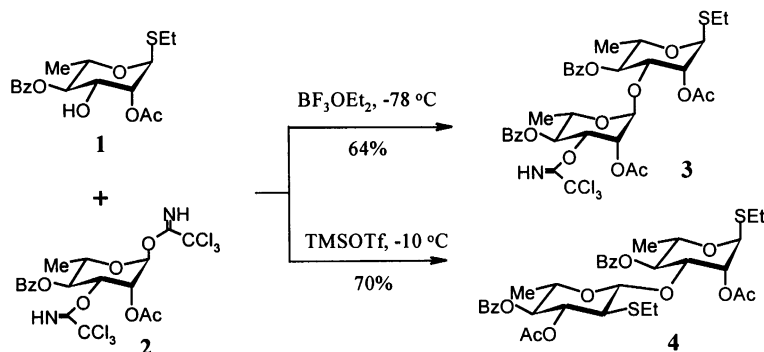
Scheme 2.

Scheme 3.

attempted preparation of ethyl 2,3-orthoester-1-thio-α-L-rhamnopyranoside derivatives.[7] Ziegler and Herold reported 1,2-migration triggered by a remote 3,4-*O*-benzyldioxonium cation, which finished with an intramolecular glycosidation leading to 1,6-anhydropyranosyl compounds.[8] 2-Thioglycosides thus produced are valuable precursors to 2-deoxy-glycosides which exit as important structural components in many antibiotics (e.g., macrolides, anthracyclines, aureolic acids, and enediynes),[9] cardiac glycosides,[10] and pregnane glycosides.[11] We report herewith a full account of preparation of 2-*S*-ethyl(phenyl)-2-thio-glucopyranosides by using ethyl(phenyl) 2,3-*O*-ethoxyethylidene-1-thio-α-D- and L-mannopyranosides as donors through 1,2-migration and consecutive glycosidation processes.[12]

2. Results and discussion

Glycosylation of ethyl 2-*O*-acetyl-4-*O*-benzoyl-1-thio-α-L-rhamnopyranoside (**1**) with trichloroacetimidate **2** under the promotion of BF$_3$·OEt$_2$ (0.1 equiv) at low temperature (−78 °C) produced the desired coupling

product **3** in 64% yield.[13] Surprisingly, when using TMSOTf (0.15 equiv) as a promoter, little of starting **1** was consumed under analogous conditions, and disaccharide **4** was isolated as the major product (70%) upon raising the reaction temperature to −10 °C (Scheme 2).

We envisaged that the production of **4** should conceivably involve the glycosylation of **1** with 1,2-episulfonium A, which was resulted from the cation D, and D from 2,3-orthoester C (Scheme 3). This 'pull–push' mechanistic process is in accordance with that known for the 1,2-migration and consecutive glycosidation of thioglycosides,[1–8] in particular in accordance with the 1,2-migration process observed incidentally by Bundle and Auzanneau during the attempted preparation of ethyl 2,3-orthoester-1-thio-α-L-rhamnopyranoside derivatives.[7]

As expected on mechanistic grounds, in the absence of the trichloroacetimidate **2**, the 1,2-migrated self-coupled product **4** was still produced in comparable yield (64%) under similar conditions. When diosgenin (as a nucleophile, 1.5 equiv) was added to the reaction, glycoside **5** formed by capture of the episulfonium A
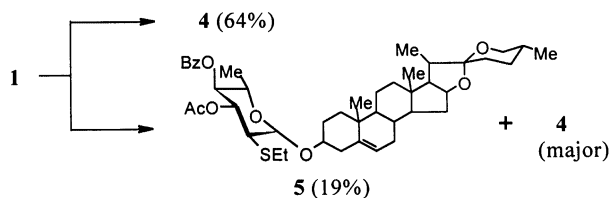
Scheme 4. Reagents and conditions: TMSOTf (0.15 equiv), CH$_2$Cl$_2$, 4Å MS, 0 °C–rt.
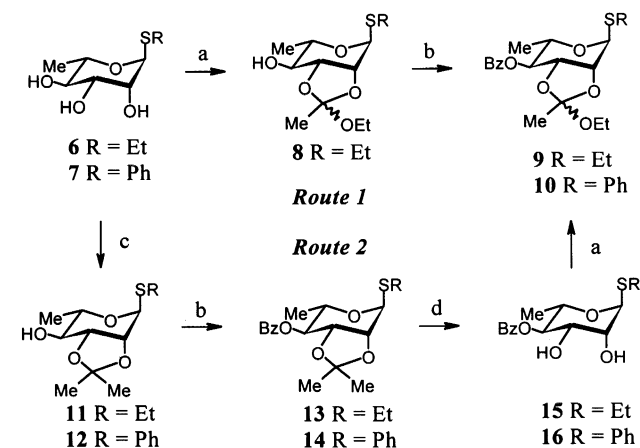
Scheme 5. Reagents and conditions: (a) CH$_3$C(OEt)$_3$, *p*-TsOH·H$_2$O (ca.), DMF, rt; (b) BzCl, pyridine, 0 °C–rt; (c) CH$_3$C(OMe)$_2$CH$_3$, *p*-TsOH·H$_2$O (ca.), CH$_2$Cl$_2$, rt; (d) 80% HOAc, 75 °C, 3 h (46% for Route 1, ~89% for Route 2).

was isolated in 19% yield, whereas the self-coupled product, **4** turned out to be the major 'byproduct' (Scheme 4). Accordingly, 2,3-or-thoester-1-thio-glycosides were expected to be

good donors for the preparation of 2-thioglycosides.

We therefore prepared several ethyl(phenyl) 2,3-*O*-ethoxyethylidene-1-thio-glycosides (**9**, **10**, **19**, and **24**) bearing the L- and D-manno configuration (see Schemes 5 and 6, respectively). Ethyl 4-*O*-benzoyl-2,3-orthoacetyl-1-thio-α-L-rhamnopyranoside (**9**) was readily obtained from ethyl 1-thio-α-L-rhamnopyran-oside (**6**) by employing two routes. Route 1 involved two steps, i.e., selective 2,3-or-thoester formation[7] and 4-OH benzoylation, and produced **9** in ~46% yield. Route 2 employed four steps, i.e., blocking of the 2,3-OH groups with an isopropylidene group, 4-OH benzoylation, removal of 2,3-*O*-iso-propylidene group, and 2,3-orthoester forma-tion, affording **9** in overall ~89% yield. Since there was no need for purification of the inter-mediate products, route 2 was preferred, and it was used in the preparation of phenyl derivative **10** (in overall ~89% yield). Ethyl 4,6-*O*-benzylidene-2,3-orthoacetyl-1-thio-α-D-mannopyranoside (**19**) was prepared from ethyl 2,3,4,6-tetra-*O*-acetyl-1-thio-α-D-man-nopyranoside (**17**) in three steps and overall 89% yield, i.e., removal of acetates, formation of the 4,6-*O*-benzylidene derivatives,[14] and 2,3-orthoacetate generation. Treatment of ethyl 1-thio-α-D-mannopyranoside with 2,2-di-methoxypropane and a catalytic amount of *p*-
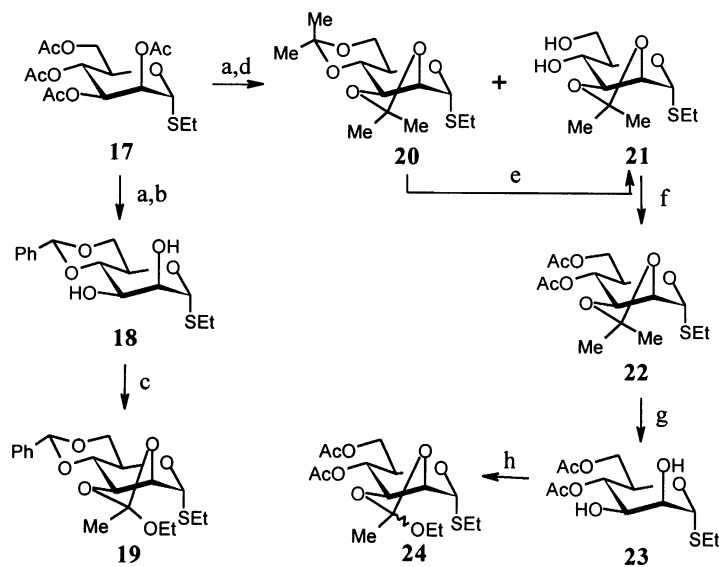
Scheme 6. Reagents and conditions: (a) NaOMe, HOMe, rt; (b) PhCH(OMe)$_2$, *p*-TsOH·H$_2$O (cat), DMF 30 °C; (c) CH$_3$C(OEt)$_3$, *p*-TsOH·H$_2$O (ca.), DMF, rt; 89% for **17**→**19**; (d) CH$_3$C(OMe)$_2$CH$_3$, *p*-TsOH·H$_2$O (cat.), acetone, rt, then H$_2$O, 33% (for **20**), 63% (for **21**); (e) 25% HOAc, rt, 70%; (f) Ac$_2$O, pyridine, rt; (g) 80% HOAc, 50 °C, 86%; (h) the same as (c); 100%.

Table 1
Glycosylation with ethyl(phenyl) 2,3-orthoester-1-thio-mannopyranoside donors (9, 10, 19, and 24) [a,b]

Entry	Donor	Acceptor	Product (yield) [c]	
1	9	cyclohexanol	26 (44%)	27 (20%)
2	9	diosgenin	5 (54%)	27 (20%)
3	9	cholesterol	28 (68%)	27 (25%)
4	9	11	29 (48%)	27 (45%)
5	9	25	30 (39%)	27 (53%)
6	10	11	31 (53%)	32 (38%)
7	10	25	33 (43%)	32 (38%)
8	19	cholesterol	34 (40%)	35 (28%)
9	19	cyclohexanol	36 (70%)	35 (24%)
10	24	cholesterol	37 (40%)	38 (28%)
11	24	25	39 (39%)	38 (18%)
12 [b]	24	25	39 (68%)	38 (40%)
13 [b]	24	cyclohexanol	40 (87%)	38 (29%)

[a] Conditions: donor (1.0 equiv), acceptor (1.2 equiv) (except in entries 12 and 13), TMSOTf (0.15 equiv), CH$_2$Cl$_2$, 4 Å MS, 0 °C–rt.

[b] Donor (1.2 equiv), acceptor (1.0 equiv).

[c] Isolated yields based on donors, except in entries 12 and 13, whereupon yields for 39 and 40 were based on acceptors.

TsOH in acetone, followed by treatment with water afforded 2,3-O-isopropylidene 21[15] as the major product (63%) and 2,3;4,6-di-O-iso-propylidene 20 in minor amount (33%).[16] Compound 20 could be readily converted to 21 in 70% yield upon treatment with 25% HOAc at room temperature. 4,6-Diol 21 was then acetylated to give 22, which was subjected to 80% HOAc at 50 °C to give 2,3-diol 23 in 86% yield. Treatment of 23 with triethyl orthoacetate afforded 2,3-orthoacetate 24 quantitatively. ^{1}H NMR analyses demonstrated that ethyl 2,3-orthoacetates 9, 10, and 24 were all mixtures of the two stereoisomers, with the ethoxy group being either exo or endo and in nearly equal amounts. However, ethyl 2,3-orthoacetate 19 was a single compound, conceivably with its ethoxy group in the exo configuration due to the steric hindrance of the endo face produced by the 4,6-O-benzylidene ring.

Employing ethyl(phenyl) 2,3-orthoacetyl-1-thio-α-mannopyranosides (9, 10, 19, and 24) as donors to prepare the corresponding 2-S-ethyl(phenyl)-2-thio-β-glucopyranosides through 1,2-migration and consecutive glycosidation was examined. A typical reaction procedure involved the addition of a catalytic amount (0.15 equiv) of TMSOTf to a solution of an alcohol acceptor (1.2 equiv) in dichloromethane at room temperature, followed by the addition of the 2,3-orthoacetate (1.0 equiv). The results are listed in the Table 1.

The reaction of ethyl 2,3-orthoacetyl-1-thio-α-L-rhamnopyranoside 9 with alcohols (cyclohexanol, diosgenin, cholesterol, as well as sugar alcohols 11 and 25) produced the expected 2-S-ethyl-2-thio-β-L-glucopyranosides (26, 5, 28–30) in moderate to good yields (39–68%); the corresponding α anomers had not previously been isolated by careful chromatography (entries 1–5). The anomeric ethylthio ether on acceptor 11 was unaffected (entry 4). However, the resulting –OEt from the 2,3-orthoacetate of donor 9 competed considerably with the alcohol acceptors for the glycosidation reactions, producing the corresponding ethyl-3-O-acetyl-4-O-benzoyl-6-deoxy-2-S-ethyl-2-thio-β-L-glucopyranoside (27) in 19–53% yields. The reaction of the phenyl 1-thio-rhamnopyranoside 10 with sugar alcohols 11 and 25 gave similar results, providing the expected products 31 and 33 stereoselectively and in 53 and 43% yields, with the byproduct ethyl glycoside 32 in 32 and 38% yields, respectively (entries 6 and 7). Raney nickel-mediated desulfurization of the SPh derivative to produce the corresponding 2-deoxy-glycoside is known to be more facile than that of the corresponding SEt derivative.[6] In contrast, the reaction of 4,6-O-benzylidene-2,3-orthoacetyl-1-thio-α-D-mannopyranoside (19) with cholesterol and cyclohexanol produced the desired 2-S-ethyl-glucopyranosides (34, 36) as their anomeric mixtures (α:β = 1:4 and 2:3, respectively), which were clearly indicated by ^{1}H NMR spectral analyses (entries 8 and 9). Nevertheless, the reaction of 4,6-di-O-acetyl-2,3-orthoacetyl-1-thio-α-D-mannopyranoside (24), gave only the β anomeric products (entries 10–13). It should be concluded that the fused 4,6-O-benzylidene ring made the pyranose ring more rigid and favored the transformation of episulphonium (A) into oxycabenium (B) (Scheme 1); capture of the oxycabenium (B) by alcohols generated the α anomers favorably due to the anomeric

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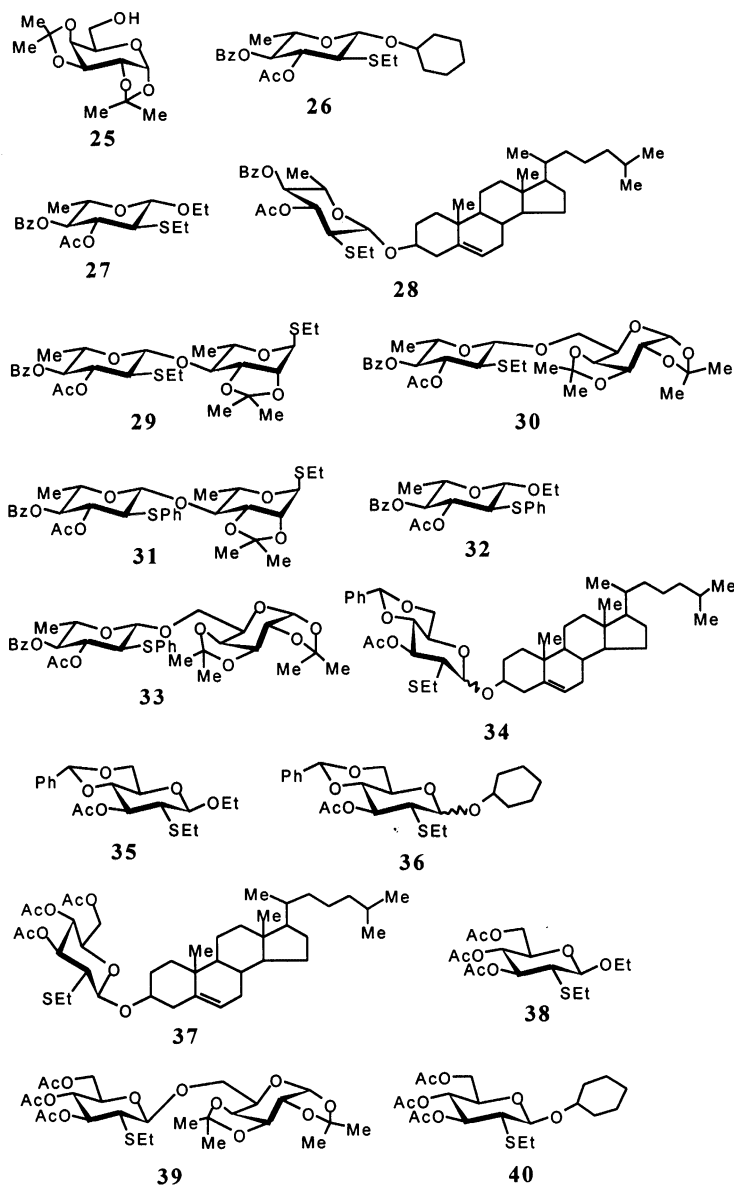
effect. The effects of fused-ring protection on the reactivity of the pyranose donors have been well observed in many studies.[17] Herein, it is difficult to interpret the results that only ethyl β-glycoside **35** was isolated along with the anomeric isomers of **34** and **36** (entries 8 and 9).

The expected 2-*S*-ethyl(phenyl)-2-thio-glycosides were produced in only moderate to good yields due to the OEt transfer side reaction in this protocol. However, it should be noted that the yields for the expected glycosides were calculated based on the 2,3-orthoester donors added (1.0 equiv). The yields would be reasonably improved on the sacrifice of the amount of donors. As shown in entries

12 and 13, using an excess amount (1.2 equiv) of the 2,3-orthoacetate donor **24** greatly increased the yields of the desired products (68% for **39**, 87% for **40**). The yields calculated on the consumed acceptors should be reasonable providing the aglycone was more precious.

3. Conclusions

Ethyl(phenyl) 2,3-orthoester-1-thio-α-mannopyranosides, which are easily accessible, were demonstrated to be good donors for the stereoselective synthesis of the corresponding 2-*S*-ethyl(phenyl)-2-thio-β-glucopyranosides, ready precursors to 2-deoxy-β-glucopyran-

osides. The reaction proceeded through the glycosidation of the 1,2-episulfonium inter-mediates. Structural variation of the 2,3-orthoacetate donors (e.g., 4,6-*O*-benzylidene protection) would facilitate the transformation of 1,2-episulfonium to oxycarbenium, hence resulting in the absence of the stereoselectivity. One major drawback of the present protocol is the competing glycosidation of the nascent OEt from the ethyl orthoacetate moiety of the donors, leading to only moderate to good yields for the desired products. Nevertheless, using excess amounts of the 2,3-orthoester donors reasonably improved the yields.

4. Experimental

General methods.—TLC was performed on precoated plates of Silica Gel HF$_{254}$ (0.5 mm, Yantai, Shandong, China). Flash-column chromatography was performed on Silica Gel H (10–40 μm, Yantai, Shandong, China). Optical rotations were determined with a Perkin–Elmer model 241 MC polarimeter, and $[\alpha]_D$ values are on units of 10^{-1} deg cm^2/g. NMR spectra were recorded on a Bruker AM 300 spectra with Me$_4$Si as the internal standard. *J* values are given in Hz. Mass spectra were obtained on a HP5989A or a VG Quatro mass spectrometer. Elemental analyses were performed on a Perkin–Elmer model 2400 instrument. Petroleum ether refers to the fraction with distillation range 60–90 °C.

Ethyl 3-O-acetyl-4-O-benzoyl-6-deoxy-2-S-ethyl-2-thio-β-L-glucopyranosyl-(1→3)-2-O-acetyl-4-O-benzoyl-1-thio-α-L-rhamnopyranoside (**4**).—To a mixture of **1** (110 mg, 0.31 mmol) and 4 Å MS (100 mg) in anhyd CH$_2$Cl$_2$ (1 mL) at −8 °C under Ar, was added a solution of TMSOTf in CH$_2$Cl$_2$ (0.05 M, 0.031 mmol). After being stirred for 30 min, the mixture was quenched with Et$_3$N, and then filtered through a pad of Celite. The filtrates were concentrated. The residue was purified by a silica gel-column chromatography (6:1–4:1, petroleum ether–EtOAc) to give **4** (68 mg, 64%) as a white amorphous solid: $[\alpha]_D$ + 20.8° (*c* 1.8, CHCl$_3$). IR (film): 1750 (Ac),

1729 (Bz) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 8.11–7.39 (m, 10 H), 5.43 (dd, 1 H, *J* 3.2, 1.6 Hz, H-2), 5.37 (t, 1 H, *J* 9.8 Hz, H-4), 5.31 (d, 1 H, *J* 1.1 Hz, H-1), 5.03 (dd, 1 H, *J* 11.6, 9.3 Hz, H-3′), 4.81 (t, 1 H, *J* 9.5 Hz, H-4′), 4.45 (d, 1 H, *J* 8.7 Hz, H-1′), 4.38–4.27 (m, 2 H, H-3, H-5), 3.54–3.45 (m, 1 H, H-5′), 2.78–2.49 (m, 3 H, H-2′, SCH$_2$), 2.18 (s, 3 H, Ac), 1.89 (s, 3 H, Ac), 1.36–0.88 (m, 12 H). EIMS (*m/z*, %): 672 ([M$^+$ − water], 0.5), 629 ([M$^+$ − water − Ac], 3.7), 105 (Bz, 100). Anal. Calcd for C$_{34}$H$_{42}$O$_{11}$S$_2$: C, 59.11; H, 6.13. Found: C, 59.32; H, 6.38.

Diosgenyl 3-O-acetyl-4-O-benzoyl-6-deoxy-2-S-ethyl-2-thio-β-L-glucopyranoside (**5**).—To a stirred solution of diosgenin (85 mg, 0.21 mmol) and 4 Å MS (120 mg) in anhyd CH$_2$Cl$_2$ (2 mL) at rt under Ar, was added a solution of TMSOTf in CH$_2$Cl$_2$ (0.1 M, 0.07 mmol), followed by addition of a solution of **1** (50 mg, 0.14 mmol) in CH$_2$Cl$_2$ (0.5 mL). After being stirred for 1 h, the reaction mixture was quenched with Et$_3$N, and then filtered through a pad of Celite. The filtrates were concentrated. The residue was applied to a silica gel column (8:1 petroleum ether–EtOAc) to give **5** (14 mg, 19%) as a white amorphous solid: $[\alpha]_D$ − 35.7° (*c* 1.4, CHCl$_3$). IR (film): 1751(Ac), 1726 (Bz) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.99–7.41 (m, 5 H), 5.39 (d, 1 H, *J* 4.9 Hz, H-6), 5.10 (t, 1 H, *J* 9.3 Hz, H-3′), 5.02 (t, 1 H, *J* 9.3 Hz, H-4′), 4.56 (d, 1 H, *J* 8.7 Hz, H-1′), 4.42 (m, 1 H, H-16), 3.67–3.60 (m, 2 H, H-3, H-5′), 3.46–3.38 (m, 2 H, H-26), 2.80–2.68 (m, 3 H, H-2′, SCH$_2$), 2.50–2.30 (m, 2 H), 1.96 (s, 3 H, Ac). EIMS (*m/z*, %): 750 ([M$^+$], 0.7), 397 (49.6), 105 (Bz, 100). Anal. Calcd for C$_{44}$H$_{62}$O$_8$S·H$_2$O: C, 68.72; H, 8.39. Found: C, 68.46; H, 8.12.

Ethyl 4-O-benzoyl-2,3-O-ethoxyethylidene-1-thio-α-L-rhamnopyranoside (**9**).—Route 1: To a stirred solution of ethyl 2,3,4-tri-*O*-acetyl-1-thio-α-L-rhamnopyranoside (3.15 g, 9.43 mmol) in MeOH (15 mL), was added a catalytic amount of NaOMe (84 mg). After being stirred at rt for 1 h, the reaction mixture was neutralized with Dowex-50WX8 (H$^+$ form), and then filtered, and concentrated in vacuo. The residue **6** was dissolved in dry DMF (15 mL), and triethyl orthoacetate (5.0 mL, 27.0 mmol) was added, followed by a catalytic amount of *p*-TsOH·H$_2$O (20 mg, 0.11 mmol).

After being stirred at 0 °C for 1 h, the reaction mixture was quenched with Et$_3$N, and then diluted with EtOAc. The organic layer, washed with water and brine, respectively, was dried over MgSO$_4$, and then filtered and concentrated in vacuo. The residue **8** was dissolved in dry pyridine (10 mL), and BzCl (1.5 mL) was added. After being stirred at rt for 1 h, the reaction mixture was quenched with Et$_3$N, and diluted with EtOAc. The organic layer was washed with brine, dried over anhyd MgSO$_4$, and then filtered and concentrated in vacuo. The residue was purified by flash chromatography (15:1 petroleum ether–EtOAc) to give **9** (1.66 g, 46% for three steps) as a colorless syrup.

Route 2: To a stirred solution of ethyl 2,3,4-tri-*O*-acetyl-1-thio-α-L-rhamnopyranoside (29.0 g, 86.7 mmol) in MeOH (100 mL), was added a catalytic amount of NaOMe (380 mg). After being stirred at rt for 5 h, the reaction mixture was neutralized with Dowex-50WX8 (H$^+$ form), and then filtered, and concentrated in vacuo. The residue **6** was dissolved in dry CH$_2$Cl$_2$ (20 mL), and 2,2-dimethoxy propane (35 mL, 285 mmol) was added, followed by a catalytic amount of *p*-TsOH·H$_2$O (420 mg). After being stirred at rt for 3 h, the reaction mixture was quenched with Et$_3$N, and then concentrated in vacuo. The residue **11** was dissolved in dry pyridine (50 mL), and BzCl (12 mL) was added. After being stirred at rt for 2 h, the reaction mixture was quenched with MeOH, and diluted with EtOAc. The organic layer was washed with brine and then concentrated in vacuo. The resulting residue **13** was dissolved in 80% HOAc (400 mL). After being stirred at 80 °C for 3 h, the solution was concentrated in vacuo. The residue was purified by flash-column chromatography (2:1 petroleum ether–EtOAc) to give **15** as a white solid. To a solution of **15** in dry DMF (40 mL) was added triethyl orthoacetate (30 mL, 162 mmol), followed by a catalytic amount of *p*-TsOH·H$_2$O (80 mg). After being stirred at rt for 2 h, the mixture was quenched with Et$_3$N and then diluted with EtOAc. The organic layer, washed with water and brine, respectively, was dried over dry MgSO$_4$, and then filtered and concentrated in vacuo. The residue

was purified by flash-column chromatography (20:1 petroleum ether–EtOAc) to give **9** (29.5 g, 89%) as a colorless syrup. Compound **9** was a mixture of the two endo/exo stereoisomers: ^{1}H NMR (CDCl$_3$): δ 8.07–7.45 (m, 5 H), 5.62, 5.60 (2 × s, 1 H, H-1), 5.48, 5.12 (2 × dd, 1 H, *J* 7.4, 10.2 Hz, H-4), 4.47–4.20 (m, 3 H, H-2, H-3, H-5), 3.78, 3.55 (2 × q, 2 H, OCH$_2$), 2.71–2.55 (m, 2 H, SCH$_2$), 1.73, 1.54 (2 × s, 3 H, CH$_3$CO$_3$), 1.35–1.14 (m, 9 H, H-6, OCH$_2$CH$_3$, SCH$_2$CH$_3$). EIMS (*m/z*, %): 337 ([M$^+$ − OEt], 3.6), 321 ([M$^+$ − SEt], 31.2), 105 (Bz, 100). Anal. Calcd for C$_{19}$H$_{26}$O$_6$S: C, 59.67; H, 6.85. Found: C, 60.02; H, 7.32.

Phenyl 4-O-benzoyl-2,3-O-ethoxyethylidene-1-thio-α-L-rhamnopyranoside (**10**).—A procedure similar to Route 2 for the preparation of **9** was employed (89% overall yield). Compound **10**, as a colorless syrup, was a mixture of the two endo/exo stereoisomers: ^{1}H NMR (CDCl$_3$): δ 8.08–7.31 (m, 10 H), 5.82, 5.80 (2 × s, 1 H, H-1), 5.53–5.47, 5.14 (m, dd, 1 H, *J* 7.4, 9.8 Hz, H-4), 4.62–4.38 (m, 2 H, H-2, H-3), 4.38–4.28 (m, 1 H, H-5), 3.80–3.72, 3.60–3.52 (2 × m, 2 H, OCH$_2$), 1.71, 1.55 (2 × s, 3 H, CH$_3$CO$_3$), 1.26–1.15 (m, 6 H, H-6, OCH$_2$CH$_3$). EIMS (*m/z*, %): 385 ([M$^+$ − OEt], 1.4), 321 ([M$^+$ − SPh], 41.0), 105 (Bz, 100). Anal. Calcd for C$_{23}$H$_{26}$O$_6$S: C, 64.17; H, 6.09. Found: C, 64.30; H, 6.24.

Ethyl 4,6-O-benzylidene-2,3-O-ethoxyethylidene-1-thio-α-D-mannopyranoside (**19**).—To a stirred solution of **18** (3.44 g, 11.02 mmol) in dry DMF (5 mL) was added triethyl orthoacetate (4.0 mL, 22.04 mmol), followed by a catalytic amount of *p*-TsOH·H$_2$O (100 mg). After being stirred at rt for 20 min, the mixture was quenched with Et$_3$N and then diluted with EtOAc. The organic layer, washed with water and brine, respectively, was dried over MgSO$_4$, and then filtered and concentrated in vacuo. The residue was purified by a flash-column chromatography (10:1 petroleum ether–EtOAc) to give **19** (3.73 g, 89%) as a colorless syrup. ^{1}H NMR (CDCl$_3$): δ 7.50–7.34 (m, 5 H), 5.60 (s, 1 H, H-1), 5.56 (s, 1 H, PhCH), 4.47–4.39 (m, 2 H, H-3, H-4), 4.28–4.08 (m, 2 H, H-6), 3.80–3.67 (m, 2 H, H-2, H-5), 3.50 (q, 2 H, OCH$_2$CH$_3$), 2.71–2.51 (m, 2 H, SCH$_2$CH$_3$), 1.70 (s, 3 H, CH$_3$CO$_3$), 1.30 (m, 3 H, OCH$_2$CH$_3$), 1.17 (m, 3 H, SCH$_2$CH$_3$).

Ethyl 4,6-di-O-acetyl-2,3-O-ethoxyethylidene-1-thio-α-D-mannopyranoside (**24**).—A procedure similar to that for the preparation of **19** from **18** was employed to prepare **24** from **23** (100%). ^{1}H NMR (CDCl$_3$): δ 5.62 (2 × s, 1 H, H-1), 5.08 (m, 1 H, H-4), 4.38 (m, 2 H, H-2, H-3), 4.24 (m, 2 H, H-6), 4.50 (m, 1 H, H-5), 3.75–3.56 (2 × m, 2 H, OCH$_2$), 2.62 (m, 2 H, SCH$_2$), 2.04 (m, 6 H, 2 Ac), 1.69, 1.55 (2 × s, 3 H, CH$_3$CO$_3$), 1.22 (m, 6 H, SCH$_2$CH$_3$, OCH$_2$CH$_3$). Anal. Calcd for C$_{16}$H$_{26}$O$_8$S: C, 50.78; H, 6.82. Found: C, 50.80; H, 7.04.

Typical procedure for the reaction of the 2,3-orthoacetates (**9**, **10**, **19**, and **24**) *with alcohol acceptors.*—To a stirred solution of an alcohol acceptor (70–110 mg, 1.2 equiv) and 4 Å MS (200 mg) in anhyd CH$_2$Cl$_2$ (2 mL) at rt under Ar was added a solution of TMSOTf in CH$_2$Cl$_2$ (0.1 M, 0.15 equiv), followed by the addition of a solution of an orthoacetate donor (1.0 equiv) in CH$_2$Cl$_2$ (0.5 mL). After being stirred for 1 h, the mixture was quenched with Et$_3$N and then filtered through a pad of Celite. The filtrates were concentrated. The residue was applied to a silica gel-column chromatography with petroleum ether–EtOAc as eluent to give the corresponding 2-thioglycosides as white amorphous solids.

Cyclohexanyl 3-O-acetyl-4-O-benzoyl-6-deoxy-2-S-ethyl-2-thio-β-L-glucopyranoside (**26**).—[α]$_D$ + 44.5° (*c* 1.3, CHCl$_3$); ^{1}H NMR (CDCl$_3$): δ 7.98–7.40 (m, 5 H), 5.09 (t, 1 H, *J* 10.2 Hz, H-3), 5.02 (t, 1 H, *J* 9.1 Hz, H-4), 4.55 (d, 1 H, *J* 8.8 Hz, H-1), 3.74–3.58 (m, 2 H, H-5, OCH(CH$_2$)$_5$), 2.80–2.60 (m, 3 H, H-2, SCH$_2$), 1.94 (s, 3 H, Ac), 1.80–1.70 (m, 2 H), 1.60–1.16 (m, 14 H). EIMS (*m/z*, %): 436 ([M$^+$], 0.1), 337 ([M$^+$], 26.3), 155 (100). Anal. Calcd for C$_{23}$H$_{32}$O$_6$S: C, 63.28; H, 7.39. Found: C, 63.30; H, 7.53.

Ethyl 3-O-acetyl-4-O-benzoyl-6-deoxy-2-S-ethyl-2-thio-β-L-glucopyranoside (**27**).—[α]$_D$ + 43.3° (*c* 1.0, CHCl$_3$); ^{1}H NMR (CDCl$_3$): 7.98–7.42 (m, 5 H), 5.10 (dd, 1 H, *J* 11.0, 9.2 Hz, H-3), 5.02 (dd, 1 H, *J* 9.5, 9.2 Hz, H-4), 4.55 (d, 1 H, *J* 8.8 Hz, H-1), 3.99 (m, 1 H, H-5), 3.68–3.61(m, 2 H, OCH$_2$), 2.80–2.61 (m, 3 H, H-2, SCH$_2$CH$_3$), 1.92 (s, 3 H, Ac), 1.30–1.20 (m, 9 H). EIMS (*m/z*, %): 337

([M$^+$ − OEt], 1.2), 105 (Bz, 100). Anal. Calcd for C$_{19}$H$_{26}$O$_6$S: C, 59.67; H, 6.85. Found: C, 59.33; H, 7.31.

Cholesteryl 3-O-acetyl-4-O-benzoyl-6-deoxy-2-S-ethyl-2-thio-β-L-glucopyranoside (**28**).—[α]$_D$ − 21.1° (*c* 1.4, CHCl$_3$); ^{1}H NMR (CDCl$_3$): δ 7.99–7.41 (m, 5 H), 5.38 (d, 1 H, *J* 4.9 Hz, H-6), 5.08 (t, 1 H, *J* 10.1 Hz, H-3′), 5.01 (t, 1 H, *J* 9.2 Hz, H-4′), 4.55 (d, 1 H, *J* 8.8 Hz, H-1′), 3.65–3.60 (m, 2 H, H-3′, H-5), 2.80–2.60 (m, 3 H, H-2, SCH$_2$), 2.48–2.30 (m, 2 H), 1.94 (s, 3 H, Ac). EIMS (*m/z*, %): 369 (100), 105 (Bz, 93.4). Anal. Calcd for C$_{44}$H$_{66}$O$_6$S: C, 73.09; H, 9.20. Found: C, 72.81; H, 9.10.

Ethyl 3-O-acetyl-4-O-benzoyl-6-deoxy-2-S-ethyl-2-thio-β-L-glucopyranosyl-(1 → 4)-2,3-O-isopropylidene-1-thio-α-L-rhamnopyranoside (**29**).—[α]$_D$ − 46.2° (*c* 0.7, CHCl$_3$); ^{1}H NMR (CDCl$_3$): δ 7.99–7.41 (m, 5 H), 5.52 (s, 1 H, H-1′), 5.17–5.08 (m, 2 H, H-3, H-4), 4.65 (d, 1 H, *J* 8.9 Hz, H-1), 4.24–4.18 (m, 2 H, H-2′, H-3′), 4.09–4.04 (m, 1 H, H-4′), 3.68–3.58 (m, 2 H, H-5′, H-5), 2.88–2.52 (m, 5 H, H-2, 2 × SCH$_2$), 1.94 (s, 3 H, Ac), 1.63, 1.56 (2 × s, 6 H, (CH$_3$)$_2$C). EIMS (*m/z*, %): 584 ([M$^+$], 0.5), 523 ([M$^+$ − SEt], 9.5), 155 (100). Anal. Calcd for C$_{28}$H$_{48}$O$_9$S$_2$: C, 57.51; H, 6.90. Found: C, 57.33; H, 7.08.

3-O-Acetyl-4-O-benzoyl-6-deoxy-2-S-ethyl-2-thio-β-L-glucopyranosyl-(1 → 6)-1,2;3,4-di-O-isopropylidene-α-D-galactopyranoside (**30**). —[α]$_D$ − 5.6° (*c* 1.0, CHCl$_3$); ^{1}H NMR (CDCl$_3$): δ 7.98–7.40 (m, 5 H), 5.54 (d, 1 H, *J* 5.1 Hz, H-1), 5.12 (dd, 1 H, *J* 9.4, 9.3 Hz, H-3′), 5.02 (t, 1 H, *J* 9.3 Hz, H-4′), 4.63 (dd, 1 H, *J* 8.0, 2.3 Hz, H-3), 4.48 (d, 1 H, *J* 8.7 Hz, H-1′), 4.33 (m, 2 H, H-2, H-4), 4.05 (m, 2 H, H-6), 3.82 (m, 1 H, H-5), 3.64 (m, 1 H, H-5′), 2.76 (m, 3 H, H-2′, SCH$_2$), 1.97 (s, 3 H, Ac), 1.53, 1.46 (2 × s, 6 H, (CH$_3$)$_2$C), 1.35, 1.33 (2 × s, 6 H, (CH$_3$)$_2$C), 1.26 (d, 3 H, *J* 6.3 Hz), 1.22 (t, 3 H, *J* 7.2 Hz, SCH$_2$CH$_3$). EIMS (*m/z*, %): 581 ([M$^+$ − Me], 0.2), 337 ([M$^+$ − galacto], 1.4), 115 (28.6), 105 (Bz, 100). Anal. Calcd for C$_{29}$H$_{40}$O$_{11}$S: C, 58.37; H, 6.76. Found: C, 58.33; H, 6.84.

Ethyl 3-O-acetyl-4-O-benzoyl-6-deoxy-2-S-phenyl-2-thio-β-L-glucopyranosyl-(1 → 4)-2,3-O-isopropylidene-1-thio-α-L-rhamnopyranoside (**31**).—[α]$_D$ − 9.4° (*c* 1.1, CHCl$_3$); ^{1}H NMR (CDCl$_3$): 7.96–7.26 (m, 10 H), 5.48 (s, 1 H,

H-1′), 5.33 (dd, 1 H, *J* 11.3, 9.3 Hz), 5.09 (t, 1 H, *J* 9.3 Hz), 4.70 (d, 1 H, *J* 9.0 Hz, H-1), 4.19–4.13 (m, 2 H, H-2′, H-3′), 4.00–3.92 (dd, 1 H, *J* 10.2, 6.3 Hz, H-4′), 3.68–3.54 (m, 2 H, H-5′, H-5), 3.38 (dd, 1 H, *J* 11.3, 8.8 Hz, H-2), 2.66–2.44 (m, 2 H, SCH$_2$), 1.83 (s, 3 H, Ac), 1.53, (s, 6 H, (CH$_3$)$_2$C), 1.36–1.25 (m, 9 H). EIMS (*m/z*, %): 571 ([M$^+$ − SEt], 1.1), 385 ([M$^+$ − Rhamno], 5.7), 203 (95.2), 105 (Bz, 100). Anal. Calcd for C$_{32}$H$_{40}$O$_9$S$_2$: C, 60.74; H, 6.37. Found: C, 61.01; H, 6.57.

Ethyl 3-O-acetyl-4-O-benzoyl-6-deoxy-2-S-phenyl-2-thio-β-L-glucopyranoside (**32**).—[α]$_D$ + 61.2° (*c* 1.0, CHCl$_3$); ^{1}H NMR (CDCl$_3$): δ 7.99–7.27 (m, 10 H), 5.28 (dd, 1 H, *J* 11.3, 9.3 Hz, H-3), 5.02 (t, 1 H, *J* 9.5 Hz, H-4), 4.34 (d, 1 H, *J* 8.8 Hz, H-1), 3.99–3.88 (m, 1 H, H-5), 3.64–3.52 (m, 2 H, OCH$_2$), 3.17 (dd, 1 H, *J* 11.3, 8.8 Hz, H-2), 1.89 (s, 3 H, Ac), 1.23 (m, 6 H). EIMS (*m/z*, %): 430 ([M$^+$], 0.6), 105 (Bz, 100). Anal. Calcd for C$_{28}$H$_{26}$O$_6$S: C, 64.17; H, 6.09. Found: C, 64.47; H, 6.32.

3-O-Acetyl-4-O-benzoyl-6-deoxy-2-S-phenyl-2-thio-β-L-glucopyranosyl-(1 → 6)-1,2;3,4-di-O-isopropylidene-α-D-galactopyranoside (**33**). —[α]$_D$ − 10.0° (*c* 0.9, CHCl$_3$); ^{1}H NMR (CDCl$_3$): δ 7.98–7.22 (m, 10 H), 5.54 (d, 1 H, *J* 4.9 Hz, H-1), 5.27 (dd, 1 H, *J* 11.2, 9.3 Hz, H-3′), 5.02 (t, 1 H, *J* 9.5 Hz, H-4′), 4.58 (dd, 1 H, *J* 8.0, 2.2 Hz, H-3), 4.42 (d, 1 H, *J* 8.8 Hz, H-1′), 4.34–4.29 (m, 2 H, H-2, H-4), 4.01–3.97 (m, 2 H, H-6), 3.81–3.74 (m, 1 H, H-5), 3.61–3.56 (m, 1 H, H-5′), 3.18 (dd, 1 H, *J* 11.3, 8.8 Hz, H-2′), 1.92 (s, 3 H, Ac), 1.49 (s, 6 H), 1.36, 1.34 (2 × s, 2 × 3 H), 1.24 (d, 3 H, *J* 6.2 Hz). EIMS (*m/z*, %): 644 ([M$^+$], 0.2), 203 (23.8), 152 (43.6), 105 (Bz, 100). Anal. Calcd for C$_{33}$H$_{40}$O$_{11}$S: C, 61.48; H, 6.25. Found: C, 61.41; H, 6.40.

Cholesteryl 3-O-acetyl-4,6-O-benzylidene-2-S-ethyl-2-thio-α/β-D-glucopyranoside (**34**).— (α:β = 1:4). ^{1}H NMR (CDCl$_3$): δ 7.44–7.32 (m, 5 H), 5.51–5.49 (m, 1.2 H, PhCH, 0.2 H-1$_a$), 5.40 (m, 0.8 H, H-6$_b'$), 5.34 (m, 0.2 H, H-6$_a'$), 5.12–5.05 (m, 1 H, H-3), 4.63 (d, 0.8 H, *J* 8.7 Hz, H-1$_b$), 4.32–4.23 (m, 1 H, H-4), 4.14–4.04 (m, 0.2 H, H-5$_a$), 3.82–3.56 (2 × m, 3 H, H-6, H-3′), 3.50–3.45 (m, 0.8 H, H-5$_b$), 2.82–2.61 (m, 3 H, H-2, SCH$_2$), 2.48–2.22 (2 × m, 2 H), 2.10 (s, 3 H, Ac). EIMS (*m/z*, %): 721 ([M$^+$], 4.1), 369 ([M$^+$ − Gluco], 100).

Anal. Calcd for C$_{44}$H$_{64}$O$_6$S: C, 73.29; H, 8.95. Found: C, 73.11; H, 9.24.

Ethyl 3-O-acetyl-4,6-O-benzylidene-2-S-ethyl-2-thio-β-D-glucopyranoside (**35**).—^{1}H NMR (CDCl$_3$): δ 7.44–7.32 (m, 5 H), 5.49 (s, 1 H, CHPh), 5.08 (dd, 1 H, *J* 11.0, 9.5 Hz, H-3), 4.52 (d, 1 H, *J* 8.8 Hz, H-1), 4.32 (dd, 1 H, *J* 10.3, 5.1 Hz, H-4), 3.97 (m, 1 H), 3.78 (t, 1 H, *J* 10.3 Hz, H-6), 3.66 (m, 1 H), 3.62 (t, 1 H, *J* 9.5 Hz, H-6′), 3.46 (dt, 1 H, *J* 9.5, 5.1 Hz, H-5), 2.79–2.60 (m, 3 H, H-2, SCH$_2$), 2.11 (s, 3 H, Ac), 1.25–1.20 (m, 6 H).

Cyclohexanyl 3-O-acetyl-4,6-O-benzylidene-2-S-ethyl-2-thio-α/β-D-glucopyranoside (**36**). —(α:β = 2:3). ^{1}H NMR (CDCl$_3$): δ 7.44–7.32 (m, 5 H), 5.52–5.50 (m, 1.4 H, PhCH, H-1$_α$), 5.12–5.05 (m, 1 H, H-3), 4.63 (d, 0.6 H, *J* 8.8 Hz, H-1$_β$), 4.62 (dd, 0.6 H, *J* 10.6, 4.9 Hz, H-4$_β$), 4.50 (dd, 0.4 H, *J* 10.2, 4.9 Hz, H-4$_α$), 4.15–4.02 (m, 0.4 H, H-5$_α$), 3.83–3.55 (2 × m, 3 H, H-6, OCH(CH$_2$)$_5$), 3.50–3.42 (m, 3 H, SCH$_2$CH$_3$).

Cholesteryl 3,4,6-tri-O-acetyl-2-S-ethyl-2-thio-β-D-glucopyranoside (**37**).—[α]$_D$ − 4.8° (*c* 0.4, CHCl$_3$); ^{1}H NMR (CDCl$_3$): δ 5.39 (m, 1 H, H-6), 5.01 (t, 1 H, *J* 9.3 Hz), 4.93 (t, 1 H, *J* 9.9 Hz), 4.54 (d, 1 H, *J* 8.8 Hz, H-1′), 4.30 (dd, 1 H, *J* 11.9, 4.8 Hz, H-6′), 4.08 (dd, 1 H, *J* 12.1, 2.2 Hz, H-6′), 3.66–3.54 (m, 2 H, H-5′, H-3), 2.80–2.60 (m, 3 H, H-2′, SCH$_2$), 2.44–2.22 (m, 2 H), 2.12, (s, 6 H, 2 × Ac), 2.02 (s, 3 H, Ac). EIMS (*m/z*, %): 703 ([M$^+$ − Me], 0.2), 659 ([M$^+$ − SEt], 0.3), 369 ([M$^+$ − Man], 100). Anal. Calcd for C$_{41}$H$_{66}$O$_8$S: C, 68.48; H, 9.25. Found: C, 68.28; H, 9.27.

Ethyl 3,4,6-tri-O-acetyl-2-S-ethyl-2-thio-β-D-glucopyranoside (**38**).—[α]$_D$ + 22.2° (*c* 1.1, CHCl$_3$); ^{1}H NMR (CDCl$_3$): δ 5.03 (t, 1 H, *J* 9.1 Hz), 4.94 (dd, 1 H, *J* 11.0, 9.1 Hz), 4.42 (d, 1 H, *J* 8.8 Hz, H-1), 4.30 (dd, 1 H, *J* 12.4, 4.9 Hz, H-6), 4.12 (dd, 1 H, *J* 12.1, 2.2 Hz, H-6), 4.04–3.94 (m, 1 H, H-5), 3.71–3.59 (m, 2 H, OCH$_2$), 2.82–2.60 (m, 3 H, H-2, SCH$_2$), 2.09, 2.08, 2.02 (3 × s, 9 H, 3 × Ac), 1.28–1.23 (m, 6 H, SCH$_2$CH$_3$, OCH$_2$CH$_3$). EIMS (*m/z*, %): 377 ([M$^+$ + 1], 0.8), 333 ([M$^+$ − OEt], 2.4). Anal. Calcd for C$_{16}$H$_{26}$O$_8$S: C, 50.78; H, 6.82. Found: C, 50.63; H, 6.83.

3,4,6-Tri-O-acetyl-2-S-ethyl-2-thio-β-D-glucopyranosyl-(1 → 6)-1,2;3,4-di-O-isopropylidene-α-D-galactopyranoside (**39**).—[α]$_D$ − 33.4° (*c* 1.0, CHCl$_3$); ^{1}H NMR (CDCl$_3$): δ

5.53 (d, 1 H, *J* 4.9 Hz, H-1′), 5.03 (t, 1 H, *J* 9.5 Hz), 4.97 (dd, 1 H, *J* 11.3, 9.1 Hz), 4.63 (dd, *J* 7.7, 2.5 Hz, H-6), 4.52 (d, 1 H, *J* 8.5 Hz, H-1), 4.46–4.24 (m, 3 H), 4.13–4.00 (m, 3 H), 3.74 (dd, 1 H, *J* 10.7, 7.1 Hz), 3.65 (m, 1 H), 2.87–2.66 (m, 3 H, H-2, SCH$_2$), 2.09, 2.08, 2.02 (3 × s, 9 H, 3 × Ac), 1.51, 1.46 (2 × s, 6 H, (CH$_3$)$_2$CO$_2$), 1.34 (s, 6 H, (CH$_3$)$_2$CO$_2$), 1.22 (m, 3 H, SCH$_2$CH$_3$). EIMS (*m/z*, %): 577 ([M$^+$ − Me], 10.7), 213 (100). Anal. Calcd for C$_{26}$H$_{40}$O$_{13}$S: C, 52.69; H, 6.80. Found: C, 52.55; H, 6.88.

*Cyclohexanyl 3,4,6-tri-*O*-acetyl-2-*S*-ethyl-2 - thio - β -* D *- glucopyranoside* (**40**).—[α]$_D$ + 24.7° (*c* 1.0, CHCl$_3$); ^{1}H NMR (CDCl$_3$): δ 5.18 (t, 1 H, *J* 9.3 Hz), 4.92 (dd, 1 H, *J* 10.7, 9.3 Hz), 4.51 (d, 1 H, *J* 8.8 Hz, H-1), 4.30 (dd, 1 H, *J* 12.1, 4.9 Hz, H-6), 4.09 (dd, 1 H, *J* 12.1, 2.2 Hz, H-6), 3.79–3.59 (m, 2 H, H-5, OCH), 2.80–2.60 (m, 3 H, H-2, SCH$_2$), 2.09 (s, 6 H, 2 × Ac), 2.03 (s, 3 H, Ac), 2.00–1.84 (m, 2 H), 1.80–1.66 (m, 2 H), 1.58–1.36 (m, 3 H), 1.36–1.19 (m, 6 H). EIMS (*m/z*, %): 415 ([M$^+$ − OH], 1.3), 333 ([M$^+$ − (CH$_2$)$_5$], 9.8), 213 (100). Anal. Calcd for C$_{20}$H$_{32}$O$_8$S: C, 55.54; H, 7.46. Found: C, 55.02; H, 7.33.

Acknowledgements

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