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Note

Intermolecular aglycon transfer of ethyl 1-thiorhamnopyranosides under Koenigs–Knorr and Helferich glycosylation conditions

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Over the past decade, carbohydrate chemists have made extensive use of alkyl (particularly methyl, ethyl, and phenyl) 1-thioglycosides as versatile and flexible building blocks for the synthesis of both simple and complex oligosaccharides [1]. The alkylthio group provides effective protection for the anomeric centre and is stable under many of the reaction conditions (including acetal formation and hydrolysis, alkylation, acylation, and reduction) that protecting group chemistry requires for hydroxyl function differentiation and manipulation [1]. Moreover, thioglycosides can be activated to act as potent glycoside donors, either directly through the use of thiophilic promoters such as methyl triflate [2], dimethyl(methylthio)sulfonium triflate [3,4], benzeneselenyl triflate [5], iodonium dicollidine perchlorate [6], nitrosyl tetrafluoroborate [7], and methylsulfenyl triflate [8], or indirectly via their facile conversion into glycosyl halides [1,9], which are themselves classical glycosyl donors activated by heavy metal salt promoters [10].

Despite this widespread synthetic utility, limitations in the applicability of alkyl thioglycosides to certain problems are becoming apparent. Intramolecular nucleophilic migrations of alkylthio groups have been reported in monosaccharide chemistry [11] and in some cases the preparation of glycosyl halides from thioglycosides, and their subsequent utilization in glycosylations, have proved difficult owing to side reactions

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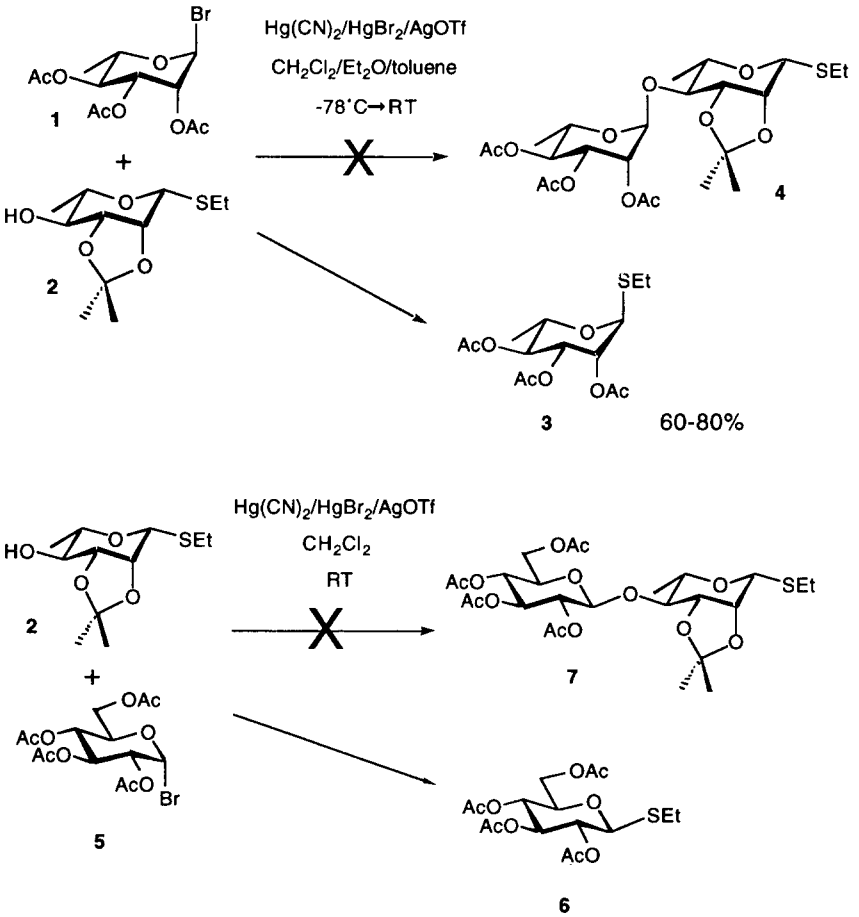


Scheme 1.

[1,9,12]. Small amounts of intermolecular aglycon transfer have been observed in glycosylation reactions when employing rhamnosyl halides as glycosyl donors [13–15] and the poor yield of a glycosylation reaction utilising an ethyl 1-thiogalactopyranoside derivative was attributed to the intermolecular transglycosylation of the thioglycoside function [16]. We report here the results of an investigation into intermolecular aglycon transfers of ethyl 1-thiorhamnopyranoside derivatives which proceed in yields of up to 80% under Koenigs–Knorr and Helferich glycosylation conditions.

During the course of our synthetic work towards novel cyclooligosaccharide derivatives, we observed that in the reaction of **1** with **2** in dichloromethane, in the presence of $Hg(CN)_2$ as the promoter and 4 Å molecular sieves (classical Helferich conditions [10]), no disaccharide was detectable and the reaction unexpectedly appeared to lead exclusively to the formation of the thioglycoside derivative **3** in 75% yield (Scheme 1). Despite varying the nature of the heavy metal salt promoter [$Hg(CN)_2$, $HgBr_2$, AgOTf

Table 1
Formation of aglycon transfer products under Koenigs–Knorr and Helferich glycosylation conditions

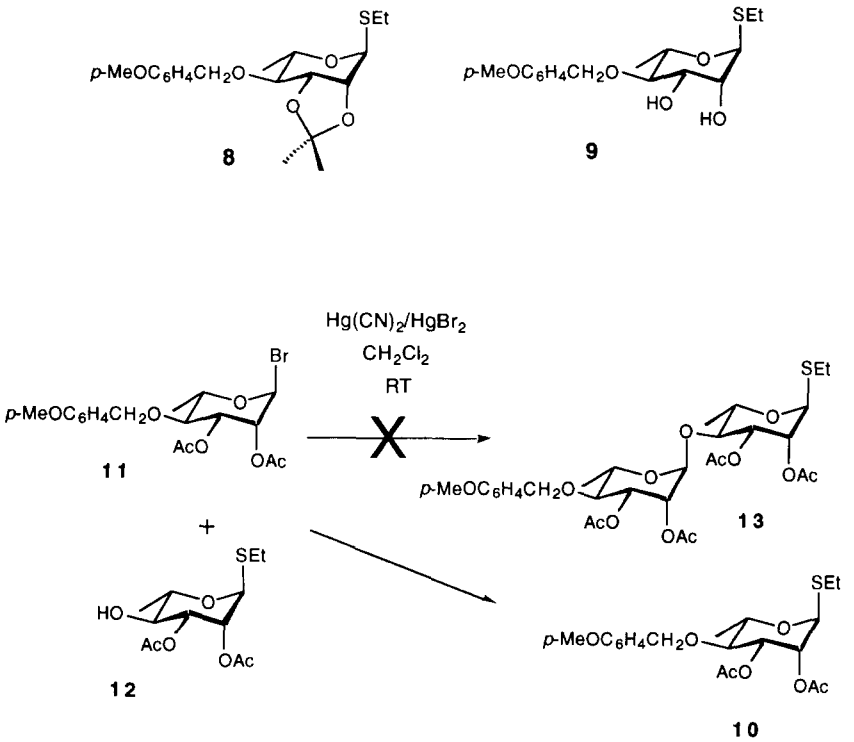
Reactants	Promoter	Solvent	Product	Yield (%)
1 + **2**	$Hg(CN)_2$	CH_2Cl_2	**3**	65
	$Hg(CN)_2$	Et_2O	**3**	60
	$Hg(CN)_2$	Toluene	**3**	63
	$HgBr_2$	CH_2Cl_2	**3**	62
	AgOTf	CH_2Cl_2	**3**	47
2 + **5**	$Hg(CN)_2$	CH_2Cl_2	**6**	80
	$HgBr_2$	CH_2Cl_2	**6**	78
	AgOTf	CH_2Cl_2	**6**	75
11 + **12**	$Hg(CN)_2$	CH_2Cl_2	**10**	10
	$HgBr_2$	CH_2Cl_2	**10**	30

(Koenigs–Knorr)], solvent (CH_2Cl_2, Et_2O, toluene), reaction times (30 min → 2 days), and temperatures (−78°C → room temperature), it was never possible to obtain a reasonable yield (> 25%) of the disaccharide **4** or to eliminate completely formation of the aglycon transfer product **3**, although smaller amounts of **3** were produced at lower temperatures and when using shorter reaction times. Further studies of the anomalous behaviour of ethyl 1-thiorhamnoside derivatives were carried out to investigate the limitations of the aglycon transfer reaction (Table 1).

Variation of the glycosyl bromide indicated that the aglycon transfer reaction was independent of the nature of the glycosyl bromide or the reaction conditions under which it was formed; the conversion of **1** into **3** occurred in identical yields whether **1** was formed from the reaction of bromine on **3** [1] or directly from L-rhamnopyranose via treatment with HBr in Ac_2O [17]. Under similar reaction conditions with either $Hg(CN)_2$, $HgBr_2$, or AgOTf as the heavy metal promoter, tetra-*O*-acetyl-α-D-glucopyranosyl bromide (**5**) was converted into the ethyl 1-thio-β-glycoside **6** in the presence of **2** in high yield (75–80%) rather than the expected disaccharide **7**.

Variations in the protecting groups at the 2- and 3-positions (acetals and esters) and the stereochemistry of the anomeric centre of the ethyl 1-thiorhamnopyranoside derivatives did not significantly change the product distribution under the reaction conditions. Protection of the 4-*O*-position of ethyl 2,3-*O*-isopropylidene-1-thio-α-L-rhamnopyranoside as its *p*-methoxybenzyl ether gave the fully protected rhamnose derivative **8**, which was deprotected at the 2,3-positions to give **9** and subsequently acetylated to give ethyl 2,3-di-*O*-acetyl-4-*O*-*p*-methoxybenzyl-1-thio-α-L-rhamnoside (**10**). Treatment of **10** with bromine gave rise to the glycosyl donor **11**, whereas removal of the *p*-methoxybenzyl function of **10** with 2,3-dichloro-5,6-dicyanobenzoquinone gave the glycosyl acceptor **12**. Reaction of **11** and **12** under Helferich conditions gave rise to **10** in 10–30% yield, depending on the promoter (Scheme 2). No disaccharide was produced. The lower yield obtained when employing **12** as the glycosyl acceptor is probably due to the electron-withdrawing group at the 2-position reducing the nucleophilicity of the sulfur atom, in the manner exploited by Veeneman and van Boom [6] in their use of "armed" and "disarmed" thioglycosides, and therefore inhibiting to some extent the transfer reaction.

This result, together with the fact that glycosylation reactions at the 2- and 3-posi-



Scheme 2.

tions of ethyl 1-thiorhamnopyranosides are well documented [1,13,18,19], supports the view that the transfer phenomena are related mainly to the nature of the relatively unreactive 4-hydroxyl group. The sulfur atoms of thioglycosides are reactive towards alkylating agents, which is utilized in their activation by thiophilic reagents such as MeOTf [1]. In the case of ethyl 1-thiorhamnopyranosides, the low nucleophilicity of the 4-OH group appears to cause it to lose the competitive alkylation (glycosylation) reaction with the sulfur atom, resulting in aglycon transfer. The use of other aglycon groups such as phenyl and *p*-nitrophenyl may well, therefore, overcome this limitation in their use.

1. Experimental

General.—TLC was performed on Silica Gel F_{254} (Merck) with detection by charring with H_2SO_4. Column chromatography was performed on Merck silica gel (60–240 mesh). ^1H NMR spectra (300 MHz) and ^{13}C NMR spectra (75 MHz) were recorded with a Bruker AC-300 spectrometer.

2,3,4-Tri-O-acetyl-α-L-rhamnopyranosyl bromide [20] (**1**).—*Method A [17].* Tetra-*O*-acetyl-β-L-rhamnopyranose (4.0 g, 12 mmol) was dissolved in AcOH (6 mL) and a

solution of HBr in AcOH (6 mL, 30%) was added dropwise at 0°C. The mixture was stirred for 3 h, after which toluene (3 × 20 mL) was added and the solvent removed to give **1** as a pale-yellow oil (4.2 g, 12 mmol).

Method B [21]. Bromine (0.15 mL, 2.95 mmol) in CH_2Cl_2 was added dropwise to a stirred solution of ethyl 2,3,4-tri-*O*-acetyl-1-thio-α-L-rhamnopyranoside (**3**) (1.0 g, 3.01 mmol) in CH_2Cl_2 (15 mL) at 0°C. Cyclohexene was added after 30 min to destroy the excess of bromine, and the solvent was removed in vacuo to give **1** as pale-yellow oil (1.1 g, 3 mmol).

Ethyl 2,3-O-isopropylidene-1-thio-β-L-rhamnopyranoside (**2**).—Ethyl 1-thio-β-L-rhamnopyranoside [11] (4.4 g, 21.2 mmol) was dissolved in dry acetone (35 mL), to which 2,3-dimethoxypropane (6 mL, 49.0 mmol) and $ZnCl_2$ (2.9 g, 21.1 mmol) in portions were added. The reaction was stirred for 10 min, triethylamine was added, and the precipitate was filtered off. The solvent was evaporated, the crude residue was dissolved in CH_2Cl_2 (50 mL), the solution was washed with water (2 × 30 mL) and dried, and the solvent was evaporated. Column chromatography (9:1 hexane–EtOAc) gave **2** (4.0 g, 16.5 mmol, 78%) as a white solid; mp 113–114°C; $[\alpha]_D$ +0.23° (*c* 2.0, CH_2Cl_2); ^{1}H NMR ($CDCl_3$): δ 4.80 (d, 1 H, $J_{1,2}$ 2 Hz, H-1), 4.25 (dd, 1 H, $J_{2,3}$ 5.5 Hz, H-2), 3.95 (dd, 1 H, $J_{3,4}$ 7 Hz, H-3), 3.43 (m, 1 H, H-4), 3.22 (m, 1 H, H-5), 2.73 (q, 2 H, *J* 7.5 Hz, SCH_2CH_3), 1.52, 1.35 [2 s, each 3 H, $C(CH_3)_2$], 1.32 (d, 3 H, $J_{5,6}$ 6 Hz, H-6), 1.29 (t, 3 H, SCH_2CH_3), and 2.43 (d, 1 H, $J_{4,OH}$ 3.5 Hz, O*H*); ^{13}C NMR (75 MHz): δ 80.6 (C-1). Anal. Calcd for $C_{11}H_{20}O_4S$: C, 53.2; H, 8.1; S, 12.9. Found: C, 53.3; H, 8.4; S, 13.2%.

Typical silver triflate-promoted glycosyl transfer reaction.—To a stirred solution of the glycosyl donor (1.0 mmol) and the glycosyl acceptor (1.0 mmol) in dried CH_2Cl_2 (15 mL) containing activated 4 Å molecular sieves was added silver triflate (1.5 mmol) and the mixture was kept at −78°C under N_2. After 30 min the mixture was warmed to room temperature, and pyridine (5 mL) and a solution of $Na_2S_2O_3$ in water (5 mL, 0.5 M) were added. The mixture was filtered on Celite, washed with water, and dried, and the solvent was evaporated. Column chromatography (9:1 hexane–EtOAc) gave the transfer products and further elution gave the starting alcohol.

Typical mercuric cyanide-promoted glycosyl transfer reaction.—To a stirred solution of the glycosyl acceptor (1.0 mmol) and $Hg(CN)_2$ (1.0 mmol) in dried CH_2Cl_2 (10 mL) containing activated 4 Å molecular sieves, the glycosyl donor (1.0 mmol) was added under N_2 at 0°C. After 24 h the mixture was filtered on Celite, washed with water, and dried, and the solvent was evaporated to give a syrup, which was subjected to column chromatography (9:1 hexane–EtOAc) to give the aglycon transfer products; further elution gave the starting alcohol.

Data for ethyl 2,3,4-tri-*O*-acetyl-1-thio-α-L-rhamnopyranoside (**3**): mp 68–70°C; $[\alpha]_D$ −0.09° (*c* 1.0, CH_2Cl_2); ^{1}H NMR ($CDCl_3$): δ 5.31 (dd, 1 H, $J_{1,2}$ 1.5, $J_{2,3}$ 3 Hz, H-2), 5.21 (dd, 1 H, $J_{3,4}$ 10 Hz, H-3), 5.17 (d, 1 H, H-1), 5.07 (t, 1 H, $J_{4,5}$ 10 Hz, H-4), 4.20 (m, 1 H, H-5), 2.60 (m, 2 H, SCH_2CH_3), 2.09, 2.02, 1.95 (3 s, each 3 H, 3 Ac), and 1.25 (m, 6 H, H-6 and SCH_2CH_3); ^{13}C NMR (75 MHz): δ 82.0 (C-1).

Data for ethyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (**6**): mp 78–79°C; $[\alpha]_D$ −37° (*c* 2.3, CH_2Cl_2); ^{1}H NMR ($CDCl_3$): δ 5.40 (t, 1 H, $J_{1,2} = J_{2,3} = 9$ Hz, H-2), 5.20 (m, 2 H, H-3, H-4), 4.68 (d, 1 H, H-1), 4.40 (dd, 1 H, $J_{5,6a}$ 4, $J_{6a,6b}$ 12 Hz,

H-6a), 4.35 (dd, 1 H, $J_{5,6b}$ 2, $J_{6a,6b}$ 12 Hz, H-6b), 3.92 (m, 1 H, H-5), 2.82 (m, 2 H, SCH_2CH_3), 2.30–2.20 (4 s, each 3 H, 4 Ac), 1.41 (t, 3 H, J 6 Hz, SCH_2CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.4, 169.9, 169.2, 169.1 (4 $COCH_3$), 83.3 (C-1), 75.6, 73.6, 69.6, 68.1, 61.9 (C-2,3,4,5,6), 23.9 (SCH_2CH_3), 20.5, 20.4, 20.4, 20.4 ($4CH_3CO$), 14.6 (SCH_2CH_3); FABMS: m/z 393 $(M+H)^+$, 415 $(M+Na)^+$. Anal. Calcd for $C_{16}H_{24}O_9S$: C, 49.0; H, 6.1; S, 8.1. Found: C, 48.9; H, 6.2; S, 8.5%.

Data for ethyl 2,3-di-*O*-acetyl-4-*O*-*p*-methoxybenzyl-1-thio-α-L-rhamnopyranoside (**10**): $[\alpha]_D$ −18° (*c* 1.72, CH_2Cl_2); ^1H NMR ($CDCl_3$): δ 7.21 (2 H, d, J 9 Hz, aromatics), 6.86 (d, 2 H, J 9 Hz, aromatics), 5.33 (dd, 1 H, $J_{1,2}$ 1.5, $J_{2,3}$ 3 Hz, H-2), 5.23 (dd, 1 H, $J_{3,4}$ 9 Hz, H-3), 5.14 (d, 1 H, H-1), 4.62, 4.53 (AB system, 2 H, J 10.5 Hz, OCH_2Ar), 4.14 (m, 1 H, H-5), 3.78 (s, 3 H, OCH_3), 3.52 (t, 1 H, $J_{4,5}$ 9 Hz, H-4), 2.60 (m, 2 H, SCH_2CH_3), 2.13, 1.98 (2 s, each 3 H, 2 Ac), 1.33 (d, 3 H, $J_{5,6}$ 6 Hz, H-6), 1.27 (t, 3 H, J 7.5 Hz, SCH_2CH_3); ^{13}C NMR (75 MHz): δ 81.9 (C-1); FABMS: m/z 413 $(M+H)^+$. Anal. Calcd for $C_{20}H_{28}O_7S$: C, 58.2; H, 6.8; S, 7.8. Found: C, 57.9; H, 7.1; S, 8.2%.

*Ethyl 2,3-*O*-isopropylidene-4-*O*-p-methoxybenzyl-1-thio-α-L-rhamnopyranoside* (**8**). —To a solution of ethyl 2,3-*O*-isopropylidene-1-thio-α-L-rhamnopyranoside [22] (8.0 g, 32.5 mmol) and *p*-methoxybenzyl chloride (6.3 mL, 42.9 mmol) in dry DMF (80 mL), NaH (1.71 g of a 60% suspension in mineral oil, 42.8 mmol) was added in portions. After 48 h the remaining hydride was destroyed with MeOH, and the mixture was washed with water, extracted into CH_2Cl_2, dried over $MgSO_4$, and concentrated to give the product (11.8 g, 99%); $[\alpha]_D$ −0.25° (*c* 1.7, CH_2Cl_2); ^1H NMR ($CDCl_3$): δ 7.30 (d, 2 H, J 9 Hz, aromatics), 6.87 (d, 2 H, aromatics), 5.50 (s, 1 H, H-1), 4.82, 4.55 (AB system, 2 H, $J_{a,b}$ 10.5 Hz, OCH_2Ar), 4.23 (t, 1 H, $J_{2,3} = J_{3,4} = 6$ Hz, H-3), 4.17 (d, 1 H, H-2), 4.01 (m, 1 H, H-5), 3.78 (s, 3 H, OCH_3), 3.25 (dd, 1 H, $J_{4,5}$ 9 Hz, H-4), 2.55 (m, 2 H, SCH_2CH_3), 1.54, 1.38 [2 s, each 3 H, $C(CH_3)_2$], and 1.27 (m, 6 H, H-6 and SCH_2CH_3); ^{13}C NMR (75 MHz): δ 80.4 (C-1).

*Ethyl 4-*O*-p-methoxybenzyl-1-thio-α-L-rhamnopyranoside* (**9**).—Compound **8** (7.0 g, 19.0 mmol) was dissolved in a solution of AcOH in water (150 mL, 4:1) and the mixture was stirred and heated at 50°C. After 3 h, TLC (3:2 hexane–EtOAc) showed that the triol was beginning to form, so the mixture was cooled to room temperature and neutralized with triethylamine, and the solvent was evaporated. Column chromatography (3:1 hexane–EtOAc) gave **9** (4.5 g, 13.8 mmol, 73%) as a white solid; mp 75–77°C; $[\alpha]_D$ −0.74° (*c* 3.3, acetone); ^1H NMR ($CDCl_3$, D_2O shake): δ 7.28 (d, 2 H, J 9 Hz, aromatics), 6.89 (d, 2 H, J 9 Hz, aromatics), 5.23 (bs, 1 H, H-1), 4.69, 4.62 (AB system, 2 H, J_{ab} 10.5 Hz, OCH_2Ar), 4.08 (m, 1 H, H-5), 4.00 (bd, 2 H, $J_{2,3}$ 3 Hz, H-2), 3.82 (m, 4 H, H-3 and OCH_3), 3.36 (t, 1 H, $J_{3,4} = J_{4,5} = 9$ Hz, H-4), 2.60 (m, 2 H, SCH_2CH_3), 1.34 (d, 3 H, $J_{5,6}$ 6 Hz, H-6), and 1.28 (t, 3 H, J 7.5 Hz, SCH_2CH_3); FABMS: m/z 329 $(M+H)^+$ and 351 $(M+Na)^+$. Anal. Calcd for $C_{16}H_{24}O_5S$: C, 58.5; H, 7.4; S, 9.8. Found: C, 58.5; H, 7.7; S, 10.0%.

Further elution of the column with EtOAc containing 5% of MeOH gave the triol (0.59 g, 2.9 mmol, 15%).

*Ethyl 2,3-di-*O*-acetyl-4-*O*-p-methoxybenzyl-1-thio-α-L-rhamnopyranoside* (**10**).—Acetic anhydride (9 mL, 95.4 mmol) was added dropwise to a cooled (0°C) stirred solution of **9** (3.0 g, 9.1 mmol) in CH_2Cl_2 (10 mL) containing triethylamine (10 mL,

71.7 mmol). After 24 h the mixture was washed with water (2 × 50 mL), dried, and concentrated. Column chromatography (5:1 hexane–EtOAc) gave **10** (3.58 g, 8.7 mmol, 95%) as a yellow oil: $[\alpha]_D$ −0.20° (*c* 1.72, CH_2Cl_2); ^{1}H NMR ($CDCl_3$): δ 7.21 (d, 2 H, *J* 9 Hz, aromatics), 6.86 (d, 2 H, aromatics), 5.33 (dd, 1 H, $J_{1,2}$ 1.5, $J_{2,3}$ 3 Hz, H-2), 5.23 (dd, 1 H, $J_{3,4}$ 9 Hz, H-3), 5.14 (d, 1 H, H-1), 4.62, 4.53 (AB system, 2 H, $J_{a,b}$ 10.5 Hz, OCH_2Ar), 4.14 (m, 1 H, H-5), 3.78 (s, 3 H, OCH_3), 3.52 (t, 1 H, $J_{4,5}$ 9 Hz, H-4), 2.60 (m, 2 H, SCH_2CH$_3$), 2.13, 1.98 (2 s, each 3 H, 2 Ac), 1.33 (d, 3 H, $J_{5,6}$ 6 Hz, H-6), and 1.27 (t, 3 H, *J* 7.5 Hz, SCH$_2$CH_3); ^{13}C NMR (75 MHz): δ 81.9 (C-1); FABMS: *m/z* 413 $(M + H)^+$. Anal. Calcd for $C_{20}H_{28}O_7S$: C, 58.2; H, 6.8; S, 7.8. Found: C, 57.9; H, 7.1; S, 8.2%.

2,3-Di-O-*acetyl-4*-O-p-*methoxybenzyl*-α-L-*rhamnopyranosyl bromide* (**11**).—Bromine (0.18 mL, 2.8 mmol) in CH_2Cl_2 was added dropwise to a stirred solution of **10** (1.5 g, 3.64 mmol) in CH_2Cl_2 (20 mL) at 0°C. Some drops of cyclohexene were added after 30 min to destroy the excess of Br_2 and the solvent was removed in vacuo to give a pale-yellow oil (1.5 g, 3.64 mmol); ^{1}H NMR ($CDCl_3$): δ 7.20 (d, 2 H, *J* 9 Hz, aromatics), 6.86 (d, 2 H, *J* 9 Hz, aromatics), 6.23 (bs, 1 H, H-1), 5.64 (dd, 1 H, $J_{2,3}$ 3, $J_{3,4}$ 9 Hz, H-3), 5.44 (dd, 1 H, $J_{1,2}$ 1.5 Hz, H-2), 4.65, 4.57 (AB system, 2 H, $J_{a,b}$ 10.5 Hz, OCH_2Ar), 4.03 (m, 1 H, H-5), 3.80 (s, 3 H, OCH_3), 3.57 (1 H, t, H-4), 2.15, 2.01 (2 s, each 3 H, 2 Ac), and 1.36 (d, 3 H, $J_{5,6}$ 6 Hz, H-6); ^{13}C NMR (75 MHz): δ 84.1 (C-1).

Ethyl 2,3-di-O-*acetyl-1-thio*-α-L-*rhamnopyranoside* (**12**).—To a stirred solution of **10** (1.53 g, 3.7 mmol) in 32:1 CH_2Cl_2–water (80 mL) was added 2,3-dichloro-5,6-dicyanobenzoquinone (0.85 mg, 3.76 mmol) in portions and the mixture was stirred overnight at room temperature. Evaporation of the solvent and column chromatography (3:1 hexane–EtOAc) gave **12** (1.03 g, 3.52 mmol, 95%) as a pale-yellow oil; $[\alpha]_D$ −0.23° (*c* 2.0, CH_2Cl_2); ^{1}H NMR ($CDCl_3$): δ 5.31 (dd, 1 H, $J_{1,2}$ 1.5, $J_{2,3}$ 3 Hz, H-2), 5.16 (d, 1 H, H-1), 5.07 (dd, 1 H, $J_{3,4}$ 9 Hz, H-3), 4.10 (m, 1 H, H-5), 3.65 (t, 1 H, H-4), 2.63 (m, 2 H, SCH_2CH$_3$), 2.12, 2.06 (2 s, each 3 H, 2 Ac), 1.36 (d, 3 H, $J_{5,6}$ 6 Hz, H-6), and 1.29 (t, 3 H, *J* 7.5 Hz, SCH$_2$CH_3); ^{13}C NMR (75 MHz): δ 82.0 (C-1); FABMS: *m/z* 293 $(M + H)^+$. Anal. Calcd for $C_{12}H_{20}O_6S$: C, 49.3; H, 6.9; S, 11.0. Found: C, 49.2; H, 6.7; S, 11.4%.

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