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A convenient synthesis for anomeric 2-thioglucobioses, 2-thiokojibiose and 2-thiosophorose [+]

Jacques Defaye * and Jean-Michel Guillot [1]

CNRS and CEA, Département de Recherche Fondamentale sur la Matière Condensée / SESAM, Centre d'Etudes de Grenoble, BP 85 X, F-38041 Grenoble (France)

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ABSTRACT

2-*S*-α-D-Glucopyranosyl-2-thio-D-glucopyranose (2-thiokojibiose, **8**) and 2-*S*-β-D-glucopyranosyl-2-thio-D-glucopyranose (2-thiosophorose, **14**) were conveniently prepared by S_N2 reaction of the corresponding anomers of 2,3,4,6-tetra-*O*-acetyl-1-thio-D-glucopyranose with 1,3,4,6-tetra-*O*-acetyl-2-*O*-triflyl-β-D-mannopyranose, followed by a deprotection sequence for the anomeric acetate involving conversion into the 1-propenyl glycosides. Alkaline *O*-deacetylation was followed by smooth hydrolysis of the propenyl group at pH ~ 2.

INTRODUCTION

The (1 → 2)-glucosidic linkage is found in a number of oligosaccharide sequences involved in specific biological systems. Sophorose (2-*O*-β-D-glucopyranosyl-D-glucose), for example, is known for its regulatory roles in the production of cellulolytic enzymes in *Trichoderma reesei*[4,5]. Cyclic β-(1 → 2)-glucans, which are produced by plant-symbiotic *Rhizobium* and phytopathogenic *Agrobacterium* strains, are believed to play a role in the interaction of plants and bacteria. Kojibiose (2-*O*-α-D-glucopyranosyl-D-glucose) is a terminal constituent of the glycolipid donor involved in the biosynthesis of asparagine-linked glycoproteins, constituents of viral and cell membranes, from which it is cleaved at a later stage of their maturation[6]. Interglycosidically linked thioglycoside analogues may thus be of interest, in view of the reported stability of the thioglycosidic linkage in enzymic processes involving the corresponding *O*-glycosides as substrates[7].

[+] Part of the Univ. D. Thesis of J.-M. Guillot (Grenoble, 1991). For a preliminary communication, see ref 1. Stereoselective Thioglycoses Synthesis, Part XVI; for Part XV, see ref 2; for Part XIV, see ref 3.

* Author for correspondence.

[1] Present address: Ecole des Mines d'Alès, F-30319 Alès, France.

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Despite the fact that the synthesis of *S*-linked thiooligosaccharides is now reasonably well handled[7], a few early attempts to prepare 2-thiosophorose proved unsuccessful * in our hands[9] as well as others[10]. Zemplén *O*-deacetylation of 2-thiosophorose octa-acetate (**10**), as reported previously by Hamacher[10] for the preparation of 2-thiosophorose, was found in fact to result[9] in the formation of a number of chromatographically faster moving products, suggesting a destruction of the molecule. A similar result was obtained by acidic hydrolysis, followed by ion-exchange neutralisation, of methyl 2-thio-α-sophoroside[9]. These failures could be ascribed to the known tendency for enolisation of 2-thio sugars related to the increased acidity of H-2 as compared with the oxygen analogues[11], which may result in elimination reactions. This observation suggested that the introduction, at the anomeric position, of a more readily cleavable protecting group, such as a prop-1-enyl substituent, could minimise the effect of the sulfur atom at C-2. This concept has already been applied to the synthesis of 2-thioxylobiose[3], and is now extended to the preparation of both 2-thioglucobioses, namely 2-*S*-α-D-glucopyranosyl-2-thio-D-glucopyranose (2-thiokojibiose, **8**) and 2-*S*-β-D-glucopyranosyl-2-thio-D-glucopyranose (2-thiosophorose, **14**).

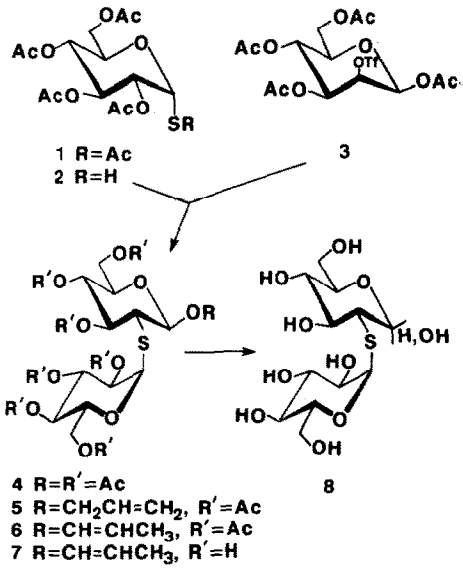
RESULTS AND DISCUSSION

The general synthetic scheme[7] for the preparation of *S*-linked thiooligosaccharides, involving S_N2 displacement of a good leaving group (sulfonate or halide) by a 1-thioglycose, was followed for both 2-thiodisaccharides **8** and **14**, using suitable anomers of 1-thio-D-glucose in reaction with a 2-*O*-triflyl-D-mannopyranose derivative **3** in an aprotic polar solvent.

2,3,4,6-Tetra-*O*-acetyl-1-thio-α-D-glucopyranose (**2**) was previously prepared[12] from its peracetylated precursor[13] **1** via the phenylmercury(II) 1-thioglycose intermediate. It was now found more convenient to use the selective *trans*-*S*-deacetylation technique of Endo et al.[14], with 2-aminoethanethiol as transfer reagent, for its preparation which was achieved by stirring at 65°C for 10 min in acetonitrile.

Reaction of the sodium salt of **2**, prepared by reaction with sodium hydride in dry tetrahydrofuran, with 1,3,4,6-tetra-*O*-acetyl-2-*O*-triflyl-β-D-mannopyranose[9,10] (**3**) in *N*,*N*-dimethylformamide at room temperature resulted in the crystalline peracetylated 2-thiokojibiose derivative **4** in 87% yield. The structure of **4** was confirmed by its ^1H NMR spectrum, which showed a signal at 5.96 ppm for H-1′ with a coupling constant of 5.9 Hz, in the range found for the 1-thioglucose

* After completion of these results, we were informed by Dr. L. Petruš (Bratislava) that he had succeeded[8] in the preparation of 2-thiosophorose, using an alternative approach which involves the addition of 1-thio-β-D-glucose to a 1,2-dideoxy-1-nitro-D-*arabino*-hex-1-enitol derivative, followed by a Nef reaction on the resulting epimeric 1-nitro-2-*S*-β-D-glucosyl-2-thiohexitol mixture. Improved yields in the 2-thiosophorose component were further obtained by Ca^{2+} epimerisation of the major *manno* isomer simultaneously formed.



precursor[13], and a doublet of doublets at high field (3.12 ppm) for H-2 with *trans*-diaxal coupling constants of 9.4 and 11.3 Hz with vicinal protons (Table I), in agreement with a *gluco* configuration at this site. The ^{13}C NMR spectrum (Table II) of **4**, with its low-field C-2 signal, further confirmed the proposed structure.

Direct *O*-deacetylation of **4** was not attempted, in view of the sensitivity previously found for this type of structure to alkaline reagents[9]. Conversion of **4** into the 1-propenyl ether **6** was readily achieved via the allyl glycoside **5**, which was obtained in quantitative yield by reaction, at room temperature in dry dichloromethane, with a slight excess of allyl alcohol in the presence of stannic chloride. The β anomer was exclusively formed, as shown by the doublet for H-1 in the ^1H NMR spectrum with a large *trans*-diaxial coupling constant, and this could suggest a possible participation of the sulfur atom at C-2 through an episulfonium ion intermediate at the glucosidation step.

Isomerisation of the allyl protecting group in **5** into the 1-propenyl glycoside **6** was achieved, in quantitative yield, with tris(triphenylphosphine)rhodium(I) chloride[15] in ethanol–toluene. ^{13}C NMR spectroscopy (Table II) confirmed the disappearance of allylic carbon atoms in favour of the *Z* and *E* propenyl isomers. This was followed by Zemplén *O*-deacetylation of **6** to **7**, followed by careful removal of salts over a mixed bed of IRC-50 (H^+)–IRA-910 (HO^-) Amberlite ion-exchange resins, yielding the 1-propenyl glycoside **7**.

Hydrolysis of the 1-propenyl protecting group of **7** was carried out at pH ~ 2, resulting in 2-thiokojibiose (**8**) which showed the expected $[M + Na]^+$ and $[M + H]^+$ pseudomolecular ions in FABMS at *m/z* 381 and 359, respectively.

TABLE I

^{1}H NMR data (400 MHz) for 2-thiokojibiose (**8**), 2 thiosophorose (**14**), and their respective precursors **4**, **5** and **10**, **11**

Compound	Chemical shift (δ) and signal multiplicities													
	H-1	H-2	H-3	H-4	H-5	H-6a	H-6b	H-1′	H-2′	H-3′	H-4′	H-5′	H-6′a	H-6′b
4	5.66d	3.12dd	5.04dd	4.97t	3.77ddd	4.04dd	4.30dd	5.96d	4.91dd	5.31t	4.99t	4.31m	4.16dd	4.25dd
5	4.50d	3.00dd	[a]	[a]	[a]	[a]	[a]	6.01d	5.04dd	5.32t	[a]	[a]	[a]	[a]
8 (α anomer)	5.48d	3.01dd	[a]	[a]	[a]	[a]	[a]	5.59d	[a]	[a]	[a]	[a]	[a]	[a]
(β anomer)	4.95d	2.77dd	[a]	[a]	[a]	[a]	[a]	5.85d	[a]	[a]	[a]	[a]	[a]	[a]
10	5.62d	3.00dd	5.14dd	4.92t	3.76ddd	4.01dd	4.23	4.61d	4.84dd	5.10t	4.98t	3.63ddd	4.05dd	4.22dd
11	5.02d	3.08dd	5.42dd	4.96t	[a]	[a]	[a]	4.67d	4.87dd	5.10t	5.03t	3.65ddd	[a]	[a]
14 (α anomer)	5.46d	3.19dd	3.88t	3.54	[a]	[a]	[a]	4.83d	3.38dd	3.58t	[a]	[a]	[a]	[a]
(β anomer)	4.86d	2.90dd	3.71dd	3.49t	[a]	[a]	[a]	4.82d	3.43dd	3.59t	[a]	[a]	[a]	[a]
	Coupling constants (Hz)													
	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6a}$	$J_{5,6b}$	$J_{6a,6b}$	$J_{1',2'}$	$J_{2',3'}$	$J_{3',4'}$	$J_{4',5'}$	$J_{5',6'a}$	$J_{5',6'b}$	$J_{6'a,6'b}$
4	9.4	11.3	9.0	9.2	2.1	4.2	12.5	5.9	10.2	9.8	9.7	1.9	5.5	11.9
5	8.9	11.3	[a]	[a]	[a]	[a]	[a]	5.8	10.2	9.9	[a]	[a]	[a]	[a]
8 (α anomer)	3.3	11.2	[a]	[a]	[a]	[a]	[a]	5.5	[a]	[a]	[a]	[a]	[a]	[a]
(β anomer)	8.9	11.0	[a]	[a]	[a]	[a]	[a]	5.5	[a]	[a]	[a]	[a]	[a]	[a]
10	9.2	10.9	9.1	9.5	2.0	4.6	12.5	10.1	9.3	9.3	9.7	1.9	5.8	12.3
11	3.5	11.0	9.5	9.7	[a]	[a]	[a]	10.0	9.0	9.0	9.5	2.0	4.9	[a]
14 (α anomer)	3.2	10.9	[a]	[a]	[a]	[a]	[a]	10.5	9.1	[a]	[a]	[a]	[a]	[a]
(β anomer)	9.1	10.6	[a]	[a]	[a]	[a]	[a]	10.5	8.9	[a]	[a]	[a]	[a]	[a]

[a] Not assigned.

TABLE II

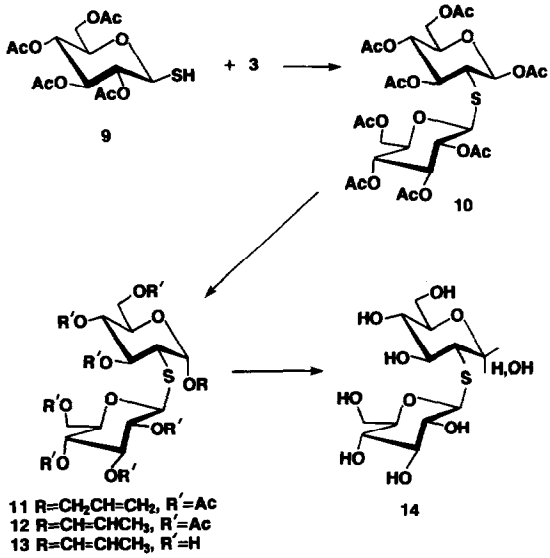
^{13}C NMR data (50 MHz) for 2-thiokojibiose (**8**), 2-thiosophorose (**14**), and their respective precursors **4,5** and **10,11,13**

Compound	Chemical shift (δ)												
	C-1	C-2	C-3	C-4	C-5	C-6	C-1′	C-2′	C-3′	C-4′	C-5′	C-6′	Other carbons
4	95.1	45.0	71.1	69.1	72.5	61.5	80.7	70.8	70.0	68.5	68.2	61.6	20.5 (Ac)
5	103.6	46.2	[a]	[a]	[a]	62.2	80.5	[a]	[a]	[a]	[a]	62.2	20.5 (Ac) 117.4, 134.3 (allyl)
8 (α anomer)	92.3	51.0	[a]	[a]	[a]	[a]	83.9	[a]	[a]	[a]	[a]	[a]	
(β anomer)	97.8	51.4	[a]	[a]	[a]	[a]	84.9	[a]	[a]	[a]	[a]	[a]	
10	92.2	48.9	73.6	68.8	72.5	61.5	83.6	70.8	73.6	68.0	75.9	61.9	20.5 (Ac)
11	98.6	47.8	73.0	67.8	69.5	61.9	84.3	70.1	73.7	68.1	75.9	61.9	20.5 (Ac) 69.2, 118.3, 133.0 (allyl)
13 (*Z* isomer)	99.9	49.6	72.9	70.5 [b]	72.9	60.5 [c]	85.7	72.9	77.4	69.6 [b]	79.9	60.9 [c]	8.8, 106.1, 141.7 (propenyl)
(*E* isomer)	99.3	49.5	72.7	70.5 [b]	72.7	60.4 [c]	85.8	72.7	77.3	69.5 [b]	79.8	60.9 [c]	11.5, 107.1, 142.5 (propenyl)
14 (α anomer)	93.7	50.5	[a]	[a]	[a]	60.9	85.8	[a]	[a]	[a]	80.0	60.9	
(β anomer)	95.4	53.0	[a]	[a]	[a]	60.9	84.6	[a]	[a]	[a]	80.0	60.9	

[a] Not assigned. [b,c] Assignments may be reversed for C-4/C-4′ and C-6/C-6′.

The ^{1}H NMR spectrum of **8** allowed the characterisation of the signals of the anomeric mixture, particularly of the high field H-2 protons at 3.01 and 2.77 ppm, respectively. From their integration, at mutarotational equilibrium, the proportion of α/β anomers was found to be 1:1, a result almost identical to the known anomeric composition[16] at equilibrium of kojibiose under similar conditions. The doublets for the H-1′ protons at δ 5.59 and 5.85 showed, furthermore, a vicinal coupling constant of 5.5 Hz, in agreement with an α configuration for the *S*-(1 → 2)-thioglycosidic linkage.

The synthesis of 2-thiosophorose followed almost the same reaction sequence, but using 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranose[17] (**9**) as precursor. Reaction of the sodium salt of **9** with **3**, in *N*,*N*-dimethylformamide at room temperature, afforded the β-(1 → 2)-linked acylated thiodisaccharide **10** in 58% yield. Hamacher[10] reported a yield of 25% for this thioglycosidation reaction using phase-transfer catalysis, while Orgeret[9] obtained a 57% yield using hexamethylphosphoramide as solvent.



Allylation of **10**, in dichloromethane at room temperature, with stannic chloride as catalyst, resulted in the crystalline allyl α-glycoside **11** in 70% yield. This anomeric specificity, which was confirmed by the 3.5-Hz vicinal coupling constant found for the anomeric proton of **11**, has to be compared with the exclusive formation of the β anomer noted above for the corresponding allyl 2-thiokojibioside derivative **5**.

Conversion into the 1-propenyl glycoside **12** was achieved, using either the Wilkinson reagent **15**, or alternatively 1,5-cyclooctadienebis(methyldiphenylphosphine)iridium hexafluorophosphate[18] as isomerisation catalyst[19], yielding from the latter process the crystalline 1′-propenyl glycoside **12** in quantitative yield. Zemplén

deacetylation of **12**, and careful demineralisation as for **7**, yielded **13** as a mixture of *E* and *Z* isomers which could be separated by LC on a Lichrosorb-NH_2 column, allowing complete assignment of their ^{13}C NMR spectra (Table II).

Mild acid hydrolysis of **13**, at pH ~2, yielded 2-thiosophorose **14**, which was characterised by its pseudomolecular ion $[M + Na]^+$ at *m/z* 381 in FABMS, and the characteristic H-2 high-field signals at 3.19 and 2.90 ppm, respectively, for the α and β anomers, in its ^1H NMR spectrum (50.5 and 53.0 ppm in ^{13}C NMR spectroscopy). Integration of the H-2 signals showed that the α/β anomeric ratio in the mixture at equilibrium was 75:25. This has to be compared with the anomeric composition at equilibrium of sophorose[16] (α/β 63:37).

EXPERIMENTAL

General methods.—The methods described in ref 3 were followed.

*2,3,4,6-Tetra-*O*-acetyl-1-thio-α-*D*-glucopyranose* (**2**).—To a solution of 2,3,4,6-tetra-*O*-acetyl-1-*S*-acetyl-1-thio-α-D-glucopyranose[13,20] (**1**; 2 g, 4.9 mmol) in MeCN was added 2-aminoethanethiol (0.42 g, 5.5 mmol). The mixture was stirred at 65°C for 10 min, then concentrated and extracted with ether. The extract was purified by passing it through a silica gel column eluted with ether, yielding **2** (1.1 g, 60%); mp 92–93°C (EtOH); $[\alpha]_D^{20}$ +165° (*c* 1.2, $CHCl_3$); lit.[11] mp 92–93°C; $[\alpha]_D^{20}$ +168° (*c* 1, $CHCl_3$).

*1,3,4,6-Tetra-*O*-acetyl-2-*S*-(2,3,4,6-tetra-*O*-acetyl-α-*D*-glucopyranosyl)-2-thio-β-*D*-glucopyranose* (**4**).—Sodium hydride (46 mg, 1.6 mmol) was added to a solution of the thiol **2** (515 mg, 1.4 mmol) in dry THF (15 mL) at room temperature. The suspension was stirred under an inert atmosphere until hydrogen formation had ceased. The resulting solution was then concentrated under reduced pressure, and the amorphous residue was dissolved in *N,N*-dimethylformamide (8 mL). To this stirred solution was added dropwise 1,3,4,6-tetra-*O*-acetyl-2-*O*-triflyl-β-D-mannopyranose[9,10] (**3**; 670 mg, 1.4 mmol) in *N,N*-dimethylformamide (8 mL). After being stirred for 4 h, at room temperature, the mixture was concentrated under reduced pressure. A solution of the residue in CH_2Cl_2 was washed with water, dried (Na_2SO_4), and concentrated to a powder (850 mg, 87%) which crystallised from CH_2Cl_2–EtOH, yielding **4** (715 mg, 73%); mp 220°C; $[\alpha]_D^{20}$ +140° (*c* 1, $CHCl_3$). Anal. Calcd for $C_{28}H_{38}O_{18}S$: C, 48.41; H, 5.48; S, 4.61. Found: C, 48.17; H, 5.47; S, 4.74.

*Allyl 3,4,6-tri-*O*-acetyl-2-*S*-(2,3,4,6-tetra-*O*-acetyl-α-*D*-glucopyranosyl)-2-thio-β-*D*-glucopyranoside* (**5**).—To a stirred solution of **4** (420 mg, 0.6 mmol) in dry CH_2Cl_2 (10 mL) was added $SnCl_4$ (110 μL, 0.88 mmol) followed after 10 min by allyl alcohol (100 μL, 1.47 mmol). The mixture was stirred for 15 h at room temperature till completion (TLC, 1:2 toluene–ether). After dilution with CH_2Cl_2, the solution was washed with aq $NaHCO_3$, then with water and concentrated to a powder (415 mg, 99%); $[\alpha]_D^{20}$ +135° (*c* 1.24, $CHCl_3$). Anal. Calcd for $C_{29}H_{40}O_{17}S$: C, 50.29; H, 5.78; S, 4.62. Found: 49.64; H, 5.72; S, 4.75.

1'-Propenyl 3,4,6-tri-O-acetyl-2-S-(2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl)-2-thio-β-D-glucopyranose (**6**).—A mixture of **5** (150 mg, 0.2 mmol), tris(triphenylphosphine)rhodium(I) chloride (63 mg), and diazabicyclo[2.2.2]octane (15 mg) in 7:3:1 EtOH–toluene–water (33 mL) was stirred for 6 h at 90°C. The solution was then concentrated under reduced pressure, and the residue was dissolved in ether (10 mL). After filtration, washing with water, and drying (Na_2SO_4), the solution was concentrated and filtered through a small column of silica gel eluted by EtOAc in order to remove the residual catalyst. Concentration of the resulting solution gave **6** as an amorphous powder (150 mg, 100%); $[\alpha]_D^{20}$ +130° (*c* 0.8, $CHCl_3$). Anal. Calcd for $C_{29}H_{40}O_{17}S$: C, 50.29; H, 5.78; S, 4.62. Found: C, 50.27; H, 5.73; S, 4.55.

2-S-α-D-Glucopyranosyl-2-thio-D-glucopyranose (2-thiokojibiose, **8**).—To a solution of the acylated thiodisaccharide **6** (150 mg, 0.2 mmol) in MeOH (10 mL) was added methanolic NaOMe (M, 37 μL). The mixture was stirred for 1.5 h at room temperature, then de-ionised by passing it through a mixed bed of Amberlite ion-exchange resins IRC-50 (H^+) and IRA-910 (HO^-). The solution was concentrated to dryness and the resulting solid was freeze-dried to an amorphous powder **7** (83 mg, 96%) which was directly used for the final step. A solution of this thiodisaccharide **7** (83 mg) in aq HCl (15 mM, 2 mL) was heated for 7 h at 65°C. The acid was then neutralised by filtration through a small column of Amberlite IRA-93. Freeze-drying of the solution gave a powder (60 mg, 80%), which was purified by LC (7:3 MeCN–water). Freeze-drying gave a white powder **8** (40 mg, 54%); $[\alpha]_D^{20}$ +113° (*c* 0.8, H_2O). FABMS: *m/z* 381 (15, MNa^+), 359 (8, $[MH]^+$), 341 (10, $[M-OH]^+$). Anal. Calcd for $C_{12}H_{22}O_{10}S$: C, 40.22; H, 6.15; S, 8.94. Found: C, 40.78; H, 6.22; S, 8.23.

1,3,4,6-Tetra-O-acetyl-2-S-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-2-thio-β-D-glucopyranose (**10**).—Sodium hydride (45 mg, 1.6 mmol) was added to a solution of 2,3,4,6-tetra-O-acetyl-1-thio-β-D-glucopyranose[17] (**9**; 523 mg, 1.44 mmol) in dry THF (15 mL), at room temperature. The suspension was stirred under an inert atmosphere until hydrogen formation had ceased. The resulting solution was then concentrated under reduced pressure and the amorphous residue was dissolved in *N,N*-dimethylformamide (8 mL). To this stirred solution, 1,3,4,6-tetra-*O*-acetyl-2-*O*-triflyl-β-D-mannopyranose[9,10] (**3**; 670 mg, 1.41 mmol) in *N,N*-dimethylformamide (8 mL) was then added dropwise. After being stirred for 3.5 h, at room temperature, the mixture was concentrated under reduced pressure. A solution of the residue in CH_2Cl_2 was washed with water (50 mL), dried (Na_2SO_4), and concentrated to a syrup (734 mg, 75%) which crystallised from EtOH, yielding **10** (570 mg, 58%); mp 160°C; $[\alpha]_D^{20}$ −5.4° (*c* 1.46, $CHCl_3$); Orgeret[9] reported mp 159–160°C; $[\alpha]_D^{20}$ +4.2° (*c* 1.5, $CHCl_3$) for this compound; lit.[10] mp 160–161°C; $[\alpha]_D^{20}$ +4° (*c* 1, $CHCl_3$). Anal. Calcd for $C_{28}H_{38}O_{18}S$: C, 48.41; H, 5.48; S, 4.61. Found: C, 48.66; H, 5.47; S, 4.67.

Allyl 3,4,6-tri-O-acetyl-2-S-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-2-thio-α-D-glucopyranoside (**11**).—To a stirred solution of **10** (500 mg, 0.72 mmol) in dry CH_2Cl_2 (10 mL) was added $SnCl_4$ (125 μL, 1 mmol) followed after 10 min by allyl

alcohol (85 μL, 1.25 mmol). The mixture was stirred for 15 h at room temperature, till completion of the reaction (TLC, 1:2 toluene–ether). After dilution with CH_2Cl_2, the solution was washed with aq $NaHCO_3$, then with water, and concentrated to a residue (464 mg, 93%) which crystallised from EtOH, yielding **11** (347 mg, 70%); mp 127–128°C; $[\alpha]_D^{20}$ +29.5° (*c* 1.22, $CHCl_3$). Anal. Calcd for $C_{29}H_{40}O_{17}S$: C, 50.29; H, 5.78; S, 4.62. Found: C, 50.38; H, 5.72; S, 4.45.

1'-Propenyl 3,4,6-tri-O-acetyl-2-S-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-2-thio-α-D-glucopyranoside (**12**).—(*a*) *With tris(triphenylphosphine)rhodium(I) chloride catalyst.* A mixture of **11** (180 mg, 0.42 mmol), the title catalyst (80 mg, 0.07 mmol), and diazabicyclo[2.2.2]octane (16 mg, 0.14 mmol) in 7:3:1 EtOH–toluene–water (44 mL) was stirred at 90°C for 6 h. The solution was then concentrated under reduced pressure and the residue was dissolved in ether (10 mL). After filtration, washing with water, and drying (Na_2SO_4), the solution was concentrated and filtered through a small column of silica gel eluted by EtOAc in order to remove the residual catalyst. Concentration of the resulting solution gave a powder (180 mg, 100%), which crystallised from EtOH, yielding **12** (135 mg, 75%); mp 127.5°C; $[\alpha]_D^{20}$ +24° (*c* 0.84, $CHCl_3$). Anal. Calcd for $C_{29}H_{40}O_{17}S$: C, 50.29; H, 5.78; S, 4.62. Found: C, 50.26; H, 5.98; S, 4.57.

(b) With 1,5-cyclooctadienebis(methyldiphenylphosphine)iridium hexafluorophosphate catalyst. To a solution of **11** (100 mg, 0.15 mmol) in dry THF (30 mL) was added the title catalyst (120 mg, 0.15 mmol) prepared as described[18]. Activation of the catalyst was achieved in situ by removing the red color of the solution under hydrogen pressure. After being stirred for 3 h, at room temperature under N_2, the solution was concentrated and extracted with ether.

The extract was filtered through a column of silica gel as described in (*a*), yielding, after concentration of the resulting solution, **12** as a powder (100 mg, 100%) which crystallised from EtOH (68 mg, 68%) and showed characteristics identical to those in (*a*).

1'-Propenyl 2-S-β-D-glucopyranosyl-2-thio-α-D-glucopyranoside (**13**).—To a solution of the acylated thiodisaccharide **12** (280 mg, 0.4 mmol) in MeOH (20 mL) was added M MeONa (73 μL). The mixture was stirred for 1.5 h, at room temperature, then de-ionised by passing it through a mixed bed of Amberlite ion-exchange resins IRC-50 (H^+) and IRA-910 (HO^-). The solution was concentrated and the resulting compound was freeze-dried to an amorphous powder **13** (160 mg, 99%); FABMS (glycerol, NaI): *m/z* 421 (42, $[MNa]^+$). Anal. Calcd for $C_{15}H_{26}O_{10}S$: C, 45.22; H, 6.53; S, 8.04. Found: C, 44.22; H, 6.51; S, 7.66.

2-S-β-D-Glucopyranosyl-2-thio-D-glucopyranose (2-thiosophorose, **14**).—A solution of **13** (210 mg, 0.53 mmol) in 0.05 M HCl (5 mL) was heated at 70°C for 7 h. The acid was then neutralised by filtration through a small column of Amberlite IRA-93 (weakly HO^-). Freeze-drying of the solution gave a powder (180 mg, 95%) which was purified by LC (7:3 MeCN–water). Freeze-drying after chromatography gave a white powder **14** (111 mg, 59%); $[\alpha]_D^{20}$ −27° (*c* 0.3, H_2O); lit.[8] mp 173–175°C; $[\alpha]_D^{20}$ −8° (3 min) → −13.1° (equil, H_2O). FABMS (glycerol, NaI):

m/z 381 (72, $[MNa]^+$). Anal. Calcd for $C_{12}H_{22}O_{10}S$: C, 40.22; H, 6.15; S, 8.94. Found: C, 39.88; H, 6.33; S, 8.93.

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