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Note

Thioanhydro sugar derivatives ☆. Action of base on methyl 6-thio-α-D-galactopyranoside derivatives

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In previous papers, we have reported on the synthesis of 2,6-[1], 3,6-[2], and 4,6-thioanhydro sugars [3] that were shown to be important intermediates for the enantiospecific preparation of polyhydroxythianes and thiolanes, structurally related to the potent glycosidase inhibitors polyhydroxypiperidines and pyrrolidines [4]. Continuing with our efforts towards the synthesis of such thioanhydro sugars, we report the preparation of a 4,6-thioanhydroglucoside by base treatment of a 3-*O*-mesyl-galactopyranoside via a novel one-pot conversion involving four consecutive steps.

1. Results and discussion

An attempt to prepare the starting compounds, methyl 2-*O*-benzoyl- (**1**) and 3-*O*-benzoyl-4,6-*O*-benzylidene-α-D-galactopyranoside (**2**), in a regioselective manner by application of the method described by Munavu and Szmant [5] was unsuccessful, giving a mixture of both isomers in a similar ratio as that obtained by Overend and co-workers [6]. Therefore, the latter and shorter procedure was used for the synthesis of **1** and **2**, requiring, however, a tedious separation of the mixture by column chromatography.

Conventional methanesulfonylation of **1** and **2** gave the corresponding 3-*O*-(**3**) and 2-*O*-methanesulfonyl derivatives (**4**). Due to close chemical shift and coupling constant

☆ Thioanhydro sugar derivatives, Part IV. For Part III, see ref. [2].

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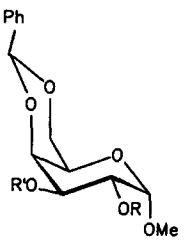
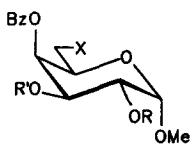
values, the respective COSY spectra were required to unequivocally assign the signals; in addition, the $^{13}C-^{1}H$ correlated spectra of **3** and **4** allowed the unequivocal assignment of the ^{13}C NMR signals.

Reaction of a mixture of **3** and **4** with *N*-bromosuccinimide in carbon tetrachloride afforded an easily separable mixture of 6-bromo-6-deoxy derivatives **5** and **6**, respectively. The structures of **5** and **6** were determined on the basis of their spectroscopic data, including COSY and $^{13}C-^{1}H$ correlated spectra and by the transformation (analytical scale) of **3** and **4** into **5** and **6**, respectively.

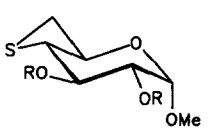
Compounds **5** and **6** were separately treated with potassium thioacetate in *N*,*N*-dimethylformamide to give methyl 6-*S*-acetyl-2,4-di-*O*-benzoyl-3-*O*-methanesulfonyl-6-thio-α-D-galactopyranoside (**7**) and methyl 6-*S*-acetyl-3,4-di-*O*-benzoyl-2-*O*-methanesulfonyl-6-thio-α-D-galactopyranoside (**8**). In both reactions, only the nucleophilic displacement of the bromine atom occurred.

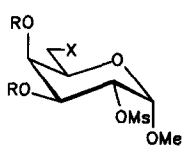




1 R = Bz; R' = H
2 R = H; R' = Bz
3 R = Bz; R' = Ms
4 R = Ms; R' = Bz

5 R = Bz; R' = Ms; X = Br
6 R = Ms; R' = Bz; X = Br
7 R = Bz; R' = Ms; X = SAc
8 R = Ms; R' = Bz; X = SAc

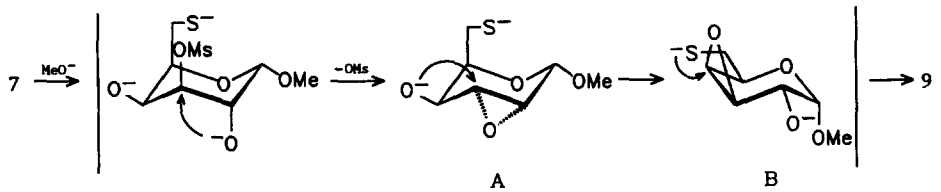




9 R = H
10 R = Ac

11 R = H; X = SH
12 R = Bz; X = SBz

Treatment of **7** with methanolic sodium methoxide gave methyl 4,6-thioanhydro-α-D-glucopyranoside (**9**) in 30% yield. Its structure was established on the basis of analytical and spectroscopic data and confirmed through its 2,3-di-*O*-acetyl derivative **10**. The formation of **9** can be explained by a methanolysis of the 6-*S*-acetyl and 2,4-di-*O*-benzoyl groups, internal nucleophilic displacement of the mesyl group at C-3 by the alkoxide anion at C-2 to produce the intermediate 2,3-epoxide (**A**), subsequent transepoxidation to the 3,4-oxirane (**A** → **B**) [7], and, finally, opening of epoxide (**B**) by an S_N2-type attack of the 6-thiolate at C-4 (Scheme 1). Surprisingly, the thiolate in **A** does not attack at C-3 as it does in the D-*gluco* analogue [2], confirming that the formation of a 3,4-epoxide is highly favoured.



Scheme 1.

On the other hand, when **8** was exposed to similar basic conditions, the deacylation product, 2-*O*-methanesulfonyl-6-thio-α-D-galactoside (**11**), was the only isolated compound, as demonstrated by its transformation into the 3,4-di-*O*-benzoyl-6-*S*-benzoyl derivative (**12**). Accordingly, a 2-*O*-mesyl group does not undergo internal displacement either by the alkoxide at C-3 or 6-thioalkoxide, although a similar reaction with methyl 2-*O*-*p*-tolylsulfonyl-β-D-galactopyranoside has been shown to give the 2,3-epoxide on a 24-h reaction time with sodium methoxide [8].

2. Experimental

General methods.—Melting points were determined with a Gallenkamp apparatus and are uncorrected. Solutions were dried over $MgSO_4$ before concentration under reduced pressure. The ^1H and ^{13}C NMR spectra were recorded with Bruker AMX-300, AM-300, and ARX-400 spectrometers for solutions in $CDCl_3$ (internal Me_4Si as standard). IR spectra were recorded with a Perkin–Elmer 782 instrument. Optical rotations were measured for solutions in $CHCl_3$ (1-dm tube) with a Jasco DIP-370 polarimeter. TLC was performed on precoated Silica 60 F_{254} aluminium sheets (E. Merck) with detection by charring with H_2SO_4. Column chromatography was performed on silica gel (E. Merck, 7734). The non-crystalline compounds, for which elemental analyses were not obtained, were shown to be homogeneous by chromatography and characterized by NMR.

Methyl 2-O-benzoyl-4,6-O-benzylidene-3-O-methanesulfonyl-α-D-galactopyranoside (**3**).—To a stirred solution of methyl 2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-galactopyranoside (**1**) [6] (120 mg, 0.31 mmol) in dry pyridine (1 mL), methanesulfonyl chloride (0.05 mL, 0.64 mmol) was added and the mixture was kept at room temperature for 30 min. TLC (9:1 CH_2Cl_2–EtOAc) then revealed the presence of a faster running compound. Conventional workup of the mixture afforded crystalline **3** (130 mg, 90%), mp 218–220°C (from diethyl ether), $[\alpha]_D^{29}$ +202° (*c* 1.1); ν_{max}^{KBr} 1729 (C=O, benzoate), 759, 720, and 702 cm^{-1} (aromatic). NMR data: ^1H, δ 8.10–8.05 and 7.60–7.35 (2 m, 10 H, 2 Ph), 5.62 (s, 1 H, C*H*Ph), 5.58 (dd, 1 H, $J_{1,2}$ 3.5, $J_{2,3}$ 10.6 Hz, H-2), 5.35 (dd, 1 H, $J_{3,4}$ 3.6 Hz, H-3), 5.23 (d, 1 H, H-1), 4.59 (dd, 1 H, $J_{4,5}$ 1 Hz, H-4), 4.33 (dd, 1 H, $J_{5,6}$ 1.6, $J_{6,6'}$ 12.6 Hz, H-6), 4.11 (dd, 1 H, $J_{5,6'}$ 1.7 Hz, H-6'), 3.80 (bs, 1 H, H-5), 3.41 (s, 3 H, OMe), and 2.97 (s, 3 H, OMs); ^{13}C, δ 165.64 (C=O), 137.33, 133.58, 129.94, 129,32, 129.19, 128.64, 128.30, and 126.28 (2 Ph), 100.98 (*C*HPh), 98.02 (C-1), 75.28

(C-4), 74.57 (C-3), 68.99 (C-6), 68.44 (C-2), 62.26 (C-5), 55.82 (OMe), and 38.77 (OMs). Anal. Calcd for $C_{22}H_{24}O_9S$: C, 56.89; H, 5.21. Found: C, 56.76; H, 5.15.

Methyl 3-O-benzoyl-4,6-O-benzylidene-2-O-methanesulfonyl-α-D-galactopyranoside (**4**).—Methyl 3-*O*-benzoyl-4,6-*O*-benzylidene-α-D-galactopyranoside (**2**) [6] (335 mg, 0.87 mmol) was treated with methanesulfonyl chloride (0.1 mL, 1.3 mmol) in dry pyridine as described above to afford crystalline **4** (317 mg, 81%), mp 152–154°C (from diethyl ether), $[\alpha]_D^{24}$ +222° (*c* 1); ν_{max}^{KBr} 1730 (C=O, benzoate), 760, 716, and 706 cm^{-1} (aromatic). NMR data: ^1H, δ 8.10–8.04 and 7.61–7.31 (2 m, 10 H, 2 Ph), 5.60 (dd, 1 H, $J_{2,3}$ 10.5, $J_{3,4}$ 3.6 Hz, H-3), 5.52 (s, 1 H, C*H*Ph), 5.27 (dd, 1 H, H-2), 5.17 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 4.62 (bd, 1 H, H-4), 4.32 (dd, 1 H, $J_{5,6}$ 1.5, $J_{6,6'}$ 12.6 Hz, H-6), 4.09 (dd, 1 H, $J_{5,6'}$ 1.6 Hz, H-6'), 3.86 (bs, 1 H, H-5), 3.52 (s, 3 H, OMe), and 2.96 (s, 3 H, OMs); ^{13}C, δ 165.82 (C=O), 137.47, 133.65, 129.92, 129,42, 129.06, 128.70, 128.25, and 126.15 (2 Ph), 100.81 (*C*HPh), 98.75 (C-1), 74.38 and 74.00 (C-2,4), 69.00 (C-6), 68.85 (C-3), 62.26 (C-5), 56.11 (OMe), and 38.46 (OMs). Anal. Calcd for $C_{22}H_{24}O_9S$: C, 56.89; H, 5.21. Found: C, 57.03; H, 5.15.

Methyl 2,4-di-O-benzoyl-6-bromo-6-deoxy-3-O-methanesulfonyl-α-D-galactopyranoside (**5**) *and methyl 3,4-di-O-benzoyl-6-bromo-6-deoxy-2-O-methanesulfonyl-α-D-galactopyranoside* (**6**).—To a stirred solution of a mixture of **1** and **2** (4.3 g, 11 mmol) in dry pyridine (20 mL) and DMAP (150 mg), methanesulfonyl chloride (1.8 mL, 22.3 mmol) was added dropwise and the mixture left at room temperature for 6 h. Conventional workup of the reaction gave a mixture of **3** and **4** (4.4 g) that was treated in dry CCl_4 (90 mL) with NBS (1.73 g, 10 mmol) and $BaCO_3$ (3.8 g, 20 mmol) under reflux for 4 h. TLC (1:2 EtOAc–hexane) then revealed the presence of two compounds with higher mobility. The reaction mixture was filtered and the filtrate washed with 10% aq sodium thiosulfate, 10% aq $NaHCO_3$, and brine, and then concentrated. Column chromatography (1:4 EtOAc–hexane) of the residue gave first crystalline **5** (1.12 g), mp 135–137°C; $[\alpha]_D^{24}$ +166° (*c* 0.7); ν_{max}^{KBr} 1730 (C=O, benzoate) and 711 cm^{-1} (aromatic). NMR data: ^1H (400 MHz), δ 8.15–7.40 (m, 10 H, 2 Bz), 5.99 (dd, 1 H, $J_{3,4}$ 3.3, $J_{4,5}$ 1.3 Hz, H-4), 5.49 (dd, 1 H, $J_{2,3}$ 10.5 Hz, H-3), 5.43 (dd, 1 H, H-2), 5.30 (d, 1 H, $J_{1,2}$ 3.4 Hz, H-1), 4.33 (dt, 1 H, H-5), 3.48 (s, 3 H, OMe), 3.43 (d, 2 H, $J_{5,6}$ 7 Hz, H-6,6), and 2.99 (s, 3 H, OMs); ^{13}C, δ 166.02 and 165.63 (2 Ph*CO*), 134.00, 133.68, 130.17, 130.12, 128.84, and 128.63 (2 CO*Ph*), 97.62 (C-1), 73.95 (C-3), 70.13 (C-4), 69.41 (C-5), 68.82 (C-2), 56.01 (OMe), 39.06 (OMs), and 28.81 (C-6). Anal. Calcd for $C_{22}H_{23}BrO_9S$: C, 48.63; H, 4.26; S, 5.90. Found: C, 48.45; H, 4.50; S, 5.84.

Eluted second was crystalline **6** (1.75 g), mp 70–72°C; $[\alpha]_D^{24}$ +203.5° (*c* 0.5); ν_{max}^{KBr} 1731 (C=O, benzoate) and 710 cm^{-1} (aromatic). NMR data: ^1H (400 MHz), δ 7.99–7.21 (m, 10 H, 2 Bz), 5.97 (dd, 1 H, $J_{3,4}$ 3.4, $J_{4,5}$ 1.1 Hz, H-4), 5.74 (m, 1 H, H-3), 5.20–5.15 (m, 2 H, H-1,2), 4.40 (dt, 1 H, H-5), 3.58 (s, 3 H, OMe), 3.42 (d, 2 H, $J_{5,6}$ 6.7 Hz, H-6,6), and 2.91 (s, 3 H, OMs); ^{13}C, δ 165.41 and 165.11 (2 Ph*CO*), 133.85, 133.54, 129.94, 129.75, 128.81, and 128.54 (2 CO*Ph*), 98.19 (C-1), 73.71 (C-2), 69.89 (C-4), 69.38 (C-5), 68.06 (C-3), 56.18 (OMe), 38.58 (OMs), and 28.83 (C-6). Anal. Calcd for $C_{22}H_{23}BrO_9S$: C, 48.63; H, 4.26; S, 5.90. Found: C, 48.35; H, 4.49; S, 6.02.

Methyl 6-S-acetyl-2,4-di-O-benzoyl-3-O-methanesulfonyl-6-thio-α-D-galactopyranoside (**7**).—To a stirred solution of **5** (1 g, 1.85 mmol) in dry DMF (6 mL) was added

potassium thioacetate (0.7 g, 6 mmol) portionwise, under argon, and the mixture left at room temperature for 2 h. TLC (1:2 EtOAc–hexane) then revealed a new compound of slightly lower mobility. The solvent was evaporated and the residue in CH_2Cl_2 washed with brine and water, then concentrated. Column chromatography (1:1 EtOAc–hexane) of the residue gave **7** (750 mg, 75%) as a pale yellow solid; mp 141–143°C; $[\alpha]_D^{25}$ +160° (*c* 0.9); ν_{max}^{KBr} 1729 (C=O, benzoate), 1696 (C=O, thioacetate), and 712 cm^{-1} (aromatic). NMR data: ^1H, δ 8.14–8.07 and 7.65–7.40 (2 m, 10 H, 2 Bz), 5.90 (bd, 1 H, H-4), 5.45 (dd, 1 H, $J_{1,2}$ 3, $J_{2,3}$ 10.6 Hz, H-2), 5.40 (dd, 1 H, $J_{3,4}$ 3 Hz, H-3), 5.25 (d, 1 H, H-1), 4.11 (bt, 1 H, H-5), 3.42 (s, 3 H, OMe), 3.11 (dd, 1 H, $J_{5,6}$ 6.3, $J_{6,6'}$ 14 Hz, H-6), 3.05 (dd 1 H, $J_{5,6'}$ 7.5 Hz, H-6'), 2.98 (s, 3 H, OMs), and 2.34 (s, 3 H, SAc); ^{13}C, δ 194.72 (S*C*OMe), 166.01 and 165.72 (2 *C*OPh), 133.86, 133.60, 130.14, 130.10, 129.12, 128.89, 128.77, and 128.57 (2 CO*Ph*), 97.49 (C-1), 74.21 (C-3), 70.52 (C-4), 68.95 (C-5), 68.09 (C-2), 55.68 (OMe), 39.06 (OMs), 32.52 (SCO*Me*), and 29.05 (C-6). Anal. Calcd for $C_{24}H_{26}O_{10}S_2$: C, 53.52; H, 4.87. Found: C, 53.68; H, 4.79.

*Methyl 6-*S*-acetyl-3,4-di-*O*-benzoyl-2-*O*-methanesulfonyl-6-thio-α-*D*-galactopyranoside* (**8**).—Compound **6** (1.85 g, 3.41 mmol) was treated as above with potassium thioacetate (1 g, 8.7 mmol) in dry DMF (10 mL). Workup of the reaction mixture gave, after column chromatography (1:3 EtOAc–hexane), **8** (1.47 g, 80%) as a pale yellow foam; $[\alpha]_D^{22}$ +162° (*c* 0.8); ν_{max}^{KBr} 1731 (C=O, benzoate), 1696 (C=O, thioacetate), and 712 cm^{-1} (aromatic). NMR data: ^1H, δ 8.04–7.26 (5 m, 10 H, 2 Bz), 5.89 (dd, 1 H, $J_{3,4}$ 3.4, $J_{4,5}$ 1.1 Hz, H-4), 5.70 (m 1 H, H-3), 5.20–5.12 (m, 2 H, H-1,2), 4.19 (dt, 1 H, H-5), 3.53 (s, 3 H, OMe), 3.08 (d, 2 H, $J_{5,6}$ 7, H-6,6), 2.89 (s, 3 H, OMs), and 2.33 (s, 3 H, SAc); ^{13}C, δ 194.63 (S*C*OMe), 165.52 and 165.11 (2 *C*OPh), 133.72, 133.48, 129.94, 129.74, 129.09, 129.02, 128.76, and 128.51 (2 CO*Ph*), 98.13 (C-1), 73.94 (C-2), 70.20 (C-4), 68.23 and 68.07 (C-3,5), 55.89 (OMe), 38.55 (OMs), 30.50 (SCO*Me*), and 28.92 (C-6). Anal. Calcd for $C_{24}H_{26}O_{10}S_2$: C, 53.52; H, 4.87. Found: C, 53.64; H, 4.61.

Treatment of **7** *with sodium methoxide: methyl 4,6-thioanhydro-α-*D*-glucopyranoside* (**9**).—To a stirred solution of **7** (0.6 g, 1.12 mmol) in dry CH_2Cl_2 (3 mL), 3 M methanolic NaOMe (1.1 mL) was added dropwise, and the mixture maintained at room temperature for 3 h. TLC (2:1 EtOAc–hexane) of the deep brown solution showed the absence of **7** and the presence of a slower running product. The mixture was neutralized with acetic acid, concentrated, and the residue extracted with EtOAc. The combined extracts were concentrated to give a residue that was chromatographed (2:1 diethyl ether–hexane) to afford crystalline **9** (60 mg, 30%), mp 137–139°C (from diethyl ether–hexane); $[\alpha]_D^{26}$ +49° (*c* 0.4); NMR data (400 MHz): ^1H, δ 6.45 (s, 1 H, H-1), 5.00 (dd, 1 H, H-5), 4.79 (d, 1 H, $J_{2,3}$ 4.4 Hz, H-2), 3.83 (m, 1 H, H-3), 3.43 (s, 3 H, OMe), 3.30 (dd, 1 H, $J_{5,6}$ 5, $J_{6,6'}$ 12.9 Hz, H-6), 2.90 (d, 1 H, H-6'), 2.84 (t, 1 H, $J_{3,4} = J_{4,5} = 7$ Hz, H-4), 2.49 (d, 1 H, $J_{3,HO}$ 10.8 Hz, OH-3), and 1.08 (bs, 1 H, HO-2); ^{13}C, δ 102.46 (C-1), 86.58, 84.16, and 76.46 (C-2,3,5), 62.14 (C-4), 54.96 (OMe), and 37.46 (C-6). Anal. Calcd for $C_7H_{12}O_4S$: C, 43.73; H, 6.29. Found: C, 43.81; H, 6.13.

Conventional acetylation of **9** (20 mg) with acetic anhydride (0.5 mL) in dry pyridine (0.5 mL) gave, after column chromatography (1:3 EtOAc–hexane), the corresponding 2,3-di-*O*-acetyl derivative **10** (13 mg), $[\alpha]_D^{25}$: −55° (*c* 0.6); NMR data (400 MHz): ^1H, δ 6.11 (s, 1 H, H-1), 5.08 (d, 1 H, $J_{2,3}$ 4.2 Hz, H-2), 5.02 (dd, 1 H, H-5), 4.66 (dd, 1 H,

H-3), 3.37 (s, 3 H, OMe), 3.21 (dd, 1 H, $J_{5,6}$ 5, $J_{6,6'}$ 13 Hz, H-6), 3.17 (t, 1 H, $J_{3,4} = J_{4,5} = 7.2$ Hz, H-4), 2.94 (d, 1 H, H-6'), 2.11 and 2.03 (2 s, 6 H, 2 Ac); ^{13}C, δ 170.52 and 169.67 (*C*OMe), 101.38 (C-1), 86.35, 82.91, and 76.65 (C-2,3,5), 56.70 (C-4), 54.98 (OMe), 37.60 (C-6), 21.27 and 20.79 (CO*Me*).

Treatment of **8** *with sodium methoxide.*—Compound **8** (1.4 g, 2.6 mmol) in dry toluene (5 mL) was treated with 1 M methanolic sodium methoxide (5 mL) at room temperature for 1 h. Workup of the reaction mixture as above gave, after column chromatography (4:1 diethyl ether–hexane), crystalline methyl 2-*O*-methanesulfonyl-6-thio-α-D-galactopyranoside (**11**, 340 mg, 45%); mp 147–149°C (from diethyl ether–hexane); $[\alpha]_D^{24}$ +99° (*c* 1.4); ν_{max}^{KBr} 3500 (OH). NMR data (400 MHz): ^{1}H, δ 4.92 (d, 1 H, $J_{1,2}$ 3.8 Hz, H-1), 4.73 (dd, 1 H, $J_{2,3}$ 10 Hz, H-2), 4.12 (bd, 1 H, H-4), 4.03 (dd, 1 H, $J_{3,4}$ 3.4 Hz, H-3), 3.79 (bt, 1 H, H-5), 3.43 (s, 3 H, OMe), 3.15 (s, 3 H, OMs), 2.83 (dt, 1 H, $J_{5,6} = J_{6,HS} = 7.5$, $J_{6,6'}$ 13.7 Hz, H-6), 2.68 (ddd, 1 H, $J_{5,6'}$ 6.3, $J_{6',HS}$ 10 Hz, H-6'), and 1.64 (dd, 1 H, SH); ^{13}C, δ 97.83 (C-1), 77.95 (C-2), 71.61, 70.32, and 67.86 (C-3,4,5), 55.71 (OMe), 38.46 (OMs), and 24.52 (C-6). Anal. Calcd for $C_8H_{16}O_7S_2$: C, 33.32; H, 5.60. Found: C, 33.48; H, 5.53.

Conventional benzoylation of **11** (270 mg, 1.41 mmol) with benzoyl chloride (0.8 mL, 5.6 mmol) in dry pyridine (3 mL) and DMAP (15 mg) gave, after workup and column chromatography (1:3 → 1:1 diethyl ether–hexane), the corresponding 3,4,-di-*O*-benzoyl-6-*S*-benzoyl derivative **12** (380 mg, 67%) as a solid foam; $[\alpha]_D^{25}$ +105° (*c* 0.6); ν_{max}^{KBr} 1732 (C=O, benzoate), 1669 (C=O, thiobenzoate), 712 and 688 cm^{-1} (aromatic). NMR data (400 MHz): ^{1}H, δ 8.10–7.29 (6 m, 15 H, 3 Bz), 5.97 (dd, 1 H, $J_{3,4}$ 3.5, $J_{4,5}$ 1.1 Hz, H-4), 5.74 (dd, 1 H, $J_{2,3}$ 10 Hz, H-3), 5.20 (dd, 1 H, H-2), 5.17 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 4.31 (dt, 1 H, H-5), 3.53 (s, 3 H, OMe), 3.28 (d, 2 H, $J_{5,6}$ 7 Hz, H-6,6), and 2.90 (s, 3 H, OMs); ^{13}C, δ 190.82 (S*C*OPh), 165.58 and 165.11 (*C*OPh), 136.59, 133.80, 133.76, 130.00, 129.78, 128.79, and 127.42 (Ph), 98.17 (C-1), 74.03 (C-2), 70.45, 68.28, and 68.22 (C-3,4,5), 55.93 (OMe), 38.59 (OMs), and 28.87 (C-6). Anal. Calcd for $C_{22}H_{24}O_9S$: C, 53.21; H, 4.87. Found: C, 53.34; H, 5.02.

References

[1] I. Izquierdo, M.T. Plaza, A.C. Richardson, and M.D. Suárez, *Carbohydr. Res.*, 242 (1993) 109–118.
[2] I. Izquierdo, M.T. Plaza, R. Asenjo, and M. Rodríguez, *Tetrahedron: Asymmetry*, 6 (1995) 1117–1122.
[3] I. Izquierdo and M.T. Plaza, *Carbohydr. Lett.*, 1 (1995) 191–198.
[4] A. Dondoni, P. Merino, and D. Perrone, *Tetrahedron*, 49 (1993) 2939–2956, and references cited therein.
[5] R.M. Munavu and H.H. Szmant, *J. Org. Chem.*, 41 (1976) 1832–1836.
[6] N. Dang, V. Ranjith, N. Munasinghe, and W.G. Overend, *J. Chem. Soc., Perkin Trans. 1*, (1983) 257–264.
[7] N.R. Williams, *Adv. Carbohydr. Chem. Biochem.*, 25 (1970) 109–179.
[8] L.F. Wiggins, *Methods Carbohydr. Chem.*, 1 (1962) 140–143.