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Action of acid on 6-thio-hexose derivatives. Synthesis of 1,6-epithio-hexofuranoses

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Abstract

Reaction of 5,6-anhydro-1,2-*O*-isopropylidene-3-*O*-methanesulfonyl-β-L-idofuranose with thioacetic acid in pyridine gave 6-*S*-acetyl-1,2-*O*-isopropylidene-3-*O*-methanesulfonyl-6-thio-β-L-idofuranose, which was deacetylated and the resultant thiol was converted into 1,2-*O*:5,6-*O*,*S*-diisopropylidene-3-*O*-methanesulfonyl-β-L-idofuranose. Alkaline cleavage of the mesyl group gave 1,2-*O*: 5,6-*O*,*S*-diisopropylidene-β-L-idofuranose, which on treatment with hot dilute hydrochloric acid gave, after acetylation, 2,3,5-tri-*O*-acetyl-1,6-dideoxy-1,6-epithio-α-L-idofuranose and not the expected idopyranose isomer. 1,2:3,5-Di-*O*-isopropylidene-6-*O*-toluene-*p*-sulfonyl-α-D-glucofuranose was converted into 6-*S*-acetyl-1,2:3,5-di-*O*-isopropylidene-6-thio-α-D-glucofuranose; conversion into the 6-thiol and isomerisation in acidified acetone gave 1,2-*O*:5,6-*O*,*S*-diisopropylidene-6-thio-α-D-glucofuranose. Acid treatment of this diacetal, or the isomeric 1,2:3,5-di-*O*-isopropylidene-6-thio-α-D-glucofuranose, followed by acetylation gave 2,3,5-tri-*O*-acetyl-1,6-dideoxy-1,6-epithio-β-D-glucofuranose. Similar treatment of 1,2:3,4-di-*O*-isopropylidene-6-thio-α-D-galactopyranose gave 2,3,5-tri-*O*-acetyl-1,6-dideoxy-1,6-epithio-α-D-galactofuranose.

Keywords: Anhydro sugars; Epithio sugars; Furanose–pyranose equilibria; 6-Thio-D-galactose derivatives; 6-Thio-D-glucose derivatives; 6-Thio-L-idose derivatives; Thio sugars

1. Introduction

In an earlier paper [1] we reported that aqueous acid hydrolysis of 1,2-*O*:5,6-*S*,*O*-diisopropylidene-5-thio-β-L-idofuranose (**1**) gave 1,6-anhydro-5-thio-β-L-idopyranose (**2**) in addition to 5-thio-L-idose (**3**); both products were isolated as their acetates **4** and **5**, respectively. The formation of the anhydro compound **2** was not unexpected, for idose itself exists in acid solution as a mixture of the free sugar and 1,6-anhydro-idose [2]. Owen and co-workers had shown [3] earlier that the corresponding 1,6-dideoxy-1,6-epithio-5-thio-β-L-idopyranose (**6**) was obtained by the action of acid on 1,2-*O*-isopropylidene-5,6-dithio-β-L-idofuranose. We therefore synthesised 1,2-*O*:5,6-*O*,*S*-diisopropylidene-6-thio-β-L-idofuranose (**7**) in the expectation that acid treatment would yield the 1,6-epithio compound **8** in good yield. Models suggested that the larger C–S bonds would facilitate the formation of the 1,6-linked system and such a system is readily formed by cyclisation in a hexopyranose bearing a thiol group at C-1 (or C-6) and a leaving group at C-6 (or C-1) [4] (Scheme 1).

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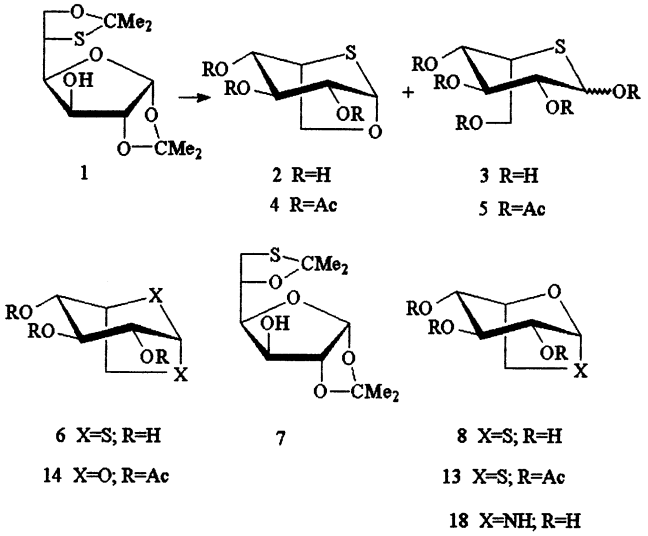


Scheme 1.

2. Results and discussion

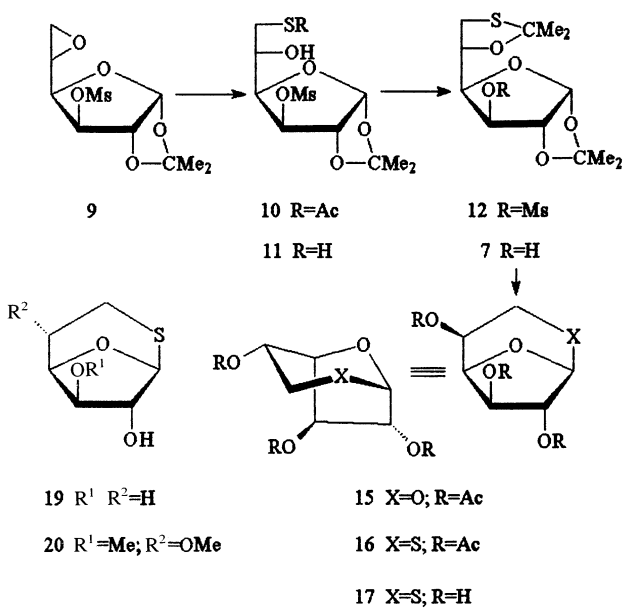
Treatment of the epoxide **9** [5] with thioacetic acid in pyridine gave the thioacetate **10**. This was deacetylated to the thiol **11**, which was immediately converted into the diacetal **12** by the action of 2,2-dimethoxypropane in acidified acetone. The mesylate ester of **12** was cleaved in refluxing methanolic sodium methoxide to give the required diacetal **7**. When **7** was heated in dilute hydrochloric acid and the products acetylated, a single crystalline product was isolated in good yield, the elemental analysis of which confirmed the expected molecular formula for **13**, the triacetate of **8**. However, the coupling constants in the ^{1}H NMR spectrum of the product bore little resemblance to those of the anhydro pyranoses **4** and **14** [6] (see Tables 1 and 2), but did show close agreement with those of the 1,6-anhydro-α-L-idofuranose triacetate (**15**) [7]. Thus, the product was 2,3,5-tri-*O*-acetyl-1,6-dideoxy-1,6-epithio-α-L-idofuranose (**16**) and not the expected epithio pyranose **13** (Scheme 2).

The isolation of the triacetate **16** indicated that the major product of the action of acid on **7** was the triol **17**. This was in sharp contrast to the action of acids on hexoses, which leads to varying amounts of 1,6-anhydro compounds, but the furanose forms are normally only minor products [8]. The exception is talose, where approximately equal amounts of furanose and pyranose forms are present, albeit in a low overall yield [9]. For idose the amount of 1,6-anhydro furanose is very low (0.08%) compared with the pyranose form (95%) [7].

The reasons for this unexpected behaviour are not clear. Both **8** and **17** have similar bicyclic systems, a five-membered ring *cis*-fused to a six-membered ring. Models and the ease of formation of 1,6-anhydro-5-thio-pyranoses referred to earlier suggest that **8** should be preferred over **17**. Energy calculations (Chem 3D Pro Version 5.0) also indicate the same preference: **8**, 16.903 kcal/mol; **17**, 21.547 kcal/mol.

The lack of formation of **8** is in further contrast to the behaviour of 6-amino-6-deoxy-L-idose, which undergoes almost quantitative dehydration, albeit in alkaline solution, to give the epimino pyranose **18** [10]. 1,6-Epithio furanose derivatives have been described previously, but in these cases formation of a pyranose compound was not possible because C-5 was blocked either by a deoxy function as in **19** [11] or by a methoxy group as in **20** [12].

Related experiments have been carried out on 6-thio-D-glucose and 6-thio-D-galactose derivatives with similar results. Treatment of the tosylate **21** [13] with potassium thioacetate gave the thioacetate **22**, which was deacetylated and the resultant thiol **23** was left in



Scheme 2.

Table 1
^{1}H NMR data: chemical shifts (ppm)

Compound	H-1	H-2	H-3	H-4	H-5	H-6a	H-6b	Other signals
10	5.99	4.91	5.11	4.22	4.03	3.26	2.96	3.25 ($MeSO_2$); 2.62 (OH); 2.37 (SAc); 1.51; 1.33 (CMe_2)
12 [a]	5.88	4.71	4.99	4.37	4.45	3.07	2.72	2.11 ($MeSO_2$); 1.58, 1.50, 1.31, 1.02 ($2\times CMe_2$)
7 [a]	5.84	4.26	4.01	4.10	4.28	3.08	2.84	2.82 (OH); 1.57, 1.48, 1.39, 1.12 ($2\times CMe_2$)
4 [b]	5.47	4.94	5.33	5.20	3.77	4.77	3.91	2.07(2), 2.02 ($3\times Ac$)
14 [c]	5.45	4.74	5.16	4.95	4.71	4.05	3.70	2.01(2), 1.97 ($3\times Ac$)
15 [d]	5.12	5.42	5.15	4.90	5.15	4.10	3.92	2.12(2), 1.99 ($3\times Ac$)
16	4.94	5.65	5.27	4.70	5.24	3.46	2.85	2.14, 2.12, 2.00 ($3\times Ac$)
22	5.99	4.65	4.21	4.25	3.63	3.37	3.00	2.35 (SAc); 1.49, 1.35, 1.33, 1.32 ($2\times CMe_2$)
24	5.97	4.55	4.35	4.17	4.50	3.35	3.15	2.73 (OH); 1.68, 1.63, 1.51, 1.33 ($2\times CMe_2$)
25 [e]	5.37	4.64	4.90	4.55	4.69	3.13	3.02	2.10, 2.09, 1.95 ($3\times Ac$)
26 [f]	4.97	4.33	4.23	4.34	3.71	4.11_{endo}	3.69_{exo}	
27	5.01	5.62	5.36	4.65	4.81	3.60	2.80	2.14, 2.07. 1.99 ($3\times Ac$)
30	5.57	5.25	5.32	4.22	5.05	2.93	2.82	2.16, 2.11, 2.10 ($3\times Ac$)
31 [f]	5.20	4.12	4.14	4.08	3.92	3.92_{exo}	3.44_{endo}	
32 [e]	5.44	4.82	5.11	5.15	4.75	3.34	3.04	2.10, 2.09, 2.03 ($3\times Ac$)

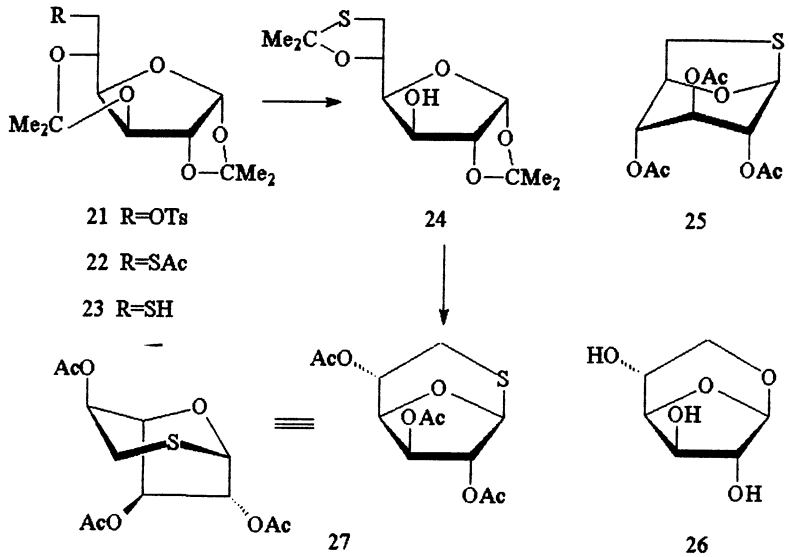
[a] In C_6D_6.
[b] Ref. [1].
[c] Ref. [6].
[d] Ref. [7].
[e] Ref. [14].
[f] Ref. [15]; in D_2O.

Table 2
^{1}H NMR data: coupling constants (Hz)

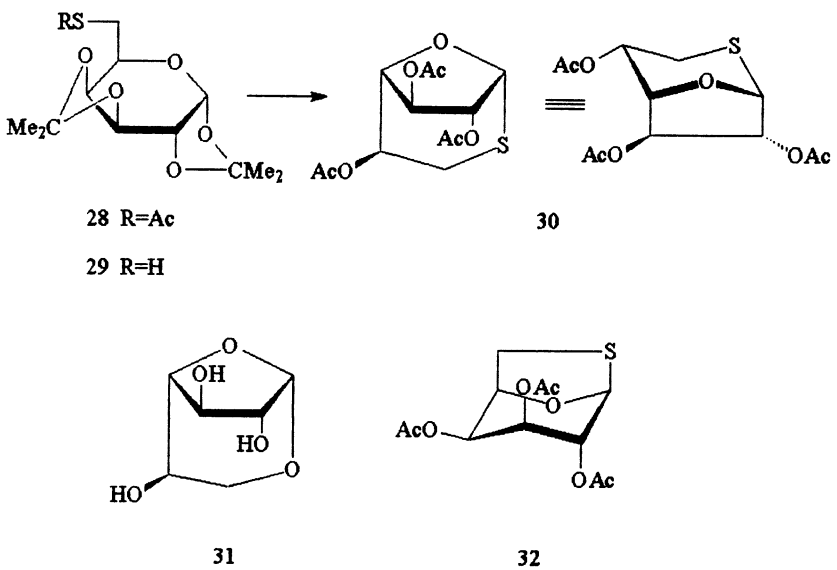
Compound	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6a}$	$J_{5,6b}$	$J_{6a,6b}$	
10	3.7	0	3.0	7.0	3.1	8.5	14.0	3.5 ($J_{5,OH}$)
12 [a]	3.8	0	3.2	7.0	5.1	9.5	10.3	
7 [a]	3.6	0	2.6	4.8	9.8	5.3	10.4	
4 [b]	0.5	8.1	8.5	3.3	0	8.3	9.3	1.5 ($J_{1,5}$)
14 [c]	1.8	8.4	8.8	4.1	0.7	5.2	8.4	
15 [d]	0	2.0	6.0	3.5	10.0	6.2	11.0	1.0 ($J_{4,6b}$)
16	0	2.5	6.4	2.7	11.2	5.4	12.8	
22	3.7	0	3.8	6.8	4.3	8.4	13.7	
24	2.6	0	2.6	7.0	5.4	8.0	10.9	3.1 ($J_{3,OH}$)
25 [e]	0.9	3.5	4.7	2.0	1.0	6.5	10.0	
26 [f]	0	2.0	7.0	1.0	3.0	0	13.5	
27	0	2.3	7.4	2.5	3.3	2.0	14.9	0.5 ($J_{1,6b}$); 0.5 ($J_{4,6b}$)
30	6.4	2.4	0	3.9	11.1	6.0	13.0	1.4 ($J_{1,6b}$); 0.9 ($J_{2,4}$); 1.5 ($J_{4,6b}$)
31 [f]	4.1	2.4	0	4.2	6.6	11.1	11.3	1.5 ($J_{4,6a}$)
32 [e]	1.6	1.5	4.9	4.9	0.8	7.2	10.0	1.4 ($J_{1,3}$); 1.4 ($J_{3,5}$)

[a] In C_6D_6.
[b] Ref. [1].
[c] Ref. [6].
[d] Ref. [7].
[e] Ref. [14].
[f] Ref. [15]; in D_2O.

acidified acetone when it was isomerised into the 1,2:5,6-diacetal **24**. The ^{1}H NMR spectrum of **24** showed the presence of a hydroxy group and coupling constants similar to those of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose. When **24** was heated in dilute hydrochloric acid followed by acetylation as for the *ido*-isomer **7**, it gave a single tri-acetate



Scheme 3.



Scheme 4.

whose ^{1}H NMR spectrum showed coupling constants (see Table 2) that differed from those of 2,3,4-tri-*O*-acetyl-1,6-dideoxy-1,6-epithio-β-D-glucopyranose (**25**) [14], but closely resembled those of 1,6-anhydro-β-D-glucofuranose (**26**) [15], thus identifying the product as the epithio furanose **27**. The same product **27** was obtained when **23** was heated in acid followed by acetylation (Scheme 3).

Deacetylation of the galactose thioacetate **28** [12] and treatment of the resultant thiol **29** as described for **23** also gave a single product, which was similarly identified as the epithio furanose **30** from comparisons of its ^{1}H NMR spectrum with those of the anhydro furanose **31** [15] and the epithio pyranose **32** [14]. In particular, the ^{1}H NMR spectrum of **30** showed small W-couplings for all the equatorial hydrogens (H-1, H-4, H-6 exo) of the 1,3-oxathiane ring (Scheme 4).

The similarity of the ^{13}C NMR chemical shifts (Table 3) for the three epithio furanose triacetates **16**, **27**, and **30** provides further evidence for their having the same bicyclic ring system. In the foregoing experiments only small quantities of the pentaacetates of the 6-thio-hexoses were detected. This was probably due to the vigour of the hydrolysis condi-

Table 3
^{13}C NMR data: chemical shifts (ppm) [a]

Compound	C-1	C-2, C-3, C-4	C-5	C-6
16	84.6	83.0, 78.8, 75.5	67.4	25.3
27	84.5	82.7, 77.5, 76.8	62.6	25.25
30	83.1	80.0, 79.9, 77.1	65.9	26.2

[a] In addition all spectra showed signals in regions: 169.5–170.5 ($COCH_3$) and 20.5–21.1 ($COCH_3$).

tions, which were chosen to maximise the formation of anhydro/epithio compounds.

Use of milder conditions, namely hot aqueous acetic acid [1], led only to free sugars and no anhydro or epithio compounds were detected.

3. Experimental

General methods.—Melting points are uncorrected. Optical rotations were measured at 22 °C for solutions in $CHCl_3$. NMR spectra were recorded at 90 or 300 MHz (^1H) or 75 MHz (^{13}C) for solutions in $CDCl_3$ unless otherwise stated. The petroleum ether (PE) used had the boiling range 60–80 °C. Kieselgel 60 was used for thin-layer chromatography (TLC) (E. Merck, 5554) and column chromatography (E. Merck, 70–230 mesh ASTM). Compounds were visualised on TLC plates with 2% H_2SO_4 in EtOH and heating to 100 °C. Solutions in Et_2O or CH_2Cl_2 were dried with $MgSO_4$.

6 - S - Acetyl - 1,2 - O - isopropylidene - 3 - O-methanesulfonyl - 6 - thio - β - L - idofuranose (**10**).—Thioacetic acid (0.30 mL, 0.32 g, 4.20 mmol) was added to a solution of 5,6-anhydro-1,2-*O*-isopropylidene-3-*O*-methanesulfonyl-β-L-idofuranose (**9**) [12] (0.73 g, 2.60 mmol) in pyridine (1.5 mL). After 1 h at room temperature (rt), the mixture was partitioned between water and CH_2Cl_2. The organic layer was washed with 2 M H_2SO_4 ($\times 2$), 1 M $KHCO_3$, dried and concentrated. The residue was chromatographed on a short silica column and eluted with 1:1 EtOAc–PE to give the thioacetate **10** (0.69g, 1.94 mmol, 75%), mp 88–89 °C (from EtOH), $[\alpha]_D - 45°$ (*c* 1.0), Anal. Calcd for $C_{12}H_{20}O_8S_2$: C, 40.44; H, 5.66. Found: C, 40.41; H, 5.61.

Acetylation of **10** was carried out in the usual way with Ac_2O and pyridine and gave 5-*O*-acetyl-6-*S*-acetyl-1,2-*O*-isopropylidene-3-*O*-methanesulfonyl-6-thio-β-L-idofuranose, mp 120–121 °C (from EtOH), $[\alpha] - 51°$ (*c* 1.0). Anal. Calcd for $C_{14}H_{22}O_9S_2$: C, 42.20; H, 5.57. Found: C, 42.36; H, 5.59.

1,2 - O:5,6 - O,S - Diisopropylidene - 3 - O-methanesulfonyl - 6 - thio - β - L - idofuranose (**12**). —The thioacetate **10** (1.50 g, 4.21 mmol) was dissolved in methanolic NaOMe [from Na (0.43 g) in MeOH (17 mL)] containing $NaBH_4$ (0.13 g).

After stirring at rt for 45 min, the mixture was neutralised (CO_2) and evaporated to dryness. The residue was partitioned between CH_2Cl_2 and H_2O, the organic extract was dried and concentrated and the resulting crude thiol **11** was dissolved in Me_2CO (10 mL) and 2,2-dimethoxypropane (2 mL) containing toluene-*p*-sulfonic acid (0.12 g). After 1 h at rt the mixture was neutralised (Na_2CO_3), filtered, evaporated and partitioned between CH_2Cl_2 and H_2O. The organic extract was dried, filtered and evaporated to give the diacetal **12** (1.22 g, 3.45 mmol, 82%), mp 125–127 °C (from EtOH), $[\alpha]_D - 72°$ (*c* 1.0). Anal. Calcd for $C_{13}H_{22}O_7S_2$: C, 44.02; H, 6.26. Found: C, 44.12; H, 6.25.

1,2-O:5,6-O,S-Diisopropylidene-6-thio-β-L-idofuranose (**7**).—A solution of **12** (0.50 g, 1.41 mmol) in methanolic NaOMe [from Na (0.17 g) in MeOH (6.5 mL)] was heated under reflux for 5 h. The solution was neutralised (CO_2) and concentrated to half volume after the addition of H_2O (6.5 mL). The remaining solution was extracted with CH_2Cl_2, which after drying and evaporation gave the diacetal **7** (0.28 g, 1.02 mmol, 72%), mp 124–125°C (from ether–PE), $[\alpha]_D - 67°$ (*c* 1.0). Anal. Calcd for $C_{12}H_{20}O_5S$: C, 52.16; H, 7.30. Found: C, 52.22; H, 7.16.

2,3,4-Tri-O-acetyl-1,6-dideoxy-1,6-epithio-α-L-idofuranose (**16**).—A mixture of the diacetal **7** (0.38 g, 1.38 mmol) and 1 M HCl (11 mL) was stirred and heated under reflux for 20 min. The solution was neutralised ($PbCO_3$), filtered and concentrated to dryness. The residue was acetylated in the usual way with Ac_2O (2 mL) and pyridine (2 mL) to give a product that was further purified by chro-

matography on silica, eluting with 1:2 Et_2O–PE to give **16** (0.23 g, 0.76 mmol, 55%) mp 78–80 °C (from EtOH), $[\alpha]_D - 33°$ (*c* 0.8). Anal. Calcd for $C_{12}H_{16}O_7S$: C, 47.36; H, 5.30. Found: C, 47.41; H, 5.20.

6-S-Acetyl-1,2:3,5-di-O-isopropylidene-6-thio-α-D-glucofuranose (**22**).—A mixture of the tosylate **21** [11] (1.00 g, 2.42 mmol) and KSAc (0.48 g, 4.21 mmol) in DMF (10 mL) was heated at 90 °C for 30 min. The mixture was partitioned between Et_2O and H_2O, the Et_2O layer was washed with 1 M $KHCO_3$ ($\times 2$), dried and concentrated. The residue was crystallised from EtOH to give the thioacetate **22** (0.58 g, 1.84 mmol, 76%), mp 73–74 °C, $[\alpha]_D + 44°$ (*c* 1.0). Anal. Calcd for $C_{14}H_{22}O_6S$: C, 52.81; H, 6.97. Found: C, 53.00; H, 6.92.

1,2-O:5,6-O,S-Diisopropylidene-6-thio-α-D-glucofuranose (**24**).—A mixture of the thioacetate **22** (0.36 g, 1.13 mmol), $NaBH_4$ (30 mg) in methanolic NaOMe [from Na (0.12 g) in MeOH (3.5 mL)] was stirred at rt for 45 min. The mixture was neutralised (CO_2), evaporated to dryness and the residue was partitioned between CH_2Cl_2 and H_2O. The organic layer was dried and evaporated to give the crude thiol **23**, which was dissolved in Me_2CO (2 mL) containing toluene-*p*-sulfonic acid (20 mg). After 1 h at rt, 1 M $KHCO_3$ was added and the mixture was extracted with CH_2Cl_2. The extract was dried and concentrated to give a crude product that was chromatographed on silica, eluting with 1:4 Et_2O–PE to give the pure diacetal **24** (0.15 g, 0.54 mmol, 48%), mp 66–67 °C (from PE), $[\alpha]_D + 18°$ (*c* 1.0). Anal. Calcd for $C_{12}H_{20}O_5S$: C, 52.16; H, 7.30. Found: C, 52.33; H, 7.20.

2,3,5-Tri-O-acetyl-1,6-dideoxy-1,6-epithio-β-D-glucofuranose (**27**).—(a) From **24**. The diacetal **24** (0.17 g, 0.62 mmol) was heated in 1 M HCl (4.5 mL) as described earlier for diacetal **7**. Work-up as before and acetylation with Ac_2O (1 mL) and pyridine (1 mL) gave, as the major product after chromatography, the furanose **27** (23 mg, 0.08 mmol, 12%), $[\alpha]_D - 90°$ (*c* 1.0); *m/z* 304.0610 ($C_{12}H_{16}O_7S$ Calcd: 304.0617).

(b) From **22**. Under a nitrogen atmosphere the thioacetate **22** (0.19 g, 0.50 mmol) was dissolved in MeOH (4 mL) containing NaOMe [from sodium (40 mg)] at rt. After 5 min AcOH (1.5 mL) was added and the solution was evaporated to dryness. Acetic acid (1.0 mL) and 1 M HCl (1.5 mL) were added to the residual thiol **23** and the mixture was heated with stirring under reflux for 5 min when more 1 M HCl (4.5 mL) was added and heating continued for 90 min. NaOAc (0.70g) was added and the mixture was evaporated to dryness. More NaOAc (0.30 g) and Ac_2O (3.0 mL) were then added and the mixture was stirred at 100 °C for 30 min. Water (10.0 mL) was added and, after 30 min, the mixture was extracted with CH_2Cl_2 (2×5 mL), the extract was washed (dilute $KHCO_3$), dried and evaporated to yield a syrup which was purified by chromatography on silica, eluting with 2:1 PE–EtOAc to give **27** (66 mg, 0.22 mmol, 36%).

2,3,5-Tri-O-acetyl-1,6-dideoxy-1,6-epithio-α-D-galactofuranose (**30**).—The thioacetate **28** (0.17 g, 0.53 mmol) was treated as described for the *gluco*-thioacetate **22** in the previous experiment to give the title compound **30** (50 mg, 0.165 mmol, 31%), mp 99–100 °C (from PE), $[\alpha]_D + 234°$ (*c* 1.0). Anal. Calcd for $C_{12}H_{16}O_7S$: C, 47.36; H, 5.30. Found: C, 47.04; H, 5.04.

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