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Syntheses and conformations of 3-acetamido-3-deoxy-5-thio-D-xylose and 4-acetamido-4-deoxy-5-thio-L-lyxose and some derivatives thereof

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ABSTRACT

In reactions with azide ions, methyl 5-thio-3-*O*-*p*-toluenesulphonyl-α-D-xylopyranoside gave methyl 3-azido-3-deoxy-5-thio-α-D-xylopyranoside, methyl 4-*O*-acetyl-2,3-anhydro-5-thio-α-D-ribofuranoside (**7**) afforded a mixture of methyl 4-*O*-acetyl-3-azido-3-deoxy-5-thio-α-D-xylopyranoside and the 2-azido-2-deoxy-D-*arabino* analogue, and methyl 2-*O*-acetyl-3,4-anhydro-5-thio-α-D-ribopyranoside (**8**) afforded, after acetylation, methyl 2,4-di-*O*-acetyl-3-azido-3-deoxy-5-thio-α-D-xylopyranoside and methyl 2,3-di-*O*-acetyl-4-azido-4-deoxy-5-thio-β-L-lyxopyranoside. Treatment of **7** and **8** with methanolic ammonia gave methyl 3-amino-3-deoxy-5-thio-α-D-xylopyranoside and the 4-amino-3-deoxy-L-*lyxo* analogue, respectively, characterised as the tetra-acetates **14** and **19**, respectively. Acetolysis of **14** and **19** followed by *O*-deacetylation gave 3-acetamido-3-deoxy-5-thio-D-xylose and 4-acetamido-4-deoxy-5-thio-L-lyxose, respectively.

INTRODUCTION

During the last few years, several 5-thio sugars of chemical and biochemical interest have been synthesised[1–8]. Recently, attention has been directed towards aminodeoxythio sugars as potentially biologically active compounds. Preparations of 2-acetamido-2-deoxy-5-thiohexoses with D-*gluco*[9–11], D-*manno*[12], D-*allo*[13], and D-*altro*[14] configurations have been reported. Syntheses of 3-acetamido-3-deoxy-5-thio-D-xylose (**16**) and 4-acetamido-4-deoxy-5-thio-L-lyxose (**21**), the first aminodeoxypentoses having sulphur in the ring, are now reported.

RESULTS AND DISCUSSION

Reaction of methyl 5-thio-3-*O*-*p*-toluenesulphonyl-α-D-glucopyranoside[8] (**1**) with lithium azide in *N*,*N*-dimethylformamide gave methyl 3-azido-3-deoxy-5-thio-α-D-glucopyranoside[15] (**2**) as the major product. The structure of **2** was confirmed[15] by X-ray crystallography of the 2,4,6-triacetate **3**. A similar reaction with methyl 5-thio-3-*O*-*p*-toluenesulphonyl-α-D-xylopyranoside[16] (**4**) gave methyl 3-azido-3-deoxy-5-thio-α-D-xylopyranoside (**9**), the structure of which was assigned from consideration of the ^{1}H-n.m.r. data for the 2,4-diacetate **11** (Table I), which showed H-2,3,4 to be axial ($J_{2,3}$ 10.5, $J_{3,4}$ 9.8, $J_{4,5}$ 11.3 Hz).

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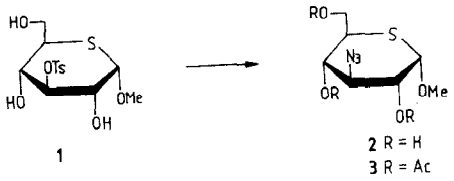


The azide displacements on **1** and **4** are unusual in that they proceed with retention of configuration. A possible explanation is that the sulphonates are converted initially into the 2,3-*allo*- or 3,4-*ribo*-epoxides, respectively, which then undergo attack at C-3 by azide ion to yield the observed products.

Accordingly, the epoxides **5** and **6** were prepared[16] from **4** and separated[17] as the 4-acetates **7**. On heating in *N,N*-dimethylformamide with lithium azide, the 2,3-epoxide **7** gave a 2:1 mixture of the xyloside **10** and the arabinoside **12**, which were separated by chromatography on silica gel. The ^{1}H-n.m.r. data for **10** (Table I) ($J_{2,3}$ 9.7, $J_{3,4}$ 10.0, $J_{4,5}$ 10.5 Hz) accord with the *xylo* configuration and a $^4C_1$ conformation. The corresponding

TABLE I

^{1}H-N.m.r. data for pyranose compounds[a]

Compound	*Chemical shifts (p.p.m.)*						*Other signals*
	H-1	*H-2*	*H-3*	*H-4*	*H-5a*	*H-5b*	
10	4.46	3.72	3.91	4.86	2.70	2.61	3.41 (OMe), 2.16 (COMe)
11	4.58	5.01	3.94	4.88	2.75	2.61	3.43 (OMe), 2.17, 2.12 (2 COMe)
12	4.38	3.82	4.13	4.88	2.96	2.55	3.40 (OMe), 2.07 (COMe)
13	4.42	3.95	3.49	3.72	2.91	2.39	3.42 (OMe), 3.49, 3.12 (2 OH), 6.52 (NH)
14	4.49	5.13	4.63	5.11	2.94	2.51	3.43 (OMe), 2.09, 2.04, 1.91 (3 COMe), 5.43 (NH)
15	5.92	5.85	4.53	5.00	3.62	2.58	2.12, 1.99, 1.95 (3 COMe), 1.86 (NHCOMe)
16	4.68	3.74	3.64	3.45	2.74	2.39	5.95, 4.93 (2 OH), 7.75 (NH), 1.81 (NHCOMe)
17	4.59	5.58	4.92	4.04	3.04	2.46	3.45 (OMe), 2.15, 2.11 (2 COMe)
18	4.48	4.05	3.64	3.37	3.13	2.18	3.37 (OMe), 3.67, 3.21, 2.17 (3 OH), 6.27 (NH)
19	4.50	5.30	5.15	4.48	3.33	2.24	3.45 (OMe), 2.12, 2.10, 2.05 (3 COMe), 6.24 (NH)
20	5.77	5.22	5.09	4.49	2.81	2.69	2.11, 2.07, 2.02 (3 COMe), 1.89 (NHCOMe)
21	4.65	3.80	3.53	3.94	3.32	2.49	6.0 (HO-1, $J_{OH,1}$ 4.8 Hz), 4.82 (HO-4, $J_{OH,4}$ 4.8 Hz), 4.41 (HO-2, $J_{OH,2}$ 6.7 Hz), 1.87 (NHCOMe)

[a]All the spectra were measured on solutions in $CDCl_3$, except **16** (Me_2SO-d_6).

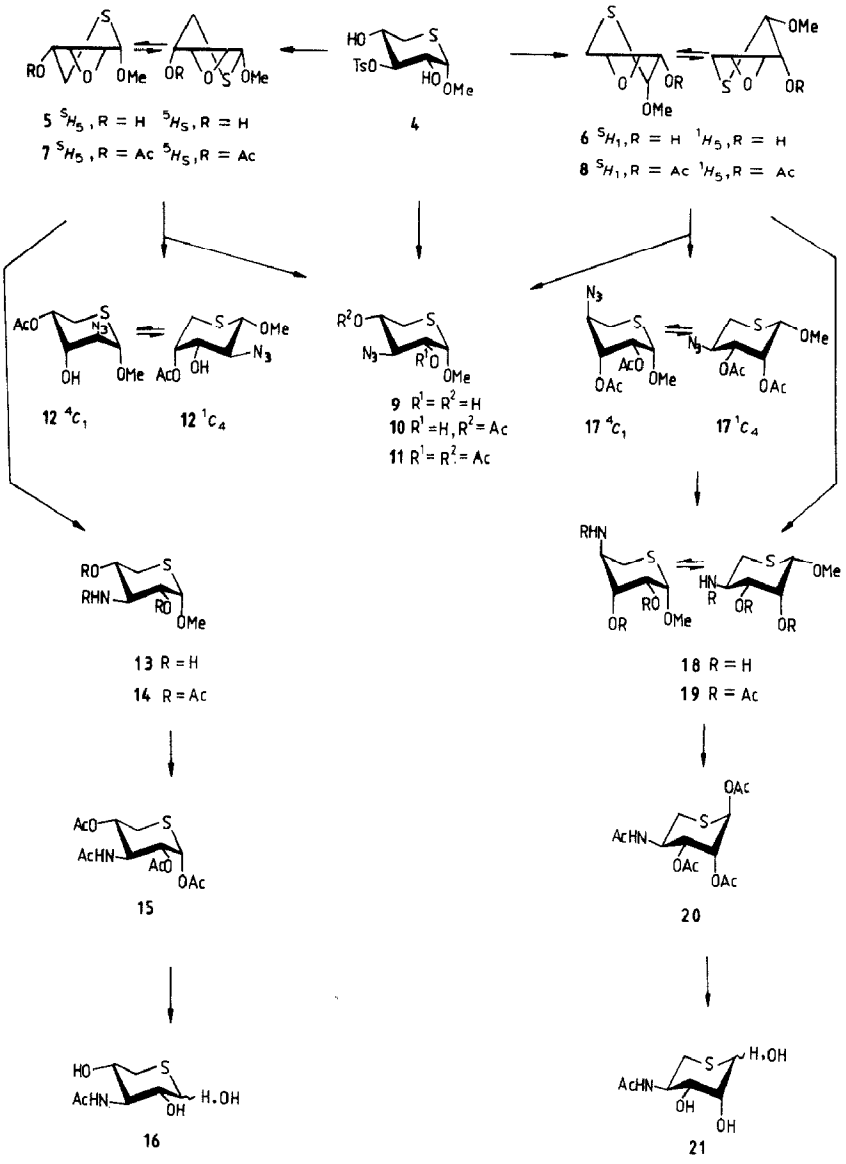
data for **12** ($J_{1,2}$ 5.4, $J_{2,3}$ 6.2, $J_{3,4}$ 6.0, $J_{4,5}$ 7.0 Hz) are similar to those reported[18] for methyl 5-thio-α-D-arabinopyranoside and suggest an equilibrium of the $^1C_4$ and the $^4C_1$ conformations. Assuming that the observed long-range coupling $J_{3,5} \sim$ 1.0 Hz is indicative of a planar W arrangement, then the equilibrium favours the $^4C_1$ conformation.

With lithium azide in hot *N,N*-dimethylformamide, the 3,4-epoxide **8** afforded a syrupy mixture of products. Acetylation followed by chromatography on silica gel gave the crystalline xyloside **11** (17%) and the crystalline lyxoside **17** (26%). The ^{1}H-n.m.r. data (Table I) for **17** ($J_{3,4}$ 7.5, $J_{4,5eq}$ 4.5, $J_{4,5ax}$ 8.0 Hz) suggested an equilibrium of the $^1C_4$ and $^4C_1$ conformations. These observations are in agreement with results obtained from the reaction of the epoxides **5** and **6** with hydroxide ions[17].

Treatment of the 2,3-epoxide **7** with methanolic ammonia gave mainly the aminodeoxyxyloside **13**, the ^{1}H-n.m.r. data (Table I) of which confirmed the *xylo* structure and the preponderance of the $^4C_1$ conformation ($J_{2,3}$ 10.0, $J_{3,4}$ 9.5, $J_{4,5ax}$ 11.0 Hz). Acetylation of **13** gave the triacetate **14**, which also existed in solution in the $^4C_1$ conformation. Reduction of **11** with lithium aluminium hydride afforded a syrupy product which gave the triacetate **14** on acetylation.

Coupling constants (Hz)

$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5a}$	$J_{4,5b}$	$J_{5a,5b}$	$J_{NH,3}$	$J_{NH,4}$	$J_{1,5a}$	$J_{1,5b}$	$J_{3,5eq}$
2.4	9.7	10.0	10.5	4.5	12.8					
2.8	10.5	9.8	11.3	4.9	13.1					
5.4	6.2	6.0	7.0	3.2	12.5					1.0
2.8	10.0	9.5	11.0	4.5	13.0					
2.7	11.0	10.0	11.3	4.3	12.8	10.1				
3.0	11.0	10.4	11.0	4.1	13.5	10.1				
2.1	9.6		11.7	3.6	13.8	8.3				
2.5	2.7	7.5	4.5	8.0	14.3					
2.4	3.1	3.1	4.6	4.1	14.0				1.0	
3.4	3.1	4.8	2.7	4.6	14.0		8.5			
3.4	2.8	10.8	3.8	11.1	13.1		5.8	1.0		
4.3	2.5	6.7	4.7	9.2	12.8		7.6			



Acetolysis of **14** afforded the tetra-acetate **15** as a syrup apparently in the α form ($J_{1,2}$ 3.0 Hz). Zemplén *O*-deacetylation[19] of **15** gave crystalline 3-acetamido-3-deoxy-5-thio-α-D-xylose (**16**).

Treatment of the epoxide **8** with methanolic ammonia afforded the crystalline lyxopyranoside **18**, for which the ^{1}H-n.m.r. data ($J_{2,3} = J_{3,4} = 3.1, J_{4,5eq}$ 4.1, $J_{4,5ax}$ 4.6 Hz) are in keeping with the $^4C_1$ conformation. Similar couplings were observed for the triacetate **19** (Table I). Treatment of **17** with lithium aluminium hydride in tetrahydrofuran also gave **18**.

TABLE II

^{13}C-N.m.r. data for pyranose compounds (chemical shift, in p.p.m.)

Compound	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*OMe*	*NHCOMe*
13	86.9	75.9	51.2	71.8	27.3	57.1	
16	77.6	74.0	51.2	71.5	28.1		22.4
18	85.3	75.6	68.2	52.5	26.1	57.4	
21	76.8	73.5	69.2	51.8	26.1		22.8

Acetolysis of **19** afforded the crystalline α-tetra-acetate **20**, the ^{1}H-n.m.r. data ($J_{3,4}$ 10.8, $J_{4,5ax}$ 11.1, $J_{1,5eq}$ ~ 1.0 Hz) of which are in agreement with a $^1C_4$ conformation. Zemplén *O*-deacetylation of **20** afforded crystalline 4-acetamido-4-deoxy-5-thio-L-lyxose (**21**).

The ^{13}C-n.m.r. spectra of **13**, **16**, **18**, and **21** (Table II) are consistent with the proposed structures.

EXPERIMENTAL

General methods. — Melting points were determined with a Gallenkamp apparatus and are uncorrected. Column chromatography was performed on silica gel (Merck, 70–230 mesh). The ^{1}H- and ^{13}C-n.m.r. spectra (internal Me_4Si) were recorded with Bruker WM-250 and AC-250 spectrometers. Solvents were evaporated *in vacuo* at 40°. Optical rotations were determined at 22–25° with a Perkin–Elmer 141 polarimeter. The amino sugars were detected in t.l.c. with ninhydrin.

Methyl 2,4-di-O-acetyl-3-azido-3-deoxy-5-thio-α-D-xylopyranoside (**11**). — (*a*) A solution of **4**[16] (0.73 g, 2.18 mmol) in *N,N*-dimethylformamide (30 mL) containing LiN_3 (0.22 g, 4.49 mmol) was heated at 120° for 3 h, then concentrated under reduced pressure to give **9** as a dark-brown syrup, which was acetylated with acetic anhydride (8 mL) and pyridine (15 mL) for 20 h at 23°. Work-up gave a product which was purified by column chromatography (toluene–ethyl acetate, 9:1) and recrystallised from di-isopropyl ether to give **11** (0.40 g, 63%), m.p. 75–77°, $[\alpha]_D^{23}$ + 188° (*c* 1, chloroform) (Found: C, 41.56; H, 5.29; N, 14.42. $C_{10}H_{15}N_3O_5S$ calc.: C, 41.52; H, 5.23; N, 14.52%).

(*b*) A solution of **7**[17] (0.99 g, 4.85 mmol) in *N,N*-dimethylformamide (25 mL) containing LiN_3 (1.0 g, 20.4 mmol) was boiled for 2 h. Evaporation of the solvent under vacuum gave a dark-brown syrup (2.0 g), which was partitioned between chloroform (50 mL) and water (50 mL). The organic extract was dried (Na_2SO_4) and filtered, and the solvent was evaporated. Column chromatography [silica gel (50 g); toluene–ether, 4:1] of the residue gave, first, **10**, isolated as a syrup (0.36 g, 30%) $[\alpha]_D^{25}$ + 140° (*c* 1, chloroform). Eluted second was **12**, isolated as a syrup (0.17 g, 15%), $[\alpha]_D^{22}$ + 120° (*c* 1.1, chloroform).

Acetylation of **10** with acetic anhydride (5 mL) in pyridine (10 mL) yielded **11** (0.40 g, 95%), m.p. and mixture m.p. 74–76°.

*Methyl 3-amino-3-deoxy-5-thio-α-*D*-xylopyranoside* (**13**). — A solution of **7** (1.00 g, 4.96 mmol) in methanolic 25% ammonia (25 mL) was stirred for 20 h at 100° under 20 bar pressure, then cooled, and decolorised with charcoal. Evaporation of the solvent yielded a crystalline product (0.70 g), which was recrystallised from ethyl acetate to yield **13** (0.62 g, 70%), m.p. 169–171°, $[\alpha]_D^{22}$ +310° (*c* 0.69, methanol) (Found: C, 39.85; H, 7.22; N, 8.24. $C_6H_{13}NO_3S$ calc.: C, 40.21; H, 7.31; N, 7.82%).

*Methyl 3-acetamido-2,4-di-*O*-acetyl-3-deoxy-5-thio-α-*D*-xylopyranoside* (**14**). — (*a*) Compound **13** (0.50 g, 2.19 mmol) was treated with acetic anhydride (6 mL) in pyridine (9 mL) for 48 h at 23°. The solvents were removed and the residue was eluted from a column of silica gel (20 g) with toluene–methanol (9:1) to afford **14** (0.72 g, 85%), which, after recrystallisation from dichloromethane–ether, had m.p. 79–80°, $[\alpha]_D$ +161° (*c* 1.1, chloroform) (Found: C, 46.98; H, 6.18; N, 4.90. $C_{12}H_{19}NO_6S$ calc.: C, 47.21; H, 6.27; N, 4.58%).

(*b*) A solution of **11** (0.13 g, 0.34 mmol) and $LiAlH_4$ (0.13 g, 3.50 mmol) in dry tetrahydrofuran (15 mL) was heated under reflux for 5 h. Ethyl acetate (20 mL) was added, the solution was extracted with water (20 mL) and then dried (Na_2SO_4), and the solvent was evaporated. Elution of the residue from a short column of silica gel with toluene–ether (1:1) gave a syrupy product (0.09 g), acetylation of which with pyridine (7 mL) and acetic anhydride (4 mL) gave **14** (0.07 g, 85%), m.p. and mixture m.p. 77–79°.

*3-Acetamido-1,2,4-tri-*O*-acetyl-3-deoxy-5-thio-α-*D*-xylopyranoside* (**15**). — To a stirred mixture of **14** (0.41 g, 1.34 mmol), acetic anhydride (20 mL), and acetic acid (5 mL) was added conc. sulphuric acid (0.4 mL) dropwise at 0°. The solution was kept at 0° for 15 min, then at 23° for 48 h. The mixture was poured into aqueous sodium hydrogen carbonate, stirred for 3 h, and extracted with chloroform (3 × 50 mL), the combined extracts were dried (Na_2SO_4), and the solvent was evaporated. The residue (0.37 g) was eluted from a short column of silica gel with chloroform–methanol (9:1), to give **15** (0.30 g, 67%), isolated as a syrup, $[\alpha]_D^{22}$ +61° (*c* 0.56, chloroform).

*3-Acetamido-3-deoxy-5-thio-*D*-xylose* (**16**). — To a cooled solution of **15** (0.25 g, 0.75 mmol) in methanol (7 mL) was added sodium methoxide (7 mg). After storage for 30 min at 0°, the mixture was neutralised with Amberlite IRC-84 (H^+) resin and filtered, and the resin was washed with methanol. The combined filtrate and washings were concentrated and the residue was recrystallised from ethanol to yield **16** (120 mg, 78%), m.p. 107–111°, $[\alpha]_D^{24}$ +49.5° → +52° (equil.; *c* 0.84, methanol) (Found: C, 40.71; H, 6.21; N, 6.73. $C_7H_{13}NO_4S$ calc.: C, 40.57; H, 6.32; N, 6.76%).

*Reaction of methyl 2-*O*-acetyl-3,4-anhydro-5-thio-α-*D*-ribopyranoside* (**8**) *with azide ion.* — A solution of **8** (0.48 g, 2.35 mmol) in *N,N*-dimethylformamide (25 mL) containing lithium azide (0.23 g, 4.70 mmol) was heated under reflux for 2 h, then concentrated, and the residue was partitioned between chloroform (20 mL) and water (20 mL). The organic extract was dried (Na_2SO_4) and filtered, and the solvent was evaporated to give a product (0.28 g), which was acetylated with acetic anhydride (4 mL) and pyridine (7 mL). Elution of the resulting syrupy product (0.31 g) from silica gel (20 g) with toluene–ethyl acetate (4:1) gave, first, **11** (0.10 g, 17%), m.p. and mixture m.p. 75–77°. Further elution afforded methyl 2,3-di-*O*-acetyl-4-azido-4-deoxy-5-thio-β-L-

lyxopyranoside (**17**; 0.15 g, 26%), m.p. 88–89° (from ethanol), $[\alpha]_D^{24}$ +178° (*c* 0.87, chloroform) (Found: C, 41.73; H, 5.11; N, 14.43. $C_{10}H_{15}N_3O_5S$ calc.: C, 41.52; H, 5.23; N, 14.52%).

*Methyl 4-amino-4-deoxy-5-thio-β-*L*-lyxopyranoside* (**18**). — A solution of **8** (0.89 g, 4.36 mmol) in methanolic 25% ammonia (25 mL) was stirred for 24 h at 80° under pressure (~ 20 bar), then cooled, and concentrated. The syrupy residue (1.0 g) crystallised on storage and was recrystallised from ethanol to give **18** (0.92 g, 91%), m.p. 191–192°, $[\alpha]_D^{22}$ +164° (*c* 0.88, methanol) (Found: C, 40.15; H, 7.11; N, 7.82. $C_6H_{13}NO_3S$ calc.: C, 40.21; H, 7.31; N, 7.82%).

*Methyl 4-acetamido-2,3-di-*O*-acetyl-4-deoxy-5-thio-β-*L*-lyxopyranoside* (**19**). — (*a*) To a solution of **18** (0.80 g, 4.46 mmol) in dry pyridine (12 mL) was added acetic anhydride (6 mL). After storage for 48 h at 25°, the mixture was worked-up in the usual way. The crude crystalline product (1.14 g) was eluted from a short column of silica gel with chloroform–methanol (9:1) to give **19** (1.11 g, 81%), m.p. 162–163° (from ethanol), $[\alpha]_D^{23}$ +166° (*c* 1.3, chloroform) (Found: C, 47.03; H, 6.32; N, 4.61. $C_{12}H_{19}NO_6S$ calc.: C, 47.21; H, 6.72; N, 4.58%).

(*b*) A solution of **17** (0.15 g, 0.52 mmol) in dry tetrahydrofuran (15 mL) containing $LiAlH_4$ (0.15 g, 4.00 mmol) was boiled under reflux for 4 h. Ethyl acetate (20 mL) was added, the solution was partitioned with water (20 mL), and the organic extract was dried (Na_2SO_4), filtered, and concentrated. The syrupy product (0.08 g) was treated with acetic anhydride (4 mL) in pyridine (7 mL) to give, after work-up, **19** (0.08 g, 50%, based on **17**), m.p. and mixture m.p. 161–163°.

*4-Acetamido-2,3-tri-*O*-acetyl-4-deoxy-5-thio-α-*L*-lyxopyranose* (**20**). — To a stirred and cooled solution of **19** (0.069 g, 2.26 mmol) in acetic acid (7 mL) and acetic anhydride (35 mL) was added conc. sulphuric acid (0.7 mL) at 0°. The mixture was stored for 30 min at 0°, then at 24° for 48 h, and poured into cold, stirred saturated aqueous sodium hydrogen carbonate. The mixture was stirred for 3 h, then extracted with chloroform (3 × 50 mL), and the combined extracts were dried (Na_2SO_4), filtered, and concentrated. The crude product (0.61 g) was eluted from a short column of silica gel with chloroform–methanol (9:1) to afford **20** (0.56 g, 74%), m.p. 182–184° (dec.) (from ethanol–hexane), $[\alpha]_D^{23}$ −71° (*c* 1.4, chloroform) (Found: C, 46.97; H, 5.71; N, 4.11. $C_{13}H_{19}NO_7S$ calc.: C, 46.84; H, 5.74; N, 4.20%).

*4-Acetamido-4-deoxy-5-thio-*L*-lyxose* (**21**). — A solution of **20** (0.50 g, 1.49 mmol) in dry methanol (40 mL) containing sodium methoxide (40 mg) was stirred for 30 min at 0°, then neutralised with Amberlite IRC-84 (H^+) resin, and filtered. The resin was washed with methanol, and the filtrate and washings were combined and concentrated to give **21** (0.25 g, 80%), m.p. 205–206° (dec.) (from ethanol), $[\alpha]_D^{25}$ −66° → −74° (equil.; *c* 0.6, methanol) (Found: C, 40.41; H, 6.41; N, 6.83. $C_7H_{13}NO_4S$ calc.: C, 40.57; H, 6.32; N, 6.76%).

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