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Carbohydrate Research 272 (1995) 111–119

CARBOHYDRATE RESEARCH

Note

# Synthesis of 2-acetamido-2-deoxy-5-thio-β-D-altropyranose

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Received 3 October 1994; accepted 11 November 1994

*Keywords:* D-*altro*; Amino sugar; Azido sugar; D-*gluco*; Thio sugar

Syntheses have been described of the 2-acetamido-2-deoxy derivatives of 5-thio-D-glucose [1–3], 5-thio-D-mannose [4], and 5-thio-D-allose [5]. We now describe the synthesis of another member of this series, 2-acetamido-2-deoxy-5-thio-D-altrose.

Treatment of oxirane **1** [6] with sodium azide and ammonium chloride in hot aqueous ethanol gave a mixture (70:30) of the *altro* and *gluco* azides, **2** and **3**, respectively. These were separated by chromatography and identified by their $^1$H NMR spectra (see Table 1). Thus, the *altro* azide **2** showed only a single diaxial coupling ($J_{4,5}$ 10.6 Hz) while the *gluco* isomer **3** displayed three such couplings ($J_{2,3}$ 9.7, $J_{3,4}$ 9.0, and $J_{4,5}$ 10.2 Hz), both compounds being constrained into the $^4C_1$ conformation by the acetal protecting group. Both **2** and **3** were further characterised as their acetates **4** and **5**. Removal of the acetal protecting group from **2** and **3** by mild acid hydrolysis afforded the azidoglycosides **6** and **8**. These were also further characterised as their triacetates **7** and **9**, and although it could not be crystallised, the *gluco* isomer **9** was shown to be identical in all other respects (NMR, $[\alpha]_D$) to that obtained earlier [7] by a different route. Sodium borohydride [8] readily reduced the *altro* azide **2** to the corresponding amine **10** in conditions which left the *gluco* isomer **3** unchanged. Indeed, it was more convenient to reduce the mixture of **2** and **3** and then separate **10** from unchanged **3** than it was to separate the mixture of **2** and **3** and then to reduce **2**. A shorter route to **10** was to treat the oxirane **1** directly with methanolic ammonia in a sealed tube. Although TLC

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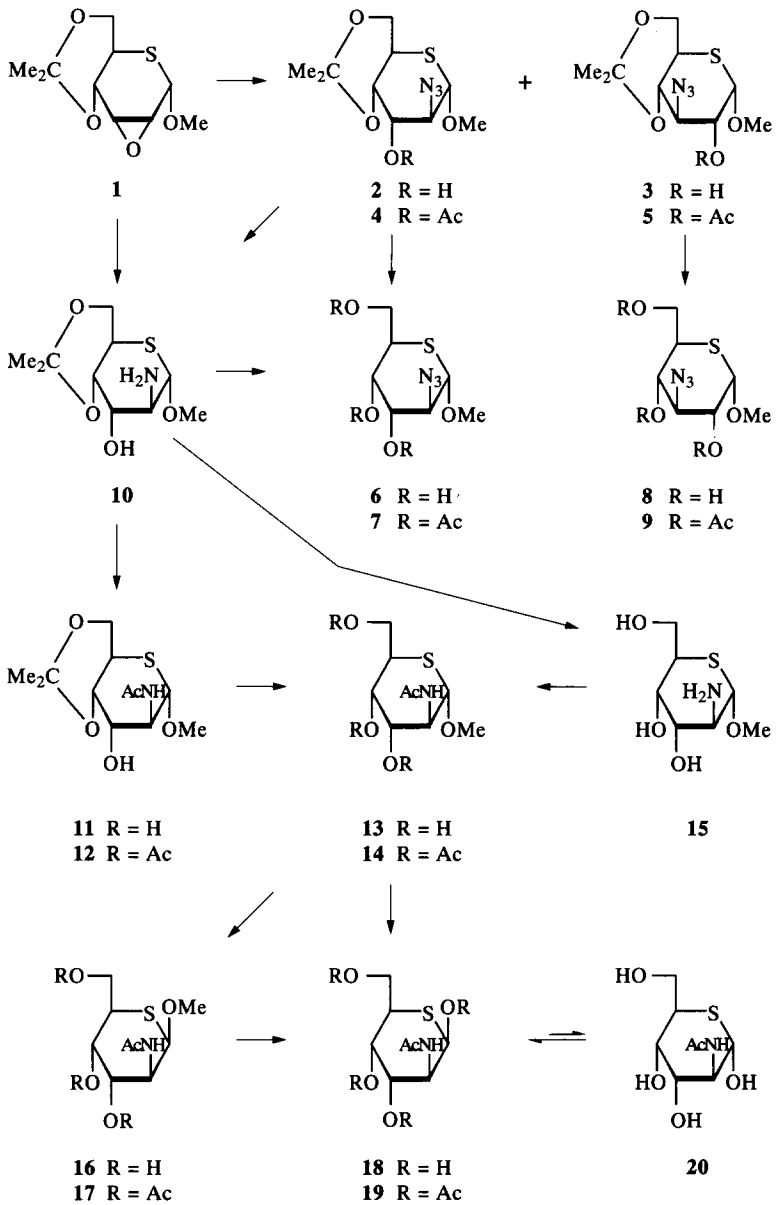
*SSDI* 0008-6215(95)00010-0

Table 1
$^1$H NMR data

| Compound | Chemical shifts (ppm) | | | | | | | Other signals | Coupling constants (Hz) | | | | | | | Other couplings |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | H-1 | H-2 | H-3 | H-4 | H-5 | H-6a | H-6b | | $J_{1,2}$ | $J_{2,3}$ | $J_{3,4}$ | $J_{4,5}$ | $J_{5,6a}$ | $J_{5,6b}$ | $J_{6a,6b}$ | |
| **2** | 4.47 | 4.31 | 3.92 | 4.16 | 3.43 | 3.80 | 3.78 | 3.48 (OMe); 3.11 (OH); 1.52, 1.44 ($CMe_2$) | 2.6 | 2.75 | 2.7 | 10.6 | 7.6 | 9.2 | 11.1 | |
| **3** | 4.54 | 3.74 | 3.62 | 3.82 | 3.10 | 3.82 | 3.73 | 3.48 (OMe); 1.43 (OH); 1.52, 1.44 ($CMe_2$) | 3.0 | 9.7 | 9.0 | 10.2 | 5.2 | 11.0 | 11.3 | |
| **4** | ← 4.36 → | | 4.95 | 4.27 | 3.54 | 3.80 | 3.74 | 3.39 (OMe); 2.09 (Ac); 1.52, 1.38 ($CMe_2$) | — | — | 2.8 | 10.3 | 7.1 | 9.8 | 11.1 | |
| **4** [a] | 3.86 | 4.16 | 5.23 | 4.39 | | 3.5 ↔ 3.9 | | 2.92 (OMe); 1.72 (Ac); 1.39, 1.15 ($CMe_2$) | 2.3 | 3.8 | 2.8 | 9.9 | — | — | — | |
| **5** [a] | 4.34 | 5.17 | 3.97 | 3.74 | 3.09 | 3.56 | 3.42 | 2.92 (OMe); 1.69 (Ac); 1.40, 1.16 ($CMe_2$) | 2.8 | 10.3 | 9.5 | 10.0 | 5.5 | 11.3 | 11.1 | |
| **6** [b,c] | 4.70 | 4.06 | 3.80 | 4.13 | 3.18 | 3.82 | 3.79 | 3.51 (OMe) | 6.8 | 7.5 | 2.9 | 6.5 | 5.9 | 6.6 | 11.9 | |
| **7** | 4.52 | 4.15 | 5.41 | 5.02 | 3.46 | 4.40 | 4.14 | 3.50 (OMe); 2.12 (2); 2.10 (Ac) | 6.2 | 6.9 | 2.9 | 7.6 | 5.8 | 6.9 | 11.8 | |
| **8** [b,c] | 4.63 | 3.86 | 3.60 | 3.65 | 3.08 | 3.91 | 3.86 | 3.47 (OMe) | 3.0 | 9.8 | 9.6 | 10.1 | 5.5 | 3.3 | 11.9 | |
| **9** | 4.66 | 5.05 | 3.95 | 5.14 | 5.33 | 4.34 | 4.04 | 3.45 (OMe); 2.18, 2.14, 2.08 (Ac) | 2.9 | 10.5 | 10.1 | 10.7 | 4.8 | 3.3 | 12.0 | |
| **10** | 4.39 | 3.62 | 3.77 | 4.13 | 3.46 | 3.80 | 3.78 | 3.46 (OMe); 2.28 (NH, OH); 1.53, 1.45 ($CMe_2$) | 2.6 | 2.5 | 2.5 | 10.6 | 7.0 | 9.7 | 11.0 | |
| **11** | 4.35 | 4.85 | 3.81 | 3.94 | 3.49 | 3.82 | 3.76 | 5.83 (NH); 3.45 (OMe); 3.15 (OH); 2.05 (Ac); 1.53, 1.44 ($CMe_2$) | 2.8 | 3.5 | 2.8 | 10.5 | 6.3 | 10.5 | 11.2 | 9.6 ($J_2$, NH); 6.5 ($J_3$, OH) |

| | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **12** | 4.23 | 4.79 | 5.02 | 4.06 | 3.56 | 3.81 | 3.72 | 5.83 (NH); 3.39 (OMe); 2.09, 2.05 (Ac); 1.51, 1.31 ($CMe_2$) | 2.5 | 3.2 | 2.9 | 10.1 | 5.9 | 10.8 | 10.9 | 9.8 ($J_2$, NH) |
| **13** [b,c] | 4.53 | 4.52 | 3.89 | 4.07 | 3.30 | 3.91 | 3.90 | 3.45 (OMe); 2.06(Ac) | 4.1 | 4.9 | 3.0 | 9.3 | 5.7 | 4.5 | 11.9 | |
| **14** | 4.25 | 4.76 | 5.18 | 5.28 | 3.72 | 4.42 | 4.10 | 5.94 (NH); 3.42 (OMe); 2.10 (2); 2.07, 2.01 (Ac) | 2.4 | 3.5 | 3.0 | 10.7 | 5.0 | 3.2 | 11.9 | 9.5 ($J_2$, NH) |
| **15** [b] | 4.71 | 3.54 | 3.85 | 4.15 | 3.20 | ← 3.85 → | | 3.48 (OMe) | 7.0 | 7.2 | 2.9 | 6.3 | ← 5.85 → | | — | |
| **16** [b] | 4.48 | 4.41 | 3.89 | 4.31 | 2.96 | 3.85 | 3.76 | 3.33 (OMe); 1.98 (Ac) | 3.0 | 10.5 | 2.8 | 4.5 | 8.4 | 6.9 | 11.8 | 1.5 ($J_{1,5}$) |
| **17** | 4.46 | 4.89 | 5.38 | 5.52 | 3.14 | 4.39 | 4.33 | 5.90 (NH); 3.41 (OMe); 2.19, 2.10, 2.04, 1.97 (Ac) | 3.1 | 11.0 | 2.7 | 3.5 | 6.5 | 9.8 | 12.0 | 1.5 ($J_{1,5}$) 9.7 ($J_2$,NH) |
| **18** [b,c] | 5.04 | 4.37 | 4.02 | 4.31 | 3.13 | 3.92 | 3.89 | 2.05 (Ac) | 2.9 | 9.9 | 2.9 | 4.2 | 7.5 | 6.1 | 11.9 | |
| **19** | 5.97 | 4.92 | 5.37 | 5.53 | 3.25 | 4.40 | 4.37 | 5.71 (NH); 2.19, 2.18, 2.11, 2.08, 1.95 (Ac) | 3.2 | 11.0 | 2.7 | 3.85 | 6.8 | 9.2 | 11.7 | 1.1 ($J_{1,5}$); 9.2 ($J_2$, NH) |
| **20** [b,c] | 4.88 | ~ 4.38 | ~ 3.85 | 4.12 | 3.29 | 3.85 | 3.84 | 2.04 (Ac) | 6.1 | — | 2.8 | 7.3 | — | 5.8 | 12.0 | |

[a] In $C_6D_6$.
[b] In $D_2O$.
[c] At 500 MHz.




of the crude product of this reaction suggested it was a single compound, the $^1$H NMR spectrum showed the product to be a mixture (3:1) of **10** and what appeared to be the isomeric methyl 3-amino-3-deoxy-4,6-*O*-isopropylidene-5-thio-α-D-glucopyranoside ($J_{2,3}$ 9.7, $J_{3,4}$ 8.1, and $J_{4,5}$ 10.3 Hz). Fortunately the required **10** could be crystallised from the mixture.

Table 2
$^{13}C$ NMR data

| Compound | Chemical shift (ppm) [a] | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | C-1 | C-2 | C-3, C-4 | C-5 | C-6 | OMe | *C*OMe | CO*Me* |
| **6** | 83.9 | 66.8 | 72.0, 70.0 | 45.7 | 62.9 | 58.9 | | |
| **8** | 84.3 | 75.7 [b] | 74.2 [b], 69.8 [c] | 44.2 | 61.3 | 57.6 | | |
| **13** | 86.1 | 59.3 | 73.6, 70.9 | 43.2 | 63.8 | 56.9 | 176.4 | 24.9 |
| **15** | 83.9 | 56.9 | 71.9, 69.8 | 46.1 | 63.1 | 58.9 | | |
| **16** | 85.2 | 53.8 | 70.8, 66.7 | 50.4 | 64.9 | 57.5 | 175.7 | 23.4 |
| **18** | 73.9 | 54.7 | 71.2, 67.3 | 49.5 | 65.0 | — | 175.9 | 23.5 |
| **20** | 74.4 | 56.7 | 72.0, 69.7 | 44.5 | 62.7 | — | 175.9 | 23.5 |

[a] In $D_2O$.
[b] May be interchanged.
[c] C-3.

Although the expected diaxial opening of the oxirane **1** is the preferred route of reaction of **1** with azide ion or ammonia, the proportion of *gluco* products is significantly higher than in comparable reactions of methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-allopyranoside where *gluco* compounds accounted for < 10% of the products [9,10]. The present observations are similar to those reported earlier on the reaction of oxirane **1** with sodium hydroxide [6], and the reaction of methyl 2,3(3,4)-anhydro-5-thio-α-D-ribopyranosides with azide or hydroxide ions [7,11] where it was suggested that axial attack by a nucleophile at C-2 is discouraged by the *syn*-diaxial interaction of the incoming nucleophile with the axial lone-pair electrons of the ring sulfur atom.

Acetylation of **10** in methanol or in pyridine gave the mono- and di-acetyl derivatives **11** and **12**, respectively, and mild acid hydrolysis converted **11** into the acetamido-glycoside **13**. Similar acid hydrolysis of **10** gave the amino-glycoside **15** which could be converted into **13** or the fully acetylated glycoside **14**. When the α-glycoside **13** was heated in acidic methanol, anomerisation occurred and it was converted into the β-glycoside **16**. Similar amomeric preference occurs in the methyl 5-thio-D-altropyranosides where the β-form is favoured [6] in keeping with the general observation that 1,2-*cis* stereochemistry is preferred in 5-thiopyranosides [12,13]. Hydrolysis of **11** or **13** with hot dilute sulfuric acid gave the free sugar **18**. Acetylation of **18** gave a syrupy pentacetate **19** whose β-configuration followed from comparison of its NMR spectrum with those of the peracetylated α- and β-glycosides **14** and **17** (see Table 1). Further evidence for the β-form of the free sugar **18** came from its mutarotation (−70.4° to −62.8°). Comparison of the $^1H$ and $^{13}C$ NMR spectra of the final solution with the spectra of the α- and β-glycosides **13** and **16** further supported this conclusion (see Tables 1 and 2) and suggested a final equilibrium ratio of 1:3 (α:β). The $^{13}C$ NMR spectrum of the final solution showed 12 lines and in the $^1H$ NMR spectrum the signals for the β-form **18** were clearly discernible, but some of the assignments of the signals of the α-form **20** are tentative. D-Altrose and 5-thio-D-altrose also crystallise in the β-pyranose forms [14,6].

In addition to the azide **2** mentioned previously, the other *altro* derivatives **4**, **10**, **11**, and **12**, all have the $^4C_1$ conformation as indicated by the large values for $J_{4,5}$ and low

values for $J_{1,2}$ and $J_{2,3}$ (see Table 1). On removal of the constraining acetal group, only the acetamido compounds **13** and **14** showed little change in these coupling constants, indicating the $^4C_1$ conformation still to be preferred. The azides **6** and **7**, the amine **15**, and possibly the $\alpha$-form **20** of the sugar have intermediate values (6.2–7.6 Hz) for all three of these coupling constants suggesting an equilibrium of $^4C_1$ and $^1C_4$ forms. All the $\beta$-compounds, **16**, **17**, **18**, and **19**, showed large values (9.9–11.0 Hz) for $J_{2,3}$ indicative of the $^1C_4$ conformation which was further confirmed by long-range couplings (1.1–1.5 Hz) between the equatorial H-1 and H-5 in compounds **16**, **17**, and **19**. The unusual *syn*-diaxial arrangement of the C-1 substituent and C-6 in the $^1C_4$ conformation has been encountered before in 5-thio-hexopyranose derivatives where it is less adverse than in a normal pyranose because of the greater length of the C–S bond [6,15].

## 1. Experimental

*General methods.*—Melting points are uncorrected. NMR spectra were recorded at 200 MHz ($^1$H) and 50 MHz ($^{13}$C) for solutions in $CDCl_3$ unless otherwise stated. Kieselgel 60 was used for TLC (Merck 5554) and column chromatography (Fluka 60738).

*Action of sodium azide on methyl 2,3-anhydro-4,6-*O*-isopropylidene-5-thio-α-*D*-allopyranoside* (**1**).—A mixture of the oxirane **1** (1.33 g), $NaN_3$ (1.33 g), and $NH_4Cl$ (0.80 g) in ethanol (37 mL) and $H_2O$ (4 mL) was heated under reflux for 4 h and then concentrated in vacuo to a syrup which was partitioned between $H_2O$ and $CH_2Cl_2$. The organic extract was purified by chromatography (2:1 light petroleum – EtOAc) to give first, methyl 3-azido-3-deoxy-4,6-*O*-isopropylidene-5-thio-α-D-glucopyranoside (**3**; 0.15 g, 10%) as a syrup, $[\alpha]_D + 40°$ (*c* 1.46, $CH_2Cl_2$). Mass spectrum: *m/z* 275.0925 ($C_{10}H_7N_3O_4S$ Calcd *m/z* 275.0940 for $M^+$). This was followed by a mixture of **2** and **3** (0.40 g, 26%) and finally methyl 2-azido-2-deoxy-4,6-*O*-isopropylidene-5-thio-α-D-altropyranoside (**2**; 0.72 g, 46%), mp 72–74°C (from diisopropyl ether–hexane), $[\alpha]_D + 30°$ (*c* 0.94, $CH_2Cl_2$). Anal. Calcd for $C_{10}H_{17}N_3O_4S$: C, 43.62; H, 6.22; N, 15.27. Found: C, 43.63; H, 6.22; N, 15.30.

The related acetates **4** and **5** were made in the usual way with $Ac_2O$ in pyridine. The *altro* acetate **4** had mp 119–121°C (from EtOH); $[\alpha]_D + 43°$ (*c* 1.05, $CH_2Cl_2$). Anal. Calcd for $C_{12}H_{19}N_3O_5S$: C, 45.42; H, 6.03; N, 13.24. Found: C, 45.13; H, 5.86; N, 13.06. The *gluco* isomer **5** was a syrup, $[\alpha]_D + 46°$ (*c* 0.58, $CH_2Cl_2$). Mass spectrum: *m/z* 317.1046 ($C_{12}H_{19}N_3O_5S$ Calcd *m/z* 317.1045 for $M^+$).

*Methyl 2-azido-2-deoxy-5-thio-α-*D*-altropyranoside* (**6**).—A solution of the acetal **2** (20 mg) in HOAc (0.2 mL) and $H_2O$ (0.05 mL) was left at room temperature for 15 h. Solvents were removed in vacuo and the residue was crystallised from ether to give the azide **6** (14 mg, 80%), mp 93–95°C, $[\alpha]_D + 76°$ (*c* 1.46, MeOH). Anal. Calcd for $C_7H_{13}N_3O_4S$: C, 35.74; H, 5.57; N, 17.86. Found: C, 36.17; H, 5.34; N, 17.54. The triacetate **7**, prepared in the usual way, had mp 107–109°C (from ether–light petroleum), $[\alpha]_D + 103°$ (*c* 0.86, $CHCl_3$). Anal. Calcd for $C_{13}H_{19}N_3O_7S$: C, 43.21; H, 5.30; N, 11.63. Found: C, 43.70; H, 5.17; N, 11.39.

*Methyl 3-azido-3-deoxy-5-thio-α-D-glucopyranoside* (**8**).—The acetal **3** (0.20 g) was treated as in the previous experiment to give the azide **8** (94 mg, 64%), mp 139–141°C, $[\alpha]_D$ + 305° (*c* 1.22, MeOH). Anal. Calcd for $C_7H_{13}N_3O_4S$: C, 35.74; H, 5.57; N, 17.86. Found: C, 36.10; H, 5.48; N, 17.67.

The triacetate **9** was a syrup, $[\alpha]_D$ + 222° (*c* 1.61, $CHCl_3$); lit. [7] +208° (*c* 0.5, $CHCl_3$).

*Methyl 2-amino-2-deoxy-4,6-O-isopropylidene-5-thio-α-D-altropyranoside* (**10**).—*(a) From the azide* **2**. A solution of **2** (50 mg) in EtOH (3 mL) and $H_2O$ (3 mL) containing $NaBH_4$ (70 mg) was stirred under reflux for 2 h. The solution was concentrated in vacuo and the residue was partitioned between $H_2O$ and $CH_2Cl_2$. The organic extract was dried ($MgSO_4$) and concentrated, and the residue was recrystallised from diisopropyl ether to give the amine **10** (32 mg, 71%), mp 127–129°C, $[\alpha]_D$ + 230° (*c* 2.05, $CH_2Cl_2$). Anal. Calcd for $C_{10}H_{19}NO_4S$: C, 48.17; H, 7.67; N, 5.62. Found: C, 47.65; H, 7.58; N, 5.48.

*(b) From the oxirane* **1** *via the azide* **2**. The oxirane **1** (0.63 g) was converted into a mixture (0.59 g) of the azides **2** and **3** as described above. This was dissolved in EtOH (10 mL) and $H_2O$ (10 mL) containing $NaBH_4$ (0.60 g) and the mixture was stirred under reflux for 2 h. Solvents were removed in vacuo and the residue was partitioned between $CH_2Cl_2$ and $H_2O$. The organic extract was dried and concentrated, and the residue was crystallised from ether to give the amine **10** (0.23 g, 33%), mp 126–128°C. The mother liquors were concentrated to give the unchanged azide **3** (0.14 g, 19%).

*(c) From the oxirane* **1** *and ammonia*. A solution of **1** (0.11 g) in MeOH (3.0 mL) and liquid $NH_3$ (1.0 mL) was heated in a sealed tube at 120°C for 20 h. Removal of solvents left a product (0.12 g) which showed only a single spot on TLC, but whose NMR spectrum suggested it was a mixture (3:1) of the required **10** and the isomeric methyl 3-amino-2-deoxy-4,6-*O*-isopropylidene-5-thio-α-D-glucopyranoside. Crystallisation from ether–light petroleum gave the amine **10** (60 mg, 48%), mp 126–128°C.

*Acetylation of methyl 2-amino-2-deoxy-4,6-O-isopropylidene-5-thio-α-D-altropyranoside* (**10**).—*(a) In acetic anhydride–methanol*. The amine **10** (0.125 g) was dissolved in MeOH (2.5 mL) and $Ac_2O$ (0.15 mL) was added. After 1 h, solvents were removed and the residue was crystallised from ether to give methyl 2-acetamido-2-deoxy-4,6-*O*-isopropylidene-5-thio-α-D-altropyranoside (**11**; 0.13 g, 89%), mp 198–200°C, $[\alpha]_D$ + 184° (*c* 0.81, $CHCl_3$). Anal. Calcd for $C_{12}H_{21}NO_5S$: C, 49.47; H, 7.27; N, 4.81. Found: C, 49.37; H, 7.22; N, 4.72.

*(b) In acetic anhydride–pyridine*. Acetic anhydride (0.5 mL) was added to a solution of the amine **10** (42 mg) in pyridine (1 mL). After 48 h at room temperature, work-up in the usual way and crystallisation from ether–diisopropyl ether gave methyl 2-acetamido-3-*O*-acetyl-2-deoxy-4,6-*O*-isopropylidene-5-thio-α-D-altropyranoside (**12**; 50 mg, 84%), mp 211–213°C, $[\alpha]_D$ + 164° (*c* 1.06, $CHCl_3$). Anal. Calcd for $C_{14}H_{23}NO_6S$: C, 50.44; H, 6.95; N, 4.20. Found: C, 50.25; H, 6.52; N, 4.15.

*Methyl 2-acetamido-2-deoxy-5-thio-α-D-altropyranoside* (**13**).—A solution of **11** (0.40 g) in aq 80% AcOH acid was kept at room temperature for 18 h. Solvents were removed and the residue was crystallised from EtOH–EtOAc to give **13** (0.21 g, 73%), mp 178–180°C, $[\alpha]_D$ +132° (*c* 1.14, MeOH). Anal. Calcd for $C_9H_{17}NO_5S$: C, 43.02; H, 6.82; N, 5.57. Found: C, 42.84; H, 6.71; N, 5.46. The triacetate **14**, prepared in the

usual way with $Ac_2O$ in pyridine, had mp 128–130°C (from ether), $[\alpha]_D$ + 174° (*c* 1.10, $CH_2Cl_2$). Anal. Calcd for $C_{15}H_{23}NO_8S$: C, 47.74; H, 6.14; N, 3.71. Found C, 47.71; H, 5.95; N, 3.70.

*Methyl 2-amino-2-deoxy-5-thio-α-*D*-altropyranoside* (**15**).—A solution of **10** (0.19 g) in aq 80% AcOH was kept at room temperature for 18 h. Concentration left a residue which was dissolved in EtOH and passed through a short column of silica gel. The eluate was concentrated to leave the amine **15** as a syrup (0.44 g, 70%), $[\alpha]_D$ + 138° (*c* 2.01, MeOH). Mass spectrum: *m/z* 209.0722 ($C_7H_{15}NO_4S$ Calcd *m/z* 209.0725 for $M^+$). *N*-Acetylation ($Ac_2O$–MeOH) gave **13**, mp and mixed mp 178–180°C, and per-acetylation ($Ac_2O$–pyridine) gave **14**, mp and mixed mp 128–130°C.

*Methyl 2-acetamido-2-deoxy-5-thio-β-*D*-altropyranoside* (**16**).—A solution of **13** (52 mg) in MeOH containing hydrogen chloride (1%) was refluxed for 10 min. The solution was passed through Dowex-1 ($AcO^-$) resin and concentrated to dryness. The residue was purified by chromatography on silica gel (60:20:3 $CHCl_3$–MeOH–$H_2O$) to give the β-glycoside **16** (24 mg, 46%), mp 168–170°C (from EtOAc), $[\alpha]_D$ −207° (*c* 1.20, MeOH). Anal. Calcd for $C_9H_{17}NO_5S$: C, 43.02; H, 6.82; N, 5.57. Found: C, 43.51; H, 6.80; N, 5.29. The triacetate **17** had mp 182–184°C (from ether), $[\alpha]_D$ −89° (*c* 1.41, $CH_2Cl_2$). Anal. Calcd for $C_{15}H_{23}NO_8S$: C, 47.74; H, 6.14; N, 3.71. Found: C, 48.12; H, 5.88; N, 3.43.

*2-Acetamido-2-deoxy-5-thio-β-*D*-altropyranose* (**18**).—A solution of **11** (0.15 g) or **13** (0.125 g) in 0.05 M $H_2SO_4$ (2.5 mL) was kept at 85°C for 3 h. The solution was then passed through Dowex-1 ($AcO^-$) resin and concentrated in vacuo. The residue was crystallised from MeOH to give the free sugar **18** (63 mg, 51%), mp 215–217°C, $[\alpha]_D$ −70.4° (5 min), −67.6° (90 min), −62.8° (final) (*c* 1.00, $H_2O$). Anal. Calcd for $C_8H_{15}NO_5S$: C, 40.49; H, 6.37; N, 5.90. Found: C, 40.92; H, 6.21; N, 5.65. The tetraacetate **19**, prepared in the usual way using $Ac_2O$–pyridine, was a syrup, $[\alpha]_D$ −132° (*c* 2.23, $CH_2Cl_2$). Mass spectrum: *m/z* 405.1143 ($C_{16}H_{23}NO_9S$ Calcd *m/z* 405.1093 for $M^+$).

## Acknowledgements

We thank the University of Basrah for a Research Studentship (to N.J.T.). NMR spectra were recorded by Mr I. McKeag and Mrs L. Cook, mass measurements were determined by Mr S. Addison, and elemental analyses were performed by Mr D. Dunbar.

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