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# ISOPROPYLIDENE ACETALS OF 5-THIOPENTOPYRANOSES*†

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ABSTRACT

Both 5-thio-D-ribose and 5-thio-D-xylose react with acetone and 2,2-dimethoxypropane, respectively, in the presence of acids to give 1,2:3,4-di-*O*-isopropylidene-5-thio-α-D-ribo- and -xylo-pyranoses (**9** and **8**); no furanoid products were detected. Partial hydrolysis of the *xylo*-diacetal **8** gave 1,2-*O*-isopropylidene-5-thio-α-D-xylopyranose, but a monoacetal could not be obtained from the *ribo*-diacetal **9**. The methyl 5-thio-D-ribopyranosides (**12**) also react with acetone, giving only the 3,4-acetal from the α anomer **12a**, and a separable mixture of 2,3- and 3,4-acetals from the β anomer **12b**.

## INTRODUCTION

Earlier papers in this series have described the synthesis and properties of 5-thio-D-ribose[3] (**1**), and such derivatives as esters[3], methyl glycosides[3], and methyl 1-thioglycosides[4], where a preference was observed for the thiopyranoid forms over the furanoid forms containing oxygen in the ring. This behaviour seems to be general for thio sugars of this type[5]. The reaction of these thio sugars with aldehydes or ketones to give acetals might also be expected to show this preference. Although acetals have been encountered in the synthesis of these thio sugars, the only prior examination of the reaction of aldehydes or ketones with this type of sugar was reported by Nestadt and van Es[6] who studied the reaction of acetone with 1,2-*O*-isopropylidene-5-thio-α-D-xylofuranose (**2**). They observed the initial formation of 5,5′-isopropylidenedithiobis(5-deoxy-1,2-*O*-isopropylidene-α-D-xylofuranose) (**3**), which underwent further reaction to give a diacetal, presumably 1,2-*O*:3,5-*O*,*S*-di-isopropylidene-5-thio-α-D-xylofuranose (**4**). In these compounds, the fact that the oxygen-ring form is retained is probably due to the nature of the starting material. It was considered that the reaction of acetone with the free sugars 5-thio-D-xylose (**5**) and 5-thio-D-ribose (**1**) would be more revealing, particularly as D-xylose and D-ribose

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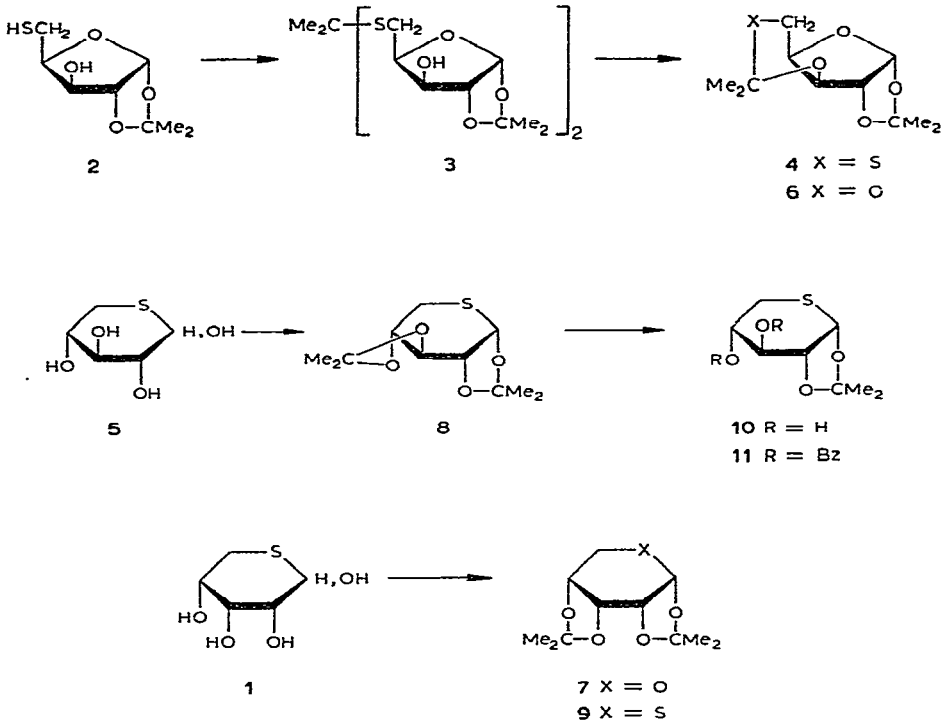
both react with acetone to give furanose derivatives, namely, 1,2:3,5-di-*O*-isopropylidene-α-D-xylofuranose (**6**) in the first case[7] and mainly a mixture of 1,2- and 2,3-*O*-isopropylidene-D-ribofuranoses in the latter case[8]. Other products in this last reaction include anhydro compounds and a small proportion of 1,2:3,4-di-*O*-isopropylidene-α-D-ribopyranose[9] (**7**).




## DISCUSSION

The work of Nestadt and van Es was repeated, and their findings and the structures of the dithioacetal **3** and the diacetal **4** were confirmed. Comparison of the $^1$H-n.m.r. spectra for **3** and **4** with those of the starting material **2** and the diacetal **6** showed the characteristic doublets for H-1 and H-2 of a 1,2-*O*-isopropylidene-α-D-xylofuranose system. The spectra of the two diacetals **4** and **6** were similar, with the exception of the signals for the sulphur-bearing methylene group of **4** which were clearly distinguished upfield of the remaining ring-hydrogen signals as the AB part of an ABX spectrum (see Table I). Although no molecular ion for the dithioacetal **3** was observed in the mass spectrum, an ion having *m/e* 246 ($M-C_8H_{14}O_4S$) corresponded to the loss of a 1,2-*O*-isopropylidene-5-thio-D-xylofuranose unit from **3**.

5-Thio-D-xylose (**5**) failed to react with acidified acetone. When recourse was had to more-forcing conditions (2,2-dimethoxypropane in *N*,*N*-dimethylformamide containing toluene-*p*-sulphonic acid[10] for two days at room temperature), a single

TABLE I

SOME FIRST-ORDER CHEMICAL SHIFTS[a] AND COUPLING CONSTANTS[b] FOR D-XYLOFURANOSE DERIVATIVES (90 MHz)

| *Compound* | *Solvent* | *H-1* | *H-2* | *Me* | $J_{1,2}$ | $J_{2,3}$ |
|---|---|---|---|---|---|---|
| 2 | $CDCl_3$ | 5.92 | 4.50 | 1.33,1.52 | 3.7 | <0.5 |
| 3 | $CDCl_3$ | 5.92 | 4.52 | 1.31,1.50,1.66 | 4.0 | <0.5 |
| 4[c] | $CCl_4$ | 5.86 | 4.40 | 1.32,1.48,1.56,1.60 | 3.6 | <0.5 |
| 6 | $CCl_4$ | 5.91 | 4.46 | 1.26,1.32,1.40,1.43 | 3.8 | <0.5 |

[a] $\delta$ values. [b] In Hz. [c] $\delta$ 2.77 (H-5, $J_{4,5}$ 5.2, $J_{5,5'}$ 14.0 Hz), $\delta$ 3.13 (H-5', $J_{4,5'}$ 4.8 Hz).

TABLE II

FIRST-ORDER CHEMICAL SHIFTS[a] FOR FOR 5-THIO-D-PENTOPYRANOSE DERIVATIVES (90 MHz)

| *Compound* | *Solvent* | *H-1* | *H-2* | *H-3* | *H-4* | *H-5e* | *H-5a* | *Me* | *OMe* | *OH* |
|---|---|---|---|---|---|---|---|---|---|---|
| 8 | $CCl_4$ | 5.05 | 4.18 | 3.29 | 3.58 | 2.73 | 2.81 | 1.36,1.39(2),1.51 | — | — |
| 10 | $CDCl_3$ | 5.13 | 4.15 | 3.58 | 3.77 | 2.91 | 2.63 | 1.47,1.64 | — | 3.67,3.84 |
| 11 | $CDCl_3$ | 5.23 | 4.50 | 5.69 | 5.36 | 3.21 | 2.92 | 1.48,1.78 | — | — |
| 7[b] | $CDCl_3$ | 5.35 | 4.35 | 4.16 | 4.37 | 3.92 | 3.76 | 1.31(2),1.45,1.57 | | |
| 9 | $CDCl_3$ | 5.36 | 4.75 | 4.17 | 4.56 | 2.88 | 3.16 | 1.38(2),1.54,1.58 | | |
| 13b | $CCl_4$ | ← 4.2–4.5 → | | | 4.08 | 2.52 | 2.63 | 1.34,1.51 | 3.35 | 2.79 |
| 14a | $CCl_4$ | ← 3.8–4.3 → | | | | 2.18 | 2.69 | 1.28,1.42 | 3.42 | 3.13 |
| 14b | $CCl_4$ | 4.59 | 3.96 | 4.2–4.5 | | 2.6–2.8 | | 1.31,1.49 | 3.37 | 2.99 |
| 15b | $CDCl_3$ | ← 4.3–4.7 → | | | 5.70 | 2.75 | 3.04 | 1.34,1.56 | 3.20 | — |
| 16a | $CDCl_3$ | 4.72 | 5.60 | 4.2–4.6 | | 2.43 | 3.03 | 1.34,1.51 | 3.42 | — |
| 16b | $CDCl_3$ | 4.95 | 5.54 | 4.6–4.9 | | 2.7–3.0 | | 1.32,1.54 | 3.38 | — |

[a] $\delta$ values. [b] Measured at 220 MHz.

TABLE III

FIRST-ORDER COUPLING CONSTANTS[a] FOR 5-THIO-D-PENTOPYRANOSE DERIVATIVES

| *Compound* | *Solvent* | $J_{1,2}$ | $J_{2,3}$ | $J_{3,4}$ | $J_{4,5e}$ | $J_{4,5a}$ | $J_{5e,5a}$ |
|---|---|---|---|---|---|---|---|
| 8 | $CCl_4$ | 4.9 | 8.6 | 9.3 | 5.7 | 8.8 | 11.2 |
| 10 | $CDCl_3$ | 5.2 | 7.2 | 9.9 | 4.0 | 9.6 | 12.7 |
| 11 | $CDCl_3$ | 5.1 | 7.8 | 9.8 | 4.0 | 9.6 | 12.8 |
| 7 | $CDCl_3$ | 5.0 | 4.0 | 7.5 | 7.5 | 9.0 | 11.0 |
| 9 | $CDCl_3$ | 6.5 | 3.0 | 8.0 | 7.6 | 10.0 | 13.0 |
| 13b | $CCl_4$ | | | 2.0 | 5.5 | 9.0 | 11.0 |
| 14a | $CCl_4$ | | | | 6.4 | 10.4 | 13.2 |
| 14b | $CCl_4$ | 6.2 | 3.2 | | | | |
| 15b | $CDCl_3$ | | | 1.4 | 5.6 | 10.0 | 11.0 |
| 16a | $CDCl_3$ | 3.6 | 4.0 | | 6.0 | 10.0 | 12.8 |
| 16b | $CDCl_3$ | 7.2 | 2.4 | | | | 14.0 |

[a] Measured in Hz.

product was obtained whose structure was readily ascertained as 1,2:3,4-di-*O*-isopropylidene-5-thio-α-D-xylopyranose (**8**) from its well-resolved $^1$H-n.m.r. spectrum. Apart from the four methyl signals of the two isopropylidene groups (see Table II). the coupling constants (see Table III) for the ring hydrogens clearly indicated an α-D-xylopyranose structure in the $^4C_1$ conformation. It is possible for this formation of the pyranose diacetal to be due more to the reaction conditions rather than the nature of the sugar, as Hasegawa and Fletcher[11] have shown that this reagent mixture often leads to unusual isopropylidene derivatives, *e.g.*, D-glucose gives 4,6-*O*-isopropylidene-D-glucopyranose. However, this appears not to be the cause in the present case, as treatment of D-xylose with this reagent mixture gave the 1,2:3,5-diacetal **6** which is the product of the more-usual acetone reaction.

Treatment of 5-thio-D-ribose (**1**) with acetone in the presence of sulphuric acid gave a crystalline, major product identified as 1,2:3,4-di-*O*-isopropylidene-5-thio-α-D-ribopyranose (**9**) by a comparison of the coupling constants of the ring hydrogens with those of the related diacetal **7*** obtained in small yield from D-ribose (see Table III). For **7** and **9**, the values of $J_{1,2}$, $J_{3,4}$, and $J_{4,5e}$ are larger than might be expected for axial–equatorial coupling constants for a $^4C_1$ pyranose conformation. They are more in keeping with a $^3S_5$ conformation, where the dihedral angles of H-1–H-2, H-3–H-4, and H-4–H-5e are less than 60° with a consequent increase in the value of the coupling constants. Skew conformations have already been encountered in other sterically crowded, pyranoid, isopropylidene derivatives[12].

The formation of the 1,2:3,4-di-*O*-isopropylidene-5-thiopentopyranoses **8** and **9** demonstrates, even more strikingly than the earlier examples, the exceedingly strong preference for the forms with sulphur in the ring. These structures are formed in spite of the considerable steric strain of a cyclic acetal derived from a *trans*-diol in one compound and of a *cis–syn–cis* arrangement of rings in the other product.

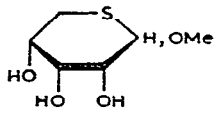
The diacetals **4**, **8**, and **9** and the dithioacetal **3** were subjected to graded, acid hydrolysis. Both the diacetal **4** and the dithioacetal **3** gave the 1,2-*O*-isopropylidene compound **2** from which they were originally prepared. The diacetal **4** thus behaves like its oxygen analogue **6**; the result for the dithioacetal **3** is perhaps a little surprising, as acetals are generally considered to be more acid-labile than dithioacetals[13]. As expected, mild hydrolysis of the *xylo*-diacetal **8** led to selective cleavage of the *trans*-acetal group, giving 1,2-*O*-isopropylidene-5-thio-α-D-xylopyranose (**10**). That the 3,4-acetal group had been cleaved followed from the different chemical shifts of the H-3 and H-4 signals of the monoacetal **10** compared to those of the diacetal **8**, and the downfield shifts of the same signals in the derived dibenzoate **11** (see Table II). Chemical evidence for the presence of the 1,2-acetal group in **10** came from the lack of reducing properties and thiol reactions. Similar treatment of the *ribo*-diacetal **9** gave only the free sugar **1**, and no evidence could be obtained for the formation of

*Since this work was submitted for publication, a paper has appeared [J. Gelas and D. Horton, *Carbohyd. Res.*, 45 (1975) 181–195] in which it is suggested that diacetal **7** may, in fact, be 1,5:2,3-di-*O*-isopropylidene-β-D-ribofuranose. Comparison of the n.m.r. spectral data for **7** and for the 1,5:2,3-diacetal described by Gelas and Horton indicates that this is not so.

either 1,2 or 3,4-acetals. This result contrasts with that for the oxygen analogue **7** where preferential cleavage of the 3,4-acetal group was achieved[9]. Methyl 5-thiopentopyranosides are[3,14] more readily hydrolysed than the related oxygen glycosides and it appears that this difference applies also to 1,2-*O*-isopropylidene-5-thiopentopyranoses. It is noteworthy that even in the successful partial hydrolysis of the *xylo*-diacetal **8**, the free sugar **5** was formed before complete reaction of the diacetal had occurred.

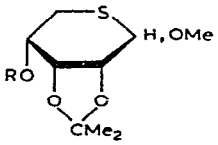
When the two *xylo*-diacetals **4** and **8** were kept in acidified acetone to see if any interconversion occurred, the furanoid diacetal **4** was recovered unchanged; this result is not surprising in view of the method of the synthesis of **4**. With the pyranoid diacetal **8**, some decomposition occurred (including hydrolysis to the monoacetal **10**, the necessary water presumably coming from the simultaneous condensation reactions of acetone), but no interconversion was observed.

Treatment of methyl 5-thio-β-D-ribopyranoside (**12b**) with acidified acetone gave an approximately equimolar mixture of the 2,3- and 3,4-acetals **13b** and **14b**, both of which were obtained crystalline after chromatography on silica gel. Their structures were assigned on the basis of the $^1$H-n.m.r. data for the crystalline benzoates **15b** and **16b** (see Tables II and III). The lowest-field signal in the spectrum of **15b** was an octet which was clearly due to H-4 and indicated the benzoate group to be at C-4. For **16b**, the lowest-field signal was a quartet; on double irradiation of this signal, the doublet due to H-1 collapsed to a singlet, thus indicating this quartet to be due to H-2 and the benzoate group to be at C-2. Only a single acetal was obtained when methyl 5-thio-α-D-ribopyranoside (**12a**) was treated with acidified acetone. That the product was the 3,4-acetal **14a** was shown in a fashion similar to that employed for the β anomer **14b**. It gave a syrupy benzoate **16a**, in whose $^1$H-n.m.r. spectrum the lowest-field signal was a triplet which collapsed to a doublet on double irradiation of the doublet due to H-1. The difference in behaviour of the two glycosides **12** in the reaction with acetone is presumably due to steric hindrance from the methoxyl group in **12a** preventing reaction at the adjacent O-2. For both compounds, the reaction was complete in minutes and more-prolonged reaction times resulted in the formation of increasing amounts of the diacetal **9**.

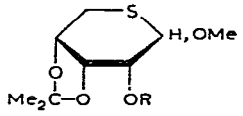



**12**

a series : α-anomers
b series : β-anomers




13 R = H
15 R = Bz




14 R = H
16 R = Bz

## EXPERIMENTAL

N.m.r. spectra were obtained at 90 MHz with a Brucker Spectrospin spectrometer, with tetramethysilane as an internal reference. $R_F$ values refer to paper

chromatography on Whatman No. 1 paper in butan-1-ol–water (86:14 v/v). Thin-layer chromatography was performed on Gelman ITLC sheets Type SA.

*5,5'-Isopropylidenedithiobis(5-deoxy-1,2-O-isopropylidene-α-D-xylofuranose)* (**3**). — 1,2-*O*-Isopropylidene-5-thio-α-D-xylofuranose[15] (**2**) (0.30 g) was dissolved in acetone (3 ml) containing sulphuric acid (0.015 ml). After a few minutes, a white, crystalline solid began to separate out; after 1 h, this was filtered off and recrystallised several times from ethanol to give **3** (0.11 g), m.p. 198–200°, $[\alpha]_D$ −89° (*c* 0.35, chloroform); lit.[6] m.p. 145°, $[\alpha]_D$ −41° (*c* 0.1, chloroform) (Found: C, 50.2; H, 7.2. $C_{19}H_{32}O_8S_2$ calc.: C, 50.4; H, 7.1%).

*1,2-O:3,5-O,S-Di-isopropylidene-5-thio-α-D-xylofuranose* (**4**). — A solution of the thiol **2** (0.17 g) in acetone (20 ml) containing sulphuric acid (0.1 ml) was kept at room temperature for 2 h and then neutralised ($Na_2CO_3$), filtered, and evaporated to dryness. The residue was sublimed (75°/0.2 mmHg) to give **4** (0.19 g), m.p. 66–69°, $[\alpha]_D$ −42° (*c* 0.37, chloroform); lit.[6] m.p. 68–70°, $[\alpha]_D$ −29.4° (*c* 0.35, chloroform) (Found: C, 53.3; H, 7.5. $C_{11}H_{18}O_4S$ calc.: C, 53.6; H, 7.3%).

*1,2:3,4-Di-O-isopropylidene-5-thio-α-D-xylopyranose* (**8**). — 5-Thio-D-xylose[15] (**5**, 0.50 g) was dissolved in *N,N*-dimethylformamide (3 ml) to which 2,2-dimethoxypropane (10 ml) containing toluene-*p*-sulphonic acid (65 mg) was added. After 48 h, the mixture was neutralised ($Na_2CO_3$), filtered, and evaporated. Chromatography of the syrupy residue on silica gel (10 g) with chloroform gave **8** (0.47 g), b.p. 100°/0.2 mmHg (bulb-distillation), $[\alpha]_D$ +118° (*c* 0.4, chloroform) (Found: C, 54.1; H, 7.8. $C_{11}H_{18}O_4S$ calc.: C, 53.6; H, 7.3%).

*Action of 2,2-dimethoxypropane on D-xylose.* — The previous experiment was repeated with D-xylose (0.50 g) in place of 5-thio-D-xylose. T.l.c. indicated the reaction to be complete after 2 h, and the mixture was worked-up as above. The major product was identified as 1,2:3,5-di-*O*-isopropylidene-α-D-xylofuranose (**6**) by comparison of its n.m.r. spectrum with that of an authentic sample. A minor, slower-running product was not identified.

*1,2:3,4-Di-O-isopropylidene-5-thio-α-D-ribopyranose* (**9**). — 5-Thio-D-ribose[3] (**1**, 2.0 g) was dissolved, with stirring, in acetone (50 ml) containing sulphuric acid (0.5 ml). After 30 min, the mixture was neutralised ($Na_2CO_3$), filtered, and evaporated. The syrupy residue was partitioned between ether and dilute, aqueous sodium hydrogen carbonate, and the ether extract was dried ($MgSO_4$) and evaporated. The crude product was purified by chromatography on silica gel (30 g) with ether, and crystallisation from light petroleum gave **9** (1.4 g), m.p. 66–67°, $[\alpha]_D$ −90° (*c* 0.25, chloroform) (Found: C, 53.8; H, 7.7; mol. wt., 246.0919. $C_{11}H_{18}O_4S$ calc.: C, 53.6; H, 7.3%; mol. wt., 246.0926).

*Hydrolysis experiments.* — (*a*) The dithioacetal **3** (20 mg) was heated in refluxing 80% acetic acid during 15 h. Paper chromatography then indicated the presence of the thiol **2** ($R_F$ 0.82) and 5-thio-D-xylose (**5**; $R_F$ 0.28) as well as starting material ($R_F$ 0.95).

(*b*) A solution of the diacetal **4** (20 mg) in 80% acetic acid was kept at 50° for

15 h; the starting material had then completely disappeared, and the thiol **2** and free sugar **5** were detected as in (*a*).

(*c*) A solution of the diacetal **8** (30 mg) in 80% acetic acid was kept at room temperature. After 2 h, t.l.c. indicated the presence of starting material, 5-thio-D-xylose (**5**), and a product (acetal **10**) of intermediate mobility.

(*d*) Experiment (*c*) was repeated with the *ribo*-diacetal **9**. After 24 h at room temperature, hydrolysis to 5-thio-D-ribose (**1**) was complete. At no intermediate time did t.l.c. indicate the presence of sizeable quantities of material other than the starting material **9** and the free sugar **1**.

*1,2-O-Isopropylidene-5-thio-α-D-xylopyranose* (**10**). — A solution of the diacetal **8** (2.5 g) in 80% acetic acid was kept at 0° for 3 days. Solvents were evaporated off, the residue was taken up in acetone, and the solution filtered to remove 5-thio-D-xylose (**5**, 0.12 g), m.p. and mixture m.p. 120–122°. Removal of the acetone from the filtrate left a residue which was dissolved in dichloromethane and chromatographed on silica gel (10 g). Elution with ether–dichloromethane (1:1) gave material which crystallised from isopropyl ether to give **10** (0.66 g), m.p. 126–128°, $[\alpha]_D$ +184° (*c* 0.65, chloroform) (Found: C, 47.0; H, 7.0; mol. wt., 206.0616. $C_8H_{14}O_4S$ calc.: C, 46.6; H, 6.8%; mol. wt., 206.0613). Earlier fractions consisted mainly of the starting material **10**.

*3,4-Di-O-benzoyl-1,2-O-isopropylidene-5-thio-α-D-xylopyranose* (**11**). — The diol **10** (20 mg) was dissolved in pyridine (0.5 ml) and treated with benzoyl chloride (0.1 ml). After 48 h at room temperature; work-up in the usual manner and crystallisation from light petroleum gave the dibenzoate **11** (30 mg), m.p. 100–101°, $[\alpha]_D$ +37° (*c* 0.54, chloroform) (Found: C, 63.9; H, 5.3. $C_{22}H_{22}O_6S$ calc.: C, 63.8; H, 5.3%).

*Effect of acidified acetone on the diacetals* **4** *and* **8**. — (*a*) The diacetal **4** (0.14 g) was dissolved in acetone (5 ml) containing sulphuric acid (0.25 ml). After 2 h at room temperature, the solution was neutralised ($Na_2CO_3$), filtered, and evaporated to dryness. Sublimation of the residue gave the starting material **4** (0.12 g), m.p. and mixture m.p. 67–69°.

(*b*) The diacetal **8** (0.14 g) was treated as in (*a*), but with less sulphuric acid (0.01 ml). Chromatography of the crude product on silica gel (15 g) with ether gave first the starting material **8** (0.12 g) and then the monoacetal **10** (11 mg), m.p. and mixture m.p. 125–126°.

*Methyl 2,3- and 3,4-O-isopropylidene-5-thio-β-D-ribopyranosides* (**13b** *and* **14b**). — Methyl 5-thio-β-D-ribopyranoside[3] (**12b**) (1.7 g) was added to a stirred solution of sulphuric acid (0.5 ml) in acetone (50 ml). Dissolution was achieved in 1.5 min; after a further 1.5 min, the acid was neutralised ($Na_2CO_3$) and the filtered solution was evaporated to a syrup (2.32 g). This was chromatographed on silica gel (100 g) with ether to give first the 2,3-acetal **13b** (0.69 g), m.p. 75–76° (from light petroleum), $[\alpha]_D$ −12° (*c* 0.52, chloroform) (Found: C, 48.9; H, 7.1; mol. wt., 220.0797. $C_9H_{16}O_4S$ calc.: C, 49.1; H, 7.3%; mol. wt. 220.0769). Further elution gave a mixture (0.24 g) of the two acetals and then the pure 3,4-acetal **14b** (0.61 g), m.p. 83–84° (from light

petroleum), $[\alpha]_D$ −22° (*c* 0.33, chloroform) (Found: C, 48.9; H, 7.3%; mol. wt., 220.0766.

*Methyl 3,4-O-isopropylidene-5-thio-α-D-ribopyranoside* (**14a**). — Treatment of methyl 5-thio-α-D-ribopyranoside[3] (**13a**, 1.0 g) with acetone containing sulphuric acid, as described above for the β anomer **12b**, gave a single product. Recrystallisation from light petroleum gave the 3,4-acetal **14a** (0.76 g), m.p. 99–100°, $[\alpha]_D$ +26° (*c* 0.51, chloroform) (Found: C, 49.2; H, 7.4%).

*Benzoylation of the acetals* **13b** *and* **14**. — These reactions were carried out as described earlier for the dibenzoate **11**, and the products were crystallised, where possible, from light petroleum.

Methyl 4-*O*-benzoyl-2,3-*O*-isopropylidene-5-thio-β-D-ribopyranoside (**15b**) had m.p. 66–68°, $[\alpha]_D$ −71° (*c* 0.40, chloroform) (Found: C, 58.9; H, 6.9. $C_{16}H_{20}O_5S$ calc.: C, 59.2; H, 6.2%).

Methyl 2-*O*-benzoyl-3,4-*O*-isopropylidene-5-thio-α-D-ribopyranoside (**16a**) was a syrup, $[\alpha]_D$ +39° (*c* 0.38, chloroform) (Found: C, 59.3; H, 6.2%).

Methyl 2-*O*-benzoyl-3,4-*O*-isopropylidene-5-thio-β-D-ribopyranoside (**16b**) had m.p. 109–110°, $[\alpha]_D$ −120° (*c* 0.32, chloroform) (Found: C, 59.0; H, 6.0%).

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