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Note

Reaction of *xylo*-pentodialdo-1,4-furanose and 2-methyl-2-propanethiol

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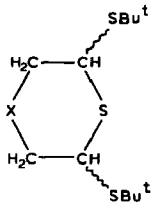
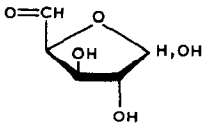
The reaction of 1,5-dialdehydes and 2-methyl-2-propanethiol in conc. hydrochloric acid affords various types of heterocyclic derivatives, such as 3,5-bis(*tert*-butylthio)-1,4-oxathiane[1] (**1**), 2,6-bis(*tert*-butylthio)-1,4-dithiane[2] (**2**), and -tetrahydrothiopyran[3] (**3**). We now report on the reaction of *xylo*-pentodialdo-1,4-furanose (**4**, *meso*-2,3,4-trihydroxypentanedial) with 2-methyl-2-propanethiol.

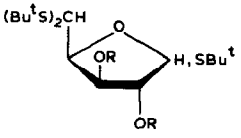
2-Methyl-2-propanethiol was treated with **4** in conc. hydrochloric acid at room temperature and the products were acetylated. Column chromatography then gave *tert*-butyl 2,3-di-*O*-acetyl-1-thio-α(or β)-DL-*xylo*-pentodialdofuranoside 5-(di-*tert*-butyl dithioacetal) (**5**, 6.1%), (5*RS*)-2,3-di-*O*-acetyl-5-*C*-(*tert*-butylthio)-1,5-thioanhydro-β-DL-xylofuranose (**8**, 5.9%), *tert*-butyl (5*SR*)-2,3,4-tri-*O*-acetyl-5-*C*-(*tert*-butylthio)-1,5-dithio-α-DL-xylopyranoside (**13**, 3.8%), (5*SR*)-1,2,3,4-tetra-*O*-acetyl-5-*C*-(*tert*-butylthio)-5-thio-α-DL-xylopyranose (**16**, 20.1%), and *tert*-butyl (5*RS*)-2,3,4-tri-*O*-acetyl-5-*C*-(*tert*-butylthio)-1,5-dithio-α-DL-xylopyranoside (**19**, 1.7%).



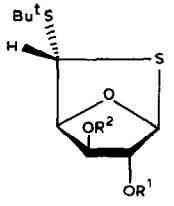
1 X = O
2 X = S
3 X = CH_2



4



5 R = Ac
6 R = H
7 R = Bz



8 $R^1 = R^2 = Ac$
9 $R^1 = R^2 = Bz$
10 $R^1 = Ac, R^2 = Bz$
11 $R^1 = R^2 = H$
12 $R^1 = Ac, R^2 = H$

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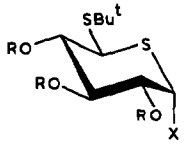

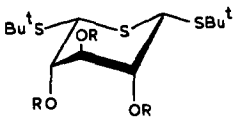

13 R = Ac, X = SBu^t 16 R = X = Ac
14 R = H, X = SBu^t 17 R = X = H
15 R = Bz, X = SBu^t 18 R = X = Bz

19 R = Ac
20 R = H
21 R = Bz

Compound **5** was identified** on the basis of its elemental analysis, i.r., and ^{1}H-n.m.r. spectra, but the configuration at the anomeric carbon atom could not be established[4,5] since $J_{1,2}$ was 5 Hz. Treatment of **5** with sodium methoxide in methanol gave *tert*-butyl 1-thio-α(or β)-DL-*xylo*-pentodialdo-1,4-furanoside 5-(di-*tert*-butyl dithioacetal) (**6**), which was further transformed into *tert*-butyl 2,3-di-*O*-benzoyl-1-thio-α(or β)-*xylo*-pentodialdo-1,4-furanoside 5-(di-*tert*-butyl dithioacetal) (**7**). As for **5** above, the anomeric configurations in **6** and **7** could not be determined from their ^{1}H-n.m.r. spectra.

Compound **8** was identified on the basis of elemental analysis, and i.r., ^{1}H-, and ^{13}C-n.m.r. spectra. Treatment of **8** with methanolic sodium methoxide gave a mixture of (5*RS*)-5-*C*-(*tert*-butylthio)-1,5-thioanhydro-β-DL-xylofuranose (**11**) with the partially deacetylated derivative (5*RS*)-2-*O*-acetyl-5-*C*-(*tert*-butylthio)-1,5-thioanhydro-β-DL-xylofuranose (**12**). No attempt was made to resolve this mixture, but it was benzoylated to give the expected (5*RS*)-2,3-di-*O*-benzoyl-5-*C*-(*tert*-butylthio)-1,5-thioanhydro-β-DL-xylofuranose (**9**) and (5*RS*)-2-*O*-acetyl-3-*O*-benzoyl-5-*C*-(*tert*-butylthio)-1,5-thioanhydro-β-DL-xylofuranose (**10**), which were isolated by column chromatography. The ^{1}H-n.m.r. spectra of **8–10** each contained three singlets in the ranges δ 5.8–5.57, 5.45–4.93, and 4.8–4.58 (H-1, H-4, and H-5, respectively), indicating zero values for $J_{1,2}$, $J_{3,4}$, and $J_{4,5}$, and therefore dihedral angles between the relevant vicinal protons of ~90°. Comparisons of this dihedral angle with the two possible angles between H-4 and H-5, determined from appropriate mechanical models, allowed the relative configuration at C-5 to be established. On the other hand, the values δ 5.57 and 5.63 (H-1), and δ 4.93 and 5.12 (H-4) for **8** and **10**, respectively, led to the view that the acetyl groups were at position 2 in **10** and **12**.

Compounds **13** and **16** were identified on the basis of elemental analysis, i.r., and ^{1}H-n.m.r. spectra. Each compound was treated with methanolic sodium methoxide, yielding *tert*-butyl (5*SR*)-5-*C*-(*tert*-butylthio)-1,5-dithio-α-DL-xylopyranoside (**14**) and (5*SR*)-5-*C*-(*tert*-butylthio)-5-thio-α-DL-xylopyranose (**17**), respectively. *tert*-Butyl (5*SR*)-2,3,4-tri-*O*-benzoyl-5-*C*-(*tert*-butylthio)-1,5-dithio-α-DL-xylopyranoside (**15**) and (5*SR*)-1,2,3,4-tetra-*O*-benzoyl-5-*C*-(*tert*-butylthio)-5-thio-α-DL-xylopyranose (**18**) were obtained by benzoylation of **14** and **17**,

**Only D forms are depicted in the formulae.

respectively. The couplings ($J_{1,2}$ 3–4.5, $J_{2,3}$ ~10, $J_{3,4}$ ~9, and $J_{4,5}$ ~1 Hz) for **13–18** were in agreement with those expected for the α anomers of the 5*SR* and DL-*xylo* configurations in their $^4C_1$ conformations.

Compound **19**, which was a *meso* form, gave *tert*-butyl (5*RS*)-5-*C*-(*tert*-butylthio)-1,5-dithio-α-DL-xylopyranoside (**20**) on transesterification with methanol, and benzoylation then gave *tert*-butyl (5*RS*)-2,3,4-tri-*O*-benzoyl-5-*C*-(*tert*-butylthio)-1,5-dithio-α-DL-xylopyranoside (**21**). The couplings $J_{1,2} = J_{4,5} = \sim 2.5$ and $J_{2,3} = J_{3,4} = \sim 4$ Hz for **19** and **21** were as expected for the α anomers with 5*RS* and DL-*xylo* configurations and $^1C_4$ conformations.

EXPERIMENTAL

General methods. — Organic solutions were dried over anhydrous Na_2SO_4. Solvents were evaporated under diminished pressure at <40°. Column chromatography was carried out on Silica Gel 60 (Merck, 70–230 mesh, ASTM). Melting points (uncorrected) were obtained with an Electrothermal apparatus. I.r. spectra were recorded for films on NaCl or KBr discs with a Pye Unicam SP 1000 spectrometer. ^{1}H- (80 MHz) and ^{13}C-n.m.r. (20 MHz) spectra were recorded with a Bruker WP-80-SY spectrometer, and, for compounds **13** and **16**, with a 200-MHz spectrometer of the University of Barcelona (Central, Spain).

Reaction of xylo-*pentodialdo-1,4-furanose* (**4**) *and 2-methyl-2-propanethiol.* — A solution of 1,2-*O*-isopropylidene-α-D-glucofuranose[7] (11 g) in water (75 mL) was treated with $NaIO_4$ (11.5 g), and the resulting[8] crude product was kept in vacuum over conc. sulfuric acid for 24 h. A mixture of this anhydrous material (7.91 g), water (10 mL), and aqueous 20% hydrochloric acid (3 mL) was heated at 80°, after ~1 h, the $[\alpha]_D$ value was ~0°, the acetone formed in the reaction had evaporated, and an aqueous solution of **4** remained.

A mixture of this solution, 2-methyl-2-propanethiol (25 mL), and conc. hydrochloric acid (16 mL) was stirred at room temperature for 2 h, then diluted with water (25 mL), basified with Na_2CO_3, and extracted with ethyl acetate (3 × 50 mL). The combined extracts were dried, filtered, and concentrated. The syrupy residue was treated conventionally with pyridine–acetic anhydride.

Chromatography (10:1 hexane–ether) of the mixture of products gave, first, *tert*-butyl 2,3-di-*O*-acetyl-1-thio-α(or β)-DL-*xylo*-pentodialdo-1,4-furanoside 5-(di-*tert*-butyl dithioacetal) (**5**; 1.47 g, 6.1%); ν_{max} 1755 and 1230 cm^{-1} (acetate). ^{1}H-N.m.r. ($CDCl_3$) data: δ 5.8 (d, 1 H, $J_{1,2}$ 5 Hz, H-1), 5.6 (dd, 1 H, $J_{2,3}$ 3.3, $J_{3,4}$ 5.5 Hz, H-3), 5.4 (dd, 1 H, $J_{1,2}$ 5, $J_{2,3}$ 3.3 Hz, H-2), 4.75 (t, 1 H, $J_{3,4} = J_{4,5} = 5.5$ Hz, H-4), 4.15 (d, 1 H, $J_{4,5}$ 5.5 Hz, H-5), 2.17 (s, 3 H, CH_3), 2.12 (s, 3 H, CH_3), and 1.4 (s, 27 H, 3 Me_3C) (Found: C, 54.2; H, 8.0. $C_{21}H_{38}O_5S_3$ calc.: C, 54.0; H, 8.2%).

Eluted second was (5*RS*)-2,3-di-*O*-acetyl-5-*C*-(*tert*-butylthio)-1,5-thioanhydro-β-DL-xylofuranose (**8**, 0.29 g), m.p. 125–127° (from hexane); ν_{max} 1735 and 1224 cm^{-1} (acetate). N.m.r. ($CDCl_3$) data: ^{1}H, δ 5.57 (bs, 1 H, H-4), 5.1 (d, 1 H, $J_{1,2}$ 6 Hz, H-1), 4.93 (m, 2 H, H-2,3), 4.58 (s, 1 H, H-5), 2.22 (s, 3 H, CH_3),

2.13 (s, 3 H, CH_3), and 1.4 (s, 9 H, Me_3C); ^{13}C, δ 170.84, 169.86, 20.73, and 20.5 (2 CH_3–CO), 86.1 and 85.86 (C-1,4), 81.26 and 78.0 (C-2,3), 47.53 (C-5), 44.79 and 30.93 (Me_3C) (Found: C, 48.6; H, 6.4. $C_{13}H_{20}O_5S_2$ calc.: C, 48.7; H, 6.3%).

Eluted third was a mixture (1.6 g) of **8** and *tert*-butyl (5*SR*)-2,3,4-tri-*O*-acetyl-5-*C*-(*tert*-butylthio)-1,5-dithio-α-DL-xylopyranoside (**13**).

Eluted fourth was a mixture (5.43 g) of (5*SR*)-1,2,3,4-tetra-*O*-acetyl-5-*C*-(*tert*-butylthio)-5-thio-α-DL-xylopyranose (**16**) and *tert*-butyl (5*RS*)-2,3,4-tri-*O*-acetyl-5-*C*-(*tert*-butylthio)-1,5-dithio-α-DL-xylopyranoside (**19**).

The mixture of **8** and **13** was rechromatographed (20:1 hexane–ether), to give **8** (0.69 g; overall yield, 5.9%) and **13** (0.894 g, 3.84%), m.p. 158–160° (from hexane); ν_{max} 1760 and 1240 cm^{-1} (acetate). ^1H-N.m.r. ($CDCl_3$) data: δ 5.24 (dd, 1 H, $J_{2,3}$ 10.2, $J_{3,4}$ 8.9 Hz, H-3), 5.1 (dd, 1 H, $J_{1,2}$ 4.25, $J_{2,3}$ 10.2 Hz, H-2), 5.05 (dd, 1 H, $J_{3,4}$ 8.9, $J_{4,5}$ 10.7 Hz, H-4), 4.26 (d, 1 H, $J_{1,2}$ 4.25 Hz, H-1), 4.16 (d, 1 H, $J_{4,5}$ 10.7 Hz, H-5), 2.04 (s, 6 H, 2 CH_3), 1.37 (s, 9 H, Me_3C), and 1.35 (s, 9 H, Me_3C) (Found: C, 50.6; H, 7.1. $C_{19}H_{32}O_6S_3$ calc.: C, 50.4; H, 7.1%).

Crystallisation of the mixture of **16** and **19** from hexane gave **16** (3.91 g), m.p. 171–173°; ν_{max} 1760, 1250, and 1216 cm^{-1} (acetate). ^1H-N.m.r. ($CDCl_3$) data: δ 6.0 (d, 1 H, $J_{1,2}$ 3 Hz, H-1), 5.43 (dd, 1 H, $J_{2,3}$ 10.3, $J_{3,4}$ 9.4 Hz, H-3), 5.25 (dd, 1 H, $J_{1,2}$ 3, $J_{2,3}$ 10.3 Hz, H-2), 5.15 (dd, 1 H, $J_{3,4}$ 9.4, $J_{4,5}$ 10.9 Hz, H-4), 4.05 (d, 1 H, $J_{4,5}$ 10.9 Hz, H-5), 2.19 (s, 3 H, CH_3), 2.06 (s, 3 H, CH_3), 2.0 (s, 3 H, CH_3), 1.98 (s, 3 H, CH_3), and 1.34 (s, 9 H, Me_3C) (Found: C, 48.6; H, 6.1. $C_{17}H_{26}O_8S_2$ calc.: C, 48.3; H, 6.2%.) The material in the mother liquor was subjected to column chromatography (10:1 hexane–ether), to give **19** (0.4 g, 1.73%), m.p. 191–193° (from hexane); ν_{max} 1778, 1760, 1750, 1240, and 1210 cm^{-1} (acetate). ^1H-N.m.r. ($CDCl_3$) data: δ 5.28 (m, 1 H, H-3), 5.07 (dd, 2 H, $J_{1,2} = J_{4,5} = 2.3$, $J_{2,3} = J_{3,4} = 4.1$ Hz, H-2,4), 4.22 (d, 2 H, $J_{1,2} = J_{4,5} = 2.3$ Hz, H-1,5), 2.14 (s, 3 H, CH_3), 2.08 (s, 6 H, CH_3), and 1.34 (s, 18 H, 2 Me_3C) (Found: C, 50.5; H, 7.1. $C_{19}H_{32}O_6S_3$ calc.: C, 50.4; H, 7.1%), and **16** (0.46 g; overall yield, 20.1%).

Deacetylation of **5, 8, 13, 16,** *and* **19,** *and formation of benzoylated derivatives.* — A mixture of the acetylated derivative, methanol, and sodium methoxide (0.1 g) was left at room temperature for 5 h and then concentrated, water (7 mL) was added, and the solution was extracted several times with ethyl acetate. The combined extracts were dried, filtered, and concentrated. The following conditions were used:

Starting material (g)	*Methanol (mL)*	*Ethyl acetate (mL)*	*Products (g, %)*
5 (0.848)	8	1 × 15	**6** (0.4, 61.4)
8 (0.688)	20	1 × 50	**11,12** (0.48)
13 (0.5)	10	1 × 25	**14** (0.16, 44.3)
16 (0.2)	25	4 × 25	**17** (0.1, 83)
19 (0.18)	18	1 × 25	**20** (0.1, 77.5)

tert-Butyl 1-thio-α(or β)-DL-*xylo*-pentodialdo-1,4-furanoside 5-(di-*tert*-butyl

dithioacetal) (**6**) had m.p. 125–127° (from hexane); ν_{max} 3500 and 1158 cm^{-1} (OH). ^{1}H-N.m.r. ($CDCl_3$) data: δ 5.62 (d, 1 H, $J_{1,2}$ 4 Hz, H-1), 4.7–4.12 (m, 4 H, H-2,3,4,5), 3.42 (d, 1 H, $J_{H,OH}$ 4.5 Hz, OH; proton exchangeable with D_2O), 2.3 (bs, 1 H, OH; proton exchangeable with D_2O), and 1.4 (s, 27 H, 3 Me_3C) (Found: C, 53.4; H, 8.9. $C_{17}H_{34}O_3S_3$ calc.: C, 53.3; H, 8.9%).

Conventional benzoylation of **6** (0.285 g) and column chromatography (hexane) of the product afforded *tert*-butyl 2,3-di-*O*-benzoyl-1-thio-α(or β)-*xylo*-pentodialdo-1,4-furanoside 5-(di-*tert*-butyl dithioacetal) (**7**; 0.22 g, 50%), m.p. 125–127° (from hexane); ν_{max} 1730 and 1255 cm^{-1} (benzoate). ^{1}H-N.m.r. ($CDCl_3$) data: δ 8.1 and 7.5 (m, 10 H, 2 C_6H_5), 6.0–5.7 (m, 3 H, H-1,2,3), 4.9 (t, 1 H, $J_{3,4} = J_{4,5}$ = 5.5 Hz, H-4), 4.17 (d, 1 H, $J_{4,5}$ 5.5 Hz, H-5), 1.42 (s, 18 H, 2 Me_3C), and 1.37 (s, 9 H, Me_3C) (Found: C, 63.2; H, 7.1. $C_{31}H_{42}O_5S_3$ calc.: C, 63.0; H, 7.1%).

The syrupy mixture (0.48 g) of (5*RS*)-5-*C*-(*tert*-butylthio)-1,5-thioanhydro-β-DL-xylofuranose (**11**) and (5*RS*)-2-*O*-acetyl-5-*C*-(*tert*-butylthio)-1,5-thioanhydro-β-DL-xylofuranose (**12**) was conventionally benzoylated, and column chromatography (15:1 hexane–ether) of the product gave, first, (5*RS*)-2,3-di-*O*-benzoyl-5-*C*-(*tert*-butylthio)-1,5-thioanhydro-β-DL-xylofuranose (**9**, 0.434 g), m.p. 109–110° (from ethanol–water); ν_{max} 1730 and 1280–1250 cm^{-1} (benzoate). N.m.r. ($CDCl_3$) data: ^{1}H, δ 8.1 and 7.57 (m, 10 H, 2 C_6H_5), 5.8 (bs, 1 H, H-4), 5.45 (m, 3 H, H-1,2,3), 4.8 (s, 1 H, H-5), and 1.4 (s, 9 H, Me_3C); ^{13}C, 165.77, 133.86, 133.5, 129.83, 129.14, 128.74, and 128.45 (2 C_6H_5CO), 86.33 and 86.21 (C-1,4), 81.81 and 78.56 (C-2,3), 47.65 (C-5), 44.79 and 30.86 (Me_3C) (Found: C, 61.9; H, 5.5. $C_{23}H_{24}O_5S_2$ calc.: C, 62.1; H, 5.4%).

Eluted second was (5*RS*)-2-*O*-acetyl-3-*O*-benzoyl-5-*C*-(*tert*-butylthio)-1,5-thioanhydro-β-DL-xylofuranose (**10**, 0.175 g), m.p. 126–127° (from ethanol–water); ν_{max} 1750 and 1270 (acetate), 1725 and 1240 cm^{-1} (benzoate). N.m.r. ($CDCl_3$) data: ^{1}H, δ 8.1 and 7.55 (m, 5 H, C_6H_5), 5.63 (bs, 1 H, H-4), 5.25 (d, 1 H, $J_{1,2}$ 6 Hz, H-1), 5.12 (m, 2 H, H-2,3), 4.66 (s, 1 H, H-5), 2.13 (s, 3 H, CH_3), and 1.3 (s, 9 H, Me_3C); ^{13}C, δ 170.15 and 20.79 (CH_3CO), 165.79, 133.92, 133.69, 130.19, 129.79, 128.8, and 128.68 (C_6H_5CO), 86.27 and 86.03 (C-1,4), 81.43 and 78.69 (C-2,3), 47.65 (C-5), 44.85 and 30.93 (Me_3C) (Found: C, 56.4; H, 5.9. $C_{18}H_{22}O_5S_2$ calc.: C, 56.5; H, 5.8%).

tert-Butyl (5*SR*)-5-*C*-(*tert*-butylthio)-1,5-dithio-α-DL-xylopyranoside (**14**) had m.p. 113–115° (from hexane–ether); ν_{max} 3550–3300 cm^{-1} (OH). ^{1}H-N.m.r. ($CDCl_3$) data: δ 4.0 (m, 3 H, H-1,3,5), 3.35 (m, 2 H, H-2,4), 3.0 and 3.2 (2 bs, each 1 H, 2 OH; protons exchangeable with D_2O), 2.62 (m, 1 H, OH; proton exchangeable with D_2O), and 1.4 (s, 18 H, 2 Me_3C) (Found: C, 47.9; H, 8.2. $C_{13}H_{26}O_3S_3$ calc.: C, 47.8; H, 8.0%).

Conventional benzoylation of **14** (0.16 g) and column chromatography (5:1 hexane–ether) of the product afforded *tert*-butyl (5*SR*)-2,3,4-tri-*O*-benzoyl-5-*C*-(*tert*-butylthio)-1,5-dithio-α-DL-xylopyranoside (**15**; 0.231 g, 80%), m.p. 153–154° (from ethanol–water); ν_{max} 1730, 1272, and 1250 cm^{-1} (benzoate). ^{1}H-N.m.r. ($CDCl_3$) data: δ 7.9 and 7.4 (m, 15 H, 3 C_6H_5), 5.9 (dd, 1 H, $J_{2,3}$ 10, $J_{3,4}$ 9 Hz, H-3),

5.62 (dd, 1 H, $J_{3,4}$ 9, $J_{4,5}$ 11 Hz, H-4), 5.55 (dd, 1 H, $J_{2,3}$ 10, $J_{1,2}$ 4.3 Hz, H-2), 4.57 (d, 1 H, $J_{1,2}$ 4.3 Hz, H-1), 4.47 (d, 1 H, $J_{4,5}$ 11 Hz, H-5), and 1.33 (s, 18 H, 2 Me_3C) (Found: C, 64.1; H, 5.9. $C_{34}H_{38}O_6S_3$ calc.: C, 63.9; H, 6.0%).

(5*SR*)-5-*C*-(*tert*-Butylthio)-5-thio-α-DL-xylopyranose (**17**) had m.p. 189–192° (from ethyl acetate); ν_{max} 3400, 3250, 1112, and 1087 cm^{-1} (OH, C-O). ^{1}H-N.m.r. [$(CD_3)_2SO$] data: δ 5.8 (bs, 1 H, OH; proton exchangeable with D_2O), 5.0 (m, 1 H, OH; proton exchangeable with D_2O), 4.65 (m, 3 H, 2 OH, H-1; two protons exchangeable with D_2O and the multiplet was transformed into a doublet $J_{1,2}$ 3 Hz), 3.9 (d, 1 H, $J_{4,5}$ 10 Hz, H-5), 3.6–3.2 (m, 3 H, H-2,3,4), and 1.4 (s, 9 H, Me_3C) (Found: C, 42.5; H, 6.9. $C_9H_{18}O_4S_2$ calc.: C, 42.5; H, 7.1%).

Conventional benzoylation of **17** gave (5*SR*)-1,2,3,4-tetra-*O*-benzoyl-5-*C*-(*tert*-butylthio)-5-thio-α-DL-xylopyranose (**18**; 0.11 g, 70%), m.p. 174–176° (from ethanol–water); ν_{max} 1736, 1284, 1262, 1250 cm^{-1} (benzoate). ^{1}H-N.m.r. ($CDCl_3$) data: δ 8.25–7.1 (m, 20 H, 4 C_6H_5), 6.5 (d, 1 H, $J_{1,2}$ 3 Hz, H-1), 6.29 (dd, 1 H, $J_{2,3}$ 11, $J_{3,4}$ 9 Hz, H-3), 5.85 (dd, 1 H, $J_{1,2}$ 3, $J_{2,3}$ 11 Hz, H-2), 5.78 (m, 1 H, H-4), 4.45 (d, 1 H, $J_{4,5}$ 11 Hz, H-5), and 1.26 (s, 9 H, Me_3C) (Found: C, 66.1; H, 5.2. $C_{37}H_{34}O_8S_2$ calc.: C, 66.2; H, 5.1%).

tert-Butyl (5*RS*)-5-*C*-(*tert*-butylthio)-1,5-dithio-α-DL-xylopyranoside (**20**) had m.p. 160–161° (from hexane–ether); ν_{max} 3500–3200 (OH), 1158, 1093, 1060, and 1050 cm^{-1} (C-O). ^{1}H-N.m.r. ($CDCl_3$) data: δ 4.41 (d, 2 H, $J_{1,2} = J_{4,5}$ = 2.3 Hz, H-1,5), 3.92 (m, 4 H, OH, H-2,3,4; one proton exchangeable with D_2O), 3.5 (m, 2 H, 2 OH; two protons exchangeable with D_2O), and 1.42 (s, 18 H, 2 Me_3C) (Found: C, 48.0; H, 7.9. $C_{13}H_{26}O_3S_3$ calc.: C, 47.8; H, 8.0%).

Conventional benzoylation of **20** (0.06 g) and column chromatography (10:1 hexane–ether) of the product afforded *tert*-butyl (5*RS*)-2,3,4-tri-*O*-benzoyl-5-*C*-(*tert*-butylthio)-1,5-dithio-α-DL-xylopyranoside (**21**; 0.106 g, 89%), m.p. 167–168° (from hexane–ether); ν_{max} 1740, 1726, 1275, and 1257 cm^{-1} (benzoate). ^{1}H-N.m.r. ($CDCl_3$) data: δ 8.1–7.1 (m, 15 H, 3 C_6H_5), 5.9 (t, 1 H, $J_{2,3} = J_{3,4}$ = 4 Hz, H-3), 5.52 (dd, 2 H, $J_{2,3} = J_{3,4}$ = 4, $J_{1,2} = J_{4,5}$ = 2.5 Hz, H-2,4), 4.58 (d, 2 H, $J_{1,2} = J_{4,5}$ = 2.5 Hz, H-1,5), and 1.4 (s, 2 Me_3C) (Found: C, 63.7; H, 5.9. $C_{34}H_{38}O_6S_3$ calc.: C, 63.9; H, 6.0%).

REFERENCES

1 F. J. Lopez Aparicio, F. Zorrilla Benitez, and F. Santoyo Gonzalez, *Carbohydr. Res.*, 102 (1982) 69–81.
2 F. J. Lopez Aparicio, F. Zorrilla Benitez, and F. Santoyo Gonzalez, *Carbohydr. Res.*, 110 (1982) 195–205.
3 F. J. Lopez Aparicio, F. Zorrilla Benitez, and F. Santoyo Gonzalez, *An. Quim., Ser. C*, 79 (1983) 158–164.
4 R. U. Lemieux, J. D. Stevens, and R. Fraser, *Can. J. Chem.*, 40 (1962) 1955–1959.
5 K. L. Rinehart, W. S. Chilton, M. Hickens, and W. Phillipsborn, *J. Am. Chem. Soc.*, 84 (1962) 3216–3218.
6 J. A. May and L. B. Townsend, *J. Org. Chem.*, 41 (1976) 1449–1456.
7 O. Th. Schmidt, *Methods Carbohydr. Chem.*, 2 (1970) 318–325.
8 M. L. Wolfrom and G. H. S. Thomas, *Methods Carbohydr. Chem.*, 2 (1970) 32–34.