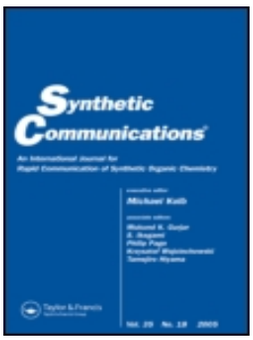

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SYNTHESIS OF FOUR ESTER PROTECTED THIOFURANOSE SUGARS

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ABSTRACT

The products obtained by titanium tetrachloride mediated dithioacetalization of four pentofuranoside derivatives were converted to thiofuranose sugars, either by direct cyclization via the unstable triflate intermediate, or by treatment of the derived mesylate. A facile inversion of a D-ribose dibenzyl dithioacetal **9** to an L-lyxose dibenzyl dithioacetal **12** via hydrolysis of the Mitsunobu derived formate intermediate is also described.

INTRODUCTION

A variety of methods have been reported in the literature for the synthesis of thiofuranose sugars,[1–7] in which the hydroxyls are protected by ester groups. In the synthesis of benzyl-2-deoxy-3,5-di-*O*-*p*-toluoyl-1,4-dithio-D-erythro-pentofuranoside, reported by Dyson et al.,[3] benzyl ether

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protection was used throughout, and after a subsequent debenzylation procedure using boron trichloride at low temperature, esterification was achieved at the end of the reaction sequence. Bredenkamp et al.[4,5] describe the synthesis of 1-thiobenzyl-2,3,5-tri-*O*-benzoyl-4-thio-D-xylose via a tin complex of L-arabinose.

Imbach et al. have described the synthesis of thioriboses protected by benzyl groups[8,9] and more recently have described a synthesis of 1-*O*-acetyl-2,3,5-tri-*O*-benzoyl-4 thioribofuranose from L-lyxose, in 14% overall yield.[7]

We now report our work in which we have synthesised a variety of 4-thiofuranoses with ester protection. We also report the synthesis of a D-thioribose starting from a readily available D-thioribose and avoiding the use of expensive L-lyxose derivatives.

Thus the L-thioarabinose **3** and L-thiolyxose **10** were made from the D-xylose **1** and the D-ribose **8** derivatives respectively, while the D-thioxylose **6** and D-thioribose **13** were made from the L-arabinose **4** and L-lyxose **11**. In addition a facile inversion at the C-4 position provided a means of converting the D-ribose dithioacetal **9** to the L-lyxose dithioacetal **12**, thus avoiding the use of the very expensive L-lyxose **11** starting material for the synthesis of D-thioribose **13**. Surprisingly an attempt to convert the D-xylose-dithioacetal **2** to the L-arabinose dithioacetal **5**, under the same conditions failed.

DISCUSSION

The initial step in the synthesis involved conversion of the appropriate tribenzoyl substituted furanoside **1**, **4**, **8** or **11** to the open chain dibenzyl dithioacetal **2**, **5**, **9** or **12** using benzyl mercaptan in the presence of a catalytic amount of titanium tetrachloride.[5] While some ester migration was observed in this reaction, under the conditions employed the required dibenzyl dithioacetals constituted the major products. In the case of **5**, a minor side-product was isolated and tentatively identified from its ^{1}H NMR spectrum as 1-thiobenzyl-2,3,5-tri-*O*-benzoyl-L-arabinose the expected intermediate in this reaction. The crystallised materials thus obtained appeared to be quite stable, whereas alcoholic solutions showed evidence of further migration. The crude dithioacetals were purified by chromatography on silica, and with the exception of **12** appeared reasonably stable to this procedure. The exception **12** underwent considerable migration and could only be obtained in 26% yield as a result.

Conversion of the dibenzyl dithioacetals to thiofuranose sugars was achieved either by mesylation of the 4-hydroxyl followed by cyclisation, or

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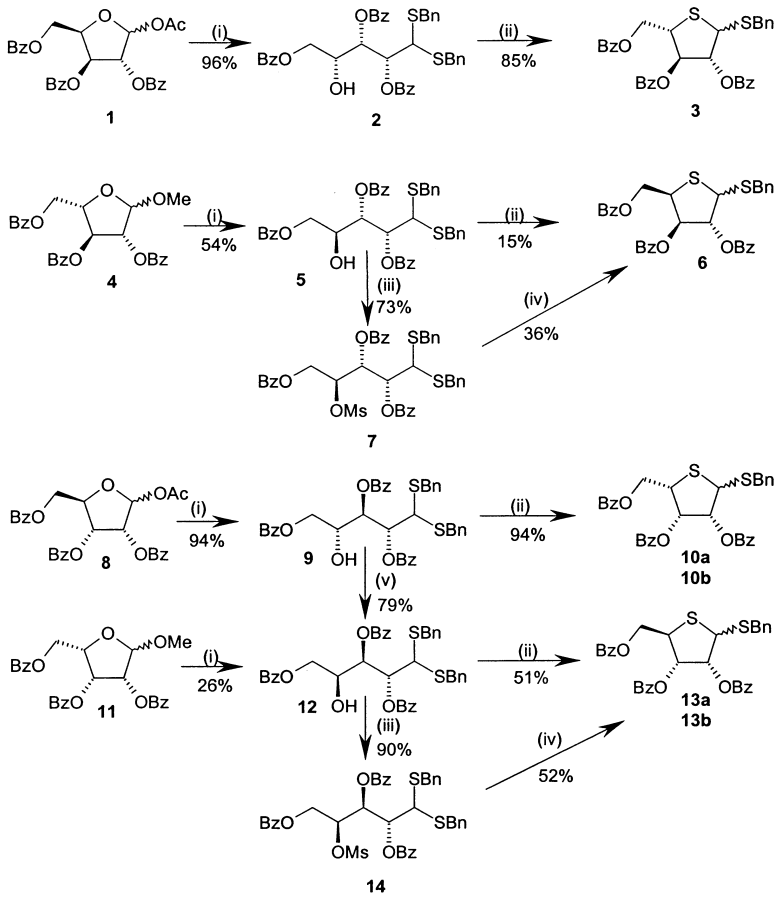
directly by treatment with triflic anhydride in pyridine. Cyclisation of the mesylate was carried out either by heating a solution of the mesylate in butan-2-one in the presence of sodium iodide and triethylamine, as in the case of **7**, or simply by heating in xylene as in the case of **14**. The more direct treatment with triflic anhydride was found when an unsuccessful attempt was made to invert the C-4 hydroxyl using the method of Coe et al.,[10] and with the exception of the L-arabinose dithioacetal **5**, gave better overall



Reagents: (i) BnSH, $TiCl_4$, toluene, (ii) trifluoromethanesulphonic anhydride, pyridine, (iii) methanesulphonyl chloride, pyridine, chloroform, (iv) NaI, Et_3N, 2-butanone, or alternatively reflux in xylene, (v) formic acid, PPh_3, DEAD, toluene, then MeOH, Amberlyst.

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yields. The exception **5** gave the D-thioxylose **6** in 15% crude yield, however no attempt was made to optimise this reaction, which may be capable of improvement. The β-anomer was the major product in each case, and in the case of L-thioarabinose **3** was formed almost exclusively.

Attempts to invert the C-4 position and simultaneously introduce a mesyl or tosyl group using the appropriate zinc sulphonate[11] under Mitsunobu conditions proved futile in our hands, as did various other means of effecting this inversion.

However, the introduction of a formate ester, using formic acid, triphenylphosphine and DEAD,[12] followed by its methanolysis in the presence of the acidic resin Amberlyst-15, provided a means of converting **9** to **12**. The reasons for the failure of **2** to undergo a similar inversion to **5** are not clear. While a variety of ester functions could be introduced in this way, attempts to remove them resulted in scrambling to give a mixture of isomeric dithioacetals having a hydroxyl in the 2,3 or 4-position, even under such mild conditions as aqueous bicarbonate. Formate proved capable of removal with only limited scrambling.

EXPERIMENTAL

IR spectra were recorded using a Perkin-Elmer 1605 FT spectrometer.

^{1}H NMR spectra were recorded in $CDCl_3$ in a Bruker AC300 instrument (300 MHz) with tetramethylsilane as internal standard (*J* values are given in Hz).

Mass spectra were recorded on a Finnigan MAT 4500 instrument.

M.p.s. were recorded with a Buchi m.p. apparatus and were uncorrected.

Solvents were dried over $MgSO_4$ and were evaporated under reduced pressure using a rotary evaporator.

Thin-layer-chromatography was carried out on silica gel plates using toluene-ethyl acetate, 10 : 1, as eluent.

Column chromatography was carried out on silica (70–230 mesh).

2,3,5-Tri-*O*-benzoyl-D-xylose Dibenzyl Dithioacetal 2

A mixture of 1-*O*-acetyl-2,3-5-tri-*O*-benzoyl-D-xylofuranose **1** (10.1 g, 0.02 mole), benzyl mercaptan (23.6 mL, 0.2 mole) and anhydrous toluene (10 mL) was stirred while cooling in an ice-bath. Titanium tetrachloride (1.1 mL, 0.01 mole) was added, giving a red solution. After 10 min the ice-bath was removed and the mixture was stirred at room temperature for 2 h.

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The solution was then poured into sat. sodium bicarbonate solution (200 mL) and the product extracted into ether (3 × 100 mL). The extracts were washed with sat. sodium bicarbonate solution (2 × 100 mL) then with sat. brine (100 mL) and dried. Removal of the ether left a colourless oil (36.7 g). Column chromatography on silica (500 g), using toluene–ethyl acetate (10 : 1) as eluent afforded 2,3,5-*tri-O-benzoyl-*D*-xylose dibenzyl dithioacetal* **2** as a colourless gum (13.26 g, 96%) which crystallised over several weeks. Recrystallisation of part (5.0 g) of this solid from methanol (40 mL) gave a white crystalline solid (2.8 g); mp 109–111°C (found: C, 69.01; H, 5.24; S. 9.73. $C_{40}H_{36}O_7S_2$ requires C, 69.34; H, 5.24; S, 9.26%); ν max (Nujol)/cm^{-1} 3532 (OH), 1728 (CO) and 1718 (CO); $^{\delta}$H 7.90–7.56 (6H, 3d, 3 ^{o}Bz), 7.50–6.75 (19H, m, 2Bn and 3^{m,p} Bz) 6.40 (1H, dd, *J* 3 and 8, H2), 5.67 (1H, dd, *J* 2 and 8. H3), 4.09 (1H, dd, *J* 6 and 12, H5), 4.03 (1H, dd *J* 4 and 12, H5′), 3.81 (1H, d, *J* 14, 1/2 SCH_2), 3.70 (1H, d, *J* 3, 1H), 3.68 (1H, d, *J* 5, 1/2 SCH_2), 3.63 (1H, d, *J* 5, 1/2 SCH_2), 3.56 (1H, d, *J* 14, 1/2 SCH_2), 3.07 (1H, m, H4).

2,3,5-Tri-*O*-benzoyl-L-arabinose Dibenzyl Dithioacetal 5

A mixture of 1-*O*-methyl-2,3,5-tri-*O*-benzoyl-L-arabinofuranose (20.0 g, 0.042 mole) and benzylmercaptan (50 mL, 0.42 mole) was treated with titanium tetrachloride (2.2 mL, 0.02 mole) as for **2** above. Work-up after 4 h followed by chromatography gave the minor component, 1-*thiobenzoyl*-2,3,5-*tri-O-benzyl-*L*-arabinose*, as a gum (0.97 g, 4%); $^{\delta}$H 8.01 (2H, d, ^{o}Bz), 7.95 (2H, d, ^{o}Bz), 7.88 (2H, d, ^{o}Bz), 7.50–7.02 (14H, m, Bn and ^{m,p}Bz), 5.52 (1H, d, *J* 4, H3), 5.46 and 5.38 (2H, 2S, H1 and H2), 4.67 (3H, m, H4 and H5), 3.38 (1H, d, *J* 13, 1/2 SCH_2), 3.27 (1H, d, *J* 13 1/2 SCH_2).

The major component 2,3,5-*tri-O-benzoyl-*L*-arabinose dibenzyl dithioacetal* **5**, was obtained as a brittle foam (15.77 g, 54%); (Found: C, 68.43; H, 5.20; S, 9.98. $C_{40}H_{36}O_7S_2$ requires C, 69.43; H, 5.24; S, 9.26%); ν max (melt)/cm^{-1} 3498 (OH), 1724 (CO); $^{\delta}$H 7.97 (2H, d, ^{o}Bz), 7.92 (2H, d, ^{o}Bz), 7.86 (2H, d, ^{o}Bz), 7.52–6.96 (19H, m, Bn and ^{m,p}Bz), 5.74 (2H, m, H2 and H3), 4.34 (1H, dd, *J* 3 and 12, H5), 4.17 (1H, dd, *J* 6 and 12, H5′), 3.81 (2H, m, H1 and H4), 3.74 (2H, s, SCH_2), 3.69 (2H, s, SCH_2).

2,3,5-Tri-*O*-benzoyl-D-ribose Dibenzyl Dithioacetal 9

A mixture of 1-*O*-acetyl-2,3,5-tri-*O*-benzoyl-β-D-ribofuranose **8** (9.68 g, 0.0192 mole) and benzylmercaptan (22.7 mL, 0.192 mole) was treated with titanium tetrachloride (1.1 mL, 0.01 mole) as for **5** above. Work-up

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after 2 h followed by chromatography gave 2,3,5-*tri-O-benzoyl-D-ribose dibenzyl dithioacetal* **9** as a colourless gum (12.57 g, 94%), which crystallised over several weeks. Recrystallisation from methanol gave colourless crystals, m.p. 92–93°C; (Found: C, 69.26; H, 5.19; S, 9.82. $C_{40}H_{36}O_7S_2$ requires C, 69.34; H, 5.24; S, 9.26%); ν max (Nujol)/cm^{-1} 3510 (OH), 1725 (CO) and 1705 (CO); $^{\delta}$H 8.08 (2H, d, ^{o}Bz), 8.01 (2H, d, ^{o}Bz), 7.78 (2H, d, ^{o}Bz), 7.62–6.88 (19H, m, Bn and ^{m,p}Bz), 5.98 (1H, dd, *J* 5 and 6, H2), 5.82 (1H, dd, *J* 5 and 6, 3H), 4.50 (1H, dd, *J* 4 and 12, H5), 4.33 (1H, dd, *J* 6 and 12, H5′), 4.22 (1H, ddd, *J* 4, 5 and 6, H4), 4.01 (1H, d, *J* 5, H1), 3.92 (1H, d, *J* 14, 1/2 SCH_2), 3.77 (1H, d, *J* 14, 1/2 SCH_2) 3.74 (2H, ABq, SCH_2).

2,3,5-Tri-*O*-benzoyl-L-lyxose Dibenzyl Dithioacetal 12

A mixture of 2,3,5-tri-*O*-benzoyl-D-ribose dibenzyl dithioacetal **9** (1.39 g, 0.002 mole), formic acid (0.15 mL, 0.004 mole) triphenylphosphine (1.04 g, 0.004 mole) and anhydrous toluene (40 mL) was stirred under nitrogen. Diethyl azodicarboxylate (0.32 mL, 0.002 mole) was added and stirring continued for 6 h. A second portion of diethyl azodicarboxylate (0.32 mL, 0.002 mole) was added and stirring continued overnight (approx. 18 h). The reaction mixture was poured into a mixture of water (150 mL) and sat. ammonium chloride solution (10 mL). The product was extracted into ether (3 × 100 mL) and the extracts washed with sat. brine (100 mL) then dried. Removal of the solvent left a pale yellow semi-solid (3.64 g). Triphenylphosphine oxide was removed by column chromatography on silica (100 g), using toluene–ethyl acetate (15 : 1) as eluent. The crude 2,3,5-*tri-O-benzoyl-4-formyl-L-lyxose dibenzyl dithioacetal* thus obtained, as a colourless gum (1.52 g), was dissolved in methanol (120 mL) and the solution stirred over Amberlyst-15 (5.0 g), at room temperature, for 22 h. The Amberlyst was filtered off, methanol removed, and the residue taken up in ether (150 mL) which was washed with water (100 mL), sat. brine (100 mL), dried and evaporated to yield 2,3,5-*tri-O-benzoyl-L-lyxose dibenzyl dithioacetal* **12** as a white foam (1.1 g, 79%). Crystallisation from methanol (20 mL) gave a white crystalline solid (0.53 g, 38%) m.p. 118–119°C. (Found: C, 69.88; H, 5.46; S, 9.37. $C_{40}H_{36}O_7S_2$ requires C, 69.34; H, 5.24; S, 9.26%); ν max (Nujol)/cm^{-1} 3500 (OH), 1735 (CO), 1725 (CO); 1700 (CO); $^{\delta}$H 8.12 (2H, d, ^{o}Bz), 7.91 (2H, d, ^{o}Bz), 7.82 (2H, d, ^{o}Bz), 7.14–6.82 (19H, m, Bn and ^{m,p}Bz), 6.02 (1H, dd, *J* 2 and 9, H2), 5.73 (1H, dd, *J* 1 and 9, H3), 4.34 (1H, dd, *J* 6 and 12, H5), 4.27 (1H, dd, *J* 7 and 12, H5′), 4.12 (1H, ddd, *J* 1, 6 and 7, H4), 3.83 (1H, d, *J* 14, 1/2 SCH_2), 3.76 (1H, d, *J* 2, H1), 3.68 (1H, d, *J* 14, 1/2 SCH_2), 3.66 (2H, ABq, SCH_2).

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2,3,5-Tri-*O*-benzoyl-L-lyxose Dibenzyl Dithioacetal 12

A mixture of 1-*O*-methyl-2,3,5-tri-*O*-benzoyl-L-lyxofuranose **11** (4.76 g, 0.01 mole) and benzylmercaptan (11.8 mL, 0.10 mole) was treated with titanium tetrachloride (0.55 mL, 0.005 mole) as for **5** above. Work-up after 2.5 h followed by chromatography gave 2,3,5-tri-*O*-benzoyl-L-lyxose dibenzyl dithioacetal **12** as a colourless glass (1.8 g, 26%). Crystallisation from methanol gave a white solid, m.p. 119–120°C. (Found: C, 69.17; H, 5.27. $C_{40}H_{36}O_7S_2$ requires C, 69.34; H, 5.24%), the ^{1}H NMR spectrum of which was identical to that of **12** made via the inversion described above.

1-Thiobenzyl-2,3,5-*O*-tribenzoyl-4-thio-β-L-arabinofuranose 3

A solution of 2,3,5-tri-*O*-benzoyl-D-xylose dibenzyl dithioacetal **2** (3.46 g, 0.005 mole) in anhydrous pyridine (40 mL) was stirred while cooling in an ice-bath. Trifluoromethanesulphonic anhydride (1.7 mL, 0.010 mole) was added and the resulting solution was then warmed to room temperature and stirred for 2 h. The solution was poured into water (250 mL) and the product extracted into ethyl acetate (3 × 100 mL). The extracts were washed with 1 N hydrochloric acid (3 × 100 mL), sat. sodium bicarbonate solution (3 × 100 mL), sat. brine (100 mL) then dried. The extracts were concentrated, filtered through silica (100 g) and the solvent removed to give a pale orange semi-solid (2.49 g, 85%). Crystallisation from ethanol (30 mL) gave 1-*thiobenzyl*-2,3,5-*tri-O-benzoyl*-4-*thio-β-L-arabinofuranose* **3** as a white crystalline solid (1.83 g, 63%) m.p. 96–97°C. (Found: C, 67.57; H, 4.77. $C_{33}H_{28}O_6S_2$ requires C, 67.78; H, 4.82%); $^{\delta}$H 8.09 (2H, d, ^{o}Bz), 8.01 (2H, d, ^{o}Bz), 7.96 (2H, d, ^{o}Bz), 7.65–6.91 (14H, m, Bn and ^{m,p}Bz), 6.17 (1H, dd, *J* 5 and 6, H3), 5.81 (1H, dd, *J* 5 and 6, 2H), 4.73 (2H, m, H5 and H1), 4.62 (1H, dd, *J* 7 and 11, 5H′), 3.87 (3H, m, H4 and SCH_2).

4-*O*-Methanesulphonyl-2,3-5-tri-*O*-benzoyl-L-arabinose Dibenzyl Dithioacetal 7

2,3,5-Tri-*O*-benzoyl-L-arabinose dibenzyl dithioacetal **5** (11.31 g, 0.0163 mole) and pyridine (5 mL) were dissolved in alcohol-free chloroform (70 mL). The solution was cooled to 0°C, methanesulphonyl chloride (1.87 mL, 0.0242 mole) added, and the reaction mixture was stirred at room temperature for 18 h. Chromatography of the reaction mixture on silica using toluene–ethyl acetate (11 : 1) as eluent gave 4-*O-methanesulphonyl*-2,3,5-*tri-O-benzoyl-L-arabinose dibenzyl dithioacetal* **7** as a sticky white

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solid (9.15 g, 73%), which appeared to be unstable and was stored below 5°C. (Found: C, 63.59; H, 4.97; S, 13.19. $C_{41}H_{38}O_9S_3$ requires C, 63.87; H, 4.97; S, 12.48%); $^{\delta}$H 7.99 (2H, d, ^{o}Bz), 7.94 (2H, d, ^{o}Bz), 7.87 (2H, d, ^{o}Bz), 7.52–6.98 (19H, m, Bn and ^{m,p}Bz), 6.06 (1H, t, *J* 5, H3), 5.65 (1H, dd, *J* 5 and 5, H2), 5.11 (1H, td, *J* 5 and 8, H4), 4.47 (1H, dd, *J* 5 and 13, H5), 4.32 (1H, dd, *J* 8 and 13, H5′), 3.80 (1H, d, *J* 6, H1), 3.76 (2H, s, SCH_2), 3.74 (2H, ABq, SCH_2), 2.89 (3H, s, Ms).

1-Thiobenzyl-2,3,5-tri-*O*-benzoyl-4-thio-D-xylofuranose 6

A mixture of 4-*O*-methanesulphonyl-2,3,5-tri-*O*-benzoyl-L-arabinose dibenzyl dithioacetal **7** (20.1 g, 0.026 mole), triethylamine (7.2 mL, 0.052 mole) and sodium iodide (38.9 g, 0.26 mole) was stirred at reflux, in methyl ethyl ketone (250 mL), for 30 h. The reaction mixture was cooled then washed with water (100 mL), 2 N hydrochloric acid (100 mL), sat. sodium bicarbonate (100 mL), brine (100 mL) and dried. Removal of the solvent followed by chromatography on silica using toluene as eluent, gave a mixture of α and β anomers of 1-thiobenzyl-2,3,5-tri-*O*-benzoyl-4-thio-D-xylofuranose **6**, as an orange gum (5.51 g, 36%). (Found: C, 67.95; H, 4.97; S, 11.47. $C_{33}H_{28}O_6S_2$ requires C, 67.78; H, 4.82; S, 10.97%); $^{\delta}$H β-anomer, 8.01 (2H, d, ^{o}Bz), 7.95 (2H, d, ^{o}Bz), 7.86 (2H, d, ^{o}Bz), 7.55–7.08 (14H, m, Bn and ^{m,p}Bz), 5.92 (1H, t, *J* 5, H3), 5.78 (1H, dd, *J* 4 and 5, H2), 4.64 (1H, dd, *J* 7 and 12, H5), 4.51 (1H, dd, *J* 6 and 12, H5′), 4.36 (1H, d, *J* 4, H1), 4.23 (1H, m, H4), 3.86 (2H, ABq, SCH_2); α-anomer, 8.07–7.80 (6H, 3d, 3^{o}Bz), 7.57–7.08 (14H, m, Bn and ^{m,p}Bz), 5.96 (1H, t, *J* 5, H3), 5.78 (1H, t, *J* 5, H2), 4.68 (1H, d, *J* 5, H1), 4.51 (1H, dd, *J* 7 and 11, H5′), 4.40 (1H, dd, *J* 11 and 6, H5′), 4.28 (1H, m, H4), 3.78 (2H, s, SCH_2).

1-Thiobenzyl-2,3,5-tri-*O*-benzoyl-4-thio-L-lyxofuranose 10

A solution of 2,3,5-tri-*O*-benzoyl-D-ribose dibenzyl dithioacetal **9** (14.10 g, 0.0204 mole) in anhydrous pyridine (30 mL) was treated with trifluoromethanesulphonic anhydride (6.0 mL, 0.0357 mole) as for **3** above. Work-up followed by chromatography gave 1-*thiobenzyl*-2,3,5-*tri-O-benzoyl*-4-*thio*-L-*lyxofuranose* **10** as a pale yellow gum (11.2 g, 94%), with the β anomer **10a** and the α anomer **10b** in the ratio of approx. 3:1. TLC showed two contiguous spots. (Found: C, 68.47; H, 5.43. $C_{33}H_{28}O_6S_2$ requires C, 67.78; H, 4.82%); $^{\delta}$H, β-anomer, 8.02–7.80 (6H, 3d, 3^{o}Bz), 7.55–7.08 (14H, m, Bn and ^{m,p}Bz), 6.19 (1H, dd, J 4 and 6, H3), 5.77 (1H, dd, J 4 and 6, 2H), 4.69 (1H, dd, J 7 and 11, H5), 4.63 (1H, d, J 6, H1), 4.59 (1H, dd, *J* 7 and 11,

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H5′), 4.32 (1H, dt, *J* 6 and 7, H4), 3.99 (2H, ABq, SCH_2); α-anomer 8.02–7.80 (6H, 3d, 3^{o}Bz), 7.55–7.08 (14H, m, Bn and ^{m,p}Bz), 6.06 (1H, dd, *J* 4 and 6, H3), 5.80 (1H, dd, *J* 4 and 6, H2), 4.74 (1H, dd, *J* 7 and 11, H5), 4.73 (1H, d, *J* 6, H1), 4.63 (1H, dd, *J* 7 and 11, H5′), 4.15 (1H, dt, *J* 6 and 7, H4), 3.83 (2H, ABq, SCH_2); *m*/*z* (C1, NH_3), 602 $(M + NH_4)^+$.

4-*O*-Methanesulphonyl-2,3,5-tri-*O*-benzoyl-L-lyxose Dibenzyl Dithioacetal 14

2,3,5-Tri-*O*-benzoyl-L-lyxose dibenzyl dithioacetal **12** (0.3 g, 0.43 m mole) and pyridine (2 mL) were dissolved in alcohol-free chloroform (10 mL). The solution was cooled to 0°C, methanesulphonyl chloride (0.05 mL, 0.65 m mole) added, and the reaction mixture was stirred at room temperature for 3 h. Chromatography of the reaction mixture on silica using toluene–ethyl acetate (9 : 1) as eluent gave 4-*O-methanesulphonyl*-2,3,5-*tri-O-benzoyl-L-lyxose dibenzyl dithioacetal* **14** as a colourless gum (0.3 g, 90%) which crystallised on standing, m.p. 55–58°C. (Found: C, 63.40; H, 4.95. $C_{41}H_{38}O_9S_3$ requires C, 63.87; H, 4.97%); $^{\delta}$H 8.11 (2H, d, ^{o}Bz), 7.99 (2H, d, ^{o}Bz), 7.78 (2H, d, ^{o}Bz), 7.65–6.85 (19H, m, Bn and ^{m,p}Bz), 5.99 (2H, m, H2 and H3), 5.77 (1H, dt, *J* 5 and 8, H4), 4.60 (1H, dd, *J* 5 and 13, H5), 4.43 (1H, dd, *J* 8 and 13, H5′), 3.90 (1H, d, *J* 14, 1/2 SCH_2), 3.82 (1H, d, *J* 3, H1), 3.73 (1H, d, *J* 14, 1/2 SCH_2), 3.70 (2H, s, SCH_2), 3.11 (3H, s, Ms).

1-Thiobenzyl-2,3,5-tri-*O*-benzoyl-4-thio-D-ribofuranose 13

A solution of 4-*O*-methanesulphonyl-2,3,5-tri-*O*-benzoyl-L-lyxose dibenzyl dithioacetal **14** (100 mg, 0.13 m mole) in xylene (1 mL) was heated at reflux for 1 h. Chromatography on silica using *n*-hexane–ethyl acetate (95 : 5) as eluent afforded 1-*thiobenzyl*-2,3,5-*tri-O-benzoyl*-4-*thio-β-D-ribofuranose* **13a** as a gum (30 mg, 39%), which was homogeneous on t.l.c.; $^{\delta}$H 8.03 ((2H, d, ^{o}Bz), 8.02 (2H, d, ^{o}Bz), 7.90 (2H, d, ^{o}Bz), 7.55–7.20 (14H, m, Bn and ^{m,p}Bz), 6.07 (1H, dd, *J* 3 and 7, H3), 5.94 (1H, t, *J* 3, H2), 4.72 (1H, dd, *J* 7 and 12, H5), 4.55 (1H, dd *J* 7 and 12, H5′), 4.44 (1H, d, *J* 3, H1), 4.18 (1H, q, *J* 7, H4), 4.00 (2H, ABq, SCH_2); *m*/*z* (C1, NH_3), 602 $(M + NH_4)^+$.

The second component, 1-*thiobenzyl*-2,3,5-*tri-O-benzoyl*-4-*thio-α-D-ribofuranose* **13b** was obtained as a gum (10 mg, 13%), which was homogeneous on t.l.c. $^{\delta}$H 8.07 (2H, d, ^{o}Bz), 7.99 (2H, d, ^{o}Bz), 7.97 (2H, d, ^{o}Bz), 7.60–7.25 (14H, m, Bn and ^{m,p}Bz), 5.95 (1H, t, *J* 4, H2), 5.68 (1H, dd, *J* 4 and 6 H3), 4.75 (1H, d, *J* 4, H1), 4.62 (1H, dd, *J* 6 and 12, H5), 4.55 (1H, dd,

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J 6 and 12, H5′), 4.31 (1H, q, *J* 6, H4), 3.86 (2H, Abq, SHC_2); *m*/*z* (C1, NH_3), 602 $(M + HN_4)^+$.

1-Thiobenzyl-2,3,5-tri-*O*-benzoyl-4-thio-β-D-ribofuranose 13a

2,3,5-*O*-Tribenzoyl-L-lyxose dibenzyl dithioacetal **12** (0.69 g, 1.0 m mole) was treated with trifluoromethanesulphonic anhydride as for **3** above. Extraction into ether followed by chromatography on silica afforded 1-thiobenzyl-2,3,5-tri-*O*-benzoyl-4-thio-β-D-ribofuranose **13a** as a colourless glass (0.3 g, 51%), the ^{1}H NMR spectrum of which was identical to that of **13a** made by cyclization of compound **14**.

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