Carbohydrate Research, 46 (1976) 237–244
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THE SYNTHESIS OF *O*-METHYL DERIVATIVES OF 4-THIOPENTOFURANOSIDES AND 2,5-ANHYDROPENTOSES

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(Received July 28th, 1975; accepted in revised form, October 23rd, 1975)

ABSTRACT

Heating of 2,3,5-tri-*O*-methyl-4-*O*-*p*-tolylsulfonyl-D-ribose diethyl dithioacetal and dibenzyl dithioacetal in aqueous pyridine gave 4-*S*-ethyl-2,3,5-tri-*O*-methyl-4-thio-L-lyxose and benzyl 2,3,5-tri-*O*-methyl-α-1,4-dithio-L-lyxofuranoside, respectively. Similar rearrangements to the 4-thiofuranoside were observed with 2,3,5-tri-*O*-methyl-4-*O*-*p*-tolylsulfonyl-D-xylose and -D-lyxose dibenzyl dithioacetals. 2,3,4-Tri-*O*-methyl-5-*O*-*p*-tolylsulfonyl-D-ribose or -D-xylose dibenzyl dithioacetal, however, gave upon heating with sodium iodide in acetone 2,5-anhydro-3,4-di-*O*-methyl-D-ribose or -D-xylose dibenzyl dithioacetal, respectively.

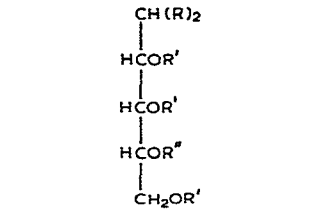
INTRODUCTION

Migrations from C-1 to C-4 have been reported for a number of *p*-toluenesulfonates. 2,3,5-Tri-*O*-benzyl-4-*O*-*p*-tolylsulfonyl-D-ribose dimethyl acetal (**1**) on treatment with a benzoate ion gave a derivative of 4-*O*-methyl-L-lyxose[1], but *p*-toluenesulfonylation of 2,3,5-tri-*O*-benzyl-D-ribose diethyl dithioacetal[2] (**2**) gave an intractable product that was ascribed to intramolecular displacement of the ethylthio group by the *p*-tolylsulfonyl group. Migrations from C-1 to C-5 occurred with 5-*O*-*p*-tolylsulfonyl-L-arabinose diethyl dithioacetal[2] and dibenzyl dithioacetal[3] to give derivatives of 5-thio-L-arabino-furanosides and -pyranosides, respectively. Previously[4], we reported the rearrangements that occurred on tosylation of the 2-*O*-methyl-, 2,3-di-*O*-methyl-, and 2,3,4-tri-*O*-methyl-D-xylose dialkyl dithioacetals. These results indicated that tosylation of various alkylated sugar dithio (or seleno) acetals may be used for the introduction of sulfur or selenium atoms into the sugar ring.

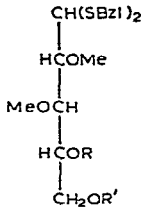
DISCUSSION

2,3,5-Tri-*O*-methyl-D-ribose diethyl (**3**) and dibenzyl dithioacetal (**4**) were obtained by treatment of methyl 2,3,5-tri-*O*-methyl-D-ribofuranosides with ethanethiol or phenylmethanethiol, respectively. *p*-Toluenesulfonylation of **3**, followed by warming

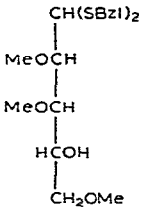
in aqueous pyridine gave 4-*S*-ethyl-2,3,5-tri-*O*-methyl-4-thio-L-lyxose (**8**), the structure of which was confirmed by spectral evidence and synthesis from 2,3,5-tri-*O*-acetyl-4-*S*-ethyl-4-thio-L-lyxose diethyl dithioacetal (**9**). This compound was prepared by the action of ethanethiol and anhydrous zinc chloride on 1,2,3,4-tetra-*O*-acetyl-β-D-ribopyranose[5]. Methylation of **9** gave **10**, and removal of the diethyl dithioacetal group gave **8**.



1 R = OMe, R' = Bzl, R'' = Ts
2 R = SEt, R' = Bzl, R'' = Ts
3 R = SEt, R' = Me, R'' = H
4 R = SBzl, R' = Me, R'' = H



5 R = H, R' = Me
6 R = Me, R' = H



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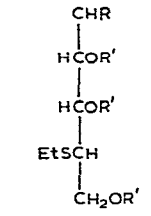
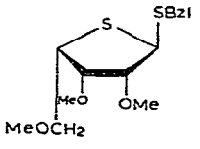


8 P = O, R' = Me
9 R = $(SEt)_2$, R = Ac
10 R = $(SEt)_2$, R = Me

p-Toluenesulfonylation of the dibenzyl dithioacetal **4**, followed either by warming the resulting tosyl compound in aqueous pyridine or heating with sodium iodide in acetone[3] gave benzyl 2,3,5-tri-*O*-methyl-1,4-dithio-α-L-lyxofuranoside (**11**). Hydrolysis of this thioglycoside was relatively slow. A slight odor of phenylmethanethiol could be detected after heating under reflux with 2% hydrogen chloride in methanol for 2 h, and most of **11** was recovered unchanged. However, treatment of **11** with mercuric chloride and cadmium carbonate in methanol gave 4,4'-dithiobis(2,3,5-tri-*O*-methyl-L-lyxose dimethyl acetal) (**14**). Reductive desulfurization of the thioglycoside **11** gave 1,4-dideoxy-2,3,5-tri-*O*-methyl-D-*erythro*-pentitol identical with that obtained from the dithioacetal **10**.



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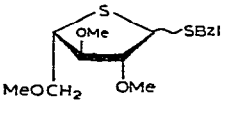

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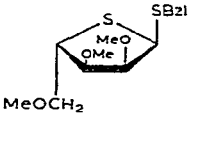

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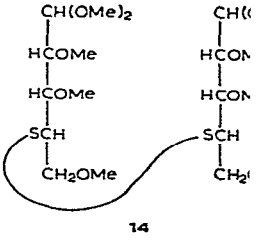
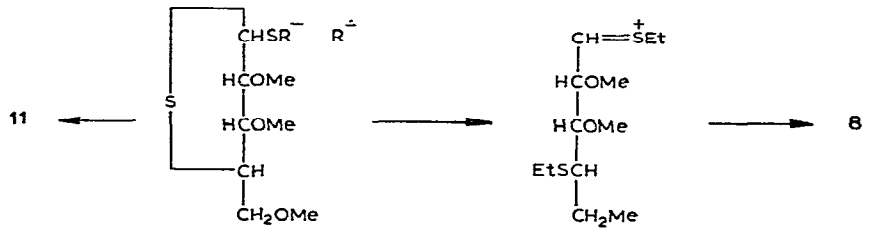


14

These reactions apparently proceeded by an intramolecular displacement resulting in a cyclic sulfonium ion (**15** or **16**) as suggested by Hughes *et al.*[2,3]. The cyclic ion **15** was opened by the second ethylthio group to give ion **17**, which was attacked by water to give **8** and ethanethiol, or ion **16** reacted with iodide ion to give **11** and benzyl iodide.

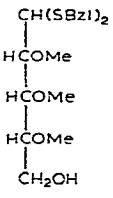
Similarly, *p*-toluenesulfonylation of 2,3,5-tri-*O*-methyl-D-xylose dibenzyl dithioacetal (**5**) and treatment of the resulting tosyl compound with sodium iodide in acetone gave benzyl 2,3,5-tri-*O*-methyl-1,4-dithio-L-arabinofuranoside (**12**), and the analogous D-lyxo compound **7** gave the L-ribofuranoside **13**.



15 R = Et
16 R = Bzl

17

This study was extended to the *p*-toluenesulfonylation of 2,3,4-tri-*O*-methyl-D-ribose (**18**) and -D-xylose (**6**) dibenzyl dithioacetals. When heated with sodium iodide in acetone, **18** and **6** gave 2,5-anhydro-3,4-di-*O*-methyl-D-ribose (**20**) and D-xylose (**22**) dibenzyl dithioacetal, respectively. The n.m.r. spectra of **20** and **22** showed the presence of two methoxyl and two benzylthio groups. Their mass spectra showed an intense peak at *m/e* 259 [$^{+}CH(SCH_2Ph)_2$] characteristic for dibenzyl



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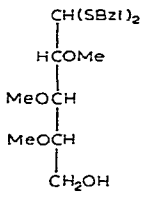

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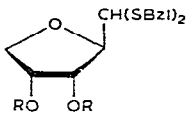
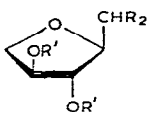
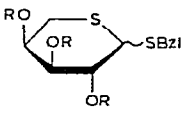


20 R = Me
21 R = H



22 R = SBzl, R' = Me
23 R = SBzl, R' = H
24 R = OMe, R' = Me
25 R = OMe, R' = H



26 R = Me
27 R = H

dithioacetals. The dibenzyl dithioacetals **20** and **22** were also prepared from the known[6] 2,5-anhydro-D-ribose (**21**) and -D-xylose dibenzyl dithioacetals (**23**) by methylation. Removal of the dithioacetal groups from **22** with mercuric chloride in neutral methanol gave the dimethyl acetal **24**. The identical compound **24** was formed by methylation of 2,5-anhydro-D-xylose dimethyl acetal[4] (**25**). The formation of the dithioacetals **20** and **22** is similar to the observed formation of 2,5-anhydro dialkyl dithioacetals on *p*-toluenesulfonylation of D-ribose, D-xylose, and D-lyxose dialkyl dithioacetals[6]. However, under the same conditions, D- and L-arabinose dialkyl dithioacetals gave the 5-*O*-*p*-tolylsulfonyl derivative. Rearrangement of 5-*O*-*p*-tolylsulfonyl-L-arabinose dibenzyl dithioacetal gave benzyl 1,5-dithio-L-arabinopyranoside[3] (**27**). Similarly, we observed that the rearrangement of 2,3,4-tri-*O*-

methyl-5-*O*-*p*-tolylsulfonyl-L-arabinose dibenzyl dithioacetal (**19**) gave benzyl 2,3,4-tri-*O*-methyl-1,5-dithio-L-arabinopyranoside (**26**), also obtained by methylation of **27**.

EXPERIMENTAL

General methods. — Column chromatography was performed on Merck Silica gel (60–200 mesh). I.r. spectra were determined on a Perkin–Elmer 700 spectrometer and n.m.r. spectra on a Varian T-60 spectrometer with tetramethylsilane as internal standard. Mass spectra were determined with a Hitachi–Perkin–Elmer RMU-7 mass spectrometer. G.l.c. analysis was performed with a Bendix Gas Chromatograph 2600 equipped with a column (1.8 m) containing 10% EGSS-X on Gas-Chrom P (Applied Sciences Labs., State College, Pa. 16801, U.S.A.) with nitrogen as the carrier gas.

*2,3,5-Tri-*O*-methyl-*D*-ribose diethyl dithioacetal* (**3**). — Methyl 2,3,5-tri-*O*-methyl-α,β-D-ribofuranoside[7] (6.9 g) was stirred overnight at room temperature with ethanethiol (10 ml) and concentrated hydrochloric acid (10 ml). The solution was diluted with water and extracted with chloroform. The extract was washed with sodium hydrogencarbonate solution and water, dried (sodium sulfate), and evaporated to give a syrup (8.3 g). Column chromatography with 1:19 methanol–benzene gave **3** as a syrup (6.99 g), $[\alpha]_D^{21}$ +18° (*c* 1.5, chloroform).

Anal. Calc. for $C_{12}H_{26}O_4S_2$: C, 48.3; H, 8.7; S, 21.5. Found: C, 48.6; H, 8.5; S, 21.2.

*2,3,5-Tri-*O*-methyl-*D*-ribose dibenzyl dithioacetal* (**4**). — This compound was prepared as described for **3**, except that phenylmethanethiol was used instead of ethanethiol. After chromatography, **4** was obtained as a syrup, $[\alpha]_D^{21}$ −142° (*c* 3.0, chloroform); n.m.r. data (dimethyl sulfoxide-d_6): τ 5.22 (d, OH-4, signal disappeared on treatment with D_2O).

Anal. Calc. for $C_{22}H_{30}O_4S_2$: C, 62.5; H, 7.1; S, 15.2. Found: C, 62.7; H, 7.0; S, 15.5.

*2,3,5-Tri-*O*-methyl-*D*-xylose dibenzyl dithioacetal* (**5**). — This compound was prepared from methyl 2,3,5-tri-*O*-methyl-α,β-D-xylofuranosides[8] and phenylmethanethiol as described for **4**. After chromatography, **5** was obtained as a syrup, $[\alpha]_D^{27}$ −34° (*c* 1.19, chloroform); n.m.r. data (dimethyl sulfoxide-d_6): τ 5.38 (d, OH-4, disappeared on treatment with D_2O).

Anal. Calc. for $C_{22}H_{30}O_4S_2$: C, 62.6; H, 7.1; S, 15.2. Found: C, 62.5; H, 7.0; S, 15.4.

*2,3,4-Tri-*O*-methyl-*D*-xylose dibenzyl dithioacetal* (**6**). — Methyl 2,3,4-tri-*O*-methyl-α,β-D-xylopyranoside[11] was treated with phenylmethanethiol as described for **4**. After the removal of the acid, the residue was partly crystalline. The excess of phenylmethanethiol was removed by washing with hexane, and the residue was crystallized from ethyl acetate–hexane to give **6**, m.p. 84–85°; $[\alpha]_D^{28}$ −30° (*c* 1.12, chloroform); n.m.r. data (dimethyl sulfoxide-d_6): τ 6.42 (t, OH-5, disappeared on treatment with D_2O).

Anal. Calc. for $C_{22}H_{30}O_4S_2$: C, 62.6; H, 7.1; S, 15.2. Found: C, 62.7; H, 7.1; S, 15.6.

2,3,5-Tri-O-methyl-D-lyxose dibenzyl dithioacetal (7). — Crude methyl 2,3,5-tri-*O*-methyl-α,β-D-lyxofuranoside, prepared by methylation of methyl α,β-D-lyxofuranoside[9] was treated with phenylmethanethiol. After chromatography, **7** was obtained as a syrup, $[\alpha]_D^{27}$ +122° (*c* 1.61, chloroform); n.m.r. data (dimethyl sulfoxide-d_6): τ 5.50 (d, OH-4, disappeared on treatment with D_2O).

Anal. Calc. for $C_{22}H_{30}O_4S_2$: C, 62.6; H, 7.1; S, 15.2. Found: C, 62.7; H, 7.0; S, 15.6.

4-S-Ethyl-2,3,5-tri-O-methyl-4-thio-L-lyxose (8). — (*a*) *From 2,3,5-tri-O-methyl-D-ribose diethyl dithioacetal* (3). A solution of the dithioacetal (3) (1.37 g) in pyridine (10 ml) was treated slowly at 0° with *p*-toluenesulfonyl chloride (2.0 g). The solution was kept overnight at room temperature, diluted with water (1 ml), and warmed for 3 h at 65–70°. A strong odor of ethanethiol was observed. The solution was extracted with chloroform and water. The chloroform extract was washed with ice-cold dilute hydrochloric acid and sodium hydrogencarbonate solution, and dried with sodium sulfate. The solution was evaporated to a syrup (1.0 g), which was chromatographed on a column of silica gel in 1:19 methanol–benzene to give **8** (0.63 g), $[\alpha]_D^{21}$ +15° (*c* 1.1, chloroform); i.r. data: ν_{max}^{film} 1720 (CHO); n.m.r. data (chloroform-*d*): τ 0.10 (d, 1 H, *J* 2.0 Hz, CHO), 6.54, 6.58, and 6.62 (s, 9 H, OCH_3), 7.43 (q, 2 H, *J* 7.8 Hz, SCH_2CH_3), and 8.73 (t, 3 H, *J* 7.8 Hz, SCH_2CH_3); g.l.c.: 10.4 min (160°).

Anal. Calc. for $C_{10}H_{20}O_4S$: C, 50.8; H, 8.5; S, 13.6; mol. wt., 236. Found: C, 50.7; H, 8.4; S, 13.7; mol. wt., 236 (mass spectrometry).

(*b*) *From 1,2,3,4-tetra-O-acetyl-β-D-ribopyranose*[5]. — The tetraacetate (5.0 g), ethanethiol (25 ml), and anhydrous zinc chloride (3.0 g) were stirred overnight at room temperature. The reaction mixture was extracted with chloroform and water. On evaporation, the dried extract gave a syrup (5.3 g) that consisted of two major and one minor components in addition to the starting material. Column chromatography on silica gel with 1:39 methanol–benzene gave 2,3,5-tri-*O*-acetyl-4-*S*-ethyl-4-thio-L-lyxose diethyl dithioacetal (**9**) (0.75 g) as a syrup; n.m.r. data (chloroform-*d*): τ 7.36 (q, 4 H, *J* 7.8 Hz, SCH_2CH_3), 7.84, 7.88 (s, 9 H, $OCOCH_3$), 8.73 (t, 6 H, *J* 7.8 Hz, SCH_2CH_3). The syrup was dissolved in dry tetrahydrofuran (25 ml), and powdered potassium hydroxide (3 g) and dimethyl sulfate (3 ml) were added. The solution was stirred for 1 h at room temperature and heated under reflux for 0.5 h. Fresh reagents were added and the treatment was repeated. Concentrated ammonia solution (10 ml) was added to destroy excess dimethyl sulfate. The reaction mixture was extracted with chloroform and water. The dried chloroform extract was evaporated to give 4-*S*-ethyl-2,3,5-tri-*O*-methyl-4-thio-L-lyxose diethyl dithioacetal (**10**) as a crude syrup (0.50 g). Without purification, this was dissolved in a solution of acetone (18 ml) and water (2 ml) containing cadmium carbonate (3.0 g) and mercuric chloride (1.5 g). The suspension was stirred overnight at room temperature, and the solid residue filtered off and washed repeatedly with chloroform. The filtrate was washed with water and evaporated to a syrup (0.30 g). Chromatography on silica

gel with 1:19 methanol–benzene gave **8** (0.24 g) as a syrup showing n.m.r. and i.r. spectra and a retention time identical with those of **8** described in (*a*).

*Benzyl 2,3,5-tri-*O*-methyl-1,4-dithio-α-*L*-lyxofuranoside* (**11**). — The dibenzyl dithioacetal **4** (2.11 g) was treated with *p*-toluenesulfonyl chloride, as described for **3**. Alternatively, after tosylation of **4**, the reaction product was isolated by extraction. This crude product was immediately heated overnight under reflux in acetone (30 ml) with sodium iodide (4.0 g) and barium carbonate (2.0 g). The suspension was filtered, and the filtrate extracted with chloroform and water. The chloroform extract was evaporated to a syrup. Column chromatography gave **11** as a syrup (1.2 g), $[\alpha]_D^{21}$ −112° (*c* 1.47, chloroform); n.m.r. data (chloroform-*d*): τ 2.79 (s, 5 H, C_6H_5), 5.70 (d, 1 H, *J* 6.0 Hz, H-1), 6.02 (s, 2 H, $CH_2C_6H_5$), 6.52, and 6.68 (s, 9 H, OCH_3); m.s.: 314 (M^+) and 191 ($M^+ - SCH_2C_6H_5$).

Anal. Calc. for $C_{15}H_{22}O_3S_2$: C, 57.3; H, 7.0; S, 20.4. Found: C, 57.6; H, 7.1; S, 20.0.

Reductive desulfurization of **10** *and* **11**. — The thioglycoside **11** (1.9 g), Raney nickel (10 g), and ethanol (25 ml) were heated under reflux overnight. The suspension was filtered and the nickel repeatedly washed with hot ethanol. The filtrate was evaporated to give a volatile oil (0.40 g). Column chromatography on silica gel with 1:99 methanol–benzene gave 1,4-dideoxy-2,3,5-tri-*O*-methyl-D-*erythro*-pentitol (0.23 g), $[\alpha]_D^{27}$ +21° (*c* 0.7, chloroform); n.m.r. data (chloroform-*d*): τ 6.44, 6.57, 6.64 (s, 9 H, OCH_3), 7.86 (m, 2 H, CH_2), and 8.75 (d, *J* 1.5 Hz, 3 H, CH_3); m.s.: 162 (M^+), 117 ($M^+ - CH_2OCH_3$), 85, 59, and 45.

Treatment of the dithioacetal (**10**) in the same manner gave an identical compound.

*Benzyl 2,3,5-tri-*O*-methyl-1,4-dithio-*L*-arabinofuranoside* (**12**). — The dibenzyl dithioacetal **5** was tosylated and then treated with sodium iodide in acetone as described for **11**. Column chromatography gave **12** as a syrup (0.90 g), $[\alpha]_D^{27}$ +197° (*c* 0.38, chloroform); n.m.r. data (chloroform-*d*): τ 2.72 (s, 5 H, C_6H_5), 5.70 (complex, 1 H, H-1), 6.13 (s, 2 H, $CH_2C_6H_5$), 6.56, 6.64, and 6.66 (s, 9 H, OCH_3); m.s.: 314 (M^+) and 191 ($M^+ - SCH_2C_6H_5$).

Anal. Calc. for $C_{15}H_{22}O_3S_2$: C, 57.3; H, 7.0; S, 20.4. Found: C, 57.2; H, 7.1; S, 20.6.

*Benzyl 2,3,5-tri-*O*-methyl-1,4-dithio-α(?)-*L*-ribofuranoside* (**13**). — This compound was prepared from **7** as described for **11**. Column chromatography gave **13** as a syrup (0.90 g), $[\alpha]_D^{27}$ −91° (*c* 0.63, chloroform); n.m.r. data (chloroform-*d*): τ 2.71 (s, 5 H, C_6H_5), 5.77 (s, 1 H, *J* 4.0 Hz, H-1), 6.14 (s, 2 H, $CH_2C_6H_5$), 6.62, and 6.65 (s, 9 H, OCH_3); m.s.: 314 (M^+), 191 ($M^+ - SCH_2C_6H_5$).

Anal. Calc. for $C_{15}H_{22}O_3S_2$: C, 57.3; H, 7.0; S, 20.4. Found: C, 57.6; H, 7.0; S, 20.5.

*4,4'-Dithiobis(2,3,5-tri-*O*-methyl-*L*-lyxose dimethyl acetal)* (**14**). — The thioglycoside **11** (1.57 g) was stirred with a suspension of cadmium carbonate (8.0 g) and mercuric chloride (4.0 g) in methanol (50 ml) for 6 h at room temperature and heated under reflux for an additional 2 h. The suspension was filtered and the residue

repeatedly washed with chloroform. The filtrate was washed with water and evaporated to a syrup (1.0 g). Column chromatography on silica gel with 1:19 methanol–benzene gave **14** as a syrup (0.65 g), $[\alpha]_D^{25}$ +32° (*c* 5.0, chloroform); n.m.r. data (chloroform-*d*): τ 5.60 (s, 1 H, H-1), 6.40, 6.50, 6.56, and 6.64 (s, 15 H, OCH_3); m.s.: 506 (M^+), 253, and 75 [very intense, $CH(OCH_3)_2^+$].

Anal. Calc. for $C_{20}H_{42}O_{10}S_2$: C, 47.4; H, 8.3; S, 12.6. Found: C, 47.6; H, 8.5; S, 12.7.

*2,3,4-Tri-*O*-methyl-*D*-ribose dibenzyl dithioacetal* (**18**). — Methyl 2,3,4-tri-*O*-methyl-α,β-D-ribopyranoside[10] was treated with phenylmethanethiol as described for **4**. Chromatography gave **18** as a syrup; $[\alpha]_D^{27}$ −105° (*c* 0.68, chloroform); n.m.r.data (dimethyl sulfoxide-d_6): τ 5.64 (t, OH-5, disappeared on treatment with D_2O).

Anal. Calc. for $C_{22}H_{30}O_4S_2$: C, 62.6; H, 7.1; S, 15.2. Found: C, 62.8; H, 7.2; S, 15.4.

*2,5-Anhydro-3,4-di-*O*-methyl-*D*-ribose dibenzyl dithioacetal* (**20**). — This compound was obtained from **18** as described for the preparation of **11**. Column chromatography gave **20** as a syrup (1.0 g), $[\alpha]_D^{27}$ −78° (*c* 0.78, chloroform); n.m.r. data (chloroform-*d*): τ 2.80 (s) and 2.90 (complex, total 10 H, $CH_2C_6H_5$), 5.80 (double doublet, 1 H, H-1), 6.63, 6.86 (s, 6 H, OCH_3); m.s.: 390 (M^+), 299 ($M^+ - CH_2C_6H_5$), 259 [$\dot{C}H(SCH_2C_6H_5)_2$].

Anal. Calc. for $C_{21}H_{26}O_3S_2$: C, 64.6; H, 6.7; S, 16.4. Found: C, 64.5; H, 6.7; S, 16.5.

2,5-Anhydro-D-ribose dibenzyl dithioacetal[6] (**21**) was methylated with dimethyl sulfate in tetrahydrofuran and powdered potassium hydroxide to give **20**.

*2,5-Anhydro-3,4-di-*O*-methyl-*D*-xylose dibenzyl dithioacetal* (**22**). — This compound was obtained from **6** as described for **11**. Column chromatography gave **22** as a syrup (0.90 g), $[\alpha]_D^{27}$ −14° (*c* 1.0, chloroform); n.m.r. data (chloroform-*d*): τ 2.68–2.85 (complex, 10 H, C_6H_5), 6.75, and 6.85 (s, 6 H, OCH_3); m.s.: 390 (M^+), 299 ($M^+ - CH_2C_6H_5$), and 259 [$\dot{C}H(SCH_2C_6H_5)_2$].

Anal. Calc. for $C_{21}H_{26}O_3S_2$: C, 64.6; H, 6.7; S, 16.4. Found: C, 64.4; H, 6.6; S, 16.6.

2,5-Anhydro-D-xylose dibenzyl dithioacetal[6] (**23**) was methylated with dimethyl sulfate in tetrahydrofuran and powdered potassium hydroxide to give **22**.

*2,5-Anhydro-3,4-di-*O*-methyl-*D*-xylose dimethyl acetal* (**24**). — Compound **22** (0.40 g), mercuric chloride (1.5 g), cadmium carbonate (3.0 g), and methanol (10 ml) were stirred overnight at room temperature, and then heated under reflux for 1 h. The suspension was diluted with chloroform and filtered. The filtrate was successively washed with water, potassium iodide solution, and water, and evaporated to give a syrup. Chromatography on silica gel with 1:19 methanol–benzene gave **24** (0.12 g) as a syrup, $[\alpha]_D^{21}$ +12° (*c* 1.3, chloroform); n.m.r. data (chloroform-*d*): τ 5.50 (d, *J* 7.8 Hz, 1 H, H-1), 6.60, and 6.64 (s, 12 H, OCH_3); g.l.c.: 8.50 min (150°). This compound was identical (by g.l.c., i.r., and n.m.r.) with the compound prepared[4] by methylation of 2,5-anhydro-D-xylose dimethyl acetal (**25**).

2,3,4-Tri-O-methyl-L-arabinose dibenzyl dithioacetal (**19**). — From methyl 2,3,4-tri-*O*-methyl-L-arabinopyranosides[13] and phenylmethanethiol as described for **4**. Chromatography gave **19** as a syrup, $[\alpha]_D^{28}$ +102° (*c* 1.0, chloroform); n.m.r. data (dimethyl sulfoxide-d_6): τ 5.55 (t, OH-5, disappeared on treatment with D_2O).

Anal. Calc. for $C_{22}H_{30}O_4S_2$: C, 62.6; H, 7.1; S, 15.5. Found: C, 62.4; H, 7.2; S, 15.5.

Benzyl 2,3,4-tri-O-methyl-1,4-dithio-(α,β)-L-arabinopyranoside (**26**). — This compound was obtained from **19** as described for **11**. Column chromatography gave **26** as a syrup, $[\alpha]_D^{27}$ +89° (*c* 0.74, chloroform); n.m.r. data (chloroform-*d*): τ 2.64 (s, 5 H, C_6H_5), 5.82–5.98 (complex, 1 H, H-1), 6.10 (s, 2 H, $CH_2C_6H_5$), 6.51, 6.58, and 6.64 (s, 9 H, OCH_3).

Anal. Calc. for $C_{15}H_{22}O_3S_2$: C, 57.3; H, 7.0; S, 20.4. Found: C, 57.1; H, 7.1; S, 20.6.

Methylation of **27** (ref. 3) with dimethyl sulfate and powdered potassium hydroxide in tetrahydrofuran also gave **26**.

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