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Note

p-Toluenesulfonylation of *O*-methyl derivatives of D-xylose dialkyl dithioacetals

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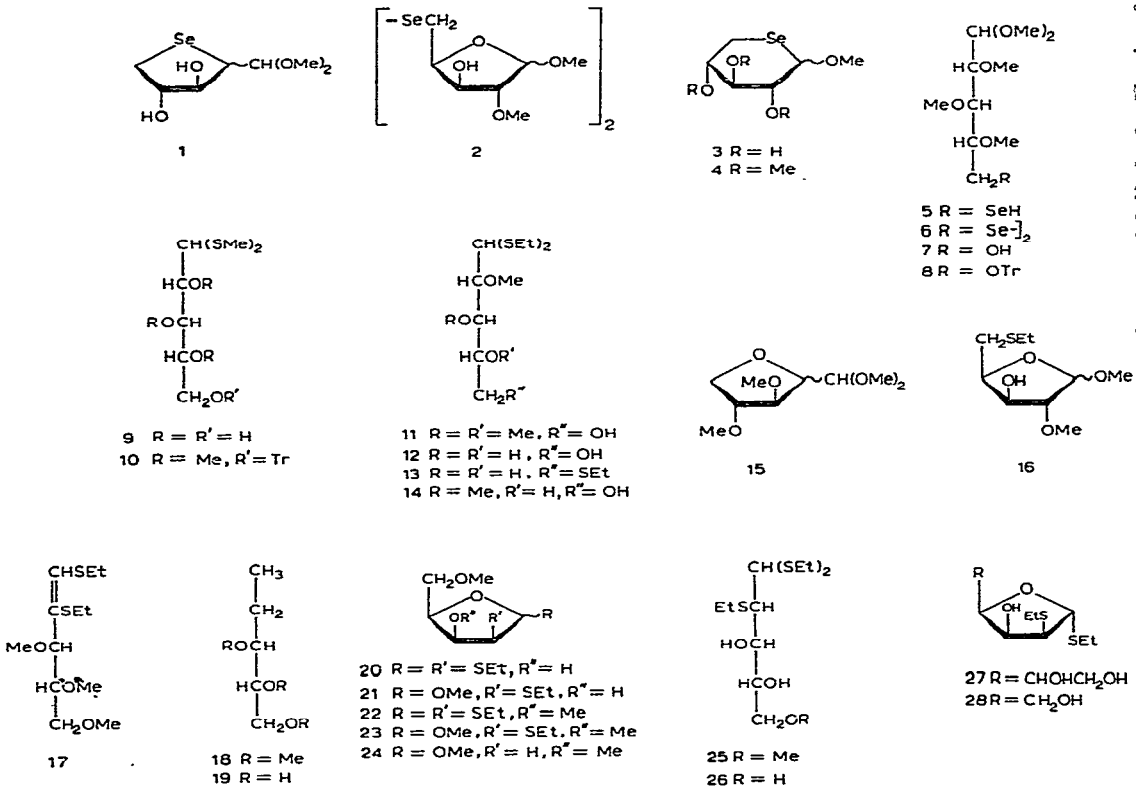
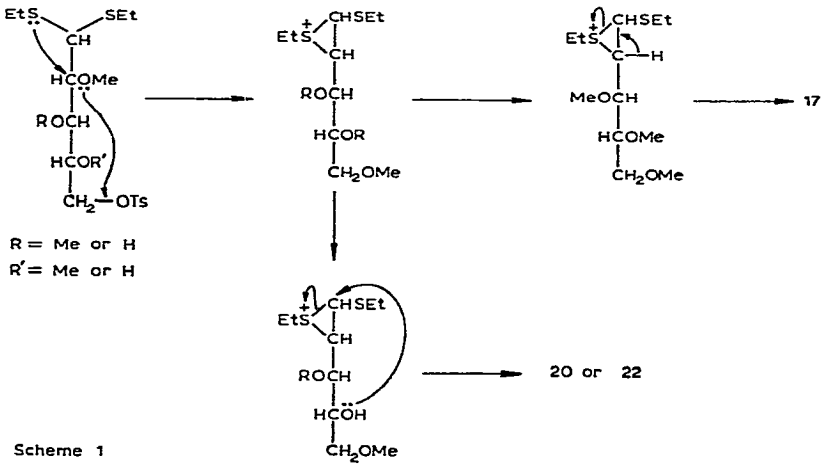
5-Seleno-D-xylose derivatives having a hydroxyl or methoxyl group at C-2 gave[1], upon treatment with acid, 2,5-anhydro-5-seleno-*aldehydo*-D-*threo*-pentose dimethyl acetal (**1**) or 5,5-diselenobis(methyl 2-*O*-methyl-D-xylofuranoside) (**2**), respectively, instead of the expected selenopyranoside (**3**). Treatment of 2,3,4-tri-*O*-methyl-5-seleno-D-xylose dimethyl acetal (**5**) with acid is expected to give either methyl 2,3,4-tri-*O*-methyl-5-seleno-D-xylopyranoside (**4**) or 5,5-diselenobis(2,3,4-tri-*O*-methyl-D-xylose dimethyl acetal) (**6**). Various routes for the preparation of 2,3,4-tri-*O*-methyl-D-xylose dimethyl acetal (**7**), an intermediate for the preparation of **4**, were tried. The one starting from D-xylose dimethyl dithioacetal (**9**) was not successful because removal of the trityl group from the dimethyl dithioacetal (**10**) or dimethyl acetal (**8**) with hydrogen bromide in acetic acid[2] or 90% trifluoroacetic acid gave methyl triphenylmethyl sulfide and methyl 2,3,4-tri-*O*-methyl-1-thio-D-xylopyranoside or methyl triphenylmethyl ether and methyl 2,3,4-tri-*O*-methyl-D-xylopyranoside, respectively. Palladium-catalyzed hydrogenolysis of the dimethyl acetal (**8**) resulted in a slow and incomplete removal of the trityl group to give compound **7**. An easier approach to the synthesis of **7** started from 2,3,4-tri-*O*-methyl-D-xylose diethyl dithioacetal (**11**), which was obtained by treatment of the known 2,3,4-tri-*O*-methyl-D-xylopyranose[3] with ethanethiol. Treatment of **7** with *p*-toluenesulfonyl chloride gave 2,5-anhydro-3,4-di-*O*-methyl-D-xylose (**15**). With *p*-toluenesulfonyl chloride, the corresponding mercaptal (**11**) gave 1,2-di-*S*-ethyl-3,4,5-tri-*O*-methyl-1,2-dithio-D-*threo*-pent-1-enitol (**17**). Spectral analysis of **17** showed the absence of the tosyloxy and hydroxyl groups and the presence of two ethylthio-, three methoxyl groups, and an olefinic proton. Reductive desulfurization of **17** with Raney nickel gave 1,2-dideoxy-3,4,5-tri-*O*-methyl-D-*threo*-pentitol (**18**), which was volatile and difficult to purify. The n.m.r. spectrum of **18** showed the presence of a terminal ethyl group and the structure was confirmed by synthesis from 1,2-dideoxy-D-*threo*-pentitol[4] (**19**).

2-*O*-Methyl-D-xylose diethyl dithioacetal (**12**), on treatment with *p*-toluenesulfonyl chloride, afforded ethyl 2-*S*-ethyl-5-*O*-methyl-1,2-dithio-D-lyxofuranoside



(**20**). This compound contained one methoxyl and two ethylthio groups. Mass-spectral analysis showed that one of the ethylthio groups was present as the aglycon; this was confirmed by the formation of methyl 2-*S*-ethyl-5-*O*-methyl-2-thio-D-lyxofuranoside (**21**) on treatment with methanolic mercuric chloride. The second ethylthio group could be present at C-5, by analogy with the findings of Hughes *et al.*[5] in the *p*-toluenesulfonylation of L-arabinose diethyl dithioacetal. If the ethylthio group were linked at C-5, treatment of **20** or methyl 5-*S*-ethyl-2-*O*-methyl-5-thio-D-xylofuranoside (**16**) with ethanethiol and acid is expected to give 2-*O*-methyl-5-*S*-ethyl-5-thio-D-xylose diethyl dithioacetal (**13**). However, **20** gave a different mercaptal, namely 5-*O*-methyl-2-*S*-ethyl-2-thio-D-lyxose diethyl dithioacetal (**25**), thus showing the absence of an ethylthio group at C-5. 2,3-Di-*O*-methyl-D-xylose diethyl dithioacetal[6] (**14**), on treatment with *p*-toluenesulfonyl chloride, gave ethyl 2-*S*-ethyl-3,5-di-*O*-methyl-1,2-dithio-D-lyxofuranoside (**22**). Treatment of this compound with methanolic mercuric chloride gave methyl 2-*S*-ethyl-3,5-di-*O*-methyl-D-lyxofuranoside (**23**) which, on reductive desulfurization with Raney nickel, gave methyl 2-deoxy-3,5-di-*O*-methyl-D-xylofuranoside (**24**). The n.m.r. spectrum of this compound showed H-1 as a triplet, indicating the presence of a 2-deoxy group. The structure of **24** was confirmed by chromatographic comparison with methylated 2-deoxy-D-pentofuranosides[7]. The second ethylthio group in **20** and **22** was therefore present at C-2.

The D-*lyxo* configuration of **20** and **22** was confirmed by the synthesis of **22** from ethyl 2-*S*-ethyl-1,2-dithio-α-D-mannofuranoside[8] (**27**) by treatment with periodate. reduction with sodium borohydride, and methylation. Compound **22** was also obtained by methylation of ethyl 2-*S*-ethyl-1,2-dithio-D-lyxofuranoside (**28**). Compound **28** was obtained from 2-*S*-ethyl-2-thio-D-lyxose diethyl dithioacetal[4] (**26**) by treatment with one mole of mercuric chloride in methanol under neutral conditions. Compound **26** was prepared from D-xylose diethyl dithioacetal and ethanethiol[4]; however, the stereochemistry of the ethylthio group at C-2 is not known. The D-*lyxo* configuration of **28** was established by analogy with the D-*manno* configuration found for the compound obtained by treatment of D-glucose diethyl dithioacetal with ethanethiol[8] and by the identity with **22** (after methylation). A possible mechanism for the formation of **17**, **20**, and **22** is described in Scheme 1.



Scheme 1

EXPERIMENTAL

Solutions were evaporated at 40° under diminished pressure. N.m.r. spectra were recorded on a Varian T-60 spectrometer, tetramethyl-silane was used as the internal standard and chemical shifts are given in p.p.m. Mass spectra were determined with a Hitachi RMU7 mass spectrograph. G.l.c. analysis was performed on a Bendix gas chromatography 2600 with a 6 ft column of 10% EGSS-X on Gas-chrom P (Applied Science Labs. Inc., State College, Pa. 16801) with nitrogen as the carrier gas.

5-O-Trityl-D-xylose dimethyl dithioacetal. — D-Xylose dimethyl dithioacetal (**9**) (5.56 g), pyridine (15 ml), and trityl chloride (6.20 g) were kept for 3 days at room temperature. The solution was extracted with chloroform and water. The chloroform extracts were washed successively with ice-cold, dilute hydrochloric acid, a sodium hydrogen carbonate solution, and water, then dried (sodium sulfate) and evaporated to a syrup (10.6 g). Part of this syrup was purified on a column of silica gel with 7:93 methanol–benzene as eluent, $[\alpha]_D^{21}$ +20° (*c* 2.6, chloroform); n.m.r. data (chloro-

form-*d*): δ 2.05, 2.14 (3-proton singlets, SCH_3) and 7.14–7.55 (15-proton complex, C_6H_5).

Anal. Calc. for $C_{26}H_{30}O_4S_2$: C, 66.39; H, 6.38. Found: C, 66.21; H, 6.45.

*2,3,4-Tri-*O*-methyl-5-*O*-trityl-*D*-xylose dimethyl dithioacetal* (**10**). — The remainder of the compound just described (9.6 g), tetrahydrofuran (30 ml), powdered potassium hydroxide (8 g), and dimethyl sulfate (5 ml) were stirred for 2 h. Further amounts of dimethyl sulfate (5 ml) and potassium hydroxide (8 g) were added, and the solution was heated under reflux for 2 h. Ammonia (10 ml) was added to destroy the excess dimethyl sulfate. The reaction mixture was extracted with chloroform and water, and the chloroform extracts were dried and evaporated to a syrup (8.6 g). The syrup crystallized from ethyl acetate and petroleum ether (40–60°), m.p. 108–109°; $[\alpha]_D^{21}$ +16° (*c* 1.6, chloroform); n.m.r. data (chloroform-*d*): δ 2.14, 2.16 (3-proton singlets, SCH_3), 3.34, 3.48 and 3.55 (3-proton singlets, OCH_3), and 7.20–7.57 (15-proton complex, C_6H_5).

Anal. Calc. for $C_{29}H_{36}O_4S_2$: C, 67.97; H, 7.03. Found: C, 67.76; H, 6.90.

*2,3,4-Tri-*O*-methyl-5-*O*-trityl-*D*-xylose dimethyl acetal* (**8**). — Compound **10**, (2.3 g), cadmium carbonate (7.0 g), and a solution of mercuric chloride (4.5 g) in methanol (30 ml) were heated under reflux for 4 h. The suspension was filtered, and the filtrate extracted with chloroform and water. The chloroform extracts were washed with 10% potassium iodide solution and water. Upon evaporation, a syrup (2.0 g) was obtained, which crystallized from petroleum ether (40–60°) to give **8**, m.p. 93°; $[\alpha]_D^{20}$ +18° (*c* 1.0, chloroform); n.m.r. data (chloroform-*d*): δ 3.13, 3.38, 3.42 and 3.48 (singlets, total 15 protons, OCH_3), and 7.21–7.62 (15-proton complex, C_6H_5).

Anal. Calc. for $C_{29}H_{36}O_6$: C, 72.51; H, 7.50. Found: C, 72.79; H, 7.63.

*2,3,4-Tri-*O*-methyl-*D*-xylose dimethyl acetal* (**7**). — Compound **8** (1.3 g), methanol (50 ml), and palladium-on-charcoal (5%) were shaken for 3 days with hydrogen at atmospheric pressure. The suspension was filtered, and the filtrate evaporated to give triphenylmethane (0.40 g) and a syrup (0.90 g). The syrup was purified on a column of silica gel with 7:93 methanol–benzene as eluent to give **7** as syrup (0.27 g), $[\alpha]_D^{25}$ +18° (*c* 3.4, chloroform); n.m.r. data (dimethyl sulfoxide-d_6): δ 3.33, 3.38 (singlets, total 15 protons, OCH_3) 4.50 (1-proton, triplet CH_2OH, disappearing upon addition of deuterium oxide).

Anal. Calc. for $C_{10}H_{22}O_6$: C, 50.42; H, 9.24. Found: C, 50.61; H, 9.16.

Compound **7** was also prepared from **11** (2.1 g) with cadmium carbonate (5.0 g), mercuric chloride (3.0 g), and methanol (20 ml) as described for **8**.

*2,3,4-Tri-*O*-methyl-*D*-xylose diethyl dithioacetal* (**11**). — 2,3,4-Tri-*O*-methyl-*D*-xylopyranose[3] (17.0 g), ethanethiol (20 ml), and hydrochloric acid (15 ml) were cooled in an ice bath and vigorously stirred for 15 min. The solution was kept for 0.5 h at room temperature and then neutralized by passage through IR 45 (OH^-) ion-exchange resin with ethanol as eluent. Compound **11** was obtained as a syrup (22.0 g) which was distilled at 0.01 mm Hg, b.p. 142–146°; $[\alpha]_D^{21}$ +20° (*c* 1.6, chloroform); n.m.r. data (dimethyl sulfoxide-d_6): δ 1.27 (6-proton triplet, *J* 7.8 Hz, SCH_2CH_3),

2.70 (4-proton quartet, *J* 7.8 Hz, SCH_2CH_3), 3.40 3.47 and 3.54 (3-proton singlets, OCH_3), and 4.56 (1-proton triplet, CH_2OH, this signal disappearing upon addition of deuterium oxide).

Anal. Calc. for $C_{12}H_{26}O_4S_2$: C, 48.30; H, 8.73. Found: C, 48.41; H, 8.69.

*1,2-Di-*S*-ethyl-3,4,5-tri-*O*-methyl-1,2-dithio-*D*-threo-pent-1-enitol* (**17**). — Compound **11** (1.0 g), *p*-toluenesulfonyl chloride (1.0 g), and pyridine were kept overnight at room temperature, and then the solution was heated for 1 h at 55–65°. The reaction mixture was extracted with chloroform and water. The chloroform extracts were washed with ice-cold hydrochloric acid, sodium hydrogen carbonate solution, and water, dried, and evaporated to a syrup (0.90 g). This was applied to a column of silica gel with 1:39 methanol–benzene as the eluent, to give **17** as a syrup, $[\alpha]_D^{22}$ −4° (*c* 1.3, chloroform); n.m.r. data (chloroform-*d*): δ 1.30, 1.35 (two 3-proton triplets, *J* 7.8 Hz, SCH_2CH_3), 2.76, 2.79 (two 2-proton quartets, *J* 7.8 Hz, SCH_2CH_3), 3.36, 3.38, 3.50 (3-proton singlets, OCH_3), and 6.66 (1-proton singlet, C=CH).

Anal. Calc. for $C_{12}H_{24}O_3S_2$: C, 51.42; H, 8.57. Found: C, 51.41; H, 8.49.

Reductive desulfurization of **17**. — Compound **17** (1.0 g), ethanol (20 ml), and Raney nickel (~15 g) were heated under reflux overnight. The nickel was filtered off and repeatedly washed with hot ethanol. The filtrate was evaporated to give a volatile liquid (0.23 g); g.l.c.: several peaks with main component (**18**, 80%); retention times, 2.86 min (100°) and 6.11 min (80°).

*2,5-Anhydro-3,4-di-*O*-methyl-*D*-xylose dimethylacetal* (**15**). — Compound **7** (0.57 g) was treated with *p*-toluenesulfonyl chloride, and the product isolated and purified, as described for **17**, to give **15** as a syrup, $[\alpha]_D^{21}$ +12° (*c* 1.3, chloroform); n.m.r. (chloroform-*d*): δ 3.40, 3.55 (3-proton singlets, OCH_3), and 3.46 [6-proton singlets, $C(OCH_3)_2$].

Anal. Calc. for $C_9H_{18}O_5$: C, 52.43; H, 8.74. Found: C, 52.50; H, 8.71.

The identical compound **15** (by g.l.c., i.r., and n.m.r.) was obtained by methylation of 2,5-anhydro-D-xylose dimethylacetal[9] with dimethyl sulfate and potassium hydroxide in tetrahydrofuran.

*2-*O*-Methyl-*D*-xylose diethyl dithioacetal* (**12**). — 2-*O*-Methyl-D-xylopyranose[1] (6.5 g), conc. hydrochloric acid (7 ml), and ethanethiol (9 ml) were vigorously stirred for 0.5 h at room temperature and **12** was isolated in the same manner as described for **11**. Crystallization from petroleum ether (60–110°) gave 9.0 g, m.p. 60–61°; $[\alpha]_D^{21}$ +3° (*c* 2.6, chloroform); n.m.r. data (chloroform-*d*): δ 1.30 (6-proton triplet, *J* 7.8 Hz, SCH_2CH_3), 2.76 (4-proton quartet, *J* 7.8 Hz, SCH_2CH_3), and 3.65 (3-proton singlet, OCH_3).

Anal. Calc. for $C_{10}H_{22}O_4S_2$: C, 44.44; H, 8.15. Found: C, 44.56; H, 8.09.

*Ethyl 2-*S*-ethyl-5-*O*-methyl-1,2-dithio-α-*D*-lyxofuranoside* (**20**). — A solution of **12** (1.08 g) in pyridine (10 ml) was cooled to 0°, and *p*-toluenesulfonyl chloride (1.53 g) was added in small portions at such a rate that the temperature did not exceed 5°. The solution was kept overnight at room temperature and then heated for 1 h at 55–65°. Compound **20** was isolated as a syrup (1.0 g), which was purified on a column of silica gel with 1:9 methanol–benzene as eluent, $[\alpha]_D^{18}$ +53° (*c* 2.04, chloro-

form); n.m.r. data (chloroform-*d*): δ 1.32 (6-proton triplet, *J* 7.8 Hz, SCH_2CH_3), 2.47–2.80 (4-proton overlapping quartets, SCH_2CH_3), 3.42 (3-proton singlet, OCH_3), and 5.20 (1-proton doublet, *J* 8.0 Hz, H-1); (dimethyl sulfoxide-d_6): δ 5.10 (1-proton doublet, *J* 8.0 Hz, H-1) and 5.28 (1-proton doublet, *J* 6.0 Hz, disappearing upon addition of deuterium oxide); m.s.: 252 (M^+) and 190 ($M^+ - C_2H_5SH$).

Anal. Calc. for $C_{10}H_{20}O_3S_2$: C, 47.60; H, 7.93. Found: C, 47.76; H, 7.89.

Acetylation of **20** with pyridine and acetic anhydride gave a syrup, $[\alpha]_D^{21}$ +42° (*c* 2.60, chloroform); n.m.r. showed the presence of one acetate group.

Anal. Calc. for $C_{12}H_{22}O_4S_2$: C, 48.99; H, 7.66. Found: C, 49.10; H, 7.56.

*Methyl 2-*S*-ethyl-5-*O*-methyl-2-thio-α(?)-*D*-lyxofuranoside* (**21**). — Compound **20** (1.0 g), cadmium carbonate (6.0 g), and a solution of mercuric chloride (2.5 g) in methanol (30 ml) were heated under reflux for 6 h. Compound **21** was isolated, as described for **8**, as a syrup (0.60 g), $[\alpha]_D^{20}$ +16° (*c* 2.15, chloroform); g.l.c. (200°): 6.33 min; n.m.r. data (chloroform-*d*): δ 1.30 (3-proton triplet, *J* 7.8 Hz, SCH_2CH_3), 2.62 (2-proton quartet, *J* 7.8 Hz, SCH_2CH_3), 3.42, 3.45 (3-proton singlets, OCH_3), and 4.91 (1-proton doublet, *J* 4.0 Hz, H-1).

Anal. Calc. for $C_9H_{18}O_4S$: C, 48.64; H, 8.11. Found: C, 48.82; H, 8.00.

*Methyl 5-*S*-ethyl-2-*O*-methyl-5-thio-α-*D*-xylofuranoside* (**16**). — Methyl 2-*O*-methyl-5-*O*-*p*-tolylsulfonyl-α-D-xylofuranoside[1] (2.5 g), ethanethiol (2 ml), and a solution of sodium (0.32 g) in methanol (30 ml) were heated under reflux overnight. The solution was extracted with chloroform and water, and the chloroform extracts were dried and evaporated to a syrup (1.58 g). This syrup was applied to a column of silica gel with 1:9 methanol–benzene as eluent to give **16** as a syrup (1.0 g), $[\alpha]_D^{25}$ +108° (*c* 2.6, chloroform); n.m.r. data (chloroform-*d*): δ 1.30 (3-proton triplet, *J* 7.8 Hz, SCH_2CH_3), 2.64 (2-proton quartet, *J* 7.8 Hz, SCH_2CH_3), 3.46, 3.54 (3-proton singlets, OCH_3), and 5.00 (1-proton doublet, *J* 4.3 Hz, H-1).

Anal. Calc. for $C_9H_{18}O_4S$: C, 48.64; H, 8.11. Found: C, 48.61; H, 8.09.

*5-*S*-Ethyl-2-*O*-methyl-5-thio-D-xylose diethyl dithioacetal* (**13**). — This compound was prepared from **16** with ethanethiol and hydrochloric acid as described for **11**, m.p. 59–60°; $[\alpha]_D^{22}$ +10° (*c* 1.76, chloroform); n.m.r. data (chloroform-*d*): δ 1.30 (9-proton triplet, *J* 7.8 Hz, SCH_2CH_3), 2.64 (6-proton complex, SCH_2CH_3), and 3.66 (3-proton singlet, OCH_3).

Anal. Calc. for $C_{12}H_{26}O_3S_3$: C, 45.86; H, 8.28. Found: C, 45.95; H, 8.23.

*2-*S*-Ethyl-5-*O*-methyl-D-lyxose diethyl dithioacetal* (**25**). — This compound was obtained from **20** by the procedure just described; syrup, $[\alpha]_D^{21}$ +14° (*c* 1.2, chloroform), n.m.r. data (chloroform-*d*): δ 1.30 (9-proton triplet, *J* 7.8 Hz, SCH_2CH_3), 2.77 (6-proton quartet, *J* 7.8 Hz, SCH_2CH_3), and 3.46 (3-proton singlet, OCH_3).

Anal. Calc. for $C_{12}H_{26}O_3S_3$: C, 45.86; H, 8.28. Found: C, 45.62; H, 8.05.

*Ethyl 2-*S*-ethyl-3,5-di-*O*-methyl-1,2-dithio-α-D-lyxofuranoside* (**22**). — (*a*). 2,3-Di-*O*-methyl-D-xylose diethyl dithioacetal[6] (**14**, 1.14 g) was treated with *p*-toluenesulfonyl chloride as described for **12** to give a syrup (1.0 g) after chromatography, $[\alpha]_D^{27}$ +42° (*c* 4.36, chloroform); g.l.c. (200°): 6.55 min; n.m.r. data (chloroform-*d*):

δ 1.30 (6-proton triplet, J 7.8 Hz, SCH_2CH_3), 2.68 (4-proton quartet, J 7.8 Hz, SCH_2CH_3), 3.40, 3.53 (3-proton singlets, OCH_3), and 5.29 (1-proton doublet, J 7.3 Hz, H-1); m.s.: 266 (M^+), 204 ($M^+ - C_2H_5SH$).

Anal. Calc. for $C_{11}H_{22}O_3S_2$: C, 49.63; H, 8.27. Found: C, 49.40; H, 8.42.

(*b*). Compound **22** was also formed by treatment of **20** with dimethyl sulfate and potassium hydroxide in tetrahydrofuran as described for **10**.

(*c*). Ethyl 2-*S*-ethyl-1,2-dithio-α-D-mannofuranoside[8] (**27**, 0.28 g) and potassium periodate in water (40 ml) were stirred at room temperature for 0.5 h. Sodium borohydride (0.50 g) was added in small portions over a period of 1 h. The solution was neutralized with acetic acid and evaporated to dryness. The residue was methylated, as described for **10**, to give a syrup (0.25 g) identical in all respects with the compound described under (*a*).

(*d*). A solution of mercuric chloride (0.70 g) in water (15 ml) was slowly added with stirring to a suspension of 2-*S*-ethyl-2-thio-D-lyxose diethyl dithioacetal[4] (**26**, 0.70 g) and barium carbonate (1.50 g) in water (15 ml), kept at 40°. When the addition was complete, the suspension was kept for an additional 0.5 h at 40°. The suspension was filtered and evaporated, and the residue extracted with ethyl acetate. The extract was evaporated to a syrup (0.60 g) which consisted of three components (t.l.c.): the starting material (**26**), the desired compound **28** (which had an R_F very similar to that of **26**), and a compound with the lowest R_F, which was probably 2-*S*-ethyl-2-thio-D-lyxose (the same compound was obtained by repeating the experiment with a double amount of mercuric chloride). The syrup was applied to a column of silica gel with 1:4 methanol–benzene as eluent to give syrupy ethyl 2-*S*-ethyl-1,2-dithio-α-D-lyxofuranoside (**28**, 0.15 g), $[\alpha]_D^{19}$ +64° (*c* 1.6, chloroform); n.m.r. data (chloroform-*d*): δ 1.33 (6-proton triplet, J 7.8 Hz, SCH_2CH_3), 2.65 (4-proton quartet, J 7.8 Hz, SCH_2CH_3), and 5.16 (1-proton doublet, J 8.0 Hz, H-1).

Anal. Calc. for $C_9H_{18}O_3S_2$: C, 45.37; H, 7.56. Found: C, 45.60; H, 7.63.

Methylation of **28** by the procedure described for **10** gave **22** showing identical g.l.c. properties, and i.r. and n.m.r. spectra identical with those of the compound described under (*a*).

Methyl 2-S-ethyl-3,5-di-O-methyl-2-thio-α(?)-D-lyxofuranoside (**23**). — As described previously for **20**, **22** gave a syrup (**23**), $[\alpha]_D^{20}$ +9° (*c* 1.2, chloroform); g.l.c. (175°): 6.50 min; n.m.r. data (chloroform-*d*); δ 1.30 (3-proton triplet, J 7.8 Hz, SCH_2CH_3), 2.62 (2-proton quartet, J 7.8 Hz, SCH_2CH_3), 3.42, 3.49 (singlets, 9 protons, OCH_3), and 5.02 (1-proton doublet, J 3.8 Hz, H-1).

Anal. Calc. for $C_{10}H_{20}O_4S$: C, 50.86; H, 8.48. Found: C, 51.06; H, 8.22.

Methyl 2-deoxy-3,5-di-O-methyl-α(?)-D-xylofuranoside (**24**). — Compound **23** (1.0 g) was treated with Raney nickel as described for **17** to give **24** as a syrup (0.35 g) after chromatography; g.l.c. (130°): 5.69 min (90%; the remaining 10% consisted of a number of unidentified peaks); $[\alpha]_D^{20}$ +29° (*c* 1.2, chloroform); n.m.r. data (chloroform-*d*): δ 3.34, 3.40, 3.45 (3-proton singlets, OCH_3), and 5.15 (1-proton triplet, J 4.0 Hz, H-1).

This compound had the same retention time as **24** prepared from 2-deoxy-

D-*threo*-pentose[10] with 0.1% hydrogen chloride in methanol for 12 min at room temperature, followed by methylation. The product of the methanolysis also contained some methyl 2-deoxy-β-D-*threo*-pentopyranoside (approximately 9%).

*1,2-Dideoxy-3,4,5-tri-O-methyl-*D-threo-*pentitol* (**18**). — 1,2-Dideoxy-D-*threo*-pentitol[4] (**19**, 0.25 g) was methylated, as described for the preparation of **10**, to give **18** (0.20 g) as a volatile liquid, $[\alpha]_D^{21}$ +16° (*c* 1.5, chloroform); g.l.c.: 2.86 min (100°) and 6.11 min (80°); n.m.r. data (chloroform-*d*): δ 0.97 (3-proton triplet, *J* 7.8 Hz, CH_2CH_3), 1.27–1.70 (2-proton distorted quartet, CH_2CH_3), 3.38, 3.45 and 3.50 (3-proton singlets, OCH_3); m.s.: M^+ absent, 133 ($M^+ - C_2H_5$), 89 ($CH_3OCH-CH_2OCH_3^+$), and 45 ($CH_2OCH_3^+$).

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