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INTRAMOLECULAR CYCLIZATION OF PENTOSE AND HEXOSE DITHIOACETALS*

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ABSTRACT

The intramolecular cyclization of *O*-tosyl derivatives of dithioacetals of D-ribose, D-arabinose, and D-glucose was investigated. *p*-Toluenesulfonylation of D-glucose diethyl dithioacetal gave 3,6-anhydro-D-glucose diethyl dithioacetal. Variously substituted 5-*O*-tosyl-D-glucose dibenzyl dithioacetals gave derivatives of either 2,5-anhydro-L-idose dibenzyl dithioacetal, benzyl 1,5-dithio-L-idopyranoside, or L-idose dibenzyl dithioacetal. Likewise, 4-*O*-tosyl-D-glucose dibenzyl dithioacetal derivatives gave benzyl 1,4-dithio-D-galactofuranoside derivatives.

INTRODUCTION

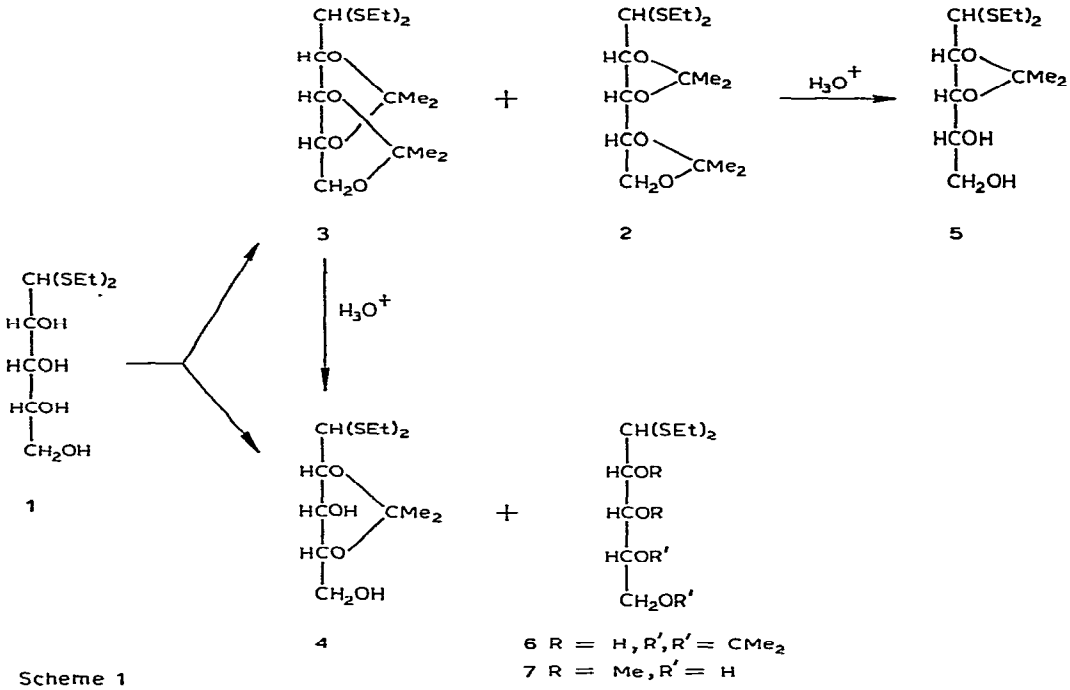
The potential of dithioacetal derivatives of pentoses as intermediates in the synthesis of furanoses and pyranoses having sulfur as the heteroatom has been reported[1]. This paper reports an extension of this synthetic approach to other pentose and D-glucose dithioacetals. For successful intramolecular cyclization, the synthesis of dithioacetals of pentoses having a sulfonic ester at O-5 or at O-4 or O-5 of hexoses is required. Suitable derivatization of the hydroxyl groups may be necessary to prevent the formation of such undesired products as 2,5-anhydro-pentose or -hexose dithioacetals.

DISCUSSION

In an attempt to form D-ribose dithioacetal derivatives having the 5-hydroxyl group free and the others protected, to allow formation of a 5-sulfonic ester, the reaction of D-ribose diethyl dithioacetal (**1**) with acetone was reinvestigated. Acid-catalyzed acetonation of D-ribose diethyl dithioacetal (**1**) has been reported to yield different isopropylidene derivatives, according to the conditions used[2,3] (see Scheme 1). Prolonged treatment of **1** with anhydrous copper(II) sulfate and acetone gave two diisopropylidene acetals, the known[3] 2,3;4,5-di-*O*-isopropylidene-D-ribose diethyl dithioacetal (**2**) and the hitherto unreported isomer 2,4;3,5-di-*O*-isopropylidene-

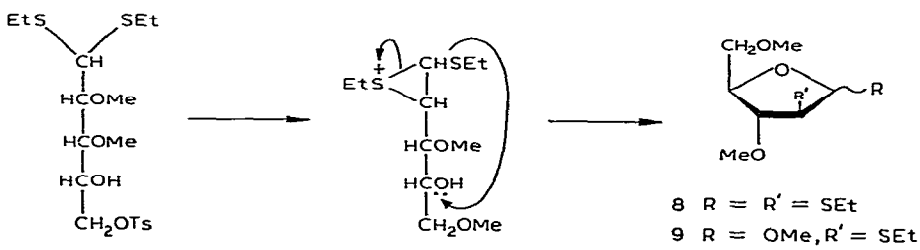
*Dedicated to Professor Roy L. Whistler.

D-ribose diethyl dithioacetal (**3**). Similar products are formed from D-xylose diethyl dithioacetal under the same conditions[4]. Partial hydrolysis of **3** gave the known[2] 2,4-*O*-isopropylidene-D-ribose diethyl dithioacetal (**4**), and similar treatment of **2** gave 2,3-*O*-isopropylidene-D-ribose diethyl dithioacetal (**5**). Compound **5** consumed



Scheme 1

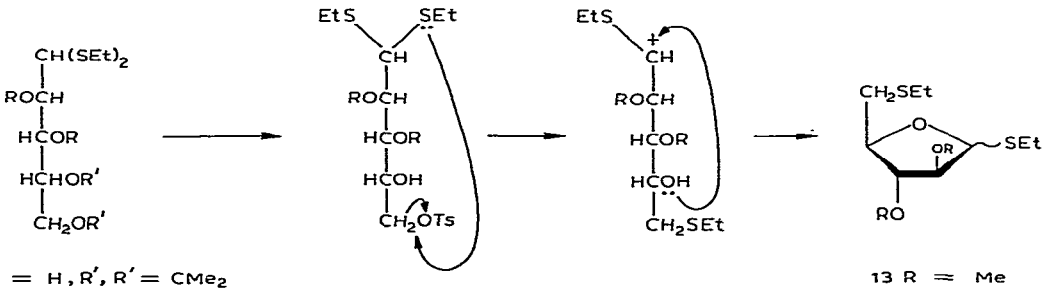
~ 1 mol of periodate and formed ~ 1 mol of formaldehyde. Methylation and subsequent hydrolysis of 4,5-*O*-isopropylidene-D-ribose diethyl dithioacetal[2] (**6**) gave 2,3-di-*O*-methyl-D-ribose diethyl dithioacetal (**7**). *p*-Toluenesulfonylation of **7** and warming of the resultant sulfonate in aqueous pyridine gave ethyl 2-*S*-ethyl-3,5-di-*O*-methyl-1,2-dithio-D-arabinofuranosides (**8**). Treatment of **8** with methanolic mercuric chloride gave methyl 2-*S*-ethyl-3,5-di-*O*-methyl-D-arabinofuranoside (**9**), reductive desulfurization of which with Raney nickel gave methyl 2-deoxy-3,5-di-*O*-methyl-D-*erythro*-pentofuranoside (**10**). This compound was also prepared by methylation of methyl 2-deoxy-D-*erythro*-pentofuranoside[5]. The stereochemistry of **8** is assumed to be



Scheme 2

D-*arabino* by analogy to the introduction of the ethylthio group at C-2 with inversion observed when 2,3-di-*O*-methyl-D-xylose diethyl dithioacetal is treated under the same conditions[5]. A probable mechanism for the formation of **8** is shown in Scheme 2. The displacement of the sulfonate by the 2-*O*-methyl group is facilitated by the formation of a 1,2-cyclic sulfonium ion. This sulfonium ion, in turn, is cyclized by the favorably disposed 4-hydroxyl group.

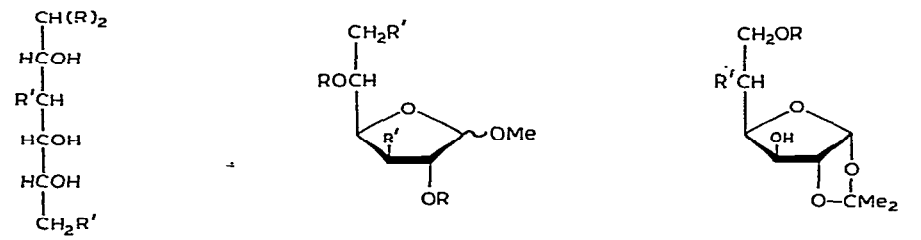
4,5-*O*-Isopropylidene-D-arabinose diethyl dithioacetal[6] (**11**) was prepared from D-arabinose diethyl dithioacetal by an improved procedure. Methylation and subsequent hydrolysis of compound **11** gave 2,3-di-*O*-methyl-D-arabinose diethyl dithioacetal (**12**). Compound **12** was treated with *p*-toluenesulfonyl chloride and the presumed sulfonic ester formed cyclized to give ethyl 5-*S*-ethyl-2,3-di-*O*-methyl-1,5-dithio-D-arabinofuranoside (**13**). The synthesis of ethyl 5-*S*-ethyl-1,5-dithiofuranoside (**14**) has been reported by Hughes[7]. Methylation of **14** gave **13**. A possible mechanism[7], involving a cyclic sulfonium ion, for the formation of **13** or **14** is shown in Scheme 3.



11 R = H, R', R' = CMe_2
12 R = Me, R' = H

13 R = Me
14 R = H

Scheme 3



15 R = SEt, R' = OH
16 R = SEt, R', R' = O

17 R = H, R' R' = O
18 R = Ac, R', R' = O

34 R = Bz, R' = OTs
39 R = Ts, R' = OTs

Treatment of D-glucose diethyl dithioacetal (**15**) with 1 mol of *p*-toluenesulfonyl chloride gave 3,6-anhydro-D-glucose diethyl dithioacetal (**16**). Compound **16** was also formed by reaction of the known[8] methyl 3,6-anhydro-D-glucofuranoside (**17**) with ethanethiol. Treatment of the acetate of **16** with mercuric chloride in buffered methanol gave methyl 2,5-di-*O*-acetyl-3,6-anhydro-D-glucofuranosides (**18**).

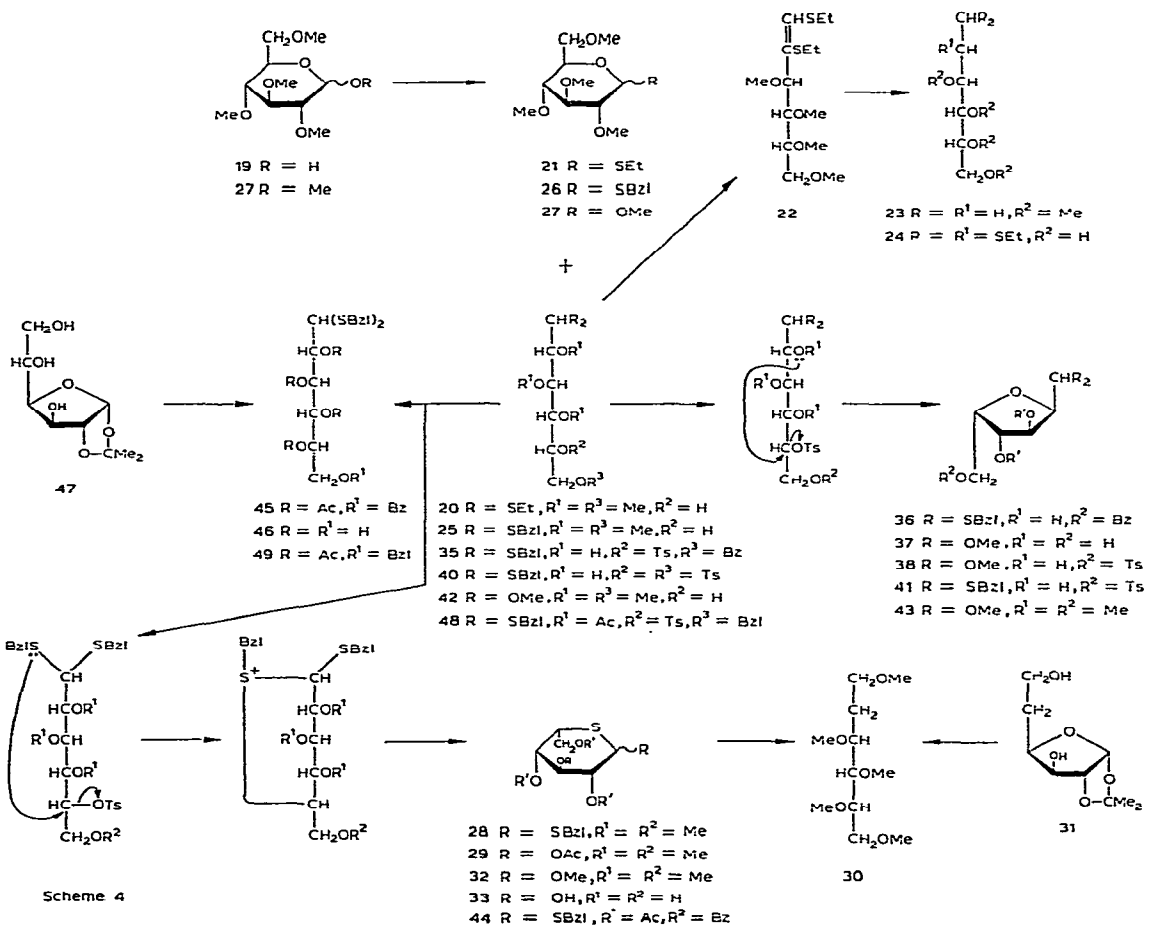
Treatment of 2,3,4,6-tetra-*O*-methyl-D-glucose[9] (**19**) with ethanethiol gave 2,3,4,6-tetra-*O*-methyl-D-glucose diethyl dithioacetal (**20**) and ethyl 2,3,4,6-tetra-*O*-methyl-1-thio-α,β-D-glucopyranosides (**21**). A brief reaction-time gave mainly **20** but longer reaction-times gave more **21**. The formation of thioglycosides following the initial rapid formation of dithioacetals has been reported[10] for the reaction of monosaccharides with thiols in acidic solution. Treatment of **20** with *p*-toluenesulfonyl chloride gave 1,2-di-*S*-ethyl-3,4,5,6-tetra-*O*-methyl-1,2-dithio-D-*arabino*-hex-1-enitol (**22**). An analogous reaction has been reported[5] for 2,3,4-tri-*O*-methyl-D-xylose diethyl dithioacetal. Reduction of **22** with Raney nickel gave 1,2-dideoxy-3,4,5,6-tetra-*O*-methyl-D-*arabino*-hexitol (**23**). Compound **23** was also formed by reductive desulfurization and subsequent methylation of 2-*S*-ethyl-2-thio-D-mannose diethyl dithioacetal[11] (**24**).

Reaction of compound **19** with phenylmethanethiol again gave two products, 2,3,4,6-tetra-*O*-methyl-D-glucose dibenzyl dithioacetal (**25**) and benzyl 2,3,4,6-tetra-*O*-methyl-1-thio-D-glucopyranoside (**26**). Treatment of compound **26** with mercuric chloride in buffered methanol gave methyl 2,3,4,6-tetra-*O*-methyl-D-glucopyranosides (**27**). The resultant sulfonate, prepared from **25**, was boiled under reflux in buffered acetone with sodium iodide to give 2,3,4,6-tetra-*O*-methyl-1,5-dithio-L-idopyranoside (**28**). Compound **28** gave n.m.r. signals for one phenyl group, four methyl groups, and an anomeric proton. Mass-spectral analysis gave the expected molecule-ion at 358 daltons. Treatment of **28** with mercuric acetate in acetic acid gave 1-*O*-acetyl-2,3,4,6-tetra-*O*-methyl-5-thio-L-idopyranoside (**29**). Treatment of **29** with Raney nickel followed by methylation gave 2-deoxy-1,3,4,5,6-penta-*O*-methyl-L-*xylo*-hexitol (**30**). This compound was also synthesized from the known[12] 5-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose (**31**) by sequential hydrolysis, reduction at C-1, and methylation. Methylation of **29** gave methyl 2,3,4,6-tetra-*O*-methyl-5-thio-L-idopyranoside (**32**), which was also prepared by methylation of 5-thio-L-idopyranose[13] (**33**).

Treatment of 6-*O*-benzoyl-1,2-*O*-isopropylidene-5-*O*-*p*-tolylsulfonyl-D-glucofuranose (**34**) with phenylmethanethiol in trifluoroacetic acid gave crystalline 6-*O*-benzoyl-5-*O*-*p*-tolylsulfonyl-D-glucose dibenzyl dithioacetal (**35**). Brief treatment of **35** with pyridine gave 2,5-anhydro-6-*O*-benzoyl-L-idose dibenzyl dithioacetal (**36**). Removal of the benzoyl groups followed by treatment with mercuric chloride in buffered methanol gave 2,5-anhydro-L-idose dimethyl acetal (**37**), which in turn was prepared from the known[14] 2,5-anhydro-6-*O*-*p*-tolylsulfonyl-L-idose dimethyl acetal (**38**) by displacement of the terminal sulfonate group by acetate ion and subsequent deacylation. Similarly, 1,2-*O*-isopropylidene-5,6-di-*O*-*p*-tolylsulfonyl-D-glucofuranose (**39**), when treated with phenylmethanethiol gave the dithioacetal (**40**), which on treatment with pyridine gave 2,5-anhydro-6-*O*-*p*-tolylsulfonyl-L-idose dibenzyl dithioacetal (**41**). Compound **41** was converted into **38** on treatment with mercuric chloride in buffered methanol. Base-catalyzed formation of 2,5-anhydro-D-ribose, -D-xylose, and -D-lyxose dithioacetal by intramolecular displacement of a 5-sulfonate by the favorably disposed 2-hydroxyl group has been reported[15]. The

formation of 2,5-anhydrides does also occur by the attack on C-5 of the oxygen atom of a 2-methoxyl group. Thus, treatment of 2,3,4,6-tetra-*O*-methyl-D-glucose dimethyl acetal (**42**) with *p*-toluenesulfonyl chloride gave 2,5-anhydro-3,4,6-tri-*O*-methyl-L-idose dimethyl acetal (**43**). Compound **43** was also prepared by methylation of **37**.

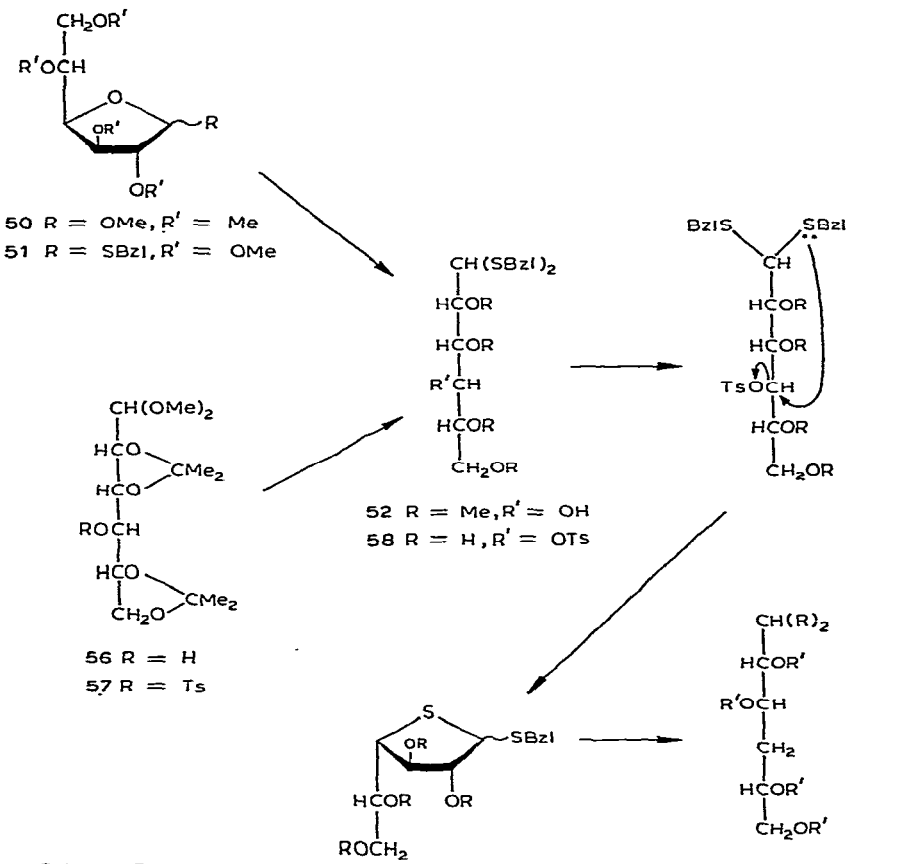
Treatment of the acetate of **35** with sodium iodide in buffered acetone did not give the expected 5-thio-L-idose derivative **44**. Instead, under these conditions the 5-sulfonate was slowly removed with inversion to afford a compound having the L-*ido* configuration. The product was acetylated to give the crystalline 2,3,4,5-tetra-*O*-acetyl-6-*O*-benzoyl-L-idose dibenzyl dithioacetal (**45**). Monobenzoylation of L-idose dibenzyl dithioacetal (**46**), followed by acetylation, also gave **45**. The dithioacetal **46** was prepared from 1,2-*O*-isopropylidene-L-idofuranose[16] (**47**) by treatment with phenylmethanethiol and trifluoroacetic acid. When the dibenzyl dithioacetal **35** was treated with sodium iodide in buffered acetone, the 2,5-anhydride **36** resulted. A change in the substituent at C-6 from benzoic ester in **35** to benzyl ether (**48**) gave an L-*ido* derivative, namely, 2,3,4,5-tetra-*O*-acetyl-6-*O*-benzyl-L-idose dibenzyl



Scheme 4

dithioacetal (**49**), on treatment sodium iodide. The various reactions of the 5-sulfonates of D-glucose dithioacetals are shown in Scheme 4. For the dibenzyl dithioacetal **23**, the sulfonic ester at C-5 is displaced, with inversion, by the benzylthio group at C-1 to form a cyclic, sulfonium ion. Under the SN2 conditions used (iodide ion in anhydrous acetone) the benzyl group was removed from the sulfonium ion to form 5-thiopyranoside **26**, rather than attack of the group at C-4, which would have resulted in the formation of 1,5-di(benzylthio) derivatives.

Methyl 2,3,5,6-tetra-*O*-methyl-D-glucofuranoside[17] (**50**) was treated with phenylmethanethiol to give benzyl 2,3,5,6-tetra-*O*-methyl-1-thio-D-glucofuranosides (**51**) and 2,3,5,6-tetra-*O*-methyl-D-glucose dibenzyl dithioacetal (**52**). Compound **51** was converted into the known methyl 2,3,5,6-tetra-*O*-methyl-α,β-D-glucofuranosides (**50**) by treatment with mercuric chloride in buffered methanol. Compound **52** was converted into benzyl 2,3,5,6-tetra-*O*-methyl-1,4-dithio-D-galactofuranoside (**53**). Treatment of **53** with Raney nickel gave 1,4-dideoxy-2,3,5,6-tetra-*O*-methyl-D-*xylo*-



Scheme 5

hexitol (**54**). This compound was synthesized from the known[18] 4-deoxy-D-*xylo*-hexose dibenzyl dithioacetal (**55**) by treatment with Raney nickel followed by methylation. Treatment of 2,3;5,6-di-*O*-isopropylidene-D-glucose dimethyl acetal[19] (**56**) with *p*-toluenesulfonyl chloride gave the 4-*O*-tosyl derivative **57**. Reaction of **57** with phenylmethanethiol in trifluoroacetic acid yielded 4-*O*-*p*-tolylsulfonyl-D-glucose dibenzyl dithioacetal (**58**). The acetate of **58** reacted with sodium iodide to give benzyl 2,3,5,6-tetra-*O*-acetyl-1,4-dithio-D-galactofuranoside (**59**), which was deacylated to afford crystalline benzyl 1,4-dithio-D-galactofuranoside (**60**). Compound **59** showed n.m.r. signals for four acetate and one benzylthio group, however, the anomeric-proton signal was obscured by an overlap of two other proton signals. Methylation of **60** gave **53**. The *galacto* configuration of **53** and **60** is assumed because the intramolecular cyclization of dibenzyl dithioacetals appears to occur with inversion (see Scheme 5).

EXPERIMENTAL

General methods. — A. Equipment and analyses. I.r. spectra were measured with a Perkin–Elmer Model 700 spectrophotometer. U.v. spectra were recorded with a Cary 11 and a Beckman DB recording spectrophotometer. Mass spectra were determined with a Hitachi–Perkin–Elmer RMU-7 mass spectrometer. Nuclear magnetic resonance spectra were recorded with a Varian T-60 spectrometer. Chemical shifts are given in p.p.m. with tetramethylsilane as the internal standard. Melting points were obtained on a Fisher–Johns apparatus and are uncorrected. G.l.c. analyses were performed on a Bendix Gas Chromatograph 2600 equipped with a column (1.8 m × 2 mm) containing 10% of EGSS-X on Gas Chrom-P (Applied Science Labs., State College, PA, USA), with nitrogen as the carrier gas. Column chromatography was performed on silica gel (60–200 mesh, Baker). High-pressure liquid chromatography (h.p.l.c.) was performed on a column (3.2 × 250 mm) of Lichrosorb (5 μm, Merck) at 160 atm, with detection at 254 nm with an Altex detector. Periodate consumption[20] was determined by the spectrophotometric method. Formaldehyde concentrations were determined by the chromotropic acid assay[20].

B. Acetylation. Acetates were prepared by dissolving the compound (1 g) in acetic anhydride (5 mL) and pyridine (5 mL). This solution was kept overnight at room temperature.

Mixtures that contained pyridine (the product of acetylation or *p*-toluenesulfonylation) were poured into saturated, aqueous sodium hydrogencarbonate and the suspension extracted with chloroform. The extracts were sequentially washed with ice-cold dilute hydrochloric acid, saturated sodium hydrogencarbonate, and water. The chloroform was dried and evaporated.

C. Methylation. Methyl ethers were prepared by addition to stirred solution of the compound (1 g) in dry oxolane (25 mL) of powdered potassium hydroxide (5 g) and methyl sulfate (5 mL) at room temperature during period of 1 h. The same amounts of fresh reagents were added and the suspension was then boiled for 1 h

under reflux. At the end of the reaction time, concentrated ammonium hydroxide was added slowly to decompose the excess of methyl sulfate. The suspension was partitioned between water and chloroform. The chloroform extract was washed with water (twice) and dried. The chloroform solution was concentrated.

D. p-*Toluenesulfonylation.* To a solution of the compound (1.0 g) in anhydrous pyridine (10 mL) at 0–5°, *p*-toluenesulfonyl chloride (1.1 mol/hydroxyl group reacted) was slowly added over a 2-h period. The mixture was stored overnight at room temperature. Water (1 mL) was added to decompose any excess sulfonyl chloride, and the solution partitioned between chloroform and water. The chloroform extracts were processed as described under (*B*).

E. Removal of alkylthio groups. A suspension of the compound (1.0 g), mercuric chloride (2.0 g), cadmium carbonate (5.0 g), and methanol (20 mL) was boiled under reflux overnight. The mixture was filtered and the filtrate partitioned between chloroform and water. The chloroform extract was washed with a concentrated solution of potassium cyanide, water, dried, and concentrated.

F. Reductive desulfurization. A mixture of compound (1.0 g), Raney nickel (~15 g), and abs. ethanol (20 mL) was boiled for 20 h under reflux. The suspension was filtered and the nickel washed 5 times with 20-mL portions of hot, abs. alcohol. The filtrate was evaporated.

G. Reaction with sodium iodide. A suspension of the compound (1.0 g), sodium iodide (2.5 g), barium carbonate (5.0 g), and acetone (30 mL) was boiled under reflux for 24 h. The suspension was filtered and the solids were washed with chloroform. The filtrate was sequentially washed with water, sodium thiosulfate solution, and water, dried, and evaporated.

2,3;4,5- and *2,4;3,5-Di-*O*-isopropylidene-*D*-ribose diethyl dithioacetal* (**2** and **3**). — D-Ribose diethyl dithioacetal[21] (**1**) (1.0 g), acetone (30 mL) and anhydrous copper sulfate (5.0 g) were stirred for 36 h at room temperature. The suspension was filtered through a Celite pad to remove the copper sulfate and the pad washed repeatedly with acetone. The filtrate was evaporated to a syrup (1.2 g). Chromatography with 1:4 (v/v) ethyl acetate–ligroin gave **2** (0.7 g) and **3** (0.4 g); **2** had $[\alpha]_D^{21}$ −4° (*c* 1.6, chloroform); n.m.r. (chloroform-*d*): δ 1.36 (complex, 18H, 2 CMe_2 and 2 SCH_2CH_3), and 2.63 (q, 4H, SCH_2CH_3); g.l.c. retention-time: 6.01 min (175°).

Anal. Calc. for $C_{15}H_{28}O_4S_2$: C, 53.6; H, 8.3. Found: C, 53.1; H, 8.0.

Compound **3** had $[\alpha]_D^{21}$ −60° (*c* 1.2, chloroform); n.m.r. (chloroform-*d*): δ 1.36 (complex, 18H, 2 CMe_2 and 2 SCH_2CH_3), and 2.63 (q, 4H, SCH_2CH_3); g.l.c. retention-time: 9.10 min (175°).

Anal. Calc. for $C_{15}H_{28}O_4S_2$: C, 53.6; H, 8.3. Found: C, 53.5; H, 8.4.

Hydrolysis of **2** *and* **3**. — Partial hydrolysis of **2** and **3** was performed by the method reported by van Es[4].

Compound **5** consumed 0.98 mol of periodate and formed 0.95 mol of formaldehyde; $[\alpha]_D^{21}$ −11° (*c* 3.32, chloroform); n.m.r. data (methyl sulfoxide-d_6): δ 1.2 (complex, 12H, CMe_2 and 2 SCH_2CH_3), 2.56 (q, 4H, SCH_2CH_3), 4.9 (t, 1H,

CH_2OH, disappeared upon addition of D_2O), and 5.2 (d, 1H, CHO*H*, disappeared upon addition of D_2O).

Anal. Calc. for $C_{12}H_{24}O_4S_2$: C, 48.7; H, 8.1. Found: C, 48.6; H, 8.0.

Hydrolysis of **3** gave syrupy 2,4-*O*-isopropylidene-D-ribose diethyl dithioacetal (**4**) (0.85 g). Compound **4** consumed no periodate when examined by the spectrometric method.

D-Ribose diethyl dithioacetal (**1**, 2.0 g), acetone (30 mL), and anhydrous copper (II) sulfate (5.0 g) were stirred for 2.5 h at 45°. The mixture was treated as described for compounds **2** and **3**. Chromatography with 2:3 (v/v) ethyl acetate–ligroin gave **6** (1.46 g), **4** (0.20 g), and the diisopropylidene acetals **2** and **3** (0.24 g). Compound **4** was converted into the acetate as described in procedure *B*. G.l.c. analysis of this acetylated compound showed its identity with acetylated compound **4**, obtained by hydrolysis; g.l.c. retention-time: 18.10 min (190°).

2,3-Di-O-methyl-D-ribose diethyl dithioacetal (**7**). — 4,5-*O*-Isopropylidene-D-ribose diethyl dithioacetal[2] (**6**) was converted into the methyl ether as described under procedure C to yield a syrup (1.1 g) that contained traces of impurities. I.r. analysis revealed no hydroxyl absorption, and the syrup was used without further purification.

The syrup (1.0 g), methanol (50 mL) and 0.5M sulfuric acid (0.4 mL) were boiled for 2.5 h under reflux. The solution was neutralized with lead carbonate, filtered, and the filtrate evaporated to a syrup (0.9 g). Chromatography with 3:2 (v/v) ethyl acetate–ligroin gave **7** (0.65 g) as a syrup; $[\alpha]_D^{21}$ +14° (*c* 1.2, chloroform); n.m.r. (chloroform-*d*): δ 1.36 (t, 6H, SCH_2CH_3), 2.66 (complex, 4H, SCH_2CH_3), 3.53 and 3.66 (s, 2 × 3 H, OCH_3). Compound **7** consumed 1.02 mol of periodate and formed 0.98 mol of formaldehyde.

Anal. Calc. for $C_{11}H_{24}O_4S_2$: C, 46.5; H, 8.5. Found: C, 47.0; H, 8.3.

Ethyl 2-S-ethyl-3,5-di-O-methyl-1,2-dithio-D-arabinofuranosides (**8**). — Compound **7** (1.0 g) was converted into the sulfonic ester by procedure *D*. The crude *p*-toluenesulfonate was dissolved in pyridine (10 mL) and water (1 mL), and the solution kept for 1 h at 60–65°. The mixture was treated as described under procedure *B* to give a syrup (0.65 g). Chromatography with 1:19 (v/v) methanol–benzene gave **8** (0.45 g); $[\alpha]_D^{21}$ −3° (*c* 1.12, chloroform); n.m.r. (chloroform-*d*): δ 1.30 (t, 6H, SCH_2CH_3), 2.63 (q, 4H, SCH_2CH_3), 3.43 (s, 6H, OCH_3), and 5.26 (s, 1H, H-1).

Anal. Calc. for $C_{11}H_{22}O_3S_2$: C, 49.6; H, 8.3. Found: C, 50.0; H, 8.3.

Methyl 2-deoxy-3,5-di-O-methyl-D-erythro-pentofuranoside (**10**). — (*a*). Compound **8** was converted into methyl 2-*S*-ethyl-3,5-di-*O*-methyl-α,β-D-arabinofuranoside (**9**) by procedure *E*. Compound **9** was reduced by procedure *F* to **10**.

(*b*). Methyl 2-deoxy-D-*erythro*-pentofuranoside[5] was methylated by procedure *C* to give **10**.

Products from (*a*) and (*b*) were identical.

4,5-O-Isopropylidene-D-arabinose diethyl dithioacetal (**11**). — D-Arabinose diethyl dithioacetal[22] (5.0 g), acetone (100 mL), and anhydrous copper(II) sulfate (25 g) were boiled for 30 min under reflux. The suspension was filtered and the

filtrate evaporated. Compound **11** (5.3 g) was crystallized from ligroin; m.p. 71° (lit.[5] m.p. 70°).

2,3-Di-O-methyl-D-arabinose diethyl dithioacetal (**12**). — Compound **11** (1.0 g), was converted into the methyl ether as described under procedure *C*; $[\alpha]_D^{21}$ −10° (*c* 1.38, chloroform); n.m.r. (chloroform-*d*): δ 1.5 (complex, 12H, CMe_2 and $2SCH_2CH_3$), 2.66 (q, 4H, SCH_2CH_3), 3.58, and 3.62 (s, 2 × 3 H, OCH_3).

The crude syrup (4.8 g), methanol (100 mL), and 0.5M sulfuric acid (25 mL) were treated exactly as described for compound **7** (except that the reaction time was shortened to 0.5 h) to yield **10** as a syrup that crystallized from ethyl acetate–ligroin; m.p. 63–65° (2.9 g). These data are in contrast with the literature[6], in which **12** was reported to be a syrup obtained in very poor yield.

Ethyl 5-S-ethyl-2,3-di-O-methyl-1,5-dithio-D-arabinofuranosides (**13**). — Compound **12** (1.42 g) was converted into the sulfonic ester as described under procedure *D*.

(*a*). A mixture of the crude syrup (2.5 g), barium carbonate (15.0 g), acetone (25 mL), and water (25 mL) was stirred and boiled for 18 h under reflux. The suspension was filtered and the filtrate evaporated to remove acetone. The residual aqueous phase was extracted three times with chloroform and the extracts evaporated to a syrup (1.35 g). Chromatography with 2:3 (v/v) ethyl acetate–ligroin gave compound **13** (0.96 g).

(*b*). A mixture of the syrup (1.0 g), pyridine (10 mL), and water (1 mL) was heated for 1 h at 65°. Chromatography with 1:19 (v/v) methanol–benzene gave **13**; $[\alpha]_D^{21}$ +1° (*c* 1.73, chloroform); n.m.r. (chloroform-*d*): δ 1.26 and 1.30 (t, 2 × 3 H, SCH_2CH_3), 2.75 and 2.70 (q, 2 × 2 H, SCH_2CH_3), 3.45 (s, 6H, OCH_3), and 5.26 (d, 1H, H-1).

Anal. Calc. for $C_{11}H_{22}O_3S_2$: C, 49.6; H, 8.3. Found: C, 49.2; H, 8.4.

(*c*). Ethyl 5-*S*-ethyl-1,5-dithio-D-arabinofuranosides[7] (**14**, 0.50 g) were converted into the methyl ethers as described under procedure *C* to yield a syrup (0.55 g) that was identical by g.l.c. to the products from the foregoing procedure (*a*) and (*b*); g.l.c. retention times: 4.50 and 6.00 min (190°).

3,6-Anhydro-D-glucose diethyl dithioacetal (**16**). — (*a*). D-Glucose diethyl dithioacetal[23] (**15**, 3.0 g), treated by procedure *D*, gave a syrup (2.23 g). Starting material (**15**) was removed from the syrup by the addition of ethanol and filtration. The filtrate was evaporated to a syrup (0.95 g). Chromatography with 1:4 (v/v) methanol–benzene gave **16** (0.42 g). Compound **16** was acetylated (procedure *B*) to give crystalline 2,4,5-tri-*O*-acetyl-3,6-anhydro-D-glucose diethyl dithioacetal (m.p. 78–80°, ethyl acetate–hexane); $[\alpha]_D^{21}$ −56° (*c* 1.12, chloroform); n.m.r. (chloroform-*d*): δ 1.26 (t, 6H SCH_2CH_3), 2.26, 2.34, 2.36 (s, 3 × 3 H, $OCOCH_3$), and 2.80 (complex, 4H, SCH_2CH_3).

Anal. Calc. for $C_{16}H_{26}O_7S_2$: C, 48.7; H, 6.6. Found: C, 48.9; H, 6.5.

(*b*). Methyl 3,6-anhydro-α-D-glucofuranoside[8] (**17**, 0.50 g), concentrated hydrochloric acid (2 mL), and ethanethiol (5 mL) were stirred for 1 h at room temperature. The mixture was made neutral with IR-45 (OH^-) resin, which was then filtered off. The filtrate was evaporated to a syrup, which was extracted with

hot ethyl acetate (5 mL). The extract was evaporated to a syrup (0.52 g) that was acetylated (procedure *B*) to yield a syrup (0.6 g) which crystallized from ethyl acetate–hexane; m.p. 78–79°, unchanged on admixture with the acetylated product from (*a*).

*Methyl 2,5-di-*O*-acetyl-3,6-anhydro-*D*-glucofuranosides* (**18**). — The acetate of compound **16** (1.48 g) was converted into **18** by procedure *E*. Chromatography with 1:19 (v/v) methanol–benzene gave **18** as a syrup (0.30 g). Methyl 3,6-anhydro-D-glucofuranosides[8] were acetylated (procedure *B*) and gave products identical by g.l.c. to **18**; $[\alpha]_D^{21}$ +4° (*c* 1.57, chloroform); n.m.r. (chloroform-*d*): δ 2.10, 2.23 (s, 2 × 3 H, $OCOCH_3$), 3.60 and 3.66 (s, 2 × 3 H, OCH_3).

*2,3,4,6-Tetra-*O*-methyl-D-glucose diethyl dithioacetal* (**20**). — 2,3,4,6-Tetra-*O*-methyl-D-glucopyranose[9] (**19**, 1.12 g), ethanethiol (3 mL), and concentrated hydrochloric acid (1 mL) were stirred for 4 min at room temperature. The mixture was immediately extracted with chloroform and water. The chloroform extract was washed with saturated sodium hydrogencarbonate and evaporated to a syrup (1.20 g). Chromatography with 1:24 (v/v) methanol–benzene gave **20** (0.80 g) and ethyl 2,3,4,6-tetra-*O*-methyl-1-thio-D-glucopyranosides (**21**) (0.35 g).

Compound **20** had $[\alpha]_D^{21}$ +39° (*c* 1.17, chloroform); n.m.r. (chloroform-*d*): δ 1.26 (t, 6H, SCH_2CH_3), 2.66 (q, 4H, SCH_2CH_3), 3.38, 3.44, 3.53, and 3.56 (s, 4 × 3 H, OCH_3).

Anal. Calc. for $C_{14}H_{30}O_5S_2$: C, 49.1; H, 8.8. Found: C, 49.5; H, 8.8.

Compound **21** had $[\alpha]_D^{21}$ −4° (*c* 1.94, chloroform); n.m.r. (chloroform-*d*): δ 1.27 (t, 3H, SCH_2CH_3), 2.60 (complex, 2H, SCH_2CH_3), 3.36, 3.46, 3.56, and 3.60 (s, 4 × 3 H, OCH_3).

Anal. Calc. for $C_{12}H_{24}O_5S$: C, 51.4; H, 8.6. Found: C, 51.8; H, 8.5.

Compound **21** (1.0 g), gave the known methyl 2,3,4,6-tetra-*O*-methyl-α,β-D-glucopyranosides[9] (0.69 g) by procedure *E*; g.l.c. retention-times 4.25 and 6.18 min (170°).

*1,2-Di-*S*-ethyl-3,4,5,6-tetra-*O*-methyl-1,2-dithio-*D*-arabino-hex-1-enitol* (**22**). — Compound **20** (0.8 g), was converted into syrupy **22** (0.7 g) by procedure *D*; $[\alpha]_D^{21}$ −60° (*c* 1.768, chloroform); ν_{max}^{film} 1580 cm^{-1} (C=C); n.m.r. (chloroform-*d*): δ 1.23, 1.33 (t, 2 × 3 H, SCH_2CH_3), 2.66, 2.70 (q, 2 × 2 H, SCH_2CH_3), 3.23, 3.26, 3.30, 3.40 (s, 4 × 3 H, OCH_3), 6.50 (s, 1H, HC=C).

Anal. Calc. for $C_{14}H_{28}O_4S_2$: C, 51.9; H, 8.6. Found: C, 52.4; H, 8.7.

Reductive desulfurization of **22**. — Compound **22** or the tetramethyl ether[11] of **24** (1.0 g, prepared from **22** by procedure *C*) was converted into **23**, a volatile oil (0.4 g) by procedure *F*. The products were identical by spectroscopy and g.l.c.; $[\alpha]_D^{21}$ −245° (*c* 1.95, chloroform); n.m.r. (chloroform-*d*): δ 0.90 (t, 3H, CH_2CH_3), 3.30, 3.36, and 3.40 (s, 3,6,3H, OCH_3).

*2,3,4,6-Tetra-*O*-methyl-D-glucose dibenzyl dithioacetal* (**25**). — 2,3,4,6-Tetra-*O*-methyl-D-glucopyranose (**19**) (3.0 g) phenylmethanethiol (5 mL), and concentrated hydrochloric acid (2 mL) were stirred for 18 h at room temperature. The mixture was diluted with chloroform and the chloroform layer washed sequentially with water and saturated sodium hydrogencarbonate. The chloroform solution was

evaporated to a syrup that was taken up in ethanol and applied to a column of IR-45 (OH^-) resin with ethanol as the mobile phase. The ethanol was evaporated at room temperature to give a syrup (3.7 g). Chromatography with 1:32 (v/v) methanol–benzene gave compound **25** (2.8 g) and benzyl 2,3,4,6-tetra-*O*-methyl-1-thio-α,β-D-glucopyranoside (**26**, 0.8 g).

Compound **25** had $[\alpha]_D^{21}$ +58° (*c* 1.13, chloroform); n.m.r. (chloroform-*d*): δ 3.03, 3.34, 3.36, 3.56 (s, 4 × 3 H, OCH_3), 3.80, 3.83 (s, 2 × 2 H, $CH_2C_6H_5$), and 7.20 (s, 10H, $CH_2C_6H_5$).

Anal. Calc. for $C_{24}H_{34}O_5S_2$: C, 61.80; H, 7.30. Found: C, 62.1; H, 7.2.

Compound **26** had $[\alpha]_D^{21}$ +2° (*c* 1.54, chloroform); n.m.r. (chloroform-*d*): δ 3.16, 3.33, 3.46, 3.50 (s, 4 × 3 H, OCH_3), 3.63 (s, 2H, $CH_2C_6H_5$), 5.26 (d, 1H, H-1) and 7.2 (complex, 5H, $CH_2C_6H_5$).

Anal. Calc. for $C_{17}H_{26}O_5S$: C, 59.7; H, 7.6. Found: C, 59.5; H, 7.6.

Compound **26** (1.0 g) was converted into the known[8] methyl 2,3,4,6-tetra-*O*-methyl-α,β-D-glucopyranoside (**27**) by procedure *E*, g.l.c. retention-times: 4.25 and 6.18 min (170°).

*Benzyl 2,3,4,6-tetra-*O*-methyl-1,5-dithio-*L*-idopyranosides* (**28**). — Compound **25** (2.8 g) was converted into the sulfonic ester (3.4 g, syrup) by procedure *D*.

The crude, syrupy sulfonate was converted into **28** by procedure *G*. Chromatography with 1:24 (v/v) methanol–benzene gave **28** (0.5 g); $[\alpha]_D^{21}$ +36° (*c* 1.64, chloroform); n.m.r. (chloroform-*d*): δ 3.16, 3.33, 3.43 (s, 3,6,3 H, OCH_3), 3.93 (complex, 2H, $CH_2C_6H_5$), 6.1 (complex, 1H, H-1), and 7.23 (s, 5H, $CH_2C_6H_5$); *m/e* 358 (M^+).

Anal. Calc. for $C_{17}H_{26}O_4S_2$: C, 57.0; H, 7.3. Found: C, 57.4; H, 7.2.

*1-O-Acetyl-2,3,4,6-tetra-*O*-methyl-5-thio-α,β-L-idopyranosides* (**29**). — Compound **28** (1.0 g), mercuric acetate (2.0 g), and glacial acetic acid (25 mL) were warmed for 18 h at 45°. The mixture was filtered through a Celite pad and the filtrate diluted with chloroform. The chloroform extract was washed sequentially with water, saturated sodium hydrogencarbonate, and 5% aqueous potassium cyanide, and evaporated to a syrup (0.8 g). Chromatography with 1:19 (v/v) methanol–benzene yielded **29** (0.6 g); $[\alpha]_D^{21}$ +15° (*c* 1.49, chloroform); n.m.r. (chloroform-*d*): δ 2.02, 2.08 (s, 3H, $OCOCH_3$), 3.36, 3.38, and 3.50 (s, 3,6,3H, OCH_3).

Anal. Calc. for $C_{12}H_{22}O_6S$: C, 49.0; H, 7.5. Found: C, 49.2; H, 7.4.

*5-Deoxy-1,2,3,4,6-penta-*O*-methyl-*D*-xylo-hexitol* (**30**). — Compound **29** (1.0 g) was reduced with Raney nickel as described under procedure *F* to yield 1-*O*-acetyl-5-deoxy-2,3,4,6-tetra-*O*-methyl-D-*xylo*-hexitol (0.7 g).

(*a*). The foregoing syrup (0.7 g), without purification, was converted into **30** by procedure *C*.

(*b*). 5-Deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose[12] (**31**) (1.0 g) was dissolved in methanol (10 mL) and M aqueous hydrochloric acid (10 mL), and the solution was boiled for 1 h under reflux. The mixture was made neutral with IR-45 (OH^-) resin, which was then filtered off. The solution was evaporated to yield syrupy 5-deoxy-D-glucofuranose (0.9 g), which was used without further purification.

5-Deoxy-D-glucofuranose (0.9 g) was dissolved in water (5 mL), and sodium borohydride (2.0 g) was added in small portions during 1 h. The solution was kept for an additional 1 h at room temperature, and glacial acetic acid was added slowly to decompose the excess of sodium borohydride. The solution was evaporated, and the residue dissolved in benzene and abs. ethanol, and the solution evaporated to remove residual water. The residue was acetylated (procedure *B*) to yield syrupy 1,2,3,4,6-penta-*O*-acetyl-5-deoxy-D-*xylo*-hexitol (0.9 g).

The syrupy (0.9 g) was converted into syrupy **30** (0.8 g) by procedure *C*. The products from (*a*) and (*b*) were identical; g.l.c. retention-times: 2.52 min (150°).

Methyl 2,3,4,6-tetra-O-methyl-5-thio-α,β-L-idopyranoside (**32**). — Compound **29** and 5-thio-L-idopyranose[13] were each methylated by procedure *C* to give **32**.

Anal. Calc. for $C_{11}H_{22}O_5S$: C, 49.6; H, 8.3. Found: C, 52.9; H, 8.5.

6-O-Benzoyl-5-O-p-tolylsulfonyl-D-glucose dibenzyl dithioacetal (**35**). — 6-*O*-Benzoyl-1,2-*O*-isopropylidene-5-*O*-*p*-tolylsulfonyl-D-glucofuranose[24] (**34**, 2.0 g) phenylmethanethiol (3.0 g), and trifluoroacetic acid (2 mL) were stirred for 2 h at room temperature. The mixture was diluted with chloroform and the chloroform was washed successively with water and saturated sodium hydrogencarbonate. The chloroform solution was evaporated to a syrup that was washed with hexane to give **35**, which crystallized from ethyl acetate–hexane, m.p. 93–94°, (3.0 g); $[\alpha]_D^{21}$ −15° (*c* 1.13, chloroform); n.m.r. (chloroform-*d*): δ 2.14 (s, 3*H*, $SO_2C_6H_4CH_3$), and 7.0–8.0 (complex, 19H, $SO_2C_6H_4CH_3$, COC_6H_5, $CH_2C_6H_5$).

2,5-Anhydro-6-O-benzoyl-L-idose dibenzyl dithioacetal (**36**). — Compound **35** (1.0 g) and pyridine (10 mL) were kept overnight at room temperature or warmed for 1 h to 60°. The mixture was treated as described in procedure *B* to give **36**; $[\alpha]_D^{20}$ +62° (*c* 3.36, chloroform).

Anal. Calc. for $C_{27}H_{28}O_5S_2$: C, 65.3; H, 5.7. Found: C, 65.5; H, 5.6.

2,5-Anhydro-L-idose dimethyl acetal (**37**). — (*a*). Syrupy **36** gave 2,5-anhydro-6-*O*-benzoyl-L-idose dimethyl acetal by procedure *E*. Deacylation of this product with sodium methoxide in methanol gave **37**.

(*b*). A mixture of dimethyl acetal[14] **38** (1.0 g), sodium acetate (2.0 g), water (1 mL), and methoxyethanol (10 mL) was boiled for 4 h under reflux. The solution was evaporated and the residue partitioned between chloroform and water. The chloroform solution was evaporated and the residue deacylated with sodium methoxide in methanol to give **37**. Compounds from (*a*) and (*b*) were identical; $[\alpha]_D^{20}$ +22° (*c* 5.3, chloroform).

Anal. Calc. for $C_8H_{16}O_6$: C, 46.2; H, 7.7. Found: C, 45.9; H, 7.4.

2,5-Anhydro-6-O-p-tolylsulfonyl-L-idose dibenzyl dithioacetal (**41**). — 1,2-*O*-Isopropylidene-5,6-di-*O*-*p*-tolylsulfonyl-D-glucofuranose[19] (**39**, 2.0 g) was converted into the dibenzyl dithioacetal (**40**) as described for **35**; n.m.r. [acetate of **40** (procedure *B*), chloroform-*d*]: δ 1.94, 2.00, 2.10 (s, 3 × 3 H, $OCOCH_3$), 2.44 (s, 6H, $C_6H_4CH_3$), 7.28 (S, 10H, $C_6H_5CH_2$), and 7.2–8.0 (complex, 8H, C_6H_4).

Compound **40** (1.0 g) and pyridine were kept overnight at room temperature and gave **41** (0.7 g); $[\alpha]_D^{20}$ +11° (*c* 1.44, chloroform); n.m.r. [acetate of **46** (proce-

dure *B*), chloroform-*d*]: δ 1.60, 1.97 (S, 2 × 3H, $OCOCH_3$), 2.37 (s, 3H, $C_6H_4CH_3$), 7.25, 7.31 (s, 2 × 5 H, $CH_2C_6H_5$), and 7.3–8.0 (complex, 4H, C_6H_4).

Anal. Calc. for $C_{27}H_{30}O_6S_3$: C, 59.3, H, 5.5. Found: C, 59.3; H, 5.9.

Compound **41** was converted into the known dimethyl acetal[14] (**38**) by procedure *E*.

*2,5-Anhydro-3,4,6-tri-*O*-methyl-*L*-idose dimethyl acetal* (**43**). — (*a*). Compound **21** (1.5 g) was converted into 2,3,4,6-tetra-*O*-methyl-D-glucose dimethyl acetal (**42**) by procedure *E*; $[\alpha]_D^{21}$ −28° (*c* 1.63, chloroform); ν_{max}^{film} 3400 cm^{-1} (OH); n.m.r. (of acetate of **42**, prepared by procedure *B*): δ 2.01, (s, 3H, $OCOCH_3$), 3.35, 3.38, 3.44, 3.46, and 3.47 (s, 3,3,6,3,3 H, OCH_3).

Compound **42** (1.0 g) by procedure *D* gave a syrup (0.8 g). G.l.c. revealed this syrup to be a mixture of **27** as minor components and **43**; n.m.r. (chloroform-*d*): δ 3.30 and 3.36 (s, 2 × 3, OCH_3); *m/e* 250 (M^+) and 75 [$CH(OCH_3)_2^+$]; g.l.c. retention-times: 4.50 and 6.20 min (methyl pyranosides), 9.25 min (**43**) (175°).

(*b*). Compound **37** was converted into the methyl ether **43** by procedure *C*. The products from (*a*) and (*b*) were identical; $[\alpha]_D^{21}$ −38° (*c* 1.33, chloroform); g.l.c. retention-time: 9.25 min (175°).

Anal. Calc. for $C_{11}H_{22}O_6$: C, 52.8, H, 8.8. Found: C, 52.8; H, 8.5.

*2,3,4,5-Tetra-*O*-acetyl-6-*O*-benzoyl-*L*-idose dibenzyl dithioacetal* (**45**). — (*a*). Compound **35** (2.0 g) was converted into the acetate by procedure *B*. The acetate (2.0 g) was treated with sodium iodide as described in procedure *G*, except that the period of reflux was 1 week. The product was converted into the acetate **45** by procedure *B*. Compound **45** was identical by h.p.l.c. to the starting material, but crystallized and was recrystallized from ethyl acetate–hexane; m.p. 102–103°; $[\alpha]_D^{20}$ +7° (*c* 9.68, chloroform); n.m.r. (chloroform-*d*): δ 1.94, 2.07, 2.10 (s, 3,3,6 H, $OCOCH_3$), 7.23, 7.28 (s, 2 × 5 H, $CH_2C_6H_5$), and 7.5–8.2 (complex, 5H, OCC_6H_5).

Anal. Calc. for $C_{35}H_{38}O_{10}S_2$: C, 61.6; H, 5.6; S, 9.4. Found: C, 61.9; H, 5.6; S, 9.8.

(*b*). 1,2-*O*-Isopropylidene-L-idofuranose[16] **47** (1.0 g) was converted into the dibenzyl dithioacetal **46** as described for **35**. Compound **46** was converted into the 6-benzoate by procedure *D*, except that benzoyl chloride replaced *p*-toluenesulfonyl chloride. The benzoate was converted into the acetate **45** by procedure *B*; yield, 1.1 g; m.p. 102–103° (ethyl acetate–hexane).

*2,3,4,5-Tetra-*O*-acetyl-6-*O*-benzyl-*L*-idose dibenzyl dithioacetal* (**49**). — (*a*). 6-*O*-Benzyl-1,2-*O*-isopropylidene-5-*O*-*p*-tolylsulfonyl-D-glucofuranose[25] was converted into 2,3,4-tri-*O*-acetyl-6-*O*-benzyl-5-*O*-*p*-tolylsulfonyl-D-glucose dibenzyl dithioacetal (**48**) as described for **35**. Compound **48** was treated with sodium iodide as described for **45**. Compound **49** was isolated as a syrup by chromatography with 1:40 (v/v) methanol–benzene; $[\alpha]_D^{20}$ +73° (*c* 4.8, chloroform); n.m.r. (carbon tetrachloride): δ 1.87, 1.93, 1.98, 2.03 (s, 4 × 3 H, $OCOCH_3$), 3.67, 3.77 (s, 2 × 2 H, $SCH_2C_6H_5$), 4.43 (s, 2H, $OCH_2C_6H_5$) and 7.13–7.27 (complex, 15H, C_6H_5).

Anal. Calc. for $C_{35}H_{40}O_9S_2$: C, 62.9; H, 6.0. Found: C, 63.3; H, 6.1.

(*b*). 6-*O*-Benzyl-1,2-*O*-isopropylidene-5-*O*-*p*-tolylsulfonyl-D-glucofuranose[25]

was converted into 3,5-di-*O*-acetyl-6-*O*-benzyl-1,2-*O*-isopropylidene-L-idofuranose with potassium acetate in boiling acetic anhydride by the procedure of Vargha[26].

The crude L-*ido* derivative was converted into the dibenzyl dithioacetal with phenylmethanethiol and trifluoroacetic acid as described for **35**, and the product of this reaction was converted by acetylation (procedure *B*) to the crude acetate **49**. Chromatography (as under *a*) gave **49**.

2,3,5,6-Tetra-O-*methyl*-D-*glucose dibenzyl dithioacetal* (**52**). — Compound **50** (ref. 17, 4.0 g), phenylmethanethiol (6.0 g), and concentrated hydrochloric acid (2 mL) were treated as described for **25** to give a syrup (5.0 g). Chromatography with 1:24 (v/v) methanol–benzene gave **52** (4.0 g) and benzyl 2,3,5,6-tetra-*O*-methyl-1-thio-D-glucofuranosides (**51**, 1.0 g).

Compound **51** had $[\alpha]_D^{21}$ +4° (*c* 1.59, chloroform); n.m.r. (chloroform-*d*): δ 3.25, 3.36, 3.43 (s, 3,6,3 H, OCH_3), and 7.24 (s, 5 H, $CH_2C_6H_5$).

Anal. Calc. for $C_{17}H_{26}O_5S$: C, 59.7; H, 7.6. Found: C, 59.4; H, 7.7.

Compound **52** had $[\alpha]_D^{21}$ +7° (*c* 1.78, chloroform); n.m.r. (chloroform-*d*): δ 3.36, 3.43, 3.53, (s, 3,6,3 H, OCH_3), 3.76 (s, 4H, $CH_2C_6H_5$), 7.20 and 7.23 (s, 2 × 5 H, $CH_2C_6H_5$).

Anal. Calc. for $C_{24}H_{34}O_5S_2$: C, 61.8; H, 7.3. Found: C, 62.0, H, 7.1.

Methyl 2,3,5,6-tetra-O-*methyl*-α,β-D-*glucofuranoside* (**50**). — Compound **51** (2.0 g) gave **50** by procedure *E*; g.l.c. retention-times, 5.20 and 5.90 min (175°).

Benzyl 2,3,5,6-tetra-O-*methyl-1,4-dithio*-D-*galactofuranoside* (**53**). — Compound **52** (4.0 g) was converted into the sulfonate by procedure *D*. The crude, syrupy sulfonate was converted into **53** by procedure *G*. Chromatography with 1:24 (v/v) methanol–benzene gave **53** (0.9 g); $[\alpha]_D^{21}$ +38° (*c* 0.85, chloroform); n.m.r. (chloroform-*d*): δ 3.24, 3.27, 3.37, 3.44 (s, 4 × 3 H, OCH_3), 3.80 (s, 2H, $SCH_2C_6H_5$), 6.16 (d, 1H, H-1), and 7.17 (s, 5H, $SCH_2C_6H_5$); *m/e* 358 (M^+).

Anal. Calc. for $C_{17}H_{26}O_4S_2$: C, 57.0; H, 7.3. Found: C, 56.8, H, 7.3.

1,4-Dideoxy-2,3,5,6-tetra-O-*methyl*-D-xylo-*hexitol* (**54**). — (*a*). Compound **53** (1.0 g) was treated with Raney nickel as described under procedure *F* to yield syrupy **54** (0.4 g).

(*b*). 4-Deoxy-D-glucose dibenzyl dithioacetal[18] (**55**, 1.0 g) was treated with Raney nickel as described for compound **54** to yield a syrup (0.3 g) that was used without further purification. The syrup (0.3 g) was converted into the methyl ether **54** by procedure *C* to yield a volatile oil (0.35 g). The two products from (*a*) and (*b*) were shown to be identical by g.l.c. analysis; g.l.c. retention-time: 1.50 min (150°).

4-O-p-*Tolylsulfonyl*-D-*glucose dibenzyl dithioacetal* (**58**). — 2,3:5,6-Di-*O*-isopropylidene-D-glucose dimethyl acetal[14] (**56**, 2.3 g) was treated by procedure *D*, to give the syrupy sulfonate **57**, which was treated without purification with phenylmethanethiol and trifluoroacetic acid as described for compound **35**, to give crystalline **58**, m.p. 54–55° (ethyl acetate–hexanes); n.m.r. [acetate of **58**, procedure *B* (chloroform-*d*)]: δ 2.04 (s, 12H, $OCOCH_3$), 2.38 (s, 3H, $C_6H_4CH_3$), 7.27, 7.31 (s, 2 × 5 H, $C_6H_5CH_2$), and 7.3–7.9 (complex, 4H, C_6H_4).

*Benzyl 1,4-dithio-*D*-galactofuranoside* (**60**). — The acetate of **58** (1.5 g) was treated with sodium iodide as described for compound **45**. Chromatography of the crude product with 1:39 (v/v) methanol–benzene gave benzyl 2,3,5,6-tetra-*O*-acetyl-1,4-dithio-D-galactofuranoside (**59**, 0.9 g) as a syrup; $[\alpha]_D^{20}$ +63° (*c* 5.5, chloroform); n.m.r. (chloroform-*d*): δ 2.04, 2.07 (s, 2 × 6 H, $OCOCH_3$), 7.24, and 7.31 (s, 5H, $C_6H_5CH_2$).

Anal. Calc. for $C_{21}H_{26}O_8S_2$: C, 53.6; H, 5.5. Found: C, 53.7; H, 5.6.

Deacylation of **59** with sodium methoxide gave **60** as a crystalline solid, m.p. 103–104° (ethyl acetate–hexane).

Anal. Calc. for $C_{13}H_{18}O_4S_2$: C, 51.7; H, 6.0; S, 21.2. Found: C, 52.2; H, 6.3; S, 21.0.

Methylation of **60** by procedure *C* gave **53**.

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