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SYNTHETIC ROUTES TO HIGHER-CARBON SUGARS. REACTION OF LACTONES WITH 2-LITHIO-1,3-DITHIANE*†

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ABSTRACT

The per(trimethylsilyl) ether of D-glucono-1,5-lactone reacted with 2-lithio-1,3-dithiane to give, after removal of protecting groups, a 62% yield of 1-*C*-(1,3-dithian-2-yl)-α-D-glucopyranose (**3**) as a single tautomer; this product is formally a derivative of a 7-carbon, 1,2-dicarbonyl sugar. The crystalline 2,3,4,6-tetraacetate (**4**) of **3** was readily obtained, again as a single tautomer, and forcing conditions of acetylation led to the acyclic, enol hexaacetate in admixture with the cyclic pentaacetate (**6**) of **3**. Desulfurization of the tetraacetate **4** with Raney nickel gave 1-deoxy-D-*gluco*-heptulose as its α-pyranose 3,4,5,7-tetraacetate, whereas similar desulfurization of the penta-acetate **6** was accompanied by removal of the tertiary acetoxyl group, providing stereospecific access to the *C*-β-D-glucosyl compound 2,6-anhydro-1-deoxy-D-*glycero*-D-*gulo*-heptitol as its 3,4,5,7-tetraacetate. To explore the effects of chain substituents on the tautomeric behavior of the lactone-derived adducts, the simple lactones 5-pentanolide, 4-butanolide, and 4-pentanolide were made to react with 2-lithio-1,3-dithiane, and the tautomeric compositions of the products were examined before and after acetylation. This work establishes preparative access to 1,2-dicarbonyl sugars, higher ketoses, and *C*-glycosyl compounds from readily available lactone precursors.

INTRODUCTION

The elaboration of synthetic routes to chain-extended sugars has been of sustained interest in this laboratory[2,3], especially through use of an ethynylmagnesium halide as the external nucleophile in reaction with the electrophilic carbonyl group of an aldehyde sugar derivative[4]. In an alternative approach employing nucleophilic acylation[5], C-1 of the sugar has been used[6] as a masked, acyl-anion equivalent[5] (reactivity umpolung[7]) in reaction with an external, carbon electrophile, as in the

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generation of a carbanion[6] from an aldose dithioacetal derivative, and its subsequent C-1 alkylation[2].

The principle of the latter route has been more commonly employed in the reverse sense, namely, by use of the acyl-anion equivalent as the external reagent attacking an electrophilic site of the substrate molecule[8]. The carbohydrate literature abounds with examples in which the 1,3-dithian-2-yl anion developed by Seebach and Corey[9] has been used[10–12], for chain extension or branching, with appropriate, protected sugar halides, sulfonates, epoxides, or free-carbonyl derivatives.

The purpose of the present study was to evaluate the reaction of 2-lithio-1,3-dithiane with protected aldonolactones as a practical route to higher ketoses, 1-deoxyketoses, and 1,2-dicarbonyl sugars. It was to be anticipated that attack by the anion on the carbonyl group would generate the ketone or its hemiacetal alkoxide, but that the product would not undergo a second addition. Literature reports concerned with the reaction of comparable anions and simple lactones[13] and aldonolactone derivatives[14,15] supported this expectation, and, in preliminary studies, the addition of 1,3-dithianyl anions to D-ribono-1,4-lactone[10,16] and L-gulono-1,4-lactone[16] derivatives were recorded; details of procedure and characterization[17] with the latter have been disclosed. It is shown here that 2-lithio-1,3-dithiane reacts with the carbonyl group of per(trimethylsilyl)ated D-glucono-1,5-lactone (**2**) to give, in good yield, a monosubstituted product (**3**) that provides convenient access to a 1-deoxyketoheptose and β-D-glucosylmethane, and comparable studies with simple lactones aided in understanding the tautomeric behavior of the 1,3-dithian-2-yl adducts.

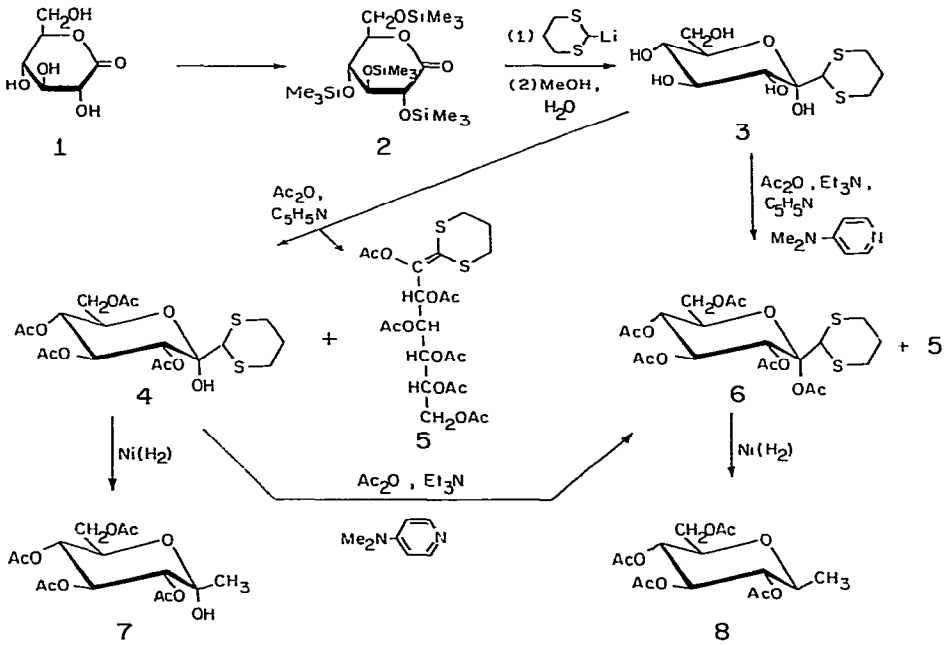
DISCUSSION

Trimethylsilyl ethers were selected as protecting groups for this work, because of their ease of formation and subsequent removal, and their inertness in the presence of strongly basic reagents. D-Glucono-1,5-lactone (**1**) was per(trimethylsilyl)ated with an excess of hexamethyldisilazane–chlorotrimethylsilane, and the resulting ether **2** was obtained in 81% yield as a distilled oil. Full ^{1}H- and ^{13}C-n.m.r.-spectral data for **2** and other compounds described in this work are recorded in the Experimental section.

The protected lactone **2** was added at −50° to a slight excess of a preformed solution of 2-lithio-1,3-dithiane in oxolane, and reaction was allowed to proceed initially at −50° and later at −14°. The product was boiled with aqueous methanol to ensure removal of the trimethylsilyl groups, and the resultant adduct (presumably at tautomeric equilibrium) was formulated, on the basis of mass-spectral and n.m.r. studies, and from further transformations, as the monoadduct in its α-pyranose form (**3**).

In principle, the addition to **2** could have generated the acyclic ketone, or a mixture of any of its tautomeric hemiacetals, or both; the pyranose tautomers would presumably be more stable than the furanoses. The analytical data precluded any possibility of the formation of a diadduct. The ^{13}C-n.m.r. spectrum indicated that

the product, although non-crystalline, was a single tautomer (to the limits of detection by n.m.r. spectroscopy), and the spectrum clearly established that it was a cyclic hemiacetal form (δ 103.1 for the carbon atom derived from the lactone carbonyl group), as the open-chain form would have given a carbonyl-group ^{13}C-resonance at very low field. Assignment of the pyranoid ring-form and α-anomeric configuration to **3** followed largely from more-detailed characterization studies on the acetylated derivatives (**4** and **6**) of **3**.



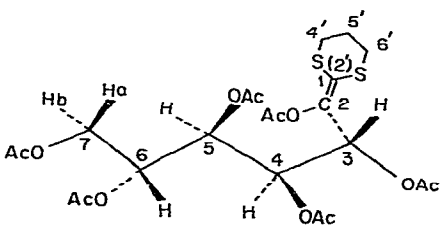
Acetylation of **3** with acetic anhydride–pyridine gave 66% of a dextrorotatory, crystalline tetraacetate **4**, whose ^{1}H-n.m.r. spectrum showed vicinal spin-couplings that demonstrated it to be a pyranose tautomer, acetylated presumably at all positions except the (tertiary) hydroxyl group of the hemiacetal. The remaining hydroxyl group could be acetylated by the action of acetic anhydride–triethylamine–4-dimethylaminopyridine at 0°, to give 52% of a crystalline, dextrorotatory pentaacetate **6**, whose ^{13}C resonance for C-1 lay 6.4 p.p.m. to lower field than the corresponding resonance for **4**; such a downfield shift accords with acetylation of a free hydroxyl group on C-1*. The uniformly large (9–10 Hz) magnitudes of $J_{2,3}$, $J_{3,4}$, and $J_{4,5}$ for **3**, **4**, and **6** clearly establish the pyranoid ring-form for all three compounds.

*For the purpose of convenience, compounds **3**, **4**, and **6** are named as 1-*C*-substituted derivatives of D-glucose, and the atom numbering is assigned accordingly; primed numbers are used for atoms in the 1,3-dithiane ring. It is recognized that strict application of established terminology would lead to the name α-D-*gluco*-heptos-2-ulo-2,6-pyranose 1,1-(propan-1,3-diyl dithioacetal) for **3**, and similarly unwieldy names for **4** and **6**. Standard nomenclature is used for the desulfurized products **7** and **8**, and accepted practice for unsaturated sugars is used for naming the acyclic, enol acetate **5**.

Acetylation of the pentol **3** with acetic anhydride–triethylamine–4-dimethylaminopyridine–pyridine gave the pentaacetate **6** directly. As anomeric interconversion under these acetylation conditions is not to be expected, compounds **3** and **6** may be judged to have the same anomeric configuration. Furthermore, the tetraacetate **4**, obtained from **3** under milder conditions of acetylation, is a single anomer (n.m.r. data) that, on the basis of its conversion into **6**, also has the same anomeric configuration. The dextrorotation exhibited by **3** ($[\alpha]_D$ +31° in methanol), **4** ($[\alpha]_D$ +38° in chloroform), and **6** ($[\alpha]_D$ +55° in chloroform) accords with their all having the α-D configuration. The specific rotations of α-D-fructopyranose pentaacetate[18] and methyl α-D-fructopyranoside[19] are +47.4° (chloroform) and +44° (water), respectively, whereas the corresponding β-pyranose anomers show −120.9° (ref. 20) and −172.1° (ref. 21), respectively.

The tetraacetate **4** showed a surprisingly large, ^4J, long-range coupling ($J_{2,2'}$ 1.9 Hz) between H-2 of the sugar ring and H-2′ of the dithiane ring. A comparable, long-range coupling is not observed for the pentaacetate **6**, even though there is little doubt that the two compounds have the same anomeric configuration. None of the C-1–C-2′ rotameric states for **4** permit H-2 and H-2′ to assume the "W" geometry considered[22] optimal for the largest $^4J_{H,H}$ couplings. The observed differences between **4** and **6** point to a difference in their favored C-1–C-2′ rotameric states, presumably dictated by the nature of the C-1 substituent (OH or OAc), but detailed speculation on this aspect is not warranted from the evidence in hand.

In addition to the tetraacetate **4**, formed as the principal product of the acetylation of **3** with acetic anhydride–pyridine, a minor, less-polar side-product was produced, especially when the acetylation was performed at ~25° rather than at 0°. The same minor product accompanied the pentaacetate **6** as prepared by acetylation of either the tetraacetate **4** or the pentol **3** with acetic anhydride–triethylamine–4-dimethylaminopyridine. This compound was obtained crystalline from **4** in 23% yield after chromatographic separation from the major product, the pentaacetate **6** (52%). Analytical and spectroscopic evidence established that this less-polar, acetylated product was the enol acetate derivative **5**. The ^{1}H- and ^{13}C-n.m.r., and elemental analytical, data were consistent with the presence of six acetoxyl groups, and i.r.-spectral absorption at 1216 cm^{-1} indicated an enol acylate group; the ^{13}C resonances at 130.7 and 136.4 p.p.m. accorded with the presence of a C=C double bond. The vicinal, proton–proton spin-couplings along the sugar chain were "extreme" values,



5a

indicative[23] of a high degree of conformational homogeneity, that led to the assignment of a favored conformation (**5a**) having carbon atoms 3–7 in essentially planar, zigzag arrangement, with the acetoxy(1,3-dithian-2-ylidene)methyl group (C-1, C-2 fragment) *gauche*-disposed; this arrangement does not lead to any 1,3-parallel alignments[23] of substituents along the chain.

The formation of the enol acetate **5**, in addition to the pentaacetate **6**, by acetylation of either **3** or **4** demonstrates that acetylation of the tertiary hydroxyl group takes place in competition with base-catalyzed opening of the hemiacetal ring and acetylation at O-5; conversion of the keto product into its enol acetate is particularly facilitated by the relative acidity of H-2′ in the dithiane ring. Access to such products as **5** from an aldonolactone precursor may provide a useful, 1-carbon homologation of sugars, as reduction of **5** would give aldoheptose dithioacetals.

The tetraacetate **4** readily underwent desulfurization by hydrogen-saturated Raney nickel in boiling ethanol, to give 1-deoxy-α-D-*gluco*-heptulopyranose in 88% yield as its crystalline 3,4,5,7-tetraacetate **7**. The ^{1}H- and ^{13}C-n.m.r. spectra indicated that the compound was a single tautomer, clearly pyranoid from the vicinal, proton–proton spin-couplings ($J_{3,4}$, $J_{4,5}$, and $J_{5,6}$ were all ~10 Hz), and of the α-D configuration from its dextrorotation ($[\alpha]_D$ +31° in chloroform). The ^{13}C-n.m.r. spectrum was assigned in detail, and showed the expected, high-field (25.9 p.p.m.) and low-field (96.6 p.p.m.) signals for C-1 and the anomeric carbon atom (C-2), respectively.

The course of desulfurization of the pentaacetate **6** by Raney nickel contrasted sharply with that observed with the tetraacetate **4**, in that desulfurization of **6** was accompanied by hydrogenolytic cleavage of the 2-acetoxyl group, with retention of configuration at C-2, so that the product obtained was the 3,4,5,7-tetraacetate (**8**) of 2,6-anhydro-1-deoxy-D-*glycero*-D-*gulo*-heptitol. Compound **8**, which may be regarded as tetra-*O*-acetyl-β-D-glucopyranosylmethane, was obtained crystalline in 92% yield as the sole product. Its structure was established by detailed ^{1}H- and ^{13}C-n.m.r. studies. The C-1 resonance appeared at high field (17.6 p.p.m.), because of the removal of O-2, and the C-2 signal no longer appeared in the anomeric-carbon region. Spin-couplings from the ^{1}H-n.m.r. spectrum established conclusively the assigned configuration at C-2, and the overall $^5C_2$(D) conformation of the ring ($J_{2,3}$, $J_{3,4}$, $J_{4,5}$, and $J_{5,6}$ were all ~9.5 Hz). The ^{1}H-n.m.r. spectrum of **8** was in accord with that of a sample of **8** obtained by Lehmann[24] by a different route.

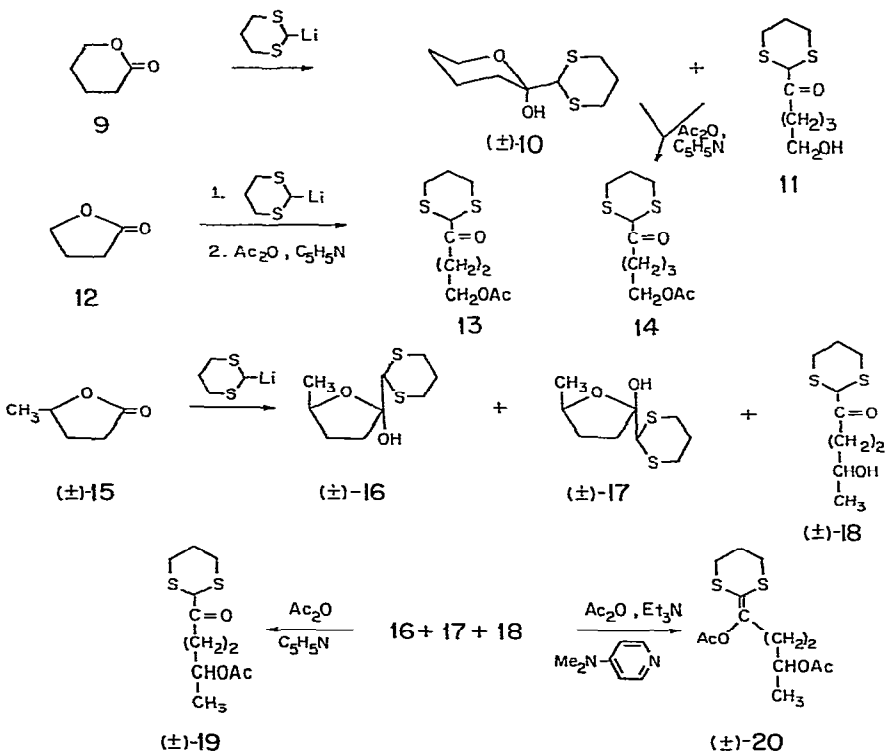
Cleavage of an acyloxy group α-disposed to the sulfur function during desulfurization is not unexpected; comparable behavior has been observed in previous work from this[25] and other[26] laboratories. The particularly clear-cut difference here between the behavior of **4** and **6** is noteworthy, as it gives the reaction preparative significance, especially because any 2-substituted 1,3-dithianyl anion could, in principle, be used in the reaction with the lactone **2**. The reaction should, therefore, be of general value for the synthesis of *C*-glycosyl derivatives based on structure **8** with further substitution at the methyl group. Such compounds are of interest as potential β-D-glucosidase inhibitors and as synthetic intermediates to various natural products.

A series of model experiments was conducted in which 2-lithio-1,3-dithiane

was brought into reaction with the simple lactones 5-pentanolide (*δ*-valerolactone, **9**), 4-butanolide (*γ*-butyrolactone, **12**), and 4-pentanolide (*γ*-valerolactone, **15**), in order to (*a*) provide reference compounds for the ^{13}C and ^{1}H assignments, (*b*) compare the keto ⇄ hemiacetal equilibrium of the products in relation to that in the product derived from D-glucono-1,5-lactone (**5**), and (*c*) examine the behavior of the products on acetylation. The ^{13}C assignments were, in all instances, verified by off-resonance decoupling, and, where necessary, by heteronuclear decoupling.

The reaction between *δ*-valerolactone (**9**) and 2-lithio-1,3-dithiane gave 78% of a chromatographically homogeneous oil whose ^{1}H- and ^{13}C-n.m.r. spectra showed it to be a 2:1 mixture of the hemiacetal **10** and the keto tautomer **11**. The former was readily recognized from its "anomeric" carbon resonance at 98.6 p.p.m., and the latter, from the carbonyl-group resonance at 202.8 p.p.m. The signals for C-2 of the 1,3-dithiane ring were also readily identified, and they served as the basis for estimating the ratio of **10** to **11** in the product, as did the corresponding H-2 resonances in the ^{1}H-n.m.r. spectrum. Acetylation of the mixture of **10** and **11** with acetic anhydride–pyridine at ~25° gave a single product, the acyclic acetate **14**, isolated in 84% yield. The ketone group of **14** showed a characteristic, low-field (202.3 p.p.m.), ^{13}C resonance; further spectroscopic details are recorded in the Experimental section.

The behavior of lactone **9** in comparison with that of the D-glucono-1,5-lactone derivative **2** shows that the cyclic hemiacetal form is less strongly favored in the



product from the non-hydroxylated lactone. Lactone **2** gives the hemiacetal exclusively, whereas one-third of the product from **9** exists as the keto form. Acetylation of the adduct (**10** + **11**) from lactone **9** gives the acetylated keto form **14** as the only detected product, whereas no appreciable proportion of keto form was encountered in the products of acetylation of compounds **3** and **4**. This difference may be occasioned by the presence of electron-withdrawing groups in the sugar derivative, especially the oxygenated substituent adjacent to the hemiacetal center. Such an inductive effect would increase the electrophilicity of the carbonyl carbon atom and promote formation of the hemiacetal.

In the reaction of γ-butyrolactone (**12**) with 2-lithio-1,3-dithiane, the product was acetylated directly. The resultant acetate was readily characterized as the keto form **13** (details of identification are given in the Experimental section), and no other products were detected, again suggesting that there is little driving force toward a stabilized, hemiacetal form.

The product from reaction of γ-valerolactone (**15**) with 2-lithio-1,3-dithiane was chromatographically homogeneous, but its ^{1}H- and ^{13}C-n.m.r. spectra indicated a 9:6:5 mixture of three components, two of which showed "anomeric" carbon resonances (107.8 and 108.3 p.p.m.) indicative of cyclic products (**16** and **17**), and the third was acyclic (C=O, ^{13}C resonance at 202.9 p.p.m.); the acyclic form (**18**) was the minor component. As for all of the 1,3-dithian-2-yl derivatives studied here, the C-2 resonance lay at ~47.0 p.p.m. for the acyclic products and several p.p.m. to lower field for the hemiacetals. Quantitation for the mixtures was based on the intensities of the C-2 signals, the corresponding H-2 signals, and the ^{1}H resonances of the chain-terminal methyl groups. The cyclic forms are evidently the geometrical isomers indicated; they were not specifically differentiated.

Acetylation of the mixture of **16**, **17**, and **18** with acetic anhydride–pyridine at ~25° gave a separable mixture of two products, the major one of which was identified as the acyclic, ketone derivative **19** (C=O, ^{13}C resonance at 201.9 p.p.m., C-2 of the 1,3-dithiane group at 47.2 p.p.m.), and the minor, less-polar one was the corresponding enol acetate **20**; acetylated hemiacetals were not detected. The enol acetate **20** was the sole product when the mixture of **16**, **17**, and **18** was acetylated with acetic anhydride–triethylamine–4-dimethylaminopyridine. The structure of **20** was readily established from the analytical data (see Experimental section), especially from the ^{13}C spectrum; the alkene resonances (117.0 p.p.m. for C-2 of the 1,3-dithiane ring and 148.0 p.p.m. for C-1 of the side chain) being particularly characteristic (compare the data for compound **5**).

The results obtained with lactone **15** are largely comparable with those observed with the 6-membered-ring analog (**9**), after making allowance for the fact that additional, isomeric hemiacetals are possible, and the data again support the concept that the hemiacetals are less stable than hemiacetals of the poly(hydroxyl)ated derivatives.

A further contrast between the simple aliphatic and the carbohydrate derivatives may be observed under the conditions for enol acylation. Whereas the aliphatic

products (**16** + **17** + **18**) are all converted into the enol acetate **20**, comparable acetylation of the sugar derivatives **3** and **4** gives a substantial proportion of the acetylated hemiacetal (**6**) accompanying the enol acetate (**5**). This difference may again be attributable to inductive factors operating to stabilize the hemiacetal form in the polyoxygenated derivatives.

EXPERIMENTAL

General methods. — Melting points were determined with a Thomas–Hoover apparatus and are uncorrected. Optical rotations were measured with a Perkin–Elmer 141 polarimeter. T.l.c. was performed on precoated, plastic sheets (0.2 mm) and glass plates (0.25 mm) coated with Silica Gel 60F-254 (E. Merck, Darmstadt, G.F.R.); components were detected by u.v. light and by spraying the plates with 0.1M ceric sulfate in 2M sulfuric acid, with subsequent heating. Solutions were dried with magnesium sulfate, and evaporations were conducted under diminished pressure. Column chromatography was performed with Silica Gel 60 (230–400 mesh) (E. Merck, Darmstadt, G.F.R.). All reactions involving use of butyllithium (2M, in hexane) were conducted under positive pressure of an inert gas (argon). The reaction procedure with 1,3-dithiane followed the general methods described by Seebach and Corey[9]. I.r. spectra were recorded with a Perkin–Elmer 457 grating spectrophotometer. ^{1}H-N.m.r. spectra were recorded, unless otherwise stated, at 200 MHz with a Bruker WP-200 spectrometer for solutions in chloroform-*d*. Spectra at 90 MHz were recorded with a Bruker HX-90, and 300-MHz spectra, with a Bruker WM-300 instrument. ^{13}C-N.m.r. spectra were recorded at 20.1 MHz with a Bruker WP-80, and at 50.3 MHz, with a Bruker WP-200, instrument, with chloroform-*d* as the solvent. N.m.r. spectra were recorded by Drs. C. Cottrell and O. Mols, and by G. Larson. Chemical shifts refer to an internal standard of tetramethylsilane ($\delta = 0.00$). Mass spectra were recorded by C. R. Weisenberger with an AEI MS9 double-focusing instrument, equipped with a direct-inlet probe (140°) at an ionization potential of 70 eV and an accelerating potential of 8 kV. Elemental analyses were performed by W. N. Rond and Dr. O. Mols.

2,3,4,6-Tetra-O-(*trimethylsilyl*)-D-*glucono-1,5-lactone* (**2**). — To a solution of D-glucono-1,5-lactone (**1**; 17.0 g, 95.43 mmol) in dry pyridine (160 mL) were added hexamethyldisilazane (79 mL, 378.8 mmol) and chlorotrimethylsilane (25 mL, 197 mmol), and the mixture was stirred vigorously for 25 min at ~25°. T.l.c. (4:1 hexane–ethyl acetate) then indicated conversion into a single, more-polar product (R_F ~0.8). Pentane (500 mL) was added, and the white precipitate that formed was filtered off through Celite. The filtrate was evaporated, and the oil remaining was distilled under high vacuum, to give **2** as the fraction boiling at 128–129°/0.4 torr; yield 36.28 g (81.4%); $[\alpha]_D^{25}$ +46° (*c* 2.3, chloroform); ν_{max}^{film} 1755 (C=O), 1250, 1100 (br), and 860 cm^{-1} (br); ^{1}H-n.m.r.: δ 4.18 (dt, 1 H, $J_{4,5}$ 6.9 Hz, H-5), 4.00 (d, 1 H, $J_{2,3}$ 7.6 Hz, H-2), 3.90 (t, 1 H, $J_{3,4}$ 7.1 Hz, H-4), 3.79 (m, 2 H, H-6), 3.75 (t, 1 H, H-3), 0.19, 0.17, 0.16, and 0.12 (s, 36 H, 4 $SiMe_3$); ^{13}C-n.m.r. (20.115 MHz):

δ 170.8 (C-1), 81.3, 76.2, 73.2, 71.0 (C-2,3,4,5), 61.5 (C-6), 0.7, 0.5, 0.2, and 0.4 (4 $SiMe_3$).

Anal. Calc. for $C_{18}H_{42}O_6Si_4$: M^+ *m/z* 466.2058. Found: *m/z* 466.2069.

1-C-(1,3-Dithian-2-yl)-α-D-glucopyranose (**3**). — To a solution of 1,3-dithiane (4.495 g, 37.38 mmol) in oxolane (180 mL) at −55° under dry argon was added butyllithium (39.3 mmol). The mixture was kept for 2.5 h at −35 to −20°, and then cooled to −50°, whereupon a solution of the trimethylsilylated lactone **2** (17.45 g, 37.38 mmol) in oxolane (60 mL) was added. The mixture was stirred for 5 h at −50 to −45°, and then kept for 2 days at −14°. The mixture was poured into water (0.5 L), and extracted with pentane. The extract was successively washed with 7% potassium hydroxide solution and water (twice), dried, and evaporated, to give a yellowish oil that was boiled with 1:1 methanol–water (500 mL) under reflux for 2.5 h. T.l.c. (5:1 chloroform–methanol) then showed one product (R_F ~0.14). The solution was cooled, washed with pentane, and evaporated, to afford **3** as a slightly yellow syrup, yield 6.95 g (62%): $[\alpha]_D^{25}$ +31° (*c* 1, methanol); ^{1}H-n.m.r. (CD_3OD): δ 4.01 (d, 1 H, $J_{2,3}$ 9.3 Hz, H-2), 3.87 (s, 1 H, H-2′), 3.67 (t, 1 H, $J_{3,4}$ 8.8 Hz, H-3), 3.92–3.34 (m, 6 H, H-4,5,5,4′a,6′a), 2.48 (m, 2 H, *J* 13.4 Hz, H-4′e,6′e), and 2.02 (m, 2 H, H-5′); ^{13}C-n.m.r. (20.115 MHz; pyridine-d_5): δ 103.1 (C-1), 76.6, 75.2, 72.6 (double intensity) (C-2,3,4,5), 63.3 (C-6), 48.1 (C-2′), 27.4, 27.2 (C-4′,6′), and 25.9 (C-5′): *m/z* (rel. int.): 298 (2.0, M^+), 280 (6.3, $M^+ - H_2O$), and 119 (100, $C_4H_7S_2^+$).

Anal. Calc. for $C_{10}H_{18}O_6S_2$: M^+ *m/z* 298.0545. Found: *m/z* 298.0552.

2,3,4,6-Tetra-O-acetyl-1-C-(1,3-dithian-2-yl)-α-D-glucopyranose (**4**). — The 1,3-dithian-2-yl derivative **3** (165 mg, 0.55 mmol) was acetylated with acetic anhydride (1.0 mL) in pyridine (8 mL) at ~25°, to give, as indicated by t.l.c. (1:1 hexane–ethyl acetate), a mixture (230 mg) of two components, a major, less-polar one (**4**, R_F ~0.27) and a minor one (**5**, R_F ~0.21). The mixture was boiled for 10 min under reflux in 2:1 hexane–ethyl acetate (8 mL), and cooled, and a small amount of petroleum ether was added; the solution was then kept for ~25 min at ~25°, to afford crystalline **4** (171 mg, 66%). The mother liquor contained compound **5** as the major component (t.l.c.), together with a detectable amount of **4**. When the acetylation was performed at 0°, t.l.c. showed that the proportion of compound **5** was significantly decreased in the product-mixture. Recrystallization of **4** from 2:1 hexane–ethyl acetate plus a small amount of petroleum ether gave the tetraacetate **4** as pure, white crystals; m.p. 198–199° (dec.), $[\alpha]_D^{23}$ +16.6°, $[\alpha]_{578}^{23}$ +17.5°, $[\alpha]_{546}^{23}$ +19.4°, $[\alpha]_{436}^{23}$ +30.1°, $[\alpha]_{365}^{23}$ +38.3° (*c* 1, chloroform); ν_{max}^{KBr} 3423 (OH), 1740 (C=O), 1385, 1259, 1246, and 1238 cm^{-1}; ^{1}H-n.m.r.: δ 5.83 (dd, 1 H, $J_{2,2'}$ 1.9, $J_{2,3}$ 9.8 Hz, H-2), 5.49 (t, 1 H, $J_{3,4}$ 9.5 Hz, H-3), 5.17 (t, 1 H, $J_{4,5}$ 9.8 Hz, H-4), 4.65 (d, 1 H, H-2′), 4.20–4.32 (m, 3 H, H-5,6), 3.35 (s, 1 H, OH), 3.25 (m, 2 H, H-4′a,6′a), 2.41 (bd, 2 H, $J_{4'a,4'e} \approx J_{6'a,6'e}$ 13.2 Hz, H-4′e,6′e), 2.07, 2.05, 2.03, 1.99 (2, 12 H, 4 OAc), and 1.90–2.08 (m, 2 H, H-5′); ^{13}C-n.m.r. (20.115 MHz): δ 170.5, 170.1, 169.6, 169.4 (C=O), 101.2 (C-1), 72.4 (C-3), 68.9 (C-2), 68.7 (double intensity), (C-4,5), 62.4 (C-6), 43.7 (C-2′), 25.5, 25.1 (C-4′,6′), 24.4 (C-5′), 20.7, and 20.6 (4

OAc); *m/z* (rel. int.): 466 (1.1, M^+), 448 (0.5, $M^+ - H_2O$), 406 (0.5, $M^+ - AcOH$), 119 (90, $C_4H_7S_2^+$), and 43 (100, Ac); X-ray powder diffraction data: 10.13 vs (1), 8.88 vw, 7.67 vw, 5.77 m (2,2), 5.37 m (2,2), 5.03 m (2,2), 4.43 vw, 4.09 vw, and 3.60 w.

Anal. Calc. for $C_{18}H_{26}O_{10}S_2$ (466.530): C, 46.34; H, 5.62; S, 13.75. Found: C, 46.14; H, 5.72; S, 13.26.

*1,2,3,4,6-Penta-*O*-acetyl-1-*C*-(1,3-dithian-2-yl)-α-*D*-glucopyranose* (**6**) *and 2-(1,2,3,4,5,6-hexa-*O*-acetyl-*D*-glucitol-1-ylidene)-1,3-dithiane* (**5**). — To a solution of tetraacetate **4** (900 mg, 1.93 mmol) in triethylamine (30 mL), cooled to 0°, were added acetic anhydride (2.0 mL) and 4-dimethylaminopyridine (100 mg). The reaction was monitored by t.l.c. (1:1 hexane–ethyl acetate), and the formation of two products (R_F 0.21 and 0.32) was observed. After 18 h, the mixture was processed conventionally, and the product resolved by column chromatography (2:1 hexane–ethyl acetate). The first fractions afforded compound **6**; yield 512 mg (52.2%); m.p. 105–107°, $[\alpha]_D^{24}$ +54.8°, $[\alpha]_{578}^{24}$ +57.4° (*c* 0.5, chloroform); ν_{max}^{film} 1750 (C=O). 1369, and 1222 cm^{-1}; ^{1}H-n.m.r.: δ 5.84 (d, 1 H, $J_{2,3}$ 9.5 Hz, H-2), 5.36 (t, 1 H, $J_{3,4}$ 9.5 Hz, H-3), 5.18 (t, 1 H, $J_{4,5}$ 9.8 Hz, H-4), 4.75 (s, 1 H, H-2′), 4.15–4.30 (m, 3 H, H-5,6), 3.11 (m, 2 H, $J_{4'a,4'e} \approx J_{6'a,6'e}$ 13.5 Hz, H-4′a,6′a), 2.56 (m, 2 H, H-4′e,6′e), 2.19, 2.09, 2.04, 2.02, 2.00 (s, 15 H, 5 OAc), and 1.82–2.11 (m, 2 H, H-5′); ^{13}C-n.m.r. (20.115 MHz): δ 170.6, 170.2, 169.4 (double intensity), 167.8 (C=O), 107.6 (C-1), 71.8, 70.4, 70.2, 67.7 (C-2,3,4,5), 61.7 (C-6), 44.0 (C-2′), 27.8 (double intensity, C-4′,6′), 25.0 (C-5′), and 22.1, 20.7 (double intensity), and 20.6 (double intensity, OAc); *m/z* (rel. int.): 508 (0.4, M^+), 448 (4.8, $M^+ - AcOH$), 388 (0.8, $M^+ - 2$ AcOH), and 119 (100, $C_4H_7S_2^+$); X-ray powder diffraction data: 12.57 w, 8.30 s (2,2), 7.65 s (2,2), 7.03 vs (1), 6.34 m (3,3), 5.89 m (3,3), and 5.60 w.

Anal. Calc. for $C_{20}H_{28}O_{11}S_2$ (508.57): C, 47.24; H, 5.55. Found: C, 47.16; H, 5.24.

Evaporation of the later fractions from the column afforded the enol acetate **5**; yield 244 mg (23%); m.p. 127–127.5°, $[\alpha]_D^{24.5}$ +11.4°, $[\alpha]_{578}^{24.5}$ +12.3°, $[\alpha]_{546}^{24.5}$ +11.9°, $[\alpha]_{436}^{24.5}$ −6.5°, $[\alpha]_{365}^{24.5}$ −102.3° (*c* 1, chloroform); ν_{max}^{KBr} 1750 (C=O) and 1216 cm^{-1} (enol acetate); ^{1}H-n.m.r.: δ 6.07 (d, 1 H, $J_{3,4}$ 9.1 Hz, H-3), 5.54 (dd, 1 H, $J_{4,5}$ 1.7 Hz, H-4), 5.35 (dd, 1 H, $J_{5,6}$ 7.6 Hz, H-5), 5.12 (8-line m, 1 H, H-6), 4.29 (q, 1 H, $J_{6,7a}$ 3.4, $J_{7a,7b}$ 12.2 Hz, H-7a), 4.06 (q, 1 H, $J_{6,7a,7b}$ 6.5 Hz, H-7b), 2.90 (m, 4 H, H-4′,6′), 2.22, 2.16, 2.07, 2.06, 2.05, 1.95 (s, 20 H, 6 OAc, H-5′); ^{13}C-n.m.r. (50.72 MHz): δ 170.5, 169.8 (double intensity), 169.7, 169.5, 167.7 (C=O), 136.4 (C-2), 130.7 [C-1 (C-2′)], 69.3, 68.9, 68.7, 68.5 (C-3,4,5,6), 62.2 (C-7), 28.9, 28.3 (C-4′,6′), 23.9 (C-5′), 21.2, 20.8, 20.7 (double intensity), 20.6, and 20.4 (OAc); X-ray powder diffraction data: 8.32 s (2), 7.46 m, 4.23 vs (1), and 3.54 w.

Anal. Calc. for $C_{22}H_{30}O_{12}S_2$ (550.60): C, 47.90; H, 5.49. Found: C, 48.36; H, 5.09.

In separate experiments, the conversion of **3** into **6** was established. The 1,3-dithian-2-yl derivative **3** (215.3 mg, 0.72 mmol) was dissolved in a mixture of triethylamine (15 mL) and pyridine (12 mL), and then acetic anhydride (3.5 mL) and 4-dimethylaminopyridine (50 mg) were added. The mixture was stirred vigorously

for 1.25 h at ~25°, whereupon it became dark-colored. The mixture was poured into ice–water, extracted with chloroform, and the extract dried, and evaporated. Toluene was 3 times added to, and evaporated from, the residue, to afford a yellow oil (260 mg). T.l.c. (1:1 hexane–ethyl acetate) showed the presence of two major compounds (**5** and **6**), together with traces of two by-products. Pure samples of compounds **5** and **6** were obtained by l.c. in a μPorasil column (7.8 mm × 30 cm) with 1:1 hexane–ethyl acetate as the eluant, at a flow rate of 2 mL/min; retention time: for **5**, 17 min; for **6**, 12 min.

3,4,5,7-Tetra-O-*acetyl-1-deoxy*-α-D-gluco-*heptulopyranose* (**7**). — To a solution of the tetraacetate **4** (98 mg, 0.21 mmol) in ethanol (5 mL) was added Raney nickel (0.35 g), and the mixture was boiled under reflux for 20 min. The mixture was cooled, and filtered through Celite, and the filter was washed with ethanol. Evaporation of the filtrate afforded compound **7** as a colorless glass; yield 67 mg (88%), m.p. 118–119°, $[\alpha]_D^{27}$ +31.1°, $[\alpha]_{578}^{27}$ +32.3° (*c* 1.4, chloroform); R_F ~0.20 (1:1 hexane–ethyl acetate); ν_{max}^{film} 3450 (OH) and 1745 cm^{-1} (C=O); ^{1}H-n.m.r.: δ 5.46 (t, 1 H, $J_{4,5}$ 9.5 Hz, H-4), 5.10 (t, 1 H, $J_{5,6}$ 9.8 Hz, H-5), 5.00 (d, 1 H, $J_{3,4}$ 10.0 Hz, H-3), 4.02–4.31 (m, 3 H, H-6,7,7') 2.83 (s, 1 H, OH), 2.10, 2.09, 2.02, 1.99 (s, 12 H, 4 OAc), and 1.44 (s, 3 H, H-1); ^{13}C-n.m.r. (50.72 MHz, assignments verified by hetero-nuclear decoupling): δ 170.8, 170.2, 169.8, 165.5 (C=O), 96.6 (C-2), 73.1 (C-3), 71.5 (C-4), 68.8 (C-5), 68.4 (C-6), 62.3 (C-7), 25.9 (C-1), and 20.7, 20.6 (4 OAc): *m/z* (rel. int.): 345 (0.5, M^+ — OH), 302 (0.6, M^+ — AcOH), 289 (0.8, M^+ — CH_2OAc), 285 (0.2, 345 — AcOH), 242 (3.4, 302 — AcOH), 200 (4.5, 242 — CH_2CO), 157 (15.5, AcO-CH_2=CH-C^+H-OAc), 145 (6.5, Ac_3O^+), 140 (5.0, 200 — AcOH), 115 (21, 157 — CH_2CO), 103 (7.5, Ac_2O^+H), 98 (12.0, 140 — CH_2CO), 73 (3.0, 115 — CH_2CO), and 43 (100, Ac); X-ray powder diffraction data: 11.18 s (3,3), 7.08 vs (1), 6.47 s, 5.70 s (3,3), 5.48 s (3,3), 4.88 vw, 4.61 w, 4.32 m, 4.08 vs (2), 3.93 vw, and 3.83 w.

Anal. Calc. for $C_{15}H_{22}O_{10}$ (362.336): C, 49.72; H, 6.12. Found: C, 49.42: H, 5.79.

Liquid chromatography [μPorasil column (7.8 mm × 30 cm), 2:1 hexane–ethyl acetate] was used to purify the analytical sample, and this material, dried at 60°/0.3 torr, afforded the first crystalline sample of **7**.

3,4,5,7-Tetra-O-*acetyl-2,6-anhydro-1-deoxy*-D-glycero-D-gulo-*heptitol* (**8**). — A solution of the pentaacetate **6** (84.4 mg, 166 μmol) in ethanol (5 mL) was boiled with Raney nickel (0.35 g) for 4 h under reflux. T.l.c. (1:1 hexane–ethyl acetate) showed conversion of **6** into a single, less-polar product (R_F ~0.35). The mixture was filtered through Celite, the filter washed with ethanol, and the filtrate evaporated, to give an oil that crystallized spontaneously after 3 months, yield 50 mg (92%); m.p. 65–67°, $[\alpha]_D^{27}$ +2.6° (*c* 1, chloroform); ν_{max}^{film} 1735 (C=O), 1430, 1370, 1220 (br), 1090, 1032, 978, and 908 cm^{-1}; ^{1}H-n.m.r.: δ 5.17 (t, 1 H, H-4), 5.05 (t, 1 H, $J_{4,5}$ 9.5 Hz, H-5), 4.83 (t, 1 H, $J_{3,4}$ 9.3 Hz, H-3), 4.22 (q, 1 H, $J_{6,7}$ 4.9, $J_{7,7'}$ 12.5 Hz, H-7), 4.10 (q, 1 H, $J_{6,7'}$ 2.4 Hz, H-7'), 3.65 (8-line m, 1 H, $J_{5,6}$ 9.5 Hz, H-6), 3.55 (dq, 1 H, $J_{2,3}$ 9.8 Hz, H-2), 2.08, 2.04, 2.02, 1.99 (s, 12 H, 4 OAc), and 1.21 (d, 3 H,

$J_{1,2}$ 6.1 Hz, H-1); ^{13}C-n.m.r. (20.115 MHz): δ 170.6, 170.3, 169.7, 169.4 (C=O), 75.7, 74.3, 73.4 (double intensity), 68.9 (C-2,3,4,5,6), 62.4 (C-7), 20.6 (4 OAc), and 17.6 (CH_3); *m/z*: 347 [0.6, $(M + 1)^+$] and 287 (5, M + 1 — AcOH).

Anal. Calc. for $C_{15}H_{22}O_9$ (346.337): C, 52.02; H, 6.40. Found: C, 52.06; H, 6.18.

For this compound, prepared by an independent route, Lehmann[24] recorded a 90-MHz, n.m.r. spectrum that was in good correspondence with the 200-MHz, ^{1}H-n.m.r. data reported here.

Reaction of 5-pentanolide (*δ-valerolactone*, **9**) *with 2-lithio-1,3-dithiane to give* (±)-*2-(1,3-dithian-2-yl)tetrahydropyran-2-ol* (**10**) *and 2-(5-hydroxypentanoyl)-1,3-dithiane* (**11**). — To a solution of 1,3-dithiane (377.4 mg, 3.14 mmol) in oxolane at −43° was added butyllithium (3.30 mmol) in hexane. For the next 3 h, the temperature was maintained at −25 to −70°. The mixture was cooled to −57°, and *δ*-valerolactone (0.29 mL, 3.1 mmol) was added. The temperature was maintained for 3 h at −50°, and then for 20 h at −16°. The mixture was poured into water (50 mL), and the mixture was extracted several times with chloroform. The extracts were combined, successively washed with 7% potassium hydroxide solution and water, and dried overnight with potassium carbonate. T.l.c. (2:1 hexane–ethyl acetate) exhibited one spot (R_F ~0.18). Filtration, and evaporation of the filtrate, afforded **10** + **11** as a slightly yellow syrup (541.7 mg, ~78%).

The ^{13}C-n.m.r. spectrum (20.115 MHz) established the presence of the adduct in its cyclic hemiacetal form (**10**) and the acyclic, ketone form (**11**). Signals at 47.1 p.p.m. (C-2′) and 202.8 p.p.m. (C=O) proved the presence of **11**, and signals at 53.5 p.p.m. (C-2′) and 98.6 (C-1) were diagnostic of the cyclic form **10**. From the intensities of the signals at 47.1 and 53.5 p.p.m., the ratio of **10** to **11** was estimated to be 17:8. Other signals present in the ^{13}C-n.m.r. spectrum: δ 62.2, 61.4, 39.7, 32.0, 31.2, 29.9, 27.8, 27.3, 26.4, 25.2, 25.1, 20.2, and 19.3.

The ^{1}H-n.m.r. spectrum (90 MHz) of the product showed two singlets, at 4.25 and 4.48 p.p.m., assigned to H-2′ of **11** and **10**, respectively, in the ratio of 33:17.

2-(5-Acetoxypentanoyl)-1,3-dithiane (**14**). — The mixture of products (**10** + **11**; 102 mg, 0.46 mmol) from the foregoing reaction was acetylated with acetic anhydride (8 mL) in pyridine (0.5 mL). After 4 h, the mixture was poured into ice–water, and the product extracted with chloroform, to afford **14** as an oil that was found (t.l.c., 4:1 hexane–ethyl acetate) to be a single product, less polar than the substrate; yield 103 mg (84%); ν_{max}^{film} 1739 (C=O), 1710 (C=O), 1428, 1331, 1236, and 1041 cm^{-1}; ^{13}C-n.m.r. (20.115 MHz): δ 202.3 (C-1), 171.0 (C=O), 64.0 (C-5), 47.0 (C-2′), 39.4 (C-2), 28.0 (C-4), 26.3 (double intensity, C-4′,6′), 25.3 (C-5′), 20.9 (OAc), and 20.6 (C-3); *m/z* (rel. int.): 262 (11.9, M^+), 202 (3.6, M^+ — 60), and 119 (100, $C_4H_7S_2^+$).

Anal. Calc. for $C_{11}H_{18}O_3S_2$: M^+ *m/z* 262.0697. Found: *m/z* 262.0704.

2-(4-Acetoxybutanoyl)-1,3-dithiane (**13**). — A solution of 1,3-dithiane (600 mg, 4.99 mmol) in oxolane (15 mL) was cooled to −43°, and butyllithium (5.25 mmol) in hexane was added. The mixture was kept for 2.5 h at −15 to −25°, and then

cooled to −60°, whereupon 4-butanolide (γ-butyrolactone; 430 mg, 5.0 mmol) was added. For the next 3 h, the temperature was maintained between −60 and −50°, and then the mixture was kept overnight at −13°, and processed as in the analogous reaction of lactone **9**, to afford 657.6 mg of a syrup that was acetylated directly with acetic anhydride in pyridine to give a single product (**13**); yield 702 mg (40.6%); ν_{max}^{film} 1748 (C=O), 1713 (C=O), 1370, 1243, and 1041 cm^{-1}; ^{13}C-n.m.r. (20.115 MHz): δ 201.8 (C-1), 171.0 (C=O), 63.4 (C-4), 47.1 (C-2′), 36.5 (C-2), 26.4 (double intensity, C-4′,6′), 25.2 (C-5′), 23.3 (C-3), and 20.9 (OAc).

Anal. Calc. for $C_{10}H_{16}O_{13}S_2$: M^+ *m/z* 248.0540. Found: *m/z* 248.0546.

Reaction of 4-pentanolide (**15**) *with 2-lithio-1,3-dithiane to give 2-(4-hydroxypentanoyl)-1,3-dithiane* (**18**), (±)-(E)-*2-(1,3-dithian-2-yl)-tetrahydro-5-methylfuran-2-ol* (**16**), *and* (±)-(*Z*)-*2-(1,3-dithian-2-yl)-tetrahydro-5-methylfuran-2-ol* (**17**). — To a mixture of 1,3-dithiane (661 mg, 5.5 mmol) in oxolane (20 mL) at −40° was added butyllithium (5.75 mmol) in hexane. After 2 h, 4-pentanolide (γ-valerolactone, **15**; 550.7 mg, 5.5 mmol) was added, and the mixture was stirred for 4.5 h at −45 to −40°, and then kept for 2 days at −14°. Further processing was conducted as for the reaction of lactone **9**. T.l.c. (4:1 hexane–ethyl acetate) showed a single spot, R_F ~0.3. Evaporation of the solvent yielded an oil (736.1 mg, 60.7%).

The ^{13}C- and ^{1}H-n.m.r. spectra of the oil in chloroform-*d* indicated a mixture of three products (**16**, **17**, and **18**) in unequal proportions; ^{13}C-n.m.r. (20.115 MHz): δ (for **18**) 77.8 (C-4), 202.9 (C-1), 47.0 (C-2′, 25% of total C-2′); [for **16** and **17** (or **17** and **16**)] 66.8, 75.5 (C-4), 107.8, 108.3 (C-1), and 51.0 and 49.6 (C-2′; 45 and 30%, respectively, of total C-2′); ^{1}H-n.m.r. (90 MHz): δ 1.22 (H-5 of **18**, 30% of total H-5), and 1.30 and 1.34 [H-5 of **17** and **16** (or **16** and **17**)], 45 and 25% of total H-5.

Acetylation of **16** + **17** + **18**. — (*a*) *To give 2-(1,4-diacetoxypentylidene)-1,3-dithiane* (**20**). The mixture from the preceding experiment (208 mg, 0.94 mmol) was acetylated at 25° with acetic anhydride (0.5 mL) in triethylamine (10 mL) in the presence of 4-dimethylaminopyridine (0.1 g). Conventional processing afforded 215 mg (75%) of a yellow oil containing the enol ester **20** as the sole product. The analytical sample was prepared by l.c. in a column (7.8 mm × 30 cm) of μPorasil with 4:1 hexane–ethyl acetate as the eluant; ν_{max}^{film} 1752 (C=O), 1726 (C=O), 1600, 1423, 1368, 1239, 1190 (br), 1159, 1065, 1019, 957, and 912 cm^{-1}; ^{1}H-n.m.r.: δ 4.89 (sextet, 1 H, *J* 6.3 Hz, H-4), 2.86 (m, 4 H, H-4′,6′), 2.61 (m, 1 H, $J_{2a,2b}$ 14.5 Hz, H-2a), 2.51 (m, 1 H, H-2b), 2.13 (m, 2 H, H-5′), 2.03, 2.17 (s, 6 H, 2 OAc), 1.68 (m, 2 H, H-3), and 1.22 (d, 3 H, $J_{4,5}$ 6.1 Hz, H-5); ^{13}C-n.m.r. (50.72 MHz): δ 170.6, 168.3 (C=O), 148.0 (C-1), 117.0 (C-2′), 70.1 (C-4), 32.6 (C-3), 30.0, 29.5 (C-4′,6′), 27.8 (C-2), 24.9 (C-5′), 21.3, 20.6 (OAc), and 20.0 (C-5); *m/z*: M^+ 304.0796; calc. for $C_{13}H_{20}O_4S_2$: 304.0803.

Anal. Calc. for $C_{13}H_{20}O_4S_2$: C, 51.29; H, 6.62. Found: C, 51.00; H, 6.25.

(*b*) *To give 2-(4-acetoxypentanoyl)-1,3-dithiane* (**19**) *and its enol acetate* **20**. The products (50 mg, 227 μmol) from the reaction of lactone **15** with 2-lithio-1,3-dithiane were acetylated with acetic anhydride (0.2 mL) in pyridine (5 mL), to give

a mixture of two components, less polar than the substrate (t.l.c., 4:1 hexane–ethyl acetate). The product was isolated conventionally, and the resultant oil was resolved on a column (7.8 × 30 cm) of μPorasil (Waters) with 4:1 hexane–ethyl acetate as the eluant, to give 16.8 mg (28%) of **19** (the less polar component of the mixture) and 11.7 mg (17%) of **20**. Compound **19** showed ν_{max}^{film} 1730–1700 (br, C=O), 1419, 1372, and 1245 cm^{-1}; ^{1}H-n.m.r. (300 MHz): δ 4.91 (q of 4-line multiplets, 1 H, H-4), 4.22 (s, 1 H, H-2'), 3.23 (m, 2 H, H-4'a,6'a), 2.72 (m, 2 H, H-2), 2.59 (8-line multiplet, 2 H, $J_{4'a,4'e} \approx J_{6'a,6'e}$ 14.2 Hz, H-4'e,6'e), 1.98–2.17 (m, 2 H, H-5'), 2.03 (s, 3 H, OAc), 1.89 (m, 2 H, H-3), and 1.24 (d, 3 H, $J_{4,5}$ 6.25 Hz, H-5); ^{13}C-n.m.r. (50.72 MHz, assignments confirmed by heteronuclear decoupling): δ 201.9 (C-1), 170.8 (C=O), 70.1 (C-4), 47.2 (C-2'), 36.1 (C-2), 30.2 (C-3), 26.4 (C-4',6'), 25.3 (C-5'), 21.4 (OAc), and 20.1 (C-5); *m/z* M^+ 262.0706; calc. for $C_{11}H_{18}O_3S_2$: 262.0697.

Anal. Calc. for $C_{11}H_{18}O_3S_2$: C, 50.35; H, 6.91. Found: C, 49.98; H, 6.54.

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