Chiral Polyhydroxylated Tetrahydrothiophene Derivatives: Novel Synthesis and Structural Elucidation by X-Ray Crystallography, NMR Spectroscopy and Molecular Mechanics Calculations

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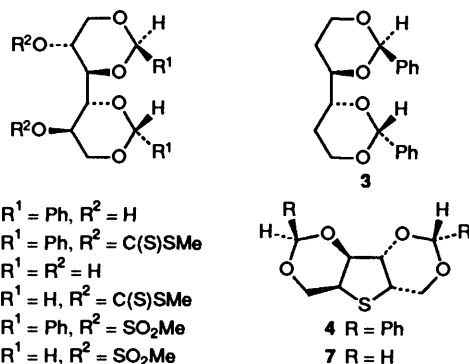S. Ramakumar,[b] M. A. Viswamitra,[b] G. V. T. Swapna,[a] B. Jagannadh[a] and A. C. Kunwar[a]
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The dideoxygenation reaction of 1,3;4,6-di-O-alkylidene-2,5-di-S-methylthiocarbonyl-D-mannitol derivatives under Barton–McCombie reaction conditions gave the hexahydrodipyranothiophenes **4** and **7** instead of the expected 2,5-dideoxy products. Structural and conformational information on these novel derivatives has been obtained by NMR spectroscopy, single-crystal X-ray crystallography and molecular mechanics calculations.

Radical deoxygenation of secondary hydroxy groups in a Barton–McCombie[1] reaction is now established methodology for obtaining deoxy compounds. In connection with a project[2] on polyether natural products[3] with a bis-tetrahydrofuran skeleton, we needed to carry out the simultaneous deoxygenation[4] of hydroxy groups present at positions 2 and 5 of 1,3;4,6-di-O-benzylidene-D-mannitol **1**.[5] Accordingly, **1** was converted into the bis-2,5-dithiocarbonate derivative **2**, by the reaction with sodium hydride, carbon disulfide and methyl iodide in dry tetrahydrofuran. Subsequent reaction[6] of **2** with freshly prepared tributyltin hydride in refluxing toluene containing a catalytic amount of azoisobutyronitrile (AIBN) resulted in a product whose ^1H NMR spectrum did not conform with the expected dideoxy structure **3**. The product obtained was given the structure **4** based on X-ray diffraction analysis and NMR spectroscopy.

Similar results were obtained when 1,3;4,6-di-O-methylene-2,5-di-O-methylthio(thiocarbonyl)-D-mannitol **6** (prepared from 1,3;4,6-di-O-methylene-D-mannitol **5**)[7] was treated with tributyltin hydride in toluene containing AIBN, to give compound **7**. Compounds **4** and **7** have also been synthesized by an alternative approach in which the corresponding dimesylate derivatives **8** and **9** were heated with sodium sulfide in dimethylformamide (DMF) at 110 °C.[8]

Table 1 Chemical shifts $(\delta)^a$ in ppm and indirect couplings $(J)^b$ in Hz for compounds **4** and **7**.

| Parameters	Value	
	4	7
$\delta[H(C\text{-}1)]$	3.938	3.836
$\delta[H(C\text{-}2)]$	4.551	4.234
$\delta[H(C\text{-}4A)]$	—	5.071
$\delta[H(C\text{-}4B)]$	5.502	4.676
$\delta[H(C\text{-}6A)]$	4.273^d	4.113
$\delta[H(C\text{-}6B)]$	4.281^d	4.066
$\delta(Phe)$	$(7.2\text{-}7.6)^c$	—
$J_{H(C\text{-}1)\text{-}H(C\text{-}2)}$	2.4	2.4
$J_{H(C\text{-}1)\text{-}H(C\text{-}4A)}$	—	0.6
$J_{H(C\text{-}1)\text{-}H(C\text{-}6A)}$	1.4^d	1.2
$J_{H(C\text{-}1)\text{-}H(C\text{-}6B)}$	2.6^d	2.5
$J_{H(C\text{-}2)\text{-}H(C\text{-}2')}$	2.0	1.8
$J_{H(C\text{-}4A)\text{-}H(C\text{-}4B)}$	—	−6.4
$J_{H(C\text{-}4A)\text{-}H(C\text{-}6A)}$	—	1.0
$J_{H(C\text{-}6A)\text{-}H(C\text{-}6B)}$	−12.9	−12.8

^{a} With respect to internal TMS. The errors in δ are ±0.001 ppm. ^{b} The errors in J are ±0.3 Hz. ^{c} No attempt was made to derive the chemical shifts and individual couplings in the phenyl ring. ^{d} It was not possible to distinguish between H(C-6A) and H(C-6B). These assignments have been made with the help of the parameters from 7.

Here we describe the structure of these unusual reaction products as obtained by NMR spectroscopy, and X-ray diffraction and molecular mechanic studies and give the mechanistic pathway for these reactions.

Conformation and Structural Studies on Compounds 4 and 7.—NMR Spectroscopy. For the two molecules **4** and **7** the relevant

^1H–^1H indirect couplings (J) and the chemical shifts (δ) are presented in Table 1. The numbering systems employed are illustrated in Figs. 1 and 2 for **4** and **7** respectively. Protons H(C-4A) and H(C-6A) are at the equatorial positions and H(C-4B) and H(C-6B) are at the axial positions. Since NMR shows C_2 symmetry for both the molecules, the numbering of the other half of **7** follows from symmetry, but for the X-ray structure the numbering shown in Fig. 2 is used. The symmetry related atoms are denoted with primes. All the vicinal proton–proton couplings are <3 Hz. The large four-bond couplings $^4J_{H(C\text{-}4A)\text{-}H(C\text{-}6A)}$ of 1.0 Hz arises due to the W configuration of the protons and the five-bond coupling $^5J_{H(C\text{-}1)\text{-}H(C\text{-}4A)}$ of 0.6 Hz is probably observed because of two 'coupling paths' contributing to it. Such long-range couplings are often observed between the equatorial protons in six-membered saturated rings.[9] For **4**, H(C-6A) and H(C-6B) are strongly coupled and misinterpretation of the spectrum can be avoided by taking note of some very weak intensity lines and careful spectral analysis.[10] Two chair conformations for **4** and **7**, consistent with the C_2 symmetry, are shown in Fig. 3. Observation of small

1 R^1 = Ph, R^2 = H
2 R^1 = Ph, R^2 = C(S)SMe
5 R^1 = R^2 = H
6 R^1 = H, R^2 = C(S)SMe
8 R^1 = Ph, R^2 = SO₂Me
9 R^1 = H, R^2 = SO₂Me

3

4 R = Ph
7 R = H

Table 2 Dihedral angles (°) between the vicinal protons in 4 and 7 by NMR, X-ray and MMX calculations

	4			7		
Dihedral angle	NMR	X-ray	MMX	NMR	X-ray[a]	MMX
H(C-6A)–C(6)–C(1)–H(C-1)	66	69	72	68	77	72
H(C-6B)–C(6)–C(1)–H(C-1)	−54	−47	−48	−55	−45	−45
H(C-1)–C(1)–C(2)–H(C-2)	54	41	45	55	40	44
H(C-2)–C(2)–C(2')–H(C-2')	75	86	63	75	76	66

[a] In the solid state the molecule does not have C_2 symmetry. For comparison with NMR and MMX calculations we have taken the average value from both the halves. The errors from the X-ray measurements are *ca.* ±4°.

Fig. 1

Fig. 2

Fig. 3

Fig. 4 ORTEP diagram for 4

Fig. 5 ORTEP diagram for 7
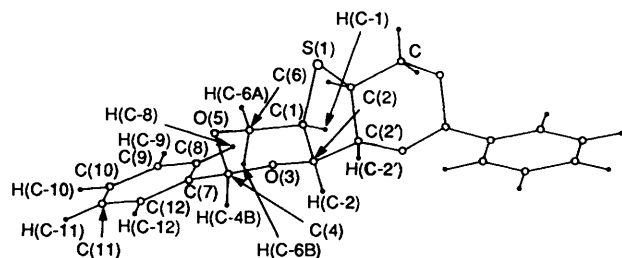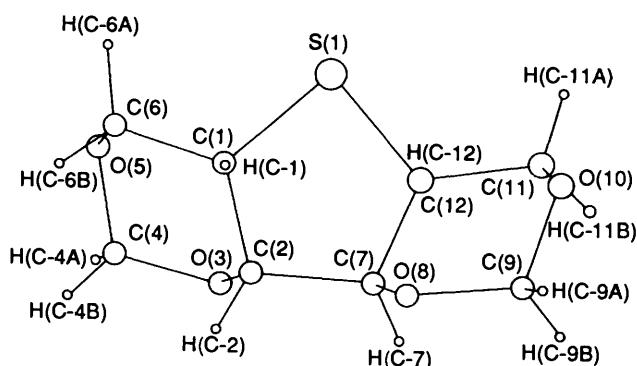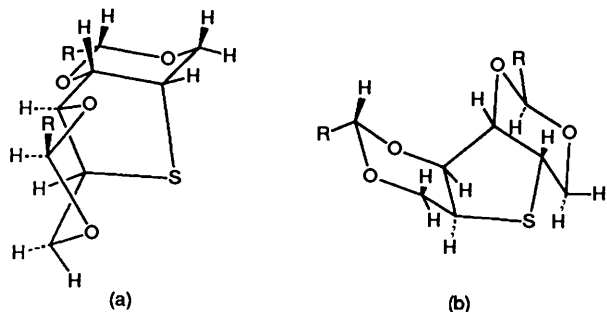
vicinal couplings (< 3 Hz) rules out structure (b), which should show vicinal coupling between two axial protons ($^3J_{H(C-1)-H(C-6B)}$) of *ca.* 10 Hz. This structure can also be ruled out on the grounds that $^3J_{H(C-2)-H(C-2')}$ is small and is not consistent with the *trans* geometry of the two protons. Further support for the chair conformation of six-membered rings is obtained by the large four-bond coupling $^4J_{H(C-4A)-H(C-6A)}$ and the NOE (nuclear Overhauser effect) experiments discussed later.

The modified Karplus equations,[11] which consider the electronegativity of the substituents, were used to determine some of the dihedral angles involving the protons in 4 and 7. The dihedral angles, H(C-6A)-C(6)-C(1)-H(C-1), H(C-6B)-C(6)-C-(1)-H(C-1), H(C-1)-C(1)-C(2)-H(C-2) and H(C-2)-C(2)-C(2')-
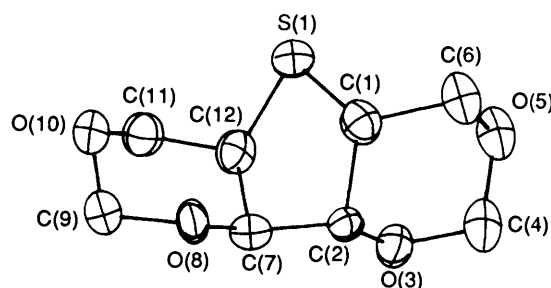
H(C-2'), are respectively, 68°, −55°, 55° and 75° for 7 (Table 2). For 4 very similar values of dihedral angles are found. Owing to the approximate nature of the Karplus relations these dihedral angles are at best accurate to ± 5°. NOE experiments have been performed, which, besides providing structural information, help in the assignments of the resonances.[12,13] The relevant results are presented in Table 3. For 4 the irradiation of H(C-2) shows large NOE enhancement at H(C-1) and H(C-4B), reflecting the proximity of these protons, resulting from the chair conformation of the six-membered ring shown in Fig. 3(a). Enhancements of the same magnitude are observed at H(C-2) when H(C-1) and H(C-4B) are irradiated. Very similar results have been obtained for 7. In both 4 and 7, H(C-6A) and H(C-6B) are strongly coupled and it is difficult to obtain the enhancement and irradiation of individual protons;[13,14] we have not, therefore, included this data in Table 3.

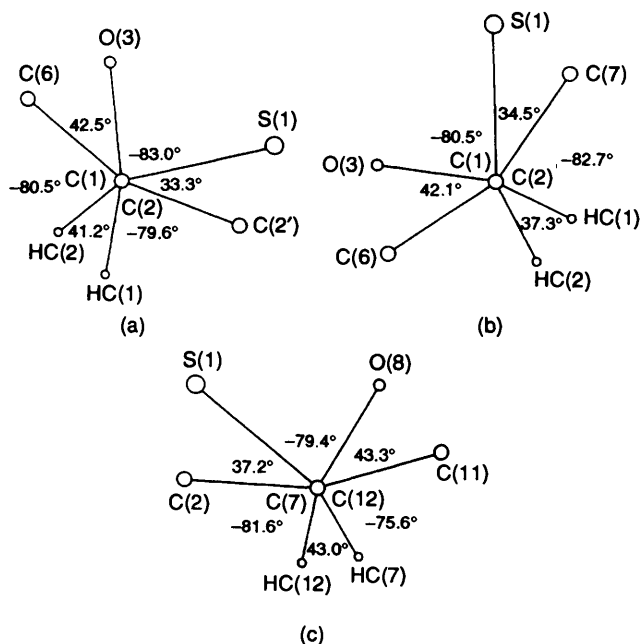*X-Ray Crystal Structure.*—The ORTEP diagrams for 4 and 7 are given in Figs. 4 and 5.

Molecule 4 shows an exact C_2 symmetry with the sulfur atom positioned on the crystallographic 2-fold axis. In contrast, molecule 7 does not show exact C_2 symmetry, the solid-state effects being responsible for such deviations. The crystal structures of both the compounds are stabilized by Van der Waals forces.

The six-membered rings are *cis* fused with the central five-membered ring in both the structures as seen from the Newman projections involved in ring fusions (Fig. 6). The heterocyclic six-membered rings are all in the chair conformation. For 4, the best mirror plane for this ring passes through C(1) and C(4), with the asymmetry parameter,[15] ΔC_s [C(1)] = 4.1°. The best mirror

Table 3 Nuclear Overhauser effects (NOE) in 4 and 7

Compound	Irradiated proton[a]	Enhancement at proton					
		H(C-1)	H(C-2)	H(C-4A)	H(C-4B)	H(C-6A)	H(C-6B)
4[b]	H(C-1)	i	10			4	
	H(C-2)	13	i		17	−7	
	H(C-4B)		14		i	4	
	H(C-6A) ⎫						
	H(C-6B) ⎭	24	−3		12	i	
7[c]	H(C-1)	i	7			3	4
	H(C-2)	4	i		6		
	H(C-4A)			i	20		
	H(C-4B)		7	23	i	1	3

[a] Irradiated protons are shown by i. [b] H(C-6A) and H(C-6B) have been irradiated simultaneously and when other protons are irradiated only the combined enhancement could be measured for them. [c] Owing to the proximity of the H(C-6A) and H(C-6B) resonances, these protons could not be individually irradiated. The data is, therefore, not presented.
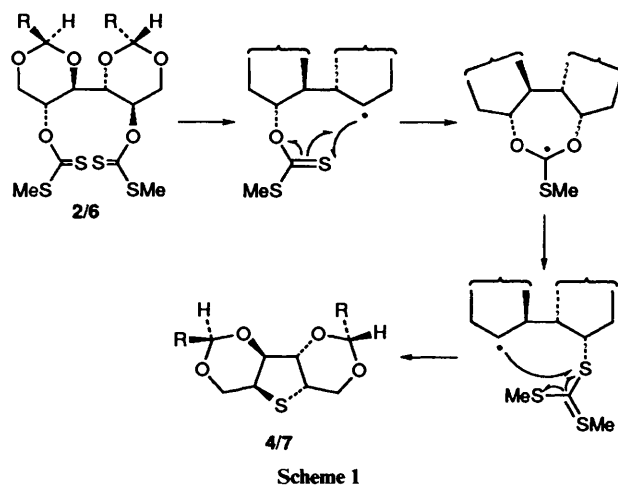

Fig. 6

rather poor and the accuracy of C–H distances is ±0.05 Å and that of H–C–C–H type torsional angles is ±4°. In order to compare the structural information derived from ¹H NMR spectral measurements some of the dihedral angles obtained from the solid-state structure are included in Table 2 along with those obtained by NMR. However, keeping in mind the low accuracy associated with the location of protons by both the techniques, it may be seen from Table 2 that all the dihedral angles involving protons as determined by NMR and X-ray are consistent with each other. In order to get further insight on the structure, we have carried out the molecular mechanics calculations discussed below.

Molecular mechanics calculations. The optimized bond lengths and bond angles of 4 and 7 using an MMX program are similar to those obtained by X-ray diffraction, but for minor deviations of the C–C bond lengths in the phenyl ring. The dihedral angles of relevance involving the protons are given in Table 2 and are, generally, in agreement with the values determined by the NMR and X-ray techniques.

Mechanistic Studies.—The outcome of these reactions can be understood in terms of the Barton–McCombie mechanism[16] for the reaction of trialkylstannanes with dithiocarbonates (Scheme 1).

planes in 7 pass through C(1) and C(4) for one of the six-membered rings and through C(9) and C(12) for the other, with the asymmetry parameters $\Delta C_s[C(1)] = 2.2°$ and $\Delta C_s[C(9)] = 1.5°$ respectively. In 4, the best four-atom least-squares plane is formed by C(1), O(3), C(4) and C(6), with C(2) and O(5) displaced by −0.6 and 0.7 Å respectively from this plane. The same four-atom plane forms the best least-squares plane for one of the six-membered rings in 7. The atoms C(2) and O(5) are −0.6 and 0.6 Å, respectively, away from this plane. The other six-membered ring has the best least-squares plane formed by the atoms C(7), O(8), O(10) and C(11), with the atoms C(9) and C(12) displaced by −0.7 and 0.6 Å, respectively, from the plane. For 4, the phenyl ring geometry is very close to regular hexagon geometry. It is interesting to note that there are significant differences in the dihedral angles involving non-hydrogen atoms between the two independent halves of molecule 7, as also between the two molecules 7 and 4. For example, in molecule 7, C(12)–S(1)–C(1)–C(2) = −11.0(2)° differs from the corresponding angle C(1)–S(1)–C(12)–C(7) = −14.8(2)° and similarly S(1)–C(1)–C(2)–C(7) = 34.5(3)° differs from S(1)–C(12)–C(7)–C(2) = −37.2(3)°. Comparing molecules 4 and 7, it may be seen that C(1)–S(1)–C(1')–C(2') = 11.9(3°) in molecule 4 differs from the corresponding angle C(1)–S(1)–C(12)–C(7) = −14.8(3)° in molecule 7. Location of hydrogens is

Scheme 1

Experimental

Materials and Methods.—*NMR spectroscopy.* NMR spectra were recorded in CDCl₃ solutions on a Bruker AM-300 NMR spectrometer. NOE difference spectra were obtained by the subtraction of two free induction decays; one accumulated with

the decoupler set on a peak of interest and the second with the decoupler set outside the spectral range. The nuclei of interest were irradiated for 5 s before acquisition of the data. The decoupler power was kept to a minimum, being just sufficient to saturate the resonance of interest.

X-Ray Crystallography.—The X-ray intensity data were collected at room temperature (295 K) on an Enraf-Nonius CAD4 diffractometer using Ni-filtered Cu-Kα radiation. Lorentz, polarization and absorption corrections[17] were applied to the intensity data. The structures were derived by direct methods using MULTAN 11/82.[18] All H atoms were located from difference electron density maps. Refinements of the structure were done with the help of SHELX76.[19] Solutions of the structure were obtained using Enraf-Nonius (1979) SDP on a PDP 11/44 computer.[15] Fractional coordinates, bond lengths and angles and thermal parameters for the two structures are available on request from the Cambridge Crystallographic Data Centre.*

X-Ray crystal structure analysis of **4**: *crystal data.* C_{20}-$H_{20}O_4S$, $M = 356.4$; Tetragonal, $a = 8.793(2)$, $b = 8.793(2)$, $c = 23.070(2)$ Å, $V = 1783.7$ Å^3, space group $P4_12_12$, $F(000) = 752$, $D_c = 1.43$ g cm^{-3}, $Z = 4$ (half molecule in the asymmetric unit), Cu-Kα radiation was used and 2109 reflections were measured. The full matrix refinement of all coordinates including anisotropic thermal parameters of non-H atoms converged at $R = 0.053$, $R_w = 0.050$ with weight $[\sigma^2(F) + P^*F^2]$ for 1306 reflections that satisfied $F \geqslant 3\sigma(F)$.

X-Ray crystal structure analysis of **7**: *crystal data.* $C_8H_{12}O_4S$, $M = 204.2$. Orthorhombic, $a = 8.825(2)$, $b = 9.274(3)$, $c = 11.050(2)$ Å, $V = 904.4$ Å,^{3} space group $P2_12_12_1$, $F(000) = 432$, $D_c = 1.50$ g cm^{-3}, $Z = 4$, Cu-Kα radiation was used and 1003 reflections were measured. The full matrix refinement of all coordinates including anisotropic thermal parameters of non-H atoms converged at $R = 0.032$, $R_w = 0.030$ with weight $[\sigma^2(F) + P^*F^2]$ for 887 reflections that satisfied $F \geqslant 3\sigma(F)$.

Molecular Mechanics Calculations.—These calculations were performed using PCMODEL,[20] a modification of MM2, which can be run on a PC in an interactive manner. PCMODEL incorporates the MMX force field from Allinger's MM2 and MMP1 programs.[21]

General Remarks.—All the solvents were evaporated on a rotavapor < 50 °C. Optical rotations were recorded on a JASCO DIP 360 digital polarimeter. Mass spectra were recorded on a VG Micromass 7070H spectrometer. Light petroleum refers to fraction b.p. 60–80 °C. M.p.s were obtained with a Mettler melting point apparatus.

1,3;4,6-*Di-O-benzylidene-2,5-di-O-methylthio(thiocarbonyl)*-D-*mannitol* **2**.—Compound **1** (3.58 g, 10.0 mmol) was dissolved in dry DMF (25 cm^3) under nitrogen and then NaH (50% dispersion in oil; 2.10 g, 43.7 mmol) was slowly added to the solution. After 2 h, dry CS$_2$ (2.2 cm^3) was introduced to the mixture, followed after 30 min by MeI (3 cm^3). The reaction mixture was stirred for 12 h, after which it was decomposed with methanol, poured into water and extracted with ether. The ether layer was washed with water, dried (Na$_2$SO$_4$) and concentrated to give a crude residue purified by column chromatography on silica gel with ethyl acetate–light petroleum as eluent to afford **2** (4.46 g, 83%); this was crystallized from ether and had m.p. 210 °C, $[\alpha]_D$ − 42.9 (c

* For details see 'Instructions for Authors (1993),' *J. Chem. Soc., Perkins Trans 1*, 1993, Issue 1.

0.5 of CHCl$_3$); δ(80 MHz) 2.59 (s, 6 H), 3.73 (2 H, t, J 10), 4.15 (2 H, d, J 9), 4.64 (2 H, q), 5.52 (2 H, s), 6.13 (2 H, dt, J 5, 10) and 7.35 (10 H, m); m/z 192 (M$^+$/2).

1,3;4,6-*Di-O-methylene-2,5-di-O-methylthio(thiocarbonyl)*-D-*mannitol* **6**.—To compound **5** (3.25 g, 15.77 mmol) in dry DMF (25 cm^3) was added sodium hydride (50% dispersion in oil; 3.4 g, 70.8 mmol) followed by dry CS$_2$ (3.0 cm^3). The reaction mixture was stirred for 20 min after which MeI (3.0 cm^3) was introduced and stirring continued for 12 h. The reaction mixture was then worked up and the residue purified on silica gel by elution with ethyl acetate–light petroleum to give **6** (4.2 g, 69%), m.p. 113 °C, $[\alpha]_D$ + 25.2 (c 0.5 of CHCl$_3$); δ(200 MHz) 2.54 (6 H, s), 3.44 (2 H, t, J 10), 3.78 (2 H, d), 4.46 (2 H, dd, J 6, 10), 4.54 (2 H, d, J 6), 5.04 (2 H, d, J 6) and 5.82 (2 H, dt).

(4aS,4bS,9aS,9bS)-2,8-*Diphenylhexahydrodipyrano*[5,6-b; 6',5'-d]*thiophene* **4**.—To a solution of compound **2** (10.76 g, 20 mmol) in dry toluene (80 cm^3) at 80 °C was added freshly prepared tributyltin hydride (14.3 cm^3) and a catalytic amount of AIBN under nitrogen. The reaction mixture was heated under reflux for 18 h and then concentrated. The residue was partitioned between water and ether and the ethereal layer then separated, dried (Na$_2$SO$_4$) and concentrated. The residue was chromatographed on silica gel with ethyl acetate–light petroleum as eluent to give the title compound **4** (5.7 g, 80%), crystallized from benzene, m.p. 209 °C, $[\alpha]_D$ − 102.8 (c 0.6 of CHCl$_3$) (Found: M, 356.1085. Calc. for $C_{20}H_{20}O_4S$: M, 356.1080).

2,5-*Di-O-mesyl*-1,3;4,6-*di-O-methylene-D-mannitol* **9**.—A mixture of compound **5** (2.0 g, 9.7 mmol), dry pyridine (10 cm^3) and mesyl chloride (2.7 g, 23.6 mmol) was stirred for 3 h at room temperature and then worked up. The residue was purified by column chromatography on silica gel with ethyl acetate–light petroleum as eluent to give the title compound **9** (2.5 g, 72%) which was crystallised from CHCl$_3$, m.p. 179–182 °C, $[\alpha]_D$ − 43.9 (c 0.5 of CHCl$_3$); δ(200 MHz) 3.04 (6 H, s), 3.58 (2 H, t, J 10), 3.80 (2 H, d, J 10), 4.40 (2 H, dd, J 5, 10), 4.58 (2 H, d, J 6), 4.88 (2 H, dt) and 5.10 (2 H, d).

2,5-*Di-O-mesyl*-1,3;4,6-*di-O-benzylidene-D-mannitol* **8**.—A mixture of compound **1** (5.0 g, 13.9 mmol), pyridine (25 cm^3) and mesyl chloride (9.5 g, 82.9 mmol) was stirred at room temperature for 3 h and then worked up. The residue was chromatographed on silica gel with ethyl acetate–light petroleum to give the title compound **8** (6.1 g, 85%), m.p. 184 °C, $[\alpha]_D$ − 18 (c 0.6 of CHCl$_3$); δ(200 MHz) 3.00 (6 H, s), 3.80 (2 H, t, J 11), 4.08 (2 H, d), 4.48 (2 H, dd, J 4.5, 11), 4.97 (2 H, m), 5.44 (2 H, s) and 7.4 (10 H, m); m/z 514 (M$^+$).

(4aS,4bS,9aS,9bS)-*Hexahydrodipyrano*[5,6-b;6',5'-d]*thio-phene* **7**.—A mixture of compound **9** (2.98 g, 8.2 mmol) sodium sulfide (2.3 g) and DMF (15 cm^3) was heated at 110 °C for 3 h and then poured into water and extracted with ether. The extract was dried and concentrated and the residue was purified by column chromatography on silica gel with ethyl acetate–light petroleum as eluent to give the title compound **7** (0.82 g, 49%), crystallized from benzene, m.p. 151–152 °C, $[\alpha]_D$ − 113.6 (c 1.7 of CHCl$_3$) (Found: M, 204.0449. Calc. for $C_8H_{12}O_4S$: M, 204.0456).

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