# Enantioselective preparation of 1,3-dithiane 1-oxides by asymmetric oxidation of 1,3-dithianes bearing a chiral auxiliary

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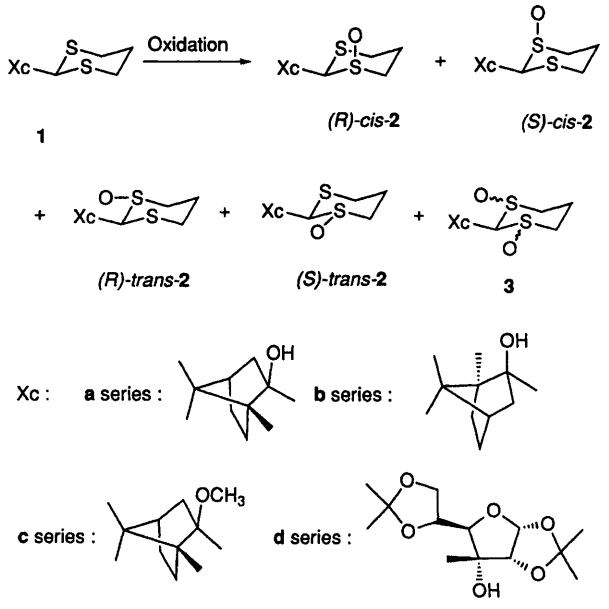
**Oxidation of 1,3-dithianes bearing a chiral auxiliary derived from (+) or (−)-camphor or diacetone D-(+)-glucose by the Sharpless reagent [$Ti(OPr^i)_4$–diethyl L-(+)- or D-(−)-tartrate–$Bu^tOOH$] affords, with high stereoselectivity, the monosulfoxides in good to excellent yields. Removal of the chiral auxiliary by base-catalysed hydrolysis yields (*R*)- and (*S*)-1,3-dithiane 1-oxides in high yields.**

Enantiomerically pure sulfoxides can be used as chiral auxiliaries as well as chiral building blocks in enantioselective carbon–carbon bond-forming reactions.[1] Recently, Page and his co-workers have demonstrated excellent asymmetric syntheses using 1,3-dithiane 1-oxides as precursors of chiral acyl anions or chiral auxiliaries.[2] A number of methods for the preparation of enantiomerically pure sulfoxides have been reported, *e.g.* the reaction of chiral sulfinates,[3] chiral sulfinyl amines[4] or chiral sulfites[5] with various organometallic reagents, and the asymmetric oxidation of sulfides.[6,7] Among the methods for the preparation of chiral sulfoxides developed so far, asymmetric oxidation would be the method of choice for the preparation of chiral 1,3-dithiane 1-oxide since there are difficulties with chiral sulfinyl transfer methods for this purpose. Asymmetric oxidation of 2-substituted 1,3-dithianes by a chiral titanium reagent has been reported to give the monosulfoxides stereoselectivity depending largely upon the substituent on the 1,3-dithiane ring.[6,8] The asymmetric oxidation of unsubstituted 1,3-dithiane, however, gives 1,3-dithiane 1-oxide with low selectivity.[9] Enantiomerically pure 1,3-dithiane 1-oxide was first prepared *via* adducts with camphor.[10] Recently, Page and his co-workers reported the preparation of enantiomerically pure 1,3-dithiane 1-oxide through the enantioselective oxidation of 2-acyl-1,3-dithianes.[11] We describe herein a convenient and highly enantioselective preparation of 1,3-dithiane 1-oxide by asymmetric oxidation of 1,3-dithianes bearing easily removable chiral auxiliaries derived from (+)- or (−)-camphor, or diacetone D-(+)-glucose (DAG).

## Results and discussion

Oxidations of (1*R*,2*R*)-2-(1,3-dithian-2-yl)-2-hydroxy-1,7,7-trimethylbicyclo[2.2.1]heptane **1a** and (1*S*,2*S*)-2-(1,3-dithian-2-yl)-2-hydroxy-1,7,7-trimethylbicyclo[2.2.1]heptane **1b** and (1*R*,2*R*)-2-(1,3-dithian-2-yl)-2-methoxy-1,7,7-trimethylbicyclo-[2.2.1]heptane **1c** were studied. The dithianylcamphors **1a** and **1b** were prepared according to the procedure reported,[10] by the reaction of (+)- or (−)-camphor with 2-lithio-1,3-dithiane, prepared from 1,3-dithiane and 1 equivalent of BuLi. The dithianyl-*O*-methylated (+)-camphor **1c** was prepared from **1a** by treatment with sodium hydride and subsequently with methyl iodide at 0 °C. Oxidation of the dithianylcamphors **1a–c** was carried out with a modified Sharpless reagent,[12] $Ti(OPr^i)_4$–diethyl L-(+)- or D-(−)-tartrate [L-(+)- or D-(−)-DET]–$Bu^tOOH$ (1 : 2 : 1.5) under anhydrous conditions (method A) and $Ti(OPr^i)_4$–L-(+)- or D-(−)-DET–$Bu^tOOH$–$H_2O$ (1 : 2 : 1.5 : 1) (method B); the latter conditions are those reported by Kagan *et al.*[6] for the oxidation of sulfides but with




**Scheme 1** Method A: $Ti(OPr^i)_4$ (1.0 equiv.), DET (2.0 equiv.), $Bu^tO_2H$ (1.5 equiv.), $CH_2Cl_2$ (0.05 M), M.S.4A (10 wt%), −23 °C. Method B: $Ti(OPr^i)_4$ (1.0 equiv.), DET (2.0 equiv.), $Bu^tO_2H$ (1.5 equiv.), $CH_2Cl_2$ (0.05M), $H_2O$ (1.0 equiv.), −23 °C. Method C: MCPBA, $CH_2Cl_2$, −23 °C

modifications (Scheme 1). Results are summarized in Table 1. When the dithianyl-(+)-camphor **1a**, prepared from (+)-camphor, was oxidized with $Ti(OPr^i)_4$–L-(+)-DET–$Bu^tOOH$ under anhydrous conditions (method A), a mixture of three diastereoisomeric monosulfoxides (*R*)-*cis*-**2a**, (*S*)-*cis*-**2a**, and (*R*)-*trans*-**2a** (ratio 82 : 15 : 3) was obtained in 95% yield together with a small amount of the disulfoxide **3a** (entry 1). The formation of (*S*)-*trans*-**2a** was not observed. High diastereoselectivity was obtained in the oxidation in the presence of 1 equiv. of water (method B), giving the monosulfoxides (*R*)-*cis*-**2a** and (*S*)-*cis*-**2a** (ratio of 92 : 8) in 79% yield without formation of (*R*)-*trans*-**2a** and (*S*)-*trans*-**2a** (entry 2). Oxidation of **1a** by methods A and B using D-(−)-DET as a ligand gave (*R*)-*cis*-**2a**, (*S*)-*cis*-**2a** and (*R*)-*trans*-**2a** (ratio 15 : 78 : 7 and 5 : 88 : 7) (entries 3 and 4). The ratios of diastereoisomers were determined by integration of the methine protons at the 2-position of the 1,3-dithiane 1-oxide in the $^1H$ NMR spectra of the crude products. Each C-2 proton of the three isomers (*R*)-*cis*-**2a**, (*S*)-*cis*-**2a** and (*R*)-*trans*-**2a** appeared at $\delta$ 3.90, 3.85, and 3.71, each as a singlet, respectively. These diastereoisomers were assigned according to the data reported by Bryan *et al.*[10] who have reported

**Table 1** Oxidation of dithianylcamphors **1**

| Entry | Compd. | Method | DET | Reaction time | Yield of **2** (%) | Diastereoisomeric ratio of **2**[a] | | | | Yield of **3** (%) |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | *R-cis* | *S-cis* | *R-trans* | *S-trans* | |
| 1 | **1a** | A | L-(+) | 6 h | 95 | 82 | 15 | 3 | 0 | 2 |
| 2 | **1a** | B | L-(+) | 4 h | 79 | 92 | 8 | 0 | 0 | 8 |
| 3 | **1a** | A | D-(−) | 9 h | 91 | 15 | 78 | 7 | 0 | 6 |
| 4 | **1a** | B | D-(−) | 9 h | 91 | 5 | 88 | 7 | 0 | 3 |
| 5 | **1b** | A | L-(+) | 8 h | 62 | 86 | 9 | 0 | 5 | 3 |
| 6 | **1b** | A | D-(−) | 10 h | 75 | 16 | 82 | 0 | 2 | 10 |
| 7 | **1c** | A | L-(+) | 10 h | 64 | 0 | 0 | >99 | 0 | 11 |
| 8 | **1c** | A | D-(−) | 27 h | 79 | 0 | 0 | >99 | 0 | 0 |
| 9 | **1c** | C | None | 10 min | 59 | —[b] | —[b] | 84 | 16[b] | 6 |

[a] Determined by $^1$H NMR. [b] A mixture of two isomers; the stereochemistry of the isomers was not determined.

**Table 2** Oxidation of the dithianyl-DAG **1d**

| Entry | Method | DET | Reaction time | Yield of **2** (%) | Diastereoisomeric ratio of **2d**[a] | | Yield of **3** (%) |
|---|---|---|---|---|---|---|---|
| | | | | | (*R*)-*trans* | Others | |
| 1 | C | None | 10 min | 58 | 79 | 21 | 25 |
| 2 | A | L-(+) | 8 h | 68 | 80 | 20 | 21 |
| 3 | B | L-(+) | 7 h | 67 | 75 | 25 | 24 |
| 4 | A | D-(−) | 8 h | 91 | 93 | 7 | 0 |
| 5 | B | D-(−) | 8 h | 85 | 84 | 16 | 0 |

[a] Determined by $^1$H NMR.

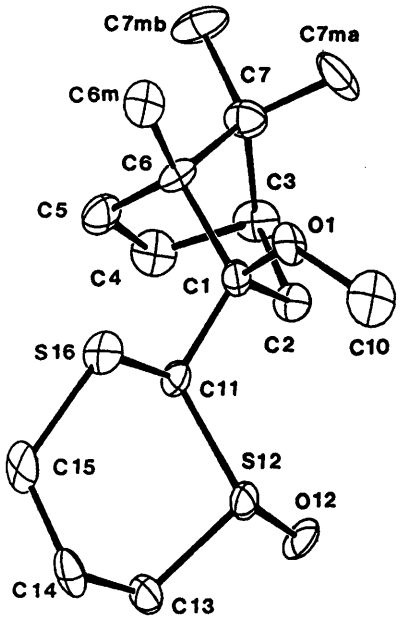



**Fig. 1** ORTEP drawing of (*R*)-*trans*-**2c**

the oxidation of **1a** with *m*-chloroperbenzoic acid (MCPBA) at −25 °C to give a diastereoisomeric mixture of the monosulfoxides (*R*)-*cis*-**2a**, (*S*)-*cis*-**2a** and (*R*)-*trans*-**2a** (ratio 40:40:20). Our results clearly show that oxidation of 1,3-dithianes having a chiral camphor-derived auxiliary with the Sharpless reagent gives monosulfoxides with higher stereoselectivity than a similar oxidation with MCPBA. Oxidation of the dithianyl-(−)-camphor, using L-(+)-DET gave (*R*)-*cis*-**2b**, (*S*)-*cis*-**2b** and (*R*)-*trans*-**2b** (ratio 86:9:5) (entry 5), whereas oxidation using D-(−)-DET gave (*S*)-*cis*-**2b** as the major product (entry 6). Oxidation of **1c**, in which the hydroxy group was protected by a methyl group, with MCPBA (method C) gave (*R*)-*trans*-**2c** and a mixture of two other isomers (ratio 84:8:8), together with a small amount of the disulfoxide **3c** (entry 7). The diastereoisomeric ratio was determined by integration of the C-2 methine protons of the 1,3-dithiane 1-oxides which appeared at $\delta$ 3.86, 4.03 and 4.02. The methoxy protons also appeared separately at $\delta$ 3.51, 3.35 and 3.23. The stereochemistry of the major isomer was assigned as (*R*)-*trans* by X-ray crystallographic analysis (see Fig. 1). The stereochemistry of other isomers has still to be determined. In contrast, oxidation of **1c** by method A gave exclusive formation of the equatorial oxidation product (*R*)-*trans*-**2c** irrespective of the chirality of the DET ligands (entries 8 and 9). The stereochemistry of the disulfoxides **3a**, **3b** and **3c**, obtained as single stereoisomers in each reaction, were not determined.

Next, oxidations of 3-*C*-(1,3-dithian-2-yl)-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose **1d** by methods A, B and C were examined and the results are summarized in Table 2. The dithianyl-D-(+)-DAG **1d** was prepared as follows. To a THF solution of 2-lithio-1,3-dithiane was added a solution of 1,2:5,6-di-*O*-isopropylidene-α-D-hexofuranose-3-urose,[13] which was prepared by oxidation of diacetone D-(−)-glucose with pyridinium chlorochromate. Oxidation of **1d** with MCPBA (method C) at −23 °C gave 3-*C*-(1-oxo-1,3-dithian-2-yl)-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose **2d** (58%) and the disulfoxide **3d** (25%). The monosulfoxide **2d** comprises two diastereoisomers (ratio 79:21) (entry 1), the absolute configuration of the major product being determined as (*R*)-*trans* by X-ray crystallographic analysis (see Fig. 2). Although the stereochemistry of the minor isomer of the monosulfoxide **2d** was not determined, the ratio of the two isomers was determined from the $^1$H NMR spectrum of the crude product, in which the C-1 methine protons of (*R*)-*trans*-**2d** and the unidentified monosulfoxide appeared at $\delta$ 5.76 and 6.19, respectively. Oxidations by methods A and B using L-(+)-DET gave two diastereoisomeric monosulfoxides in similar ratios to the above together with a considerable amount of the disulfoxide **3d** (entries 2 and 3). Although (*R*)-*trans*-**2d** was also the major product in these reactions, the minor isomer of the monosulfoxide **2d** has different stereochemistry from that described above, its C-1 methine proton appearing at $\delta$ 6.01. A particular feature of the oxidations employing D-(−)-DET as the ligand was the absence of any **3d**. The monosulfoxides **2d**, however, were formed in 91% yield in a high diastereoisomeric

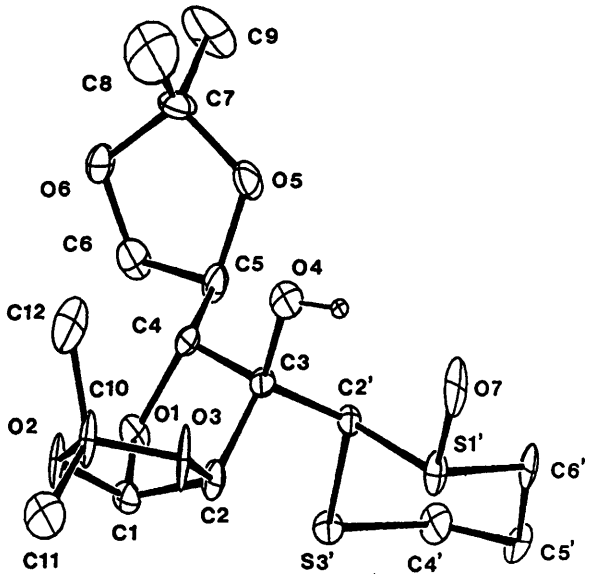
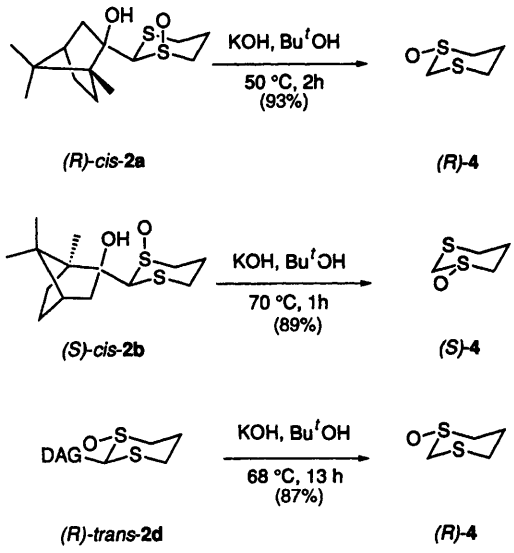



**Fig. 2** ORTEP drawing of (*R*)-*trans*-**2d**




**Scheme 2**

ratio (93:7) by method A and in 85% yield (ratio 84:16) by method B (entries 4 and 5). The diastereoisomeric ratios were determined from the $^1$H NMR signals of the C-1 protons which appeared at $\delta$ 5.76 and 5.75.

It is interesting that the (*R*)-*trans* isomer is the major product in both oxidations of the dithianyl-D-(+)-DAG **1d** with L-(+)- and D-(−)-DET. The steric bulkiness of the DAG-derived auxiliary reflects on the stereoselection irrespective of the DET ligands without coordination of the hindered hydroxy group to the titanium reagent. A similar stereochemical outcome irrespective of the chirality of the DET ligands was also observed in oxidations of the *O*-methylated dithianyl-camphor **1c**. These oxidations afforded (*R*)-*trans*-**2c** with strikingly high stereoselectivity, suggesting the non-coordination of the hydroxy or the methoxy group with titanium. On the other hand, oxidation of the dithianyl-camphors **1a** and **1b** resulted in a different stereochemical outcome depending upon the ligand used; this suggests that the hydroxy group may coordinate with the titanium to effect the determination of the stereoselectivity. There is a report which suggests that in the asymmetric oxidation of sulfides[14] a stereochemical effect is induced by coordination of a polar group to a metal such as Ti$^{IV}$. Although the role of water in the oxidation is unclear, Kagan and his collaborators have reported that water is added to deactivate the titanium reagent and to minimize further oxidation of the sulfoxide to the sulfone.[6] Our results fail to show any significant changes in the stereoselectivity or in disulfoxide formation for reactions carried out in the presence of water compared with those carried out under anhydrous conditions.

Oxidation of dithianes having a chiral auxiliary afforded monosulfoxides with high stereoselectivities. Such (*R*)- and (*S*)-monosulfoxides as (*R*)-*cis*-**2a**, (*R*)-*trans*-**2d** and (*S*)-*cis*-**2b** could be easily isolated by column chromatography. Chiral auxiliaries were easily removed by the base-catalysed hydrolysis (Scheme 2). Thus, the monosulfoxide (*R*)-*cis*-**2a** was treated with potassium hydroxide in Bu$^t$OH at 50 °C for 2 h to give (*R*)-1,3-dithiane 1-oxide (*R*)-**4** (93%). Similarly, (*S*)-1,3-dithiane 1-oxide (*S*)-**4** was obtained from (*S*)-*cis*-**2b** (89%). Both (*R*)-**4** and (*S*)-**4** were confirmed as >98% ee by NMR studies using a chiral shift reagent, (*R*)-(−)-2,2,2-trifluoro-1-(9-anthryl)ethanol.[11] DAG was removed upon treatment of (*R*)-*trans*-**2d** with potassium hydroxide at 70 °C for 13 h to give (*R*)-**4** (87%).

In summary, 1,3-dithianes bearing a chiral auxiliary derived from (+)- or (−)-camphor, or D-(+)-DAG gave the 1,3-dithiane 1-oxides with high stereoselectivity in the oxidation with Ti(OPr$^i$)$_4$–L-(+)- and D-(−)-DET–Bu$^t$OOH (1:2:1.5). Since the chiral auxiliary can be readily removed, the present reaction provides a method for the efficient preparation of (*R*)- and (*S*)-1,3-dithiane 1-oxides.

## Experimental

$^1$H NMR spectra for solutions in $CDCl_3$ were recorded on a Varian Gemini-200 operating at 200 MHz, chemical shifts ($\delta$) are expressed in ppm downfield from tetramethylsilane and *J* values are given in Hz. $^{13}$C NMR spectra for solutions in $CDCl_3$ were recorded on a Varian Gemini-200 operating at 50 MHz. IR spectra were recorded on a JASCO FT/IR 200 spectrometer; absorptions are given in reciprocal centimeter. Melting points were determined on a Yanaco micro-melting point apparatus and are uncorrected. Optical rotations were measured on a JASCO DIP-4 (100 mm, 1 cm$^3$ cell) in the indicated solvent and concentration in grams of solute per 100 cm$^3$. Microanalyses were performed with a Perkin-Elmer-240 machine. Reactions involving air- or moisture-sensitive compounds were carried out in appropriate round-bottom flasks under argon. All reactions were monitored by thin-layer chromatography on 0.25-mm Merk silica gel plates (60F-254). TLC plates were visualized with UV light and 7% phosphomolybdic acid or *p*-anisaldehyde in ethanol. Column chromatography was carried out on a column packed with Fuji Devison silica gel BW-200. A *tert*-butyl hydroperoxide solution in dichloromethane (5.22 mol dm$^{-3}$) was prepared according to the literature[15] and stored over molecular sieves under argon in a refrigerator. Diethyl L-(+)- and D-(−)-tartrate were purified by distillation before use.

### (1*R*,2*R*)-2-(1,3-Dithian-2-yl)-2-hydroxy-1,7,7-trimethylbicyclo-[2.2.1]heptane 1a

To a solution of 1,3-dithiane (5.26 g, 42.42 mmol) in THF (55 cm$^3$) was added BuLi (1.45 mol dm$^{-3}$ hexane solution; 29.3 cm$^3$, 42.49 mmol) at −50 °C after which the mixture was allowed to warm to −10 °C. After the mixture had been stirred for 1 h, it was treated with (+)-camphor (7.10 g, 45.72 mmol) dissolved in THF (10 cm$^3$), added at −10 °C, and then was stirred at room temperature for 13 h. After this the reaction mixture was diluted with aqueous $NH_4Cl$ and extracted with ether (5 × 20 ml). The combined extracts were dried ($Na_2SO_4$) and evaporated to give the crude product (4.30 g). Recrystallization of this from hexane gave the title compound **1a** as a colourless solid (4.01 g, 35%), mp 130–131 °C (Found: C, 61.59; H, 9.17. Calc. for $C_{14}H_{24}OS_2$: C, 61.71; H, 8.88%); $[\alpha]_D^{22}$ +3.3 (*c* 2.30 in ethanol) [lit.,[10]

$[\alpha]_D^{20}$ +2.9 (*c* 1.5 in ethanol)]; $\nu_{max}$(KBr)/cm$^{-1}$ 3480 (OH); $\delta_H$ 0.83 (3 H, s, $CH_3$), 1.05 (3 H, s, $CH_3$), 1.08 (3 H, s, $CH_3$), 1.10–2.12 (9 H, m, $CH_2$), 2.30 (1 H, s, OH), 2.76–3.05 (4 H, m, H-4′ and H-6′) and 4.27 (s, 1 H, H-2′); $\delta_C$ 12.4, 21.0, 21.1, 25.6, 27.5, 29.3, 30.3, 30.7, 44.5, 46.4, 50.6, 53.7, 61.6 and 82.8.

**(1*S*,2*S*)-2-(1,3-Dithian-2-yl)-2-hydroxy-1,7,7-trimethylbicyclo[2.2.1]heptane 1b**

The reaction was carried out as described above using 2-lithio-1,3-dithiane, prepared from 1,3-dithiane (1.62 g, 13.07 mmol) and BuLi (1.45 mol dm$^{-3}$; 9 cm$^3$, 13.05 mmol), and (−)-camphor (1.88 g, 1.17 mmol) for 15 h. The crude product was purified by column chromatography on silica gel with hexane–ethyl acetate (95:5 and then 9:1) as the eluent. Further purification was carried out by recrystallization of the solid from hexane to give **1b** (1.19 g, 37%), mp 129.5–131 °C; $[\alpha]_D^{22}$ −2.8 (*c* 1.72 in ethanol).

**(1*R*,2*R*)-2-(1,3-Dithian-2-yl)-2-methoxy-1,7,7-trimethylbicyclo-[2.2.1]heptane 1c**

To a solution of **1a** (547 mg, 2.01 mmol) in THF (6 cm$^3$) was added sodium hydride (60% dispersion in mineral oil; 125 mg, 3.11 mmol) at 0 °C and the mixture was stirred for 1 h. Methyl iodide (0.377 cm$^3$, 6.02 mmol) was added to the reaction mixture which was then stirred at 0 °C for 4 h. After this it was diluted with aqueous $NH_4Cl$ and the aqueous layer separated and extracted with ether (5 × 10 cm$^3$). The combined organic extracts were washed with brine, dried ($Na_2SO_4$) and concentrated to give a crude oil. This was purified by column chromatography on silica gel with hexane–ethyl acetate (95:5) as the eluent to give the title compound **1c** (517 mg, 90%) as a colourless solid, mp (Found: C, 63.03; H, 9.22. Calc. for $C_{15}H_{26}OS_2$: C, 62.88; H, 9.15%); $[\alpha]_D^{23}$ −29.2 (*c* 0.50 in ethanol); $\nu_{max}$(KBr)/cm$^{-1}$ 1275 (C–O) and 1050 (C–O); $\delta_H$ 0.83 (3 H, s, $CH_3$), 0.93 (3 H, s, $CH_3$), 1.13 (3 H, s, $CH_3$), 1.05–1.20 (1 H, m, H-5′), 1.35–1.97 (7 H, m, H-5′ and $CH_2$), 2.13 (2 H, ddt, *J* 3.8, 3.8, 13.8, $CH_2$), 2.73–3.00 (4 H, m, H-4′ and H-6′), 3.45 (3 H, s, $OCH_3$), and 4.40 (1 H, s, H-2′); $\delta_C$ 13.2, 20.8, 21.4, 26.5, 27.3, 31.0, 31.9, 33.6, 38.5, 44.8, 50.6, 51.2, 55.7, 60.6 and 87.7.

**3-*C*-(1,3-Dithian-2-yl)-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose 1d**

A solution of D-(+)-DAG (1.00 g, 3.77 mmol), pyridinium chlorochromate (3.39 g, 15.74 mmol) and 3 Å molecular sieves (3.21 g) in $CH_2Cl_2$ (20 cm$^3$) was stirred at room temperature for 3 h and then diluted with ether (50 cm$^3$), filtered and evaporated under reduced pressure. The crude product was purified by column chromatography on Florisil with hexane–ethyl acetate (4:6) as eluent to give 1,2:5,6-di-*O*-isopropylidene-α-D-ribo-hexofuranos-3-urose (0.970 g, 92%),[13] $\nu_{max}$(KBr)/cm$^{-1}$ 1763 (C=O), 1210 (C–O), and 1060 (C–O); $\delta_H$ 1.34 (6 H, s, $CH_3$). 1.44 (3 H, s, $CH_3$), 1.46 (3 H, s, $CH_3$), 4.03 (2 H, d, *J* 6.3, H-6), 4.32–4.40 (3 H, m, H-2, H-4 and H-5) and 6.14 (1 H, d, *J* 4.5, H-1). A solution of 1,3-dithiane (1.54 g, 12.46 mmol) in THF (40 cm$^3$) was treated with BuLi (1.54 mol dm$^{-3}$; 6.23 cm$^3$, 12.46 mmol) at −78 °C and then allowed to warm to 0 °C. After the mixture had been stirred for 15 min, the urose (1.57 g, 5.69 mmol) described above in THF (10 cm$^3$) was added at −78 °C, and stirring continued for 5 h. The reaction mixture was then quenched with aqueous $NH_4Cl$ and the aqueous layer was separated and extracted with ether (5 × 20 cm$^3$). The combined organic extracts were washed with brine, dried ($Na_2SO_4$) and then concentrated to give the crude product, which was purified by column chromatography on silica gel with benzene–ethyl acetate (8:2) as eluent to give the title compound **1d** as colourless solid (1.65 g, 76%), mp 117–118 °C (from hexane–$CH_2Cl_2$) (Found: C, 50.51; H, 7.18. Calc. for $C_{16}H_{26}O_6S_2$: C, 50.77; H, 6.92%); $\nu_{max}$(KBr)/cm$^{-1}$ 3500 (OH), 1250 (C–O) and 1070 (C–O); $\delta_H$ 1.38 (3 H, s, $CH_3$), 1.39 (3 H, s, $CH_3$), 1.46 (3 H, s, $CH_3$), 1.54 (3 H, s, $CH_3$), 1.72–1.95 (1 H, s, H-5′*ax*), 2.04–2.19 (1 H, m, H-5′*ax*), 2.78–3.08 (4 H, m, H-4′ and H-6′), 3.10 (1 H, s, OH), 3.86 (1 H, d, *J* 9.2, H-4), 3.95 (1 H, dd, *J* 8.7, 4.8, H-6), 4.12 (1 H, dd, *J* 8.7, 6.0, H-6), 4.68 (1 H, ddd, *J* 4.8, 9.2, 5.9, H-5), 4.77 (1 H, s, H-2′), 4.81 (1 H, d, *J* 4.1, H-2) and 5.86 (1 H, d, *J* 4.1, H-1); $\delta_C$ 25.5, 25.6, 26.6, 27.0, 30.1, 50.8, 68.2, 73.2, 80.7, 81.0, 83.4, 96.1, 104.8, 110.0 and 112.4

**Oxidation of the dithianyl-(+)-camphor 1a with the titanium reagent under anhydrous conditions: Method A**

A suspension of 4 Å molecular sieves powder (14 mg) in $CH_2Cl_2$ (10 cm$^3$) was treated with Ti(OPr$^i$)$_4$ (0.172 cm$^3$, 0.577 mmol) and L-(+)-DET (0.198 cm$^3$, 1.50 mmol) at −23 °C, after which the mixture was stirred for 15 min. A solution of the dithianyl-(+)-camphor **1a** (143 mg, 0.525 mmol) in $CH_2Cl_2$ (5 cm$^3$) was then added to the titanium reagent at −30 °C. After the mixture had been stirred for 15 min, a solution of Bu$^t$OOH in $CH_2Cl_2$ (0.15 cm$^3$, 0.787 mmol) was added dropwise to it over a period of 20 min. The reaction mixture was then stirred for 6 h before being diluted with water (0.094 cm$^3$, 5.25 mmol) and then allowed to warm to room temperature. The resulting white gel was filtered through Celite 500, the latter then being washed with $CH_2Cl_2$. The filtrate was washed subsequently with 5% (w/v) aq. sodium thiosulfate and 5% (w/v) aq. sodium hydroxide, dried ($Na_2SO_4$) and concentrated under reduced pressure to give a crude product. This was purified by column chromatography on silica gel with $CH_2Cl_2$–ethyl acetate–ethanol (40:12:1) as the eluent to give the monosulfoxides **2a** (143 mg, 95%) and the disulfoxide **3a** (3 mg, 2%). The diastereoisomeric ratio of **2a** was determined by integration of the C-2 methine proton of the 1,3-dithianes in the $^1$H NMR spectrum of the crude product; (*R*)-*cis*-**2a** (δ):(*S*)-*cis*-**2a** (δ):(*R*)-*trans*-**2a** (δ) = 82 (3.90):15 (3.71):3 (3.85) (1*R*,2*R*)-2-[(1*R*,2*S*)-(1-oxo-1,3-dithian-2-yl)]-2-hydroxy-1,7,7-trimethylbicyclo[2.2.1]heptane (*R*)-*cis*-**2a**, mp 176–179 °C (from hexane–$CH_2Cl_2$) (decomp.) (Found: C, 58.16; H, 8.65. Calc. for $C_{14}H_{24}O_2S_2$: C, 58.29; H, 8.39%); $[\alpha]_D^{22}$ +63.1 (*c* 0.98 in ethanol); $\nu_{max}$(KBr)/cm$^{-1}$ 3450 (OH) and 1055 (SO); $\delta_H$ 0.85 (3 H, S), 1.02 (3 H, s), 1.00–1.14 (1 H, m), 1.20 (3 H, s), 1.25–1.40 (1 H, m), 1.52–1.90 (5 H, m), 2.03 (1 H, dt, *J* 3.8, 13.8), 2.40–2.73 (3 H, m), 2.78–3.17 (2 H, m), 3.32 (1 H, s, OH) and 3.90 (1 H, s, H-2′); $\delta_C$ 12.4, 15.3, 20.9, 21.0, 27.3, 29.1, 29.6, 43.8, 46.7, 47.2, 50.7, 53.7, 70.2 and 84.8. (1*R*,2*R*)-2-[(1*S*,2*R*)-(1-oxo-1,3-dithian-2-yl)]-2-hydroxy-1,7,7-trimethylbicyclo[2.2.1]heptane (*S*)-*cis*-**2a**, mp 175–178 °C (from hexane–$CH_2Cl_2$) (decomp); $[\alpha]_D^{22}$ −68.8 (*c* 0.85 in ethanol) [lit.,[10] $[\alpha]_D^{22}$ −74.4 (*c* 2.7 in ethanol)] $\nu_{max}$(KBr)/cm$^{-1}$ 3450 (OH) and 1055 (SO); $\delta_H$ 0.84 (3 H, s, $CH_3$), 0.90–1.10 (1 H, m), 1.03 (3 H, s), 1.08 (3 H, s), 1.45–1.58 (2 H, m), 1.68–1.89 (4 H, m), 2.38 (1 H, dt, *J* 4.3, 13.7, H-5′ *eq*), 2.51–2.73 (3 H, m), 2.82–2.99 (1 H, m), 3.21 (1 H, ddd, *J* 1.6, 4.7, 11.8, H-6′*eq*), 3.69 (1 H, s, OH) and 3.71 (1 H, s, H-2′); $\delta_C$ 12.3, 14.1, 21.0, 21.3, 27.6, 28.3, 29.5, 44.8, 47.6, 48.0, 50.5, 54.5, 70.6 and 84.0. (1*R*,2*R*)-2-[(1*R*,2*R*)-(1-oxo-1,3-dithian-2-yl)]-2-hydroxy-1,7,7-trimethylbicyclo[2.2.1]heptane (*R*)-*trans*-**2a** mp 168–171 °C (from hexane–$CH_2Cl_2$) (decomp.); $[\alpha]_D^{25}$ +23.5 (*c* 0.49 in chloroform) [lit.,[10] $[\alpha]_D^{20}$ +25.9 (*c* 1.3 in chloroform)]; $\nu_{max}$(KBr)/cm$^{-1}$ 3450 (OH) and 1055 (SO); $\delta_H$ 0.84 (3 H, s, $CH_3$), 1.07 (3 H, s, $CH_3$), 1.10 (3 H, s, $CH_3$), 1.10–1.27 (1 H, m), 1.50–1.82 (4 H, m), 2.08–2.50 (5 H, m), 2.63–2.90 (2 H, m), 2.83 (1 H, dt, *J* 3.4, 12.5, H-6′ax), 3.41 (1 H, dt, *J* 3.4, 13.2, H-6′eq) and 3.85 (1 H, s, H-2′); $\delta_C$ 12.5, 20.6, 21.0, 27.0, 28.8, 29.3, 30.5, 44.8, 46.9, 49.5, 54.1, 54.6, 77.8 and 82.7. (1*R*,2*R*)-2-(1,3-dioxo-1,3-dithian-2-yl)-2-hydroxy-1,7,7-trimethylbicyclo[2.2.1]heptane **3a**, mp 192–195 °C (from hexane–$CH_2Cl_2$) (decomp.) (Found: C, 54.90; H, 8.28. Calc. for $C_{14}H_{24}O_3S_2$: C, 55.23; H, 7.95%); $[\alpha]_D^{20}$ +74.5 (*c* 1.03 in ethanol); $\nu_{max}$(KBr)/cm$^{-1}$ 3400 (OH) and 1055 (SO); $\delta_H$ 0.90 (3 H, s, $CH_3$), 1.05 (3 H, s, $CH_3$), 1.21 (3 H, s, $CH_3$), 1.10–1.40 (2 H, m), 1.55–1.95 (3 H, m), 2.06 (1 H, d, *J* 13.8), 2.30 (1 H, dt, *J* 3.8, 13.8), 2.41–2.58 (2 H, m), 3.14 (1 H, s, H-2′), 3.29–3.42 (3 H, m), 3.65–3.81 (1 H, m) and 4.04 (1 H, s, OH); $\delta_C$ 8.0, 12.7, 20.8, 21.0, 27.3, 30.4, 38.3, 40.0, 44.2, 48.3, 50.5, 53.7, 79.6 and 85.1.

**Oxidation of the dithianyl-(+)-camphor 1a with the titanium reagent in the presence of water: method B**

A mixture of $Ti(OPr^i)_4$ (0.144 $cm^3$, 0.485 mmol), L-(+)-DET (0.167 $cm^3$, 0.975 mmol) and water (0.009 $cm^3$) in $CH_2Cl_2$ (10 $cm^3$) was stirred at room temperature for 30 min after which a solution of **1a** (121 mg, 0.444 mmol) in $CH_2Cl_2$ (1 $cm^3$) was added to it at −23 °C. Stirring was continued for 30 min after which a solution of $Bu^tOOH$ in $CH_2Cl_2$ (0.080 $cm^3$, 0.418 mmol) was added dropwise at −23 °C over a period of 5 min. The mixture was stirred for 4 h after which it was diluted with water (0.1 $cm^3$, 5.56 mmol), and allowed to warm to room temperature. The white gel was filtered through Celite 500 the latter then being washed with $CH_2Cl_2$. The filtrate was washed with 5% (w/v) aq. sodium thiosulfate and 5% (w/v) aq. sodium hydroxide, dried ($Na_2SO_4$) and concentrated under reduced pressure to give the crude product. This was purified by column chromatography on silica gel with $CH_2Cl_2$–ethyl acetate–ethanol (40:12:1) as eluent to give the monosulfoxides **2a** (101 mg, 79%) and the disulfoxide **3a** (11 mg, 8%). The diastereoisomeric ratio of **2a** was determined by the integration of the C-2 methine proton of the 1,3-dithianes in the $^1H$ NMR spectrum of the crude product; (*R*)-*cis*-**2a** (δ):(*S*)-*cis*-**2a** (δ) = 92 (3.90):8 (3.71).

**Oxidation of the dithianyl-(+)-camphor 1a using D-(−)-DET by method A**

Oxidation was carried out as described with 4 Å molecular sieves (43 mg), the dithianyl-(+)-camphor **1a** (568 mg, 2.08 mmol), $Ti(OPr^i)_4$ (0.682 $cm^3$, 2.30 mmol), D-(−)-DET (0.785 $cm^3$, 4.58 mmol) and $Bu^tOOH$ (0.612 $cm^3$, 3.19 mmol). The diastereoisomeric ratio of **2a** was determined by integration of the C-2 methine proton of the 1,3-dithianes in the $^1H$ NMR spectrum of the crude product; (*R*)-*cis*-**2a** (δ):(*S*)-*cis*-**2a** (δ):(*R*)-*trans*-**2a** (δ) = 15 (3.90):78 (3.71):7 (3.85). Purification by column chromatography on silica gel with $CH_2Cl_2$–ethyl acetate–methanol (40:12:1) as eluent afforded the monosulfoxide **2a** (546 mg, 91%).

**Oxidation of the dithianyl-(+)-camphor 1a using D-(−)-DET by method B**

Oxidation was carried out as described above with the thianyl-(+)-camphor **1a** (59 mg, 0.218 mmol), $Ti(OPr^i)_4$ (0.071 $cm^3$, 0.239 mmol), D-(−)-DET (0.082 $cm^3$, 0.479 mmol), water (0.004 $cm^3$, 0.222 mmol) and $Bu^tOOH$ (0.063 $cm^3$, 0.329 mmol). The diastereoisomeric ratio of **2a** was determined by integration of the C-2 methine proton of the 1,3-dithianes in the $^1H$ NMR spectrum of the crude product; (*R*)-*cis*-**2a** (δ):(*S*)-*cis*-**2a** (δ):(*R*)-*trans*-**2a** (δ) = 5 (3.90):88 (3.71):7 (3.85). Purification by column chromatography on silica gel with $CH_2Cl_2$–ethyl acetate–methanol (40:12:1) as eluent afforded the monosulfoxide **2a** (57 mg, 91%).

**Oxidation of the dithianyl-(−)-camphor 1b using L-(+)-DET by method A**

Oxidation was carried out as described above with the 1-dithianyl-(−)-camphor (121 mg, 0.444 mmol), $Ti(OPr^i)_4$ (0.144 $cm^3$, 0.485 mmol), L-(+)-DET (0.167 $cm^3$, 0.975 mmol), and $Bu^tOOH$ (0.131 $cm^3$, 0.418 mmol). The diastereoisomeric ratio of **2b** was determined by integration of the C-2 methine proton of the 1,3-dithianes in the $^1H$ NMR spectrum of the crude product; (*R*)-*cis*-**2b** (δ):(*S*)-*cis*-**2b** (δ):(*S*)-*trans*-**2b** (δ) = 86 (3.90):9 (3.71):5 (3.82). Purification by column chromatography on silica gel with $CH_2Cl_2$–ethyl acetate–methanol (40:12:1) as eluent afforded the monosulfoxide **2b** (79 mg, 62%) and the disulfoxide **3b** (4 mg, 3%). The mixture of monosulfoxides **2b** was recrystallized from hexane–$CH_2Cl_2$ to give (*R*)-*cis*-**2b**. (1*S*,2*S*)-2-[(1*R*,2*S*)-1-oxo-1,3-dithian-2-yl]-2-hydroxy-1,7,7-trimethylbicyclo[2.2.1]heptane (*R*)-*cis*-**2b**, mp 176–180 °C (from hexane–$CH_2Cl_2$) (decomp.); $[\alpha]_D^{22}$ −67.0 (*c* 0.70 in ethanol) (Found: C, 58.16; H, 8.65. Calc. for $C_{14}H_{24}O_2S_2$: C, 58.29; H, 8.39%); $\nu_{max}$(KBr)/$cm^{-1}$ 3450 (OH) and 1055 (SO); $\delta_H$ 0.86 (3 H, s), 1.04 (3 H, s), 1.00–1.14 (1 H, m), 1.21 (3 H, s), 1.25–1.40 (1 H, m), 1.52–1.90 (5 H, m), 2.03 (1 H, dt, *J* 3.8, 13.8), 2.40–2.73 (3 H, m), 2.78–3.17 (2 H, m), 3.40 (1 H, s, OH) and 3.90 (1 H, s, H-2′); $\delta_C$ 12.4, 15.3, 20.9, 21.0, 27.3, 29.1, 29.6, 43.8, 46.7, 47.2, 50.7, 53.7, 70.2 and 84.8. (1*S*,2*S*)-(1,3-dioxo-1,3-dithian-2-yl)-2-hydroxy-1,7,7-trimethylbicyclo[2.2.1]heptane **3b**, mp 190 °C (from hexane–$CH_2Cl_2$) (decomp.); $[\alpha]_D^{21}$ −81.0 (*c* 0.12, in ethanol) (Found: C, 55.05; H, 8.13. Calc. for $C_{14}H_{24}O_3S_2$: C, 55.23; H, 7.95%).

**Oxidation of the dithianyl-(−)-camphor 1b using D-(−)-DET by method A**

Oxidation was carried out as described above with 4 Å molecular sieves (54 mg), the dithianyl-(+)-camphor **1b** (544 mg, 2.00 mmol), $Ti(OPr^i)_4$ (0.65 $cm^3$, 2.19 mmol), D-(−)-DET (0.753 $cm^3$, 4.39 mmol), and $Bu^tOOH$ (0.587 $cm^3$, 3.06 mmol). The diastereoisomeric ratio of **2a** was determined by integration of the C-2 methine proton of the 1,3-dithianes in the $^1H$ NMR spectrum of the crude product; (*R*)-*cis*-**2b** (δ):(*S*)-*cis*-**2b** (δ):(*S*)-*trans*-**2b** (δ) = 16 (3.90):82 (3.71):2 (3.82). Purification by column chromatography on silica gel with $CH_2Cl_2$–ethyl acetate–methanol (40:12:1) as eluent afforded the monosulfoxide **2b** (433 mg, 75%).

**Oxidation of the *O*-methylated dithianyl-(+)-camphor 1c by method A**

Oxidation was carried out as described above with 4 Å molecular sieves (13 mg), the *O*-methylated dithianyl-(+)-camphor **1c** (106 mg, 0.369 mmol), $Ti(OPr^i)_4$ (0.120 $cm^3$, 0.404 mmol), L-(+)-DET (0.139 $cm^3$, 0.811 mmol), and $Bu^tOOH$ (0.109 $cm^3$, 0.569 mmol). Purification by column chromatography on silica gel with $CH_2Cl_2$–ethyl acetate (4:1) as eluent afforded the monosulfoxide **2c** (72 mg, 64%) and the disulfoxide **3c** (13 mg, 11%). (1*R*,2*R*)-2-[(1*R*,2*R*)-(1-oxo-1,3-dithian-2-yl)]-2-methoxy-1,7,7-trimethylbicyclo[2.2.1]heptane (*R*)-*trans*-**2c**, mp 193–194 °C (Found: C, 59.57; H, 8.70. Calc. for $C_{15}H_{26}O_2S_2$: C, 59.56; H, 8.67%); $[\alpha]_D^{22}$ −0.86 (*c* 0.58 in ethanol); $\nu_{max}$(KBr)/$cm^{-1}$ 1070 (SO), 1045 (C–O) and 1020 (C–O); $\delta_H$ 0.84 (3 H, s, $CH_3$), 0.89 (3 H, s, $CH_3$), 1.12 (3 H, s, $CH_3$), 1.13–1.26 (1 H, m), 1.50–1.61 (2 H, m), 1.70–1.90 (2 H, m), 2.15–2.48 (4 H, m), 2.56–2.77 (3 H, m), 3.43 (1 H, ddt, *J* 12.6, 3.66, 1.1, H-6′ *eq*), 3.51 (3 H, s, $OCH_3$) and 3.86 (1 H, s, H-2′); $\delta_C$ 13.2, 20.4, 21.0, 27.1, 29.9, 30.5, 30.8, 36.8, 44.9, 48.6, 50.1, 51.4, 57.1, 78.5 and 87.0. (1*R*,2*R*)-2-[(1,3-Dioxo-1,3-dithian-2-yl))-2-methoxy-1,7,7-trimethylbicyclo[2.2.1]heptane **3c** (Found: C, 56.66; H, 8.31. Calc. for $C_{15}H_{26}O_3S_2$: C, 56.57; H, 8.23%); $\nu_{max}$(KBr)/$cm^{-1}$ 1070 (SO), 1045 1055 (C–O), and 1020 (C–O); $\delta_H$ 0.86 (3 H, s, $CH_3$), 0.92 (3 H, s, $CH_3$), 1.13 (3 H, s, $CH_3$), 1.10–1.38, (2 H, m), 1.55–1.83 (3 H, m), 2.15–2.50 (4 H, m), 2.99–3.16 (3 H, m), 3.40–3.51 (1 H, m), 3.26 (3 H, s, $OCH_3$) and 4.20 (1 H, s, H-2′).

**Oxidation of the *O*-methylated dithianyl-(+)-camphor 1c using D-(−)-DET by method A**

Oxidation was carried out as described above with 4 Å molecular sieves (15.0 mg), the *O*-methylated dithianyl-camphor **1c** (118 mg, 0.409 mmol), $Ti(OPr^i)_4$ (0.134 $cm^3$, 0.451 mmol), D-(−)-DET (0.155 $cm^3$, 0.905 mmol), and $Bu^tOOH$ (0.121 $cm^3$, 0.632 mmol). Purification by column chromatography on silica gel with $CH_2Cl_2$–ethyl acetate (4:1) as eluent afforded the monosulfoxide **2c** (98 mg, 79%).

**Oxidation of the *O*-methylated dithianyl-(+)-camphor 1c with MCPBA: method C**

To a solution of the dithianyl-camphor **1c** (217 mg, 0.757 mmol) in $CH_2Cl_2$ (10 $cm^3$) was added dropwise a solution of MCPBA (99.5 mg, 0.403 mmol) in $CH_2Cl_2$ (5 $cm^3$) at −23 °C and the mixture was stirred for 10 min. The reaction mixture was washed successively with aqueous $Na_2CO_3$ and brine, and dried

($Na_2SO_4$) and evaporated under reduced pressure to give the crude product. The diastereoisomeric ratio was determined by integration of the C-2 methine proton of the 1,3-dithiane which appeared at $\delta$ 4.03, 4.02 and 3.86 (8:8:84) or the methoxy protons which appeared at $\delta$ 3.51, 3.35 and 3.23. The mixture was purified by column chromatography on silica gel with $CH_2Cl_2$–ethyl acetate (4:1) as eluent to give the monosulfoxides **2c** (136 mg, 59%) and the disulfoxide **3c** (14 mg, 6%). (1*R*,2*R*)-2-[(1,3-Dioxo-1,3-dithian-2-yl)-2-methoxy-1,7,7-trimethylbicyclo[2.2.1]heptane **3c** (Found: C, 56.66; H, 8.31. Calc. for $C_{15}H_{26}O_3S_2$: C, 56.56; H, 8.24%); $\nu_{max}$(KBr)/cm$^{-1}$ 1070 (SO), 1045 1055 (C–O), and 1020 (C–O); $\delta_H$ 0.86 (3 H, s, $CH_3$), 0.92 (3 H, s, $CH_3$), 1.13 (3 H, s, $CH_3$), 1.10–1.38, (2 H, m), 1.55–1.83 (3 H, m), 2.15–2.50 (4 H, m), 2.99–3.16 (3 H, m), 3.40–3.51 (1 H, m), 3.26 (3 H, s, $OCH_3$) and 4.20 (1 H, s, H-2′).

### Oxidation of the dithianyl-D-(+)-DAG 1d with MCPBA: method C

Oxidation was carried out as described above with dithianyl-D-(+)-DAG **1d** (85 mg, 0.225 mmol) and MCPBA (69 mg, 0.282 mmol) at −23 °C during 10 min. The mixture was purified by column chromatography on silica gel with $CH_2Cl_2$–ethyl acetate–ethanol (20:12:1) as eluent to afford the monosulfoxide **2d** (91 mg, 58%) and the disulfoxide **3d** (23 mg, 25%). The diastereoisomeric ratio of **2d** was determined by integration of the C-1 methine proton of the glucose in the $^1$H NMR spectrum of the crude product; (*R*)-*trans*-**2d** ($\delta$): unidentified isomer ($\delta$) = 79 (5.76):21 (6.18). 3-*C*-[(1*R*,2*R*)-(1-oxo-1,3-dithian-2-yl)]-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (*R*)-*trans*-**2d**, mp 221–229 °C (decomp.) (Found: C, 47.48; H, 6.87. Calc. for $C_{16}H_{26}O_7S_2$: C, 47.71; H, 6.64%); $[\alpha]_D^{22}$ +42.3 (*c* 0.94 in acetone); $\nu_{max}$(KBr)/cm$^{-1}$ 3325 (OH), 1065 (SO) and 1030 (COC); $\delta_H$ 1.39 (6 H, s, $CH_3$), 1.48 (3 H, s, $CH_3$), 1.62 (3 H, s, $CH_3$), 2.15–2.88, (4 H, m), 2.99 (1 H, dt, *J* 3.6, 12.5), 3.50 (1 H, dt *J* 3.6, 12.5 H-6′ *eq*), 3.95 (1 H, d, *J* 9.0, H-4), 3.99 (1 H, dd, *J* 8.8, 4.8, H-6), 4.12 (1 H, dd, *J* 8.8, 5.7, H-6), 4.37 (1 H, s, H-2′), 4.47 (1 H, ddd, *J* 5.2, 5.2, 9.4, H-5), 4.77 (1 H, d, *J* 4.0, H-2), 5.00 (1 H, s, OH) and 5.76 (1 H, d, *J* 4.0, H-1); $\delta_C$ 25.8, 26.8, 27.0, 29.0, 30.4, 54.4, 66.5, 68.4, 73.3, 81.7, 82.8, 83.6, 104.6, 110.4 and 113.2. 3-*C*-(1,3-Dioxo-1,3-dithian-2-yl)-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose **3d**, mp 201–203 °C (Found: C, 46.70; H, 6.53. Calc. for $C_{16}H_{26}O_8S_2$: C, 46.81; H, 6.38%); $[\alpha]_D^{22}$ +20.6 (*c* 0.94 in acetone); $\nu_{max}$(KBr)/cm$^{-1}$ 3300 (OH), 1070 (SO) and 1040 (C–O); $\delta_H$ 1.36 (3 H, s, $CH_3$), 1.41 (3 H, s, $CH_3$), 1.49 (3 H, s, $CH_3$), 1.63 (3 H, s, $CH_3$), 2.42–2.60 (1 H, m, H-5′ *ax*), 2.72–2.95 (2 H, m), 3.15–3.32 (2 H, m), 3.78 (1 H, ddd, *J* 3.0, 5.8, 12.3, H-6′ *eq*), 4.03–4.18 (4 H, m), 4.42 (1 H, dt, *J* 6.3, 7.4, H-5), 4.79 (1 H, s, OH), 5.05 (1 H, d, *J* 4.0, H-2) and 6.12 (1 H, d, *J* 4.0, H-1); $\delta_C$ 13.8, 25.5, 26.4, 26.5, 26.8, 45.4, 50.3, 68.1, 73.3, 76.2, 81.2, 82.1, 82.8, 104.8, 110.5 and 113.0.

### Oxidation of the dithianyl-D-(+)-DAG 1d by method A

Oxidation was carried out as described above with 4 Å molecular sieves (76 mg), the dithianyl-D-(+)-DAG **1d** (758 mg, 2.00 mmol), Ti(OPr$^i$)$_4$ (0.652 cm$^3$, 2.19 mmol), L-(+)-DET (0.755 cm$^3$, 4.41 mmol) and Bu$^t$OOH (0.589 cm$^3$, 3.07 mmol) for 8 h. Purification by column chromatography on silica gel with $CH_2Cl_2$–ethyl acetate–methanol (20:12:1) as eluent afforded the monosulfoxide **2d** (536 mg, 68%) and the disulfoxide **3d** (172 mg, 21%). The diastereoisomeric ratio of **2d** was determined by integration of the C-1 methine proton of the glucose in the $^1$H NMR spectrum of the crude product; (*R*)-*trans*-**2d** ($\delta$): unidentified isomer ($\delta$) = 80 (5.76):20 (6.01).

### Oxidation of the dithianyl-D-(+)-DAG 1d by method B

Oxidation was carried out as described above with dithianyl-D-(+)-DAG **1d** (55 mg, 0.145 mmol), Ti(OPr$^i$)$_4$ (0.047 cm$^3$, 0.158 mmol), L-(+)-DET (0.055 ml, 0.321 mmol), water (0.0029 cm$^3$) and Bu$^t$OOH (0.042 cm$^3$, 0.218 mmol) for 7 h. The crude product was purified by column chromatography on silica gel with $CH_2Cl_2$–ethyl acetate–ethanol (40:12:1) as eluent to give the monosulfoxide **2d** (52 mg, 67%) and the disulfoxide **3d** (14 mg, 24%). The diastereoisomeric ratio of **2d** was determined by integration of the C-1 methine proton of the glucose in the $^1$H NMR spectrum of the crude product; (*R*)-*trans*-**2d** ($\delta$): unidentified isomer ($\delta$) = 75 (5.76):25 (6.01).

### Oxidation of the dithianyl-D-(+)-DAG 1d by method A

Oxidation was carried out as described above with molecular sieves (40 mg), the dithianyl-D-(+)-DAG **1d** (368 mg, 0.971 mmol), Ti(OPr$^i$)$_4$ (0.318 cm$^3$, 1.07 mmol), D-(−)-DET (0.366 cm$^3$, 2.14 mmol), and Bu$^t$OOH (0.285 cm$^3$, 1.46 mmol). Purification by column chromatography on silica gel with $CH_2Cl_2$–ethyl acetate–ethanol (20:12:1) as eluent afforded the monosulfoxide **2d** (347 mg, 91%). The diastereoisomeric ratio of **2d** was determined by integration of the C-1 methine proton of the glucose in the $^1$H NMR spectrum of the crude product; (*R*)-*trans*-**2d** ($\delta$): unidentified isomer ($\delta$) = 93 (5.76):7 (5.75).

### Oxidation of the dithianyl-D-(+)-DAG 1d by method B

Oxidation was carried out as described above with dithianyl-D-(+)-DAG **1d** (52 mg, 0.138 mmol), Ti(OPr$^i$)$_4$ (0.045 cm$^3$, 0.166 mmol), D-(−)-DET (0.052 cm$^3$, 0.304 mmol), water (0.003 cm$^3$) and Bu$^t$OOH (0.040 cm$^3$, 0.209 mmol). Purification by column chromatography on silica gel with $CH_2Cl_2$–ethyl acetate–methanol (20:12:1) as eluent afforded the monosulfoxide **2d** (46 mg, 85%). The diastereoisomeric ratio of **2d** was determined by integration of the C-1 methine proton of the glucose in the $^1$H NMR spectrum of the crude product; (*R*)-*trans*-**2d** ($\delta$): unidentified isomer ($\delta$) = 84 (5.76):16 (5.75).

### Base-catalysed hydrolysis of the monosulfoxide 2

**Preparation of (*R*)-1,3-dithiane 1-oxide (*R*)-4 from (*R*)-*cis*-2a.** A mixture of the monosulfoxide (*R*)-*cis*-**2a** (215 mg, 0.745 mmol) and potassium hydroxide (47 mg, 0.831 mmol) in Bu$^t$OH (6 cm$^3$) was stirred at 50 °C for 2 h. The reaction mixture was diluted with aqueous $NH_4Cl$ and extracted with chloroform. The extract was washed with brine, dried ($Na_2SO_4$), and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel with ethyl acetate as eluent to give (*R*)-**4** (94.5 mg, 93%), mp 108–110 °C (from ethanol–hexane); $[\alpha]_D^{22}$ +224 (*c* 0.580 in ethanol) [lit.,[10] $[\alpha]_D^{24}$ +227 (*c* 1.0 in ethanol)]; $\nu_{max}$(KBr)/cm$^{-1}$ 1040 (SO); $\delta_H$ 2.10–2.34 (1 H, m, H-5 *eq*), 2.44–2.74 (4 H, m), 3.28–3.41 (1 H, m, H-6 *eq*), 3.65 (1 H, d, *J* 12.5, H-2 *ax*) and 4.02 (1 H, dd, *J* 2.5, 12.5, H-2 *eq*).

### Preparation of (*S*)-4 from (*S*)-*cis*-2c

Hydrolysis was carried out as described above except using (*S*)-*cis*-**2c** (45 mg, 0.155 mmol) and potassium hydroxide (9 mg, 0.136 mmol) in Bu$^t$OH (1.5 cm$^3$). Purification by column chromatography afforded (*S*)-**4** (19 mg, 89%), mp 108–110 °C (from ethanol–hexane); $[\alpha]_D^{22}$ −230 (*c* 0.38 in ethanol) [lit.,[10] $[\alpha]_D^{20}$ −224° (c 0.85 in ethanol)].

### Preparation of (*R*)-4 from (*R*)-*trans*-2d

Hydrolysis was carried out as described above with (*R*)-*trans*-**2d** (91 mg, 0.231 mmol) and potassium hydroxide (29 mg, 0.435 mmol) in Bu$^t$OH (1 cm$^3$) at 70 °C for 13 h. Purification by column chromatography on silica gel with $CH_2Cl_2$–ethyl acetate–methanol (20:12:2) as eluent afforded (*R*)-**4** (27 mg, 87%), mp 108–110 °C (from ethanol–hexane); $[\alpha]_D^{20}$ +214 (*c* 0.52 in ethanol).

### Crystal data for (*R*)-*trans*-2c

$C_{15}H_{26}O_2S_2$, *M* = 302.48. Orthorhombic, *a* = 7.1710(6), *b* = 15.525(2), *c* = 14.4851(6) Å, *V* = 1612.6(2) Å$^3$, space group $P2_12_12_1$, *Z* = 4, $D_x$ = 1.246 g cm$^{-3}$. Colourless, acicular crystal dimensions: 0.30 × 0.35 × 0.35, $\mu$(Mo-K$\alpha$) = 3.131 cm$^{-1}$.

### Crystal data for (*R*)-*trans*-2d

$C_{16}H_{26}O_7S_2$, $M$ = 394.49. Orthorhombic, $a$ = 7.6593(4), $b$ = 13.1659(5), $c$ = 18.8906(7) Å, $V$ = 1905.13(14) Å$^3$ space group $P2_12_12_1$, $Z$ = 4, $D_x$ = 1.375 g cm$^{-3}$. Colourless, acicular crystal dimensions: 0.30 × 0.40 × 0.40, μ(Mo-Kα) = 2.993 cm$^{-1}$.

### Data collection and processing

Diffraction data for (*R*)-*trans*-**2c** and (*R*)-*trans*-**2d** were obtained with an Enraf-Nonius CAD4 four-circle automated diffractometer. The reflection intensities were monitored by three standard reflections at every 2 h, and these showed less than 2% decay over the period of the data collection. Reflection data were corrected for Lorentz and polarization effects. Absorption corrections for the crystals were applied according to the DIFABS procedure in both the cases.[16] The absorption corrections for compounds **2c** and **2d** are max./min. = 1.01–0.89 and 1.12–0.78, respectively.

### Structure analysis and refinement

The structure was solved by direct methods and non-H atoms were refined with anisotropic thermal parameters by full-matrix least-squares calculations. Refinement was continued until all shifts were smaller than one-third of the standard deviations of the parameters involved. Atomic scattering factors and anomalous dispersion terms were taken from literature.[17] Hydrogen atoms were located from difference Fourier syntheses and included in the refinement with isotropic thermal parameters; their positions were located on the positions obtained form the difference Fourier maps. The thermal parameters of the O(2), O(3) and O(10) atoms for compound **2d** have been refined with a large anisotropic distortion. These atoms may be disordered, but the Fourier maps did not give electron densities at the different positions under the conditions used here. The final $R$ and $R_w$ values were 0.032 and 0.045 for (*R*)-*trans*-**2c**, 0.033 and 0.045 for (*R*)-*trans*-**2d**, respectively. The weighting scheme $w^{-1} = \{\sigma^2(|F_o|) + (0.02|F_o|)^2\}$ was employed for both crystals. The final difference Fourier maps did not show any significant features. The calculations were performed on a VAX-3100 computer by using the program system SDP-MolEN.[18] Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Perkin Trans 1*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 207/30.



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