Synthesis of a Thiashikimic Acid Derivative

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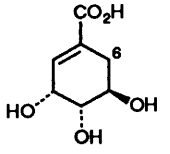
6-Thiashikimic acid has been synthesised as its racemic ethyl ester acetate **10**. Ethyl thioxoacetate **3**, generated thermally from the anthracene cycloadduct **2**, reacted with 1,4-diacetoxybuta-1,3-diene **4** to give a pair of epimeric, Diels–Alder adducts **5** and **6**. Each was converted with osmium tetroxide into the corresponding diol **7** and **8**. The diol **7** underwent *trans* elimination of acetic acid in hot pyridine to give the 6-thiashikimic acid derivative **10**. The configurations of both diols **7** and **8** were confirmed by X-ray crystal structure analysis. The conformations of the diols in the crystals and in solution are discussed in the light of their ^{1}H NMR spectra.

Shikimic acid [1] **1** is a pivotal intermediate in the biosynthesis of aromatic amino acids from carbohydrates in organisms of the



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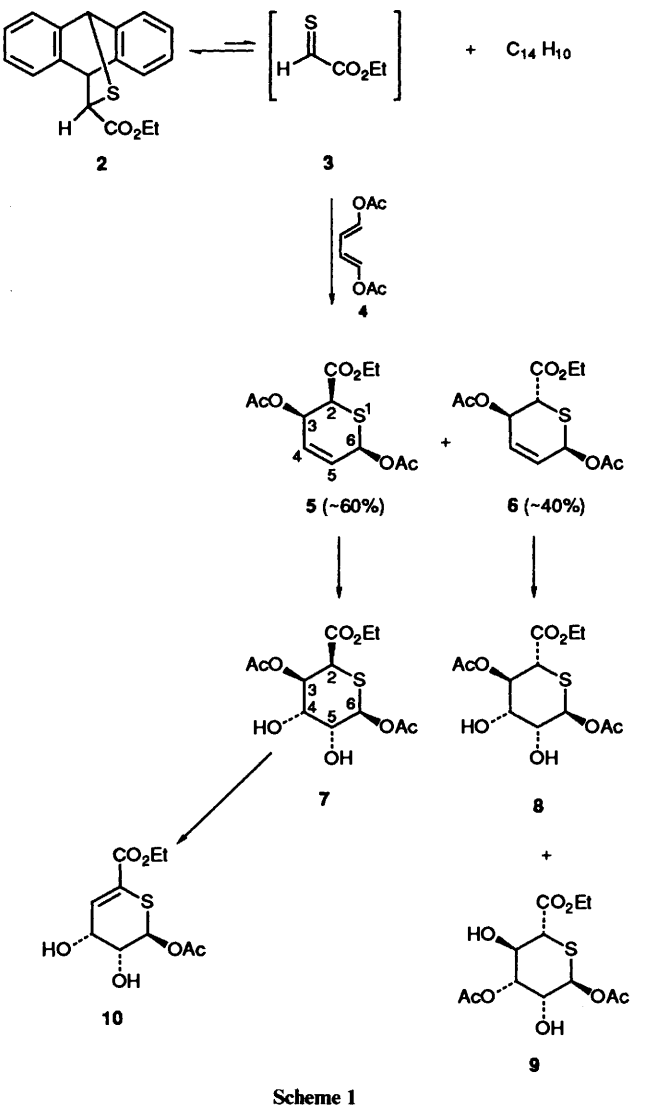
plant Kingdom. The enzymes of the shikimate pathway are now available in quantity through the modern techniques of molecular biology, and there is current interest in the synthesis of inhibitors of potential use in crop protection.[2] We report here the synthesis (Scheme 1) of racemic 6-thiashikimic acid as the ester acetate **10**.

Thioaldehydes, for example ethyl thioxoacetate **3**, are readily formed as transient intermediates by 1,2-elimination reactions of sulfenyl derivatives, ZCH_2SX, and may be trapped *in situ* by conjugated dienes.[3,4] The resulting cycloadducts of anthracene and cyclopentadiene may serve as convenient, ancillary precursors of the thials by retro-Diels–Alder cleavage at moderate temperatures. The following synthesis of the racemic thiashikimic derivative **10** was modelled on syntheses of shikimic acid **1** itself, which began with the cycloaddition of 1,4-diacetoxybuta-1,3-diene **4** and methyl acrylate [5] or acrylic acid.[6]

The cycloadduct **2** of ethyl thioxoacetate **3** was heated under reflux in toluene with the diacetoxybutadiene **4** to give, in high yield, a mixture of the *cis,cis*-**5** and *trans,trans*-cycloadduct **6** of the diene. The 2,3-*cis* isomer **5** was the major product (59%), as expected from preferential, *endo* cycloaddition. The crystalline adduct **5** gave, with osmium tetroxide in pyridine, the corresponding *cis*-diol **7** (66%), by attack from the less hindered side of the molecule. In the synthesis [5,6] of shikimic acid **1**, the diols corresponding to the sulfur analogues **7** and **8** were protected as isopropylidene derivatives before undergoing elimination of acetic acid. This was found to be unnecessary with the diol **7**, presumably because the sulfur facilitated base-catalysed, 1,2-elimination. Thus, when the diol **7** was heated under reflux in dry pyridine, the thiashikimic derivative **10** was formed directly in good yield. The oily 2,3-*trans* cycloadduct **6** likewise gave, with osmium tetroxide, the corresponding diol **8**. However, on some occasions the major product **8** was accompanied by an isomeric by-product **9**, apparently arising from 1,2-migration of an acetyl group. The diol **8**, unlike its epimer **7**, did not eliminate acetic acid in hot pyridine; as expected, base-catalysed 1,2-elimination required a *trans* arrangement of the relevant proton



Scheme 1

and acetoxy group. So far, attempts to cleave the ester groups in the thiashikimic derivative **10**, under even mildly alkaline conditions, have led to extensive decomposition of the molecule, apparently reflecting the instability of 6-thiashikimic acid, a hemiacetal of an enethiol, towards alkalis. The hydrolysis of the diester **10** and other thiopyrans (Scheme 1) with esterase enzymes is being studied.

Table 1 Vicinal coupling constants (J) and torsional angles (φ) for the 2,3-*cis*-7 and 2,3-*trans*-diol **8**

Torsional angle	Isomer	φ^a (°)	Conformation[b]	J^c/Hz
H–C(2)–C(3)–H	**7**	−54	*ax.–eq.*	4.6
	8	−174	*ax.–ax.*	10.5
H–C(3)–C(4)–H	**7**	−53	*eq.–eq.*	8.8
	8	180	*ax.–ax.*	9.8
H–C(4)–C(5)–H	**7**	−73	*eq.–ax.*	2.7
	8	67	*ax.–eq.*	2.9
H–C(5)–C(6)–H	**7**	180	*ax.–ax.*	5.3
	8	60	*eq.–eq.*	3.5

[a] Torsional angles from the X-ray structures Figs. 1 and 2 for the diols **7** and **8**, respectively. [b] Conformations in the crystal structures of the vicinal protons. [c] ^{1}H NMR (200 MHz; $CDCl_3$) vicinal coupling constants.

The stereochemistry of the cycloadducts **5** and **6** was deduced initially from the relative magnitudes of the relevant, vicinal coupling constants; $J_{2,3}$ 5.9 and 10.6 Hz for the epimers **5** and **6**, respectively. Further, hydroxylation of both epimers was expected[5,6] to occur *anti* to the two acetoxy groups, to give diols with the stereochemistry shown in structures **7** and **8**. However, to place the relative stereochemistry of these racemates beyond doubt, X-ray crystallographic analyses were carried out on both diols. This was especially desirable because of difficulties in reconciling the magnitudes of the vicinal proton coupling constants for the 2,3-*cis* isomer **7** (Table 1) with those expected for a conformation having three equatorial and two axial groups (see below).

X-Ray Structures.—Atomic coordinates for the racemic, epimeric 2,3-*cis* **7** and 2,3-*trans* **8** diols are given in Tables 2 and 3, respectively. Structures with the absolute configuration (6*R*) corresponding to that of shikimic acid **1** are displayed in Figs. 1 and 2 for the epimers **7** and **8**, respectively. The epimers adopt opposite chair conformations in the crystals, both having three equatorial and two axial, rather than two equatorial and three axial, groups. The 2,3-*trans* epimer **8** appears to adopt predominantly the same conformation in deuteriochloroform solution (Table 1). Thus, the ^{1}H NMR spectrum showed large vicinal coupling constants for two pairs of *trans* diaxial protons, $J_{2,3}$ 10.5 (φ −174°) and $J_{3,4}$ 9.8 Hz (φ 180°), as expected. However, in the spectrum of the 2,3-*cis* epimer **7**, the vicinal coupling constant $J_{5,6}$ 5.3 Hz was smaller than that expected (*ca.* 10 Hz) for *trans*-diaxial protons (φ 180°). Also, the coupling constant $J_{3,4}$ 8.8 Hz was larger than that expected (*ca.* 4 Hz) for *trans*-diequatorial protons (φ = −53°). These J values would be better accommodated by the alternative chair conformation, that is the one adopted by the epimer **8**, which showed $J_{5,6}$ 3.5 and $J_{3,4}$ 9.8 Hz. It appears that the 2,3-*cis epimer* **7** exists in solution as an equilibrium mixture of the conformation (Fig. 1) adopted in the crystal and, unexpectedly, the alternative (like Fig. 2) having three axial and two equatorial groups. The latter, which apparently predominates, might be stabilised by an anomeric effect of the 6-axial acetoxy group. An indication of the magnitude of this effect is provided by the relative stabilities of the anomers of the thiopyranose 5-thio-D-glucose.[7] At equilibrium, the α anomer, having an axial 1-hydroxy group, predominates (85%), whereas for glucose itself the corresponding figure is only 38%.* The *trans*-diaxial coupling constants reported for α- and β-5-thioglucose were in the range 8.9–9.8 Hz.

* Changes in bond angles and lengths arising from the replacement of oxygen by sulfur also may affect the relative positions of these equilibria.[7] Further, the relative stabilities of conformations in crystals (Figs. 1 and 2) may depend in part upon the requirements for efficient crystal packing.

Table 2 Fractional atomic coordinates for the 2,3-*cis*-diol **7** with esds in parentheses

Atom	x	y	z
S(1)	0.8400(2)	0.2119(2)	0.3704(2)
O(1)	0.7960(5)	0.3052(5)	0.0379(4)
O(2)	0.7146(5)	−0.0040(5)	−0.0104(5)
O(3)	0.7993(7)	0.4882(6)	0.5293(5)
O(4)	0.5015(4)	0.3224(4)	0.2080(4)
O(5)	0.3431(6)	0.4493(6)	0.0613(6)
O(6)	0.8914(5)	−0.0443(5)	0.2465(5)
O(7)	1.1138(7)	−0.0435(6)	0.1907(7)
O(8)	0.7105(7)	0.6250(5)	0.3717(5)
C(2)	0.7946(7)	0.3865(6)	0.3104(6)
C(3)	0.6439(6)	0.3680(6)	0.1798(6)
C(4)	0.6634(7)	0.2530(7)	0.0696(6)
C(5)	0.7023(7)	0.0967(7)	0.1004(6)
C(6)	0.8613(7)	0.1056(6)	0.2216(6)
C(7)	0.7688(8)	0.5039(7)	0.4186(6)
C(8)	0.6663(13)	0.7478(10)	0.4571(9)
C(9)	0.540(3)	0.802(3)	0.410(3)
C(10)	0.3557(7)	0.3725(7)	0.1409(6)
C(11)	0.2218(7)	0.3223(8)	0.1793(7)
C(12)	1.0192(8)	−0.1093(7)	0.2213(7)
C(13)	1.0217(10)	−0.2695(8)	0.2369(8)

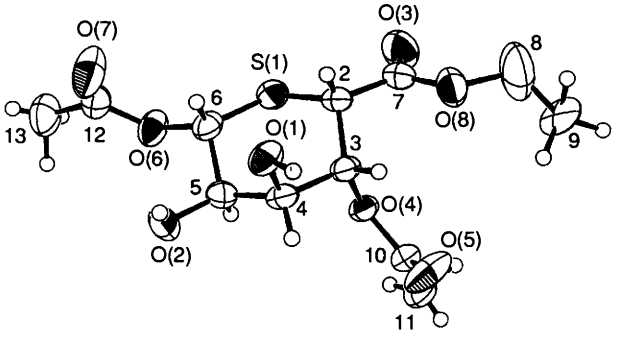


Fig. 1 X-Ray crystal structure of the 2,3-*cis*-diol **7**

Experimental

General.—NMR spectra were obtained with a Bruker WP 200 spectrometer and IR spectra with either a Perkin–Elmer 580 or 953 spectrometer. J Values are in Hz. Mass spectra were obtained by EI at 70 eV with AEI MS 12 and MS 9 spectrometers. TLC was carried out on Merck silica gel GF_{254} plates. Column chromatography employed Merck, TLC grade silica gel, the solvent flow being assisted with a water pump.[8] Solutions were evaporated in a Büchi rotary evaporator.

Ethyl 3-c,6-c- *and* 3-t,6-t-*Diacetoxythiacyclohex*-4-*ene*-2-r-*carboxylate* **5** and **6**.—The adduct[4] **2** (1.40 g, 4.73 mmol) of anthracene and ethyl thioxoacetate **3** and *trans,trans*-1,4-diacetoxybuta-1,3-diene[9] **4** (0.98 g, 5.76 mmol) were heated under

Table 3 Fractional atomic coordinates for the 2,3-*trans*-diol **8** with esds in parentheses

Atom	*x*	*y*	*z*
S(1)	0.843 10(12)	0.459 16(13)	0.857 43(12)
O(1)	0.789 0(3)	0.017 3(3)	0.481 0(3)
O(2)	0.724 3(3)	0.335 7(4)	0.545 0(3)
O(3)	0.649 4(4)	0.287 6(5)	1.004 2(4)
O(4)	0.762 5(3)	−0.010 4(3)	0.732 5(3)
O(5)	0.506 7(3)	−0.038 2(4)	0.661 9(4)
O(6)	1.108 4(3)	0.381 6(3)	0.748 3(3)
O(7)	1.200 3(4)	0.489 8(5)	0.610 1(4)
O(8)	0.871 9(5)	0.177 5(5)	1.046 6(4)
C(2)	0.851 6(4)	0.257 8(5)	0.857 2(4)
C(3)	0.769 2(4)	0.145 6(4)	0.722 9(4)
C(4)	0.858 4(4)	0.134 0(5)	0.602 6(4)
C(5)	0.876 5(4)	0.292 6(5)	0.584 6(4)
C(6)	0.949 2(4)	0.424 1(5)	0.712 1(4)
C(7)	0.777 6(5)	0.244 6(6)	0.976 8(5)
C(8)	0.813 5(9)	0.130 2(8)	1.152 5(6)
C(9)	0.756 4(9)	−0.029 5(9)	1.099 0(8)
C(10)	0.623 7(5)	−0.092 6(5)	0.695 1(5)
C(11)	0.636 1(7)	−0.253 8(6)	0.700 9(6)
C(12)	1.223 8(5)	0.420 9(5)	0.687 4(5)
C(13)	1.378 1(5)	0.365 6(6)	0.729 4(5)

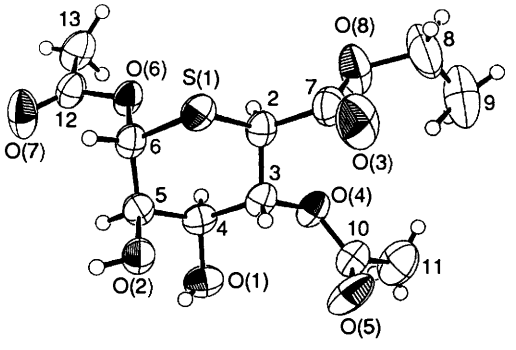


Fig. 2 X-Ray crystal structure of the 2,3-*trans*-diol **8**

reflux in dry toluene (65 cm^3) under nitrogen for 6 h. The mixture was cooled, filtered to remove anthracene, then evaporated. The residue was agitated with methanol and the resulting suspension was again filtered to remove anthracene. The filtrate was evaporated to give the cycloadducts **5** and **6** together with a little anthracene. Chromatography on a silica gel (TLC grade) column eluted with hexane, to remove anthracene, then with mixtures of hexane and ethyl acetate gave, successively, the trans-trans-*diacetoxy ester* **6** (0.47 g, 35%) as an oil (Found: C, 50.2; H, 5.1. $C_{12}H_{16}O_6S$ requires C, 50.0; H, 5.6%); $\nu_{max}(CHCl_3)/cm^{-1}$ 1750, 1370 and 1215; δ_H(200 MHz; $CDCl_3$) 1.24 (t, *J* 7.1, OCH_2Me), 2.05 and 2.08 (2 × s, 2 × Ac), 3.86 (d, *J* 10.6, 2-H), 4.17 (q, *J* 7.1, OCH_2), 5.74 (d, *J* 10.5, with fine splitting, 3-H), 5.80–5.98 (m, 4- and 5-H) and 6.01 (m, 6-H); δ_C(50.3 MHz; $CDCl_3$) 14.0 (OCH_2Me), 20.8 and 21.0 (2 × $COMe$), 41.3 (C-2), 62.1 (OCH_2), 67.7 (C-3 or -6), 69.0 (C-6 or -3), 125.1 (C-4 or -5), 132.8 (C-5 or -4) and 168.3, 169.7 and 169.8 (3 × C=O); then the cis,cis-*diacetoxy ester* **5** (0.80 g, 59%), m.p. 77–78 °C (from diethyl ether) (Found: C, 50.0; H, 5.6; S, 11.5. $C_{12}H_{16}O_6S$ requires C, 50.0; H, 5.6; S, 11.1%); $\nu_{max}(CHCl_3)/cm^{-1}$ 1745, 1370 and 1226; δ_H(200 MHz; $CDCl_3$) 1.26 (t, *J* 7.1, OCH_2Me), 2.06 and 2.09 (2 × s, 2 × Ac), 3.71 (ddd, *J* 5.9, 1.1 and 0.5, 2-H), 4.17 (q, *J* 7.1, OCH_2), 5.62 (dm, *J* 5.9, 3-H), 5.88 and 5.94 (2 × m, 4- and 5-H) and 6.01 (m, 6-H); δ_C(50.3 MHz; $CDCl_3$) 13.9 (OCH_2Me), 20.8 and 20.85 (2 × $COMe$), 37.3 (C-2), 61.1 (OCH_2), 65.8 (C-3 or -6), 67.4 (C-6 or -3), 124.5 (C-4 or -5), 130.3 (C-5 or -4), and 168.4, 169.9 and 170.1 (3 × C=O).

The mass spectra of the adducts **5** and **6** showed no molecular ion peaks; in both, the fragment of highest mass, *m/z* 228 (*ca.* 11%), corresponded to $M^{\cdot+}$ − AcOH, and the fragment with *m/z* 113 (100) to $C_5H_5OS^+$.

Ethyl 3-c,6-c-*Diacetoxy*-4-t,5-t-*dihydroxythiacyclohexane*-2-r-*carboxylate* **7**.—Solutions of osmium tetroxide (1.0 g, 3.94 mmol) in dry, freshly distilled pyridine (5 cm^3) and the *cis,cis*-diacetoxy ester **5** (1.13 g, 3.92 mmol) in dry pyridine (5 cm^3) were mixed and stirred for 25 h at room temperature. Sodium hydrogen sulfite (1.8 g, 17.3 mmol) in water (30 cm^3) and pyridine (20 cm^3) was added to the mixture, which was stirred for 4 h and then extracted with dichloromethane (6 × 30 cm^3). The extracts were dried ($MgSO_4$) and evaporated to give an oily residue, which was kept *in vacuo* over phosphorus pentoxide to remove pyridine. The resulting brown syrup (1.17 g) was triturated with dichloromethane and light petroleum (b.p. 60–80 °C) to yield the diol **7** as a white powder. Crystallisation from benzene gave the cis,cis-*diacetoxy diol* **7** (0.83 g, 66%), m.p. 145–146 °C (Found: C, 44.6; H, 5.7; S, 9.3%; M^+, 322.0738. $C_{12}H_{18}O_8S$ requires C, 44.7; H, 5.6; S, 9.9%; *M*, 322.0722); ν_{max}(KBr)/cm^{-1} 3502, 3243, 1749, 1735 and 1715; δ_H(200 MHz; $CDCl_3$) 1.26 (t, *J* 7.1, OCH_2Me), 2.09 and 2.10 (2 × s, 2 × Ac), 2.86 (br s, 2 × OH, exch. with D_2O), 3.96 (d, *J* 4.6, 2-H), 4.17 (q, *J* 7.1, OCH_2), 4.20 (dd, *J* 5.3 and 2.7, 5-H), 4.62 (dd, *J* 8.8 and 2.7, with fine splitting, 4-H), 5.43 (dd, *J* 8.8 and 4.6, 3-H) and 5.89 (d, *J* 5.3, 6-H); δ_C(50.3 MHz; $CDCl_3$) 14.0 (OCH_2Me), 20.8 and 20.9 (2 × $COMe$), 42.9 (C-2), 61.7 (OCH_2), 66.8, 70.5, 71.6 and 74.6 (C-3, -4, -5 and -6) and 169.1, 169.3 and 170.8 (3 × C=O).

Ethyl 3-t,6-t-*Diacetoxy*-4-c,5-c-*dihydroxythiacyclohexane*-2-r-*carboxylate* **8** *and the Isomer* **9**.—The *trans,trans*-diacetoxy ester **6** was converted into the corresponding diol **8** by treatment with osmium tetroxide in pyridine, as described for the isomer **5**. The syrupy product was chromatographed on a silica gel (TLC grade) column. Elution with dichloromethane–hexane (4:1) then dichloromethane–ethyl acetate (9:1) gave the diol **8** as a white powder (84%). The trans,trans-*diacetoxy diol* **8** (66%) has m.p. 110–111 °C [from light petroleum (b.p. 40–60 °C)] (Found: C, 44.7; H, 5.8%; M^+, 322.0731. $C_{12}H_{18}O_8S$ requires C, 44.7; H, 5.6%; *M*, 322.0722); $\nu_{max}(CHCl_3)/cm^{-1}$ 3480br and 1745; δ_H(200 MHz; $CDCl_3$) 1.18 (t, *J* 7.1, OCH_2Me), 2.02 and 2.08 (2 × s, 2 × Ac), 3.65 (br s, OH, exch. with D_2O), 3.72 (dd, *J* 9.8 and 2.9, 4-H), 3.83 (d, *J* 10.5, 2-H), 4.09 (q, *J* 7.1, with fine splitting, OCH_2), *ca.* 4.15 (br s, OH, exch. with D_2O), 4.18 (dd, *J* 3.5 and 2.9, 5-H), 5.43 (br t, *J* 10.2, 3-H) and 5.81 (d, *J* 3.5, 6-H); δ_C(50.3 MHz; $CDCl_3$) 13.8 (OCH_2Me), 20.8 and 20.9 (2 × $COMe$), 44.0 (C-2), 62.2 (OCH_2), 70.5, 71.2, 71.5 and 75.8 (C-3, -4, -5, and -6) and 167.5, 168.7 and 170.9 (3 × C=O).

Occasionally (see main text) the diol **8** was accompanied by an isomeric by-product, tentatively assigned the structure **9**, which was eluted with hexane–ethyl acetate (97:3) from a silica gel column, in advance of the major product **8**. *Ethyl* 4-c,6-t-*diacetoxy*-3-t,5-c-*dihydroxythiacyclohexane*-2-r-*carboxylate* **9** was obtained as a syrup (Found: M^+, 322.0748. $C_{12}H_{18}O_8S$ requires *M*, 322.0722); $\nu_{max}(CHCl_3)/cm^{-1}$ 3602, 3515br and 1740; δ_H(200 MHz; $CDCl_3$) 1.26 (t, *J* 7.1, OCH_2Me), 2.14 and 2.15 (2 × s, 2 × Ac), 2.95 and 3.43 (2 × br s, 2 × OH, exch. with D_2O), 3.88 (d, *J* 10.3, 2-H), 4.17 (dd, *J* 4.2 and 2.8, 5-H), 4.20 (q, *J* 7.1, OCH_2), 4.38 (br t, *J* 10.3, 3-H), 5.04 (dd, *J* 10.0 and 2.8, 4-H) and 5.84 (d, *J* 4.2, 6-H); δ_C(50.3 MHz; $CDCl_3$) 13.9 (OCH_2Me), 21.0 (2 × $COMe$), 45.5 (C-2), 62.4 (OCH_2), 68.2, 69.5, 73.3 and 75.8 (C-3, -4, -5 and -6) and 168.7, 169.0 and 170.7 (3 × C=O).

Ethyl 6-t-*Acetoxy*-4-r,5-c-*dihydroxythiacyclohex*-2-*ene*-2-*carboxylate* **10**.—The 2,3-*cis*-acetoxy ester **7** (500 mg) was heated under reflux in dry pyridine (20 cm^3) under nitrogen for 6 h. The mixture was evaporated, and the residue was freed from

traces of pyridine by storage in a vacuum desiccator over phosphorus pentoxide. A solution of the dark residue in diethyl ether was warmed with activated charcoal and then filtered. The filtrate was evaporated to give the unsaturated ester **10** as a syrup (350 mg, 86%). This material was judged to be substantially pure (*ca.* 95%) by ^{1}H NMR spectroscopy. A portion was purified, for final characterisation, by TLC on silica plates, but the recovery from the plates was poor. The *thiashikimic derivative* **10** (Found: M^+, 262.0499. $C_{10}H_{14}O_6S$ requires *M*, 262.0511) gave $\nu_{max}(CHCl_3)/cm^{-1}$ 3440br, 1758 and 1730; δ_H(200 MHz; $CDCl_3$) 1.29 (t, *J* 7.1, CH_2*Me*), 2.08 (s, Ac), 3.42 (br s, OH, exch. with D_2O), 4.05 (ddd, *J* 4.9, 3.8 and 1.2, 5-H), 4.23 (q, *J* 7.1, OCH_2), 4.43 (dd, *J* 3.8 and 2.4, 4-H), 6.00 (d, *J* 4.9, 6-H) and 6.85 (dd, *J* 2.4 and 1.2, 3-H); δ_C(50.3 MHz; $CDCl_3$) 13.9 (CH_2*Me*), 20.8 (CO*Me*), 62.1 (OCH_2), 64.6, 65.4 and 74.3 (C-4, -5 and -6), 125.4 (C-2), 132.7 (C-3), 163.3 (*C*O_2Et) and 169.3 (*C*OMe).

X-Ray Crystal Structure Analysis of the Racemic 2,3-Cis *Epimer* **7**.—*Crystal data.* $C_{12}H_{18}O_8S$, *M* = 322.33, triclinic, *a* = 8.642(3), *b* = 8.993(5), *c* = 11.037(3) Å, α = 100.8(5), β = 111.1(3), γ = 90.2(4)°, *U* = 784 Å^3, *F*(000) = 340, D_c = 1.37 g cm^{-3}, *Z* = 2, λ(Mo-Kα) 0.710 69 Å; space group $P\bar{1}$.

Crystallographic measurements. Cell dimensions were derived by least-squares treatments of the setting angles of 18 reflections measured on an Enraf–Nonius CAD-4 diffractometer with Cu-Kα radiation. 2954 Independent intensities were collected in the range θ 1.0–25.0°.

Structure analysis. The crystal structure was solved using the direct phasing procedure MITHRIL.[10] Full matrix refinement of all coordinates and anisotropic thermal parameters of non-H atoms converged at *R* 0.0781, R_w 0.0871 with weights $W\alpha 1/\sigma^2(F_o)$ for 2104 reflections which satisfied the criterion $I \geqslant 3.0\sigma(I)$. H Atom coordinates are in calculated positions. Fourier, least-squares, geometry and ORTEP calculations were performed with the GX system of programs.[11]

X-Ray Crystal Structure Analysis of the Racemic 2,3-*trans Epimer* **8**.—*Crystal data.* $C_{12}H_{18}O_8S$, *M* = 322.33, triclinic, *a* = 8.591(8), *b* = 9.025(1), *c* = 10.517(2) Å, α = 110.7(1), β = 96.02(4), γ = 90.2(3)°, *U* = 757.85 Å^3, *F*(000) = 340, D_c = 1.41 g cm^{-3}, *Z* = 2, λ(Mo-Kα) 0.710 69 Å; space group $P\bar{1}$.

Crystallographic measurements. Cell dimensions were derived by least-squares treatment of the setting angles of 25 reflections measured on an Enraf-Nonius CAD-4 diffractometer with Mo-Kα radiation. 3175 Independent intensities were collected in the range θ 2.0–26.0°.

Structure analysis. The crystal structure was solved using the direct phasing procedure MITHRIL.[10] Full matrix refinement of all coordinates and anisotropic thermal parameters of non-H atoms converged at *R* 0.0647, R_w 0.0653 with weights $W\alpha 1/\sigma^2(F_o)$ for 2440 reflections which satisfied the criterion $I \geqslant 3.0\sigma(I)$. H Atom coordinates are in calculated positions. Fourier, least-squares, geometry and ORTEP calculations were performed with the GX system of programs.[11]

Bond angles, lengths and H-atom coordinates have been deposited with CCDC.

Acknowledgements

We thank the SERC, the MRC, the Association of Commonwealth Universities and the Loudon Bequest for financial support and Professor J. R. Coggins for his interest in this project.

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Paper 1/06255G
Received 12*th December* 1991
Accepted 9*th March* 1992