Data collection: *DIF*4 (Stoe & Cie, 1988*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1988*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1992). Software used to prepare material for publication: *SHELXL*93.

We thank the SERC for provision of a four-circle diffractometer and acknowledge the use of the Cambridge Structural Database implementation at CCLRC Daresbury Laboratory.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1326). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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The Diels–Alder Adduct of an Enantiopure Sulfinyl Trialkoxycarbonyl Ethene and Cyclopentadiene

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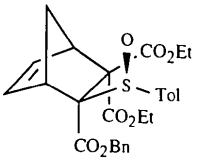
Abstract

The absolute configuration of (1*S*,2*S*,4*R*,*SS*)-2-benzyl 3,3-diethyl 2-(*p*-tolylsulfinyl)bicyclo[2.2.1]hept-5-ene-2,3,3-tricarboxylate, $C_{28}H_{30}O_7S$, has been determined.

Comment

The ability of the sulfinyl group to control the π-facial selectivity in the asymmetric Diels–Alder reaction has provided the impetus for the use of enantiopure α,β-unsaturated sulfoxides as dienophiles. Nevertheless, the low dienophilic reactivity of vinyl sulfoxides determines that other activating groups must be attached to the double bond (Arai, Matsui, Koizumi & Shiro, 1991; Takahashi, Kotsubo & Koizumi, 1991; Carreño, García-Ruano & Urbano, 1992; Fuji *et al.*, 1994). In this sense, sulfinyl maleates (Alonso, Carretero & García-Ruano, 1994) reacted with a variety of dienes in high yields and stereoselectivities. However, the cyclohexenes resulting from the reaction with acyclic dienes evolve quickly at room temperature into cyclohexadienes by non-regioselective pyrolitic elimination of the sulfinyl group. In order to avoid this problem, a triactivated enantiopure vinyl sulfoxide was prepared (Carretero, García-Ruano & Martín Cabrejas, 1995) and the determination of the absolute configuration of its Diels–Alder adduct with cyclopentadiene was performed by X-ray analysis. The molecular structure of this compound, (I), and the atomic numbering scheme are shown in Fig. 1.



(I)

The angle between the carbonyl groups C13—O6 and C10—O4 is −167.5 (5)°, whereas the angle between the sulfinyl group S1—O1 and the carbonyl group C8—O2 is −79.8 (4)°. The angle between the aromatic rings is 132.3 (2)°. An intermolecular hydrogen bond was found [H36···O6^i = 2.527 (8), C36···O6^i = 3.366 (8) Å, C36—H36···O6^i = 150.2 (2)°; symmetry code: (i) $x - 1, y, z$].

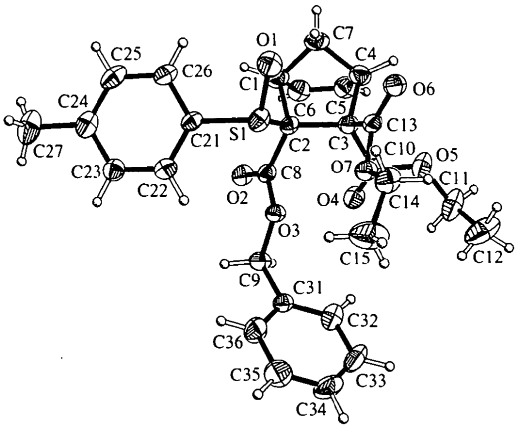


Fig. 1. Molecular structure of the compound showing 20% probability displacement ellipsoids.

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Experimental

The crystals were grown at 253 K from a dichloromethane–hexane solution of the compound (Carretero *et al.*, 1995).

Crystal data

$C_{28}H_{30}O_7S$
$M_r = 510.58$
Monoclinic
$P2_1$
$a = 8.738\ (2)$ Å
$b = 9.998\ (2)$ Å
$c = 15.307\ (3)$ Å
$\beta = 91.02\ (3)^\circ$
$V = 1337.0\ (5)$ Å^3
$Z = 2$
$D_x = 1.268$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 25 reflections
$\theta = 20\text{–}25^\circ$
$\mu = 1.441$ mm^{-1}
$T = 293\ (2)$ K
Transparent block
$0.32 \times 0.30 \times 0.27$ mm
Colourless

Data collection

Rigaku AFC-7*R* four-circle diffractometer
$2\theta/\omega$ scans
Absorption correction: none
2273 measured reflections
2117 independent reflections
1790 observed reflections $[I > 2\sigma(I)]$

$R_{\text{int}} = 0.0434$
$\theta_{\text{max}} = 60.06^\circ$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 11$
$l = -17 \rightarrow 17$
3 standard reflections monitored every 100 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0505$
$wR(F^2) = 0.1290$
$S = 1.065$
2117 reflections
325 parameters
Only coordinates of H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0934P)^2 + 0.0923P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\text{max}} = 0.030$

$\Delta\rho_{\text{max}} = 0.310$ e Å^{-3}
$\Delta\rho_{\text{min}} = -0.231$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983) parameter = 0.01 (4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
S1	0.0428 (2)	0.49589 (13)	0.14456 (9)	0.0733 (4)
O1	0.1692 (5)	0.4368 (5)	0.0947 (3)	0.0965 (14)
O2	−0.1495 (4)	0.4140 (4)	0.3474 (3)	0.0773 (11)
O3	−0.1118 (3)	0.6161 (3)	0.2879 (2)	0.0629 (8)
O4	0.0870 (4)	0.6212 (5)	0.4289 (3)	0.0839 (11)
O5	0.3197 (6)	0.6968 (5)	0.3984 (3)	0.102 (2)
O6	0.4117 (4)	0.6205 (4)	0.1994 (3)	0.0843 (11)
O7	0.1980 (4)	0.7369 (4)	0.2222 (2)	0.0725 (9)
C1	0.1326 (7)	0.3103 (6)	0.2822 (4)	0.0760 (15)
C2	0.0813 (5)	0.4567 (5)	0.2669 (3)	0.0596 (12)
C3	0.2243 (5)	0.5391 (6)	0.3018 (4)	0.0661 (13)
C4	0.3385 (6)	0.4237 (6)	0.3279 (4)	0.082 (2)
C5	0.2715 (8)	0.3571 (7)	0.4053 (5)	0.090 (2)
C6	0.1484 (7)	0.2922 (6)	0.3797 (4)	0.084 (2)
C7	0.3002 (7)	0.3203 (6)	0.2575 (5)	0.087 (2)
C8	−0.0704 (5)	0.4902 (5)	0.3081 (3)	0.0617 (11)
C9	−0.2468 (6)	0.6650 (6)	0.3317 (4)	0.0751 (15)
C10	0.1958 (6)	0.6249 (6)	0.3830 (4)	0.0711 (14)
C11	0.3172 (11)	0.7915 (10)	0.4731 (5)	0.127 (3)
C12	0.3445 (16)	0.9200 (10)	0.4445 (7)	0.167 (5)
C13	0.2913 (6)	0.6354 (5)	0.2341 (4)	0.0659 (13)
C14	0.2407 (8)	0.8403 (7)	0.1608 (5)	0.091 (2)
C15	0.1130 (11)	0.9323 (10)	0.1473 (8)	0.151 (4)
C21	−0.1206 (6)	0.3906 (5)	0.1234 (3)	0.0642 (12)
C22	−0.2652 (6)	0.4459 (6)	0.1272 (3)	0.0750 (14)
C23	−0.3893 (7)	0.3740 (7)	0.1001 (4)	0.079 (2)
C24	−0.3736 (8)	0.2485 (8)	0.0661 (4)	0.088 (2)
C25	−0.2271 (9)	0.1949 (7)	0.0623 (4)	0.096 (2)
C26	−0.1002 (7)	0.2643 (6)	0.0894 (4)	0.078 (2)
C27	−0.5137 (11)	0.1755 (11)	0.0321 (5)	0.135 (4)
C31	−0.2521 (6)	0.8133 (5)	0.3178 (4)	0.0670 (14)
C32	−0.1649 (8)	0.8988 (8)	0.3668 (5)	0.098 (2)
C33	−0.1714 (12)	1.0367 (10)	0.3546 (6)	0.118 (3)
C34	−0.2662 (12)	1.0867 (8)	0.2960 (8)	0.123 (3)
C35	−0.3506 (10)	1.0062 (9)	0.2447 (7)	0.128 (3)
C36	−0.3440 (8)	0.8678 (7)	0.2552 (6)	0.101 (2)

Table 2. *Selected geometric parameters (Å, °)*

S1—O1	1.477 (4)	C1—C7	1.523 (8)
S1—C21	1.799 (5)	C1—C2	1.547 (7)
S1—C2	1.937 (5)	C2—C8	1.515 (7)
O2—C8	1.198 (6)	C2—C3	1.582 (7)
O3—C8	1.344 (6)	C3—C10	1.534 (8)
O3—C9	1.452 (6)	C3—C13	1.538 (8)
O4—C10	1.192 (6)	C3—C4	1.572 (8)
O5—C10	1.317 (7)	C4—C5	1.488 (9)
O5—C11	1.485 (9)	C4—C7	1.527 (10)
O6—C13	1.196 (6)	C5—C6	1.311 (9)
O7—C13	1.312 (7)	C9—C31	1.498 (8)
O7—C14	1.450 (7)	C11—C12	1.379 (14)
C1—C6	1.507 (9)	C14—C15	1.458 (10)
O1—S1—C21	105.7 (3)	C5—C4—C7	100.1 (5)
O1—S1—C2	107.4 (2)	C5—C4—C3	105.9 (5)
C21—S1—C2	100.3 (2)	C7—C4—C3	100.8 (5)
C8—O3—C9	115.3 (4)	C6—C5—C4	108.4 (6)
C10—O5—C11	117.5 (5)	C5—C6—C1	107.3 (6)
C13—O7—C14	118.3 (4)	C1—C7—C4	93.9 (5)
C6—C1—C7	100.5 (5)	O2—C8—O3	123.8 (4)
C6—C1—C2	106.5 (5)	O2—C8—C2	125.8 (5)
C7—C1—C2	100.2 (4)	O3—C8—C2	110.2 (4)
C8—C2—C1	113.6 (4)	O3—C9—C31	106.9 (4)
C8—C2—C3	115.8 (4)	O4—C10—O5	125.0 (5)
C1—C2—C3	102.5 (4)	O4—C10—C3	127.0 (5)
C8—C2—S1	102.7 (3)	O5—C10—C3	107.7 (5)
C1—C2—S1	112.5 (4)	C12—C11—O5	110.2 (7)
C3—C2—S1	110.1 (3)	O6—C13—O7	125.7 (5)
C10—C3—C13	105.4 (4)	O6—C13—C3	124.7 (5)
C10—C3—C4	108.4 (5)	O7—C13—C3	109.5 (4)
C13—C3—C4	112.5 (4)	O7—C14—C15	109.7 (5)
C10—C3—C2	115.2 (4)	C26—C21—S1	119.8 (4)
C13—C3—C2	114.0 (4)	C22—C21—S1	118.8 (4)
C4—C3—C2	101.4 (4)		

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992*a*). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1992*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990*a*). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1990*b*). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NS1006). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(14α,22*E*)-14-Hydroxyergosta-4,7,22-triene-3,6-dione, $C_{28}H_{40}O_3$

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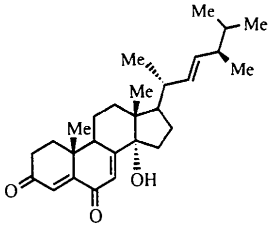
(*Received 27 September 1995; accepted 2 January 1996*)

Abstract

The rings *A*, *B*, *C* and *D* in the title compound adopt twist, sofa, chair and twist conformations, respectively. The C17 side chain has an extended conformation. There is an intermolecular hydrogen bond between the O3 carbonyl and the O14 hydroxy groups.

Comment

The title compound, (I), is a natural product which has been isolated from *Phellinus igniarius*. To determine the structure unequivocally, an X-ray analysis has been undertaken.



(I)

An *ORTEP*II (Johnson, 1976) drawing of the title compound, together with the atomic numbering and ring-labelling scheme, is shown in Fig. 1. Ring *A* adopts a twist conformation with atoms C1 and C2 deviating 0.384 (2) and −0.265 (2) Å, respectively, from the least-squares planes defined by C3, C4, C5 and C10. Ring *B* adopts a sofa conformation with the C10 atom deviating 0.610 (2) Å from the least-squares plane defined by the other five atoms in the ring. The *C* ring has a chair conformation and ring *D* adopts a twist conformation with the C13 and C14 atoms deviating −0.509 (2) and 0.227 (2) Å, respectively, from the plane defined by the other three atoms in the ring. The alkyl chain attached to atom C17 has an extended conformation.

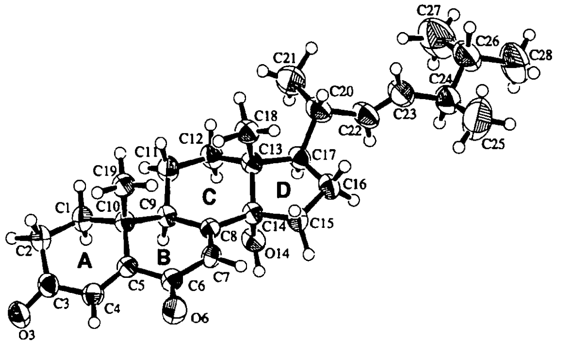


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the title compound showing the atomic numbering and ring-labelling schemes. Displacement ellipsoids are shown at the 50% probability level for non-H atoms and H atoms are shown as small spheres of arbitrary radii.

The C22=C23 bond is relatively short for a C=C double bond. The C6—C7 bond is significantly shorter than the C5—C6 bond. The exocyclic bond angles around atom C17 are highly asymmetric. Other bond lengths and angles are within normal ranges.