

All H atoms were inserted using a riding model and given isotropic displacement parameters equal to  $1.2U_{eq}$  (or  $1.5U_{eq}$  for methyl groups) of the parent atom.

Data collection and cell refinement: Siemens R3m system. Data reduction: *SHELXTL-Plus* (Sheldrick, 1991). Program(s) used to solve structure: *SHELXTL-Plus*. Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1994).

We thank the SERC for financial support (to TJS).

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: HR1035). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## References

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## Dimethyl 1-(4-Acetoxy-3,5-dimethoxyphenyl)-4,7,9-trimethoxy-8-oxospiro[4.5]-deca-6,9-diene-*trans*-2,3-dicarboxylate Acetone Solvate

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## Abstract

In this isomer of the title compound,  $C_{27}H_{32}O_{12} \cdot C_3H_6O$ , the five-membered ring adopts an envelope conformation and the ester groups occupy *trans* positions with respect to the ring.

## Comment

The structure of a product of peroxidatic oxidation of methyl sinapate was determined as a part of a

study on the stereoselectivity of the oxidative coupling of phenols. The title compound (I) was the main product and the *trans* configuration of the ester groups demonstrates a degree of diastereoselectivity in the coupling reaction. The details of the synthetic work and the crystal structure of the *cis* diastereomer have been published elsewhere (Setälä, Pajunen, Kilpeläinen & Brunow, 1994). The five-membered ring is in an envelope conformation with C10 the out-of-plane atom. The angle between the least-squares plane through atoms C6, C7, C8 and C9 and the plane of C6, C9 and C10 is  $39.5(5)^\circ$ . Disorder of one of the ester groups was resolved. The ester group O5, O6, C21 has two orientations with 0.43 (2) and 0.57 (2) occupancy. The structure contains a poorly defined acetone molecule.

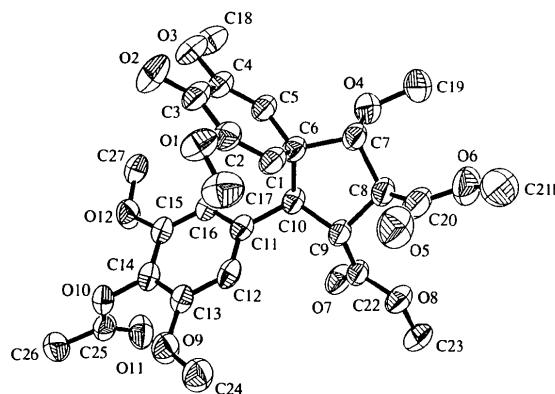
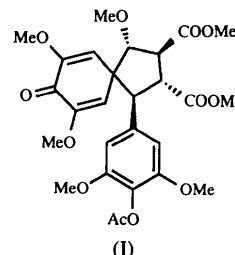


Fig. 1. A drawing of the molecule with the numbering of the non-H atoms. The displacement ellipsoids represent 30% probability levels. Only one orientation of the disordered ester group is shown.

## Experimental

### Crystal data

$C_{27}H_{32}O_{12} \cdot C_3H_6O$

$M_r = 606.60$

Triclinic

$P\bar{1}$

$a = 9.278(4) \text{ \AA}$

$b = 11.635(8) \text{ \AA}$

$c = 15.812(4) \text{ \AA}$

$\alpha = 76.46(5)^\circ$

$\beta = 78.46(4)^\circ$

$\gamma = 72.77(5)^\circ$

$V = 1569.2(13) \text{ \AA}^3$

$Z = 2$

$D_x = 1.284 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation

$\lambda = 0.71069 \text{ \AA}$

Cell parameters from 20 reflections

$\theta = 7\text{--}14^\circ$

$\mu = 0.101 \text{ mm}^{-1}$

$T = 297(2) \text{ K}$

Transparent block

$0.40 \times 0.30 \times 0.30 \text{ mm}$

Colourless

## Data collection

Nicolet P3 diffractometer

 $\omega$ -2 $\theta$  scans

Absorption correction:

empirical

 $T_{\min} = 0.795$ ,  $T_{\max} = 0.992$ 

5890 measured reflections

5514 independent reflections

2598 observed reflections

 $[I > 2\sigma(I)]$ 

## Refinement

Refinement on  $F^2$  $R[F^2 > 2\sigma(F^2)] = 0.0955$  $wR(F^2) = 0.2855$  $S = 1.353$ 

5509 reflections

368 parameters

H atoms refined as riding

model

 $w = 1/[\sigma^2(F_o^2) + (0.1947P)^2]$ where  $P = (F_o^2 + 2F_c^2)/3$  $R_{\text{int}} = 0.0370$  $\theta_{\text{max}} = 25.00^\circ$  $h = 0 \rightarrow 11$  $k = -13 \rightarrow 13$  $l = -18 \rightarrow 18$ 

5 standard reflections

monitored every 60

reflections

intensity variation:

insignificant

 $(\Delta/\sigma)_{\text{max}} = 0.39$  $\Delta\rho_{\text{max}} = 0.68 \text{ e } \text{\AA}^{-3}$  $\Delta\rho_{\text{min}} = -0.26 \text{ e } \text{\AA}^{-3}$ 

Extinction correction: none

Atomic scattering factors

from *International Tables*for *Crystallography* (1992),

Vol. C, Tables 4.2.6.8 and

6.1.1.4)

O13	0.3653 (30)	0.4554 (24)	0.1414 (18)	0.45 (2)
C28	0.1906 (27)	0.3986 (19)	0.2362 (15)	0.31 (1)
C29	0.3149 (48)	0.4183 (37)	0.1802 (29)	0.39 (2)
C30	0.3436 (22)	0.2505 (22)	0.1982 (14)	0.34 (1)

† Occupancy = 0.43 (2).

‡ Occupancy = 0.57 (2).

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

O1—C2	1.359 (6)	O11—C25	1.181 (6)
O1—C17	1.393 (7)	O12—C15	1.369 (5)
O2—C3	1.225 (6)	O12—C27	1.398 (6)
O3—C4	1.339 (6)	C1—C2	1.327 (6)
O3—C18	1.439 (7)	C1—C6	1.497 (7)
O4—C19	1.409 (7)	C2—C3	1.459 (7)
O4—C7	1.416 (6)	C3—C4	1.472 (7)
O5—C20*	1.242 (9)	C4—C5	1.328 (6)
O5—C21A*	1.29 (2)	C5—C6	1.478 (6)
O6—C20*	1.255 (8)	C6—C7	1.556 (6)
O6—C21B*	1.477 (12)	C6—C10	1.587 (6)
O7—C22	1.191 (5)	C7—C8	1.562 (7)
O8—C22	1.315 (5)	C8—C20	1.492 (9)
O8—C23	1.452 (6)	C8—C9	1.542 (7)
O9—C13	1.376 (6)	C9—C22	1.518 (6)
O9—C24	1.415 (6)	C9—C10	1.527 (6)
O10—C25	1.360 (6)	C10—C11	1.512 (6)
O10—C14	1.386 (5)		
C2—O1—C17	115.8 (4)	C20—C8—C7	111.0 (4)
C4—O3—C18	115.4 (4)	C9—C8—C7	107.0 (4)
C19—O4—C7	113.3 (5)	C22—C9—C8	113.2 (4)
C20—O5—C21A*	108.5 (13)	C22—C9—C8	113.5 (4)
C20—O6—C21B*	114.7 (8)	C10—C9—C8	105.5 (4)
C22—O8—C23	115.4 (4)	C11—C10—C9	117.3 (4)
C13—O9—C24	117.8 (4)	C11—C10—C6	115.2 (3)
C25—O10—C14	116.3 (4)	C9—C10—C6	103.0 (3)
C15—O12—C27	117.0 (4)	C12—C11—C10	123.4 (4)
C1—C2—O1	127.5 (5)	C16—C11—C10	118.6 (4)
O1—C2—C3	110.5 (4)	O9—C13—C12	125.3 (4)
O2—C3—C2	120.6 (5)	C13—C14—O10	121.0 (5)
O2—C3—O4	123.0 (5)	O12—C15—C16	125.7 (5)
C5—C4—O3	127.8 (5)	O12—C15—C14	113.7 (4)
O3—C4—C3	111.2 (4)	O5—C20—O6*	123.0 (8)
C5—C6—C7	112.5 (4)	O5—C20—C8*	119.4 (7)
C1—C6—C7	109.7 (4)	O6—C20—C8*	117.5 (9)
C5—C6—C10	110.5 (4)	O7—C22—O8	124.1 (4)
C1—C6—C10	108.9 (4)	O7—C22—C9	125.8 (4)
C7—C6—C10	101.9 (3)	O8—C22—C9	110.1 (4)
O4—C7—C6	109.9 (4)	O11—C25—O10	121.8 (5)
O4—C7—C8	109.7 (4)	O11—C25—C26	126.4 (6)
C6—C7—C8	105.3 (4)	O10—C25—C26	111.7 (5)
C20—C8—C9	114.5 (5)		

\* These values are affected by the disorder of the ester group.

C12 and atoms of the ill-defined acetone molecule were refined isotropically.

Data collection, cell refinement and data reduction: Nicolet P3 software (Nicolet, 1980). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1994). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991). Software used to prepare material for publication: *SHELXL93*.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: HR1032). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{\text{eq}}$
O1	0.2533 (5)	0.9300 (4)	0.0330 (3)	0.105 (1)
O2	0.1696 (5)	1.1526 (4)	0.0566 (3)	0.132 (2)
O3	-0.0779 (5)	1.2518 (3)	0.1565 (3)	0.108 (1)
O4	-0.3795 (5)	0.9656 (4)	0.2080 (3)	0.108 (1)
O5	-0.0562 (8)	0.6266 (5)	0.1288 (3)	0.139 (2)
O6	-0.3023 (7)	0.6555 (5)	0.1340 (3)	0.142 (2)
O7	-0.1521 (5)	0.6721 (3)	0.4421 (2)	0.100 (1)
O8	-0.1544 (4)	0.5417 (3)	0.3607 (2)	0.090 (1)
O9	0.4415 (4)	0.6574 (3)	0.3716 (3)	0.099 (1)
O10	0.4303 (3)	0.8538 (3)	0.4346 (2)	0.081 (1)
O11	0.3170 (5)	0.7896 (5)	0.5678 (3)	0.122 (2)
O12	0.1876 (4)	1.0441 (3)	0.4299 (3)	0.097 (1)
C1	0.0365 (6)	0.8862 (4)	0.1341 (3)	0.080 (1)
C2	0.1229 (6)	0.9594 (5)	0.0896 (3)	0.084 (1)
C3	0.0864 (7)	1.0877 (5)	0.0974 (4)	0.093 (2)
C4	-0.0542 (6)	1.1328 (4)	0.1557 (3)	0.081 (1)
C5	-0.1411 (6)	1.0592 (4)	0.1987 (3)	0.079 (1)
C6	-0.1042 (5)	0.9273 (4)	0.1964 (3)	0.074 (1)
C7	-0.2390 (6)	0.8906 (5)	0.1746 (3)	0.084 (2)
C8	-0.2230 (6)	0.7548 (5)	0.2229 (3)	0.086 (1)
C9	-0.1009 (6)	0.7242 (4)	0.2839 (3)	0.075 (1)
C10	-0.0833 (5)	0.8475 (4)	0.2916 (3)	0.073 (1)
C11	0.0575 (5)	0.8468 (4)	0.3263 (3)	0.069 (1)
C12	0.1868 (6)	0.7504 (4)	0.3279 (3)	0.075 (1)
C13	0.3106 (6)	0.7514 (4)	0.3641 (3)	0.076 (1)
C14	0.3069 (5)	0.8504 (4)	0.3991 (3)	0.072 (1)
C15	0.1783 (6)	0.9501 (4)	0.3947 (3)	0.075 (1)
C16	0.0558 (5)	0.9467 (4)	0.3602 (3)	0.074 (1)
C17	0.3075 (8)	0.8069 (7)	0.0260 (4)	0.126 (2)
C18	-0.2082 (10)	1.3030 (6)	0.2155 (5)	0.139 (3)
C19	-0.5053 (7)	0.9575 (7)	0.1748 (5)	0.131 (2)
C20	-0.1904 (13)	0.6716 (6)	0.1586 (5)	0.120 (2)
C21A†	-0.0561 (29)	0.5699 (23)	0.0679 (17)	0.20 (1)
C21B‡	-0.2641 (15)	0.5952 (12)	0.0570 (8)	0.136 (6)
C22	-0.1385 (5)	0.6454 (4)	0.3721 (3)	0.076 (1)
C23	-0.1899 (7)	0.4577 (5)	0.4407 (4)	0.109 (2)
C24	0.4578 (7)	0.5557 (5)	0.3325 (5)	0.115 (2)
C25	0.4219 (6)	0.8216 (5)	0.5235 (4)	0.086 (1)
C26	0.5541 (6)	0.8336 (6)	0.5542 (4)	0.108 (2)
C27	0.0709 (7)	1.1524 (5)	0.4191 (4)	0.095 (2)

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### 3-Chloro- and 3-Bromo-2-oxopropyl *p*-Toluenesulfonate

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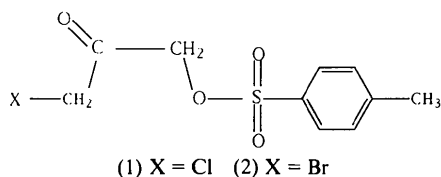
(Received 1 February 1994; accepted 6 June 1994)

#### Abstract

The crystal structures of 3-chloro-2-oxopropyl *p*-toluenesulfonate,  $C_{10}H_{11}ClO_4S$ , and 3-bromo-2-oxopropyl *p*-toluenesulfonate,  $C_{10}H_{11}BrO_4S$ , were determined at 150 and 293 K, respectively. They have essentially identical molecular structures and conformations, but different, though closely related, crystal structures. The Cl(or Br)—CH<sub>2</sub>—CO—CH<sub>2</sub>—O chain has an almost planar conformation.

#### Comment

The title compounds 3-chloro- (1) and 3-bromo-2-oxopropyl *p*-toluenesulfonate (2) are of interest as intermediates in a recently developed synthesis of isotopically labelled epichlorohydrins (O'Hagan, White & Jones, 1994). In order to provide additional insight into the potential reactivity of these molecules, we undertook structural studies.



The molecular structures of (1) and (2) in the crystalline form are essentially identical (Fig. 1). An interesting feature to emerge was the conformation of the O1, C8, C9, O4, C10, X moiety (X = Cl or Br), which is planar to within 0.11 Å for (1) and 0.05 Å for (2). The planes of this moiety and the benzene ring form

dihedral angles of 93.9 (1) and 91.5 (1)° with each other in (1) and (2), respectively, and both are approximately perpendicular to the O1, S, C1 plane. This apparently unfavourable conformation, on steric grounds, may be eased by hyperconjugation in the planar moiety, or by donation from the lone pair of O1 onto the  $\sigma^*$  orbital of the X—C10 bond [in both molecules, O1...C10 2.68 Å]. The latter explanation, however, seems less likely as the X—C10 bonds are not weakened, but rather are shorter than the average Cl—CH<sub>2</sub> and Br—CH<sub>2</sub> bond lengths of 1.790 (7) and 1.966 (29) Å, respectively (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987), and the S—O1 bond is not lengthened. The *cis*-planar orientation of the halogen and O4 atoms is quite common for  $\alpha$ -halogenoketones and can be attributed to O...Cl charge-transfer bonds (e.g. Sørensen, 1974; Watson, Go & Purdy, 1973).

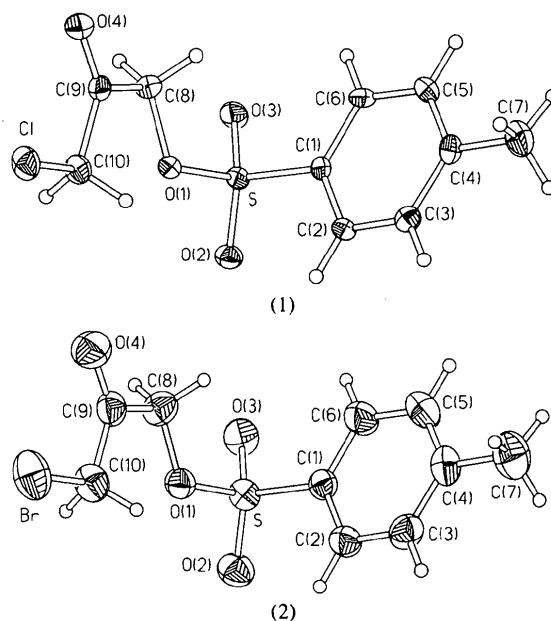


Fig. 1. Molecular structures of compounds (1) and (2), showing 50% probability displacement ellipsoids.

It is noteworthy that the deviation of the C1—S—O1—C8 torsion angle from 0 or 180° makes the molecular conformation chiral and the actual conformations of (1) and (2) are those of maximum chirality.

With the van der Waals radii of Cl and Br being similar (1.75 versus 1.85 Å; see Bondi, 1964), crystals of (1) and (2) might be expected to be isomorphous. In fact, (1) forms chiral crystals (space group  $P2_1$ ) with the polarity along the  $2_1$  axis defined by parallel orientation of S(=O)<sub>2</sub> groups along this axis, while (2) crystallizes in space group  $P2_1/c$  (Fig. 2) with the unit cell equal to that of (1) with the *c* parameter doubled. The latter contains enantiomers differing by rotation of *ca* 160° around the S—O1 bond and oriented antiparallel along