Experimental

The title compound was obtained as a product of a dyotropic ring-enlargement reaction of the isomeric β-lactone, with the ester O and the *trans*-diaxial-positioned H atom migrating (Mulzer *et al.*, 1997). The substance was isolated as the major reaction product and was separated from a minor isomer by high-performance liquid chromatography. The compound was recrystallized from a mixture of ethyl acetate and diethyl ether.

Crystal data

$C_{22}H_{24}O_2$	Mo $K\alpha$ radiation
$M_r = 320.41$	$\lambda = 0.71073$ Å
Triclinic	Cell parameters from 165
$P\bar{1}$	reflections
$a = 8.4311\ (12)$ Å	$\theta = 3–23°$
$b = 14.505\ (2)$ Å	$\mu = 0.073$ mm^{-1}
$c = 15.609\ (3)$ Å	$T = 158\ (2)$ K
$\alpha = 73.317\ (10)°$	Plate
$\beta = 85.702\ (18)°$	$0.44 \times 0.20 \times 0.08$ mm
$\gamma = 89.375\ (10)°$	Colorless
$V = 1823.2\ (5)$ Å^3	
$Z = 4$	
$D_x = 1.167$ Mg m^{-3}	
D_m not measured	

Data collection

Siemens SMART diffractom-eter	$R_{int} = 0.074$
	$\theta_{max} = 28.5°$
ω scans	$h = -11 \rightarrow 11$
Absorption correction: none	$k = -19 \rightarrow 19$
23 262 measured reflections	$l = -19 \rightarrow 20$
8657 independent reflections	282 standard reflections
5776 reflections with	frequency: 540 min
$I > 2\sigma(I)$	intensity decay: none

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.002$
$R[F^2 > 2\sigma(F^2)] = 0.097$	$\Delta\rho_{max} = 0.300$ e Å^{-3}
$wR(F^2) = 0.147$	$\Delta\rho_{min} = -0.275$ e Å^{-3}
$S = 1.708$	Extinction correction:
8657 reflections	SHELXL97
626 parameters	Extinction coefficient:
All H-atom parameters	0.0059 (10)
refined	Scattering factors from
$w = 1/[\sigma^2(F_o^2) + (0.03P)^2]$	International Tables for
where $P = (F_o^2 + 2F_c^2)/3$	Crystallography (Vol. C)

All H atoms were refined and C—H distances are in the range 0.94 (3)–1.04 (3) Å.

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SMART*. Data reduction: *SAINT* (Siemens, 1995). Program(s) used to solve structure: *SHELXS96* (Sheldrick, 1996a). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *XP* in *SHELXTL* (Sheldrick, 1996b). Software used to prepare material for publication: *CIF* in *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1338). Services for accessing these data are described at the back of the journal.

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Pseudosymmetry with $Z' = 4$ in 1,3-propanesultone at 100 K

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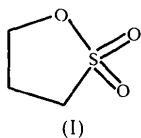
Abstract

The asymmetric unit of the low-melting title compound, $C_3H_6O_3S$, contains four molecules at low temperature. The conformations of two of the five-membered rings are envelopes, one has the half-chair conformation, and the fourth is intermediate between an envelope and a half-chair. S=O distances range from 1.424 (2) to 1.436 (2) Å, S—O distances from 1.582 (2) to 1.587 (2) Å, and S—C distances from 1.760 (3) to 1.776 (3) Å. The crystal structure contains approximate centers, 2_1 screw axes, and translations. Above 180 K, the compound exists as a polymorph in which these symmetry operations are exact, and $Z' = 1$.

Comment

The title compound, (I), is a common reagent used to introduce sulfonate groups into hydrophobic mol-

ecules in order to enhance water solubility, and is available in bulk quantities from commercial suppliers. While the structures of 3,5-diphenylpropanesultone (Bondarenko *et al.*, 1987), 3,3-diphenylpropanesultone (Petit *et al.*, 1980), 3,3,5-triphenylpropanesultone (Hellier & Motevalli, 1994), and several other substituted propanesultones (Brown *et al.*, 1983, 1987; Tafeenko *et al.*, 1987; Aslanov *et al.*, 1989; Duffy *et al.*, 1993) have been reported, the structure of the unsubstituted title compound has not been previously described. This is doubtless a result of its low melting point (306 K). We have obtained suitable crystals from the melt, and determined the structure at 100 K, at which temperature the displacement parameters for non-H atoms are quite low, 0.016–0.029 $\mathring{A}^2$.
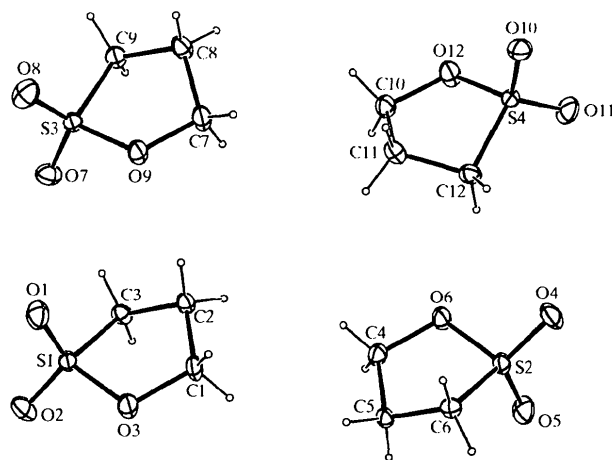
(I)

Fig. 1. The asymmetric unit of the title compound showing the four independent γ-sultone molecules, with ellipsoids at the 50% probability level.

The structure of the title compound has four independent γ-sultone molecules in space group $P2_1$, as illustrated in Fig. 1. $Z' = 4$ is quite rare in this space group, occurring in less than 1% of structures in the compilation of Brock & Dunitz (1994). While the crystallographic symmetry is low, significant pseudosymmetry exists, as is evident in Fig. 2. An approximate translation of $c/2$ relates the S1 and S3 molecules, as well as the S2 and S4 molecules. Further, an approximate center exists near $\frac{1}{4}$, $\frac{1}{2}$, $\frac{1}{2}$, and an approximate screw axis near $\frac{1}{2}$, y, $\frac{1}{4}$. Thus, the structure with the c axis halved resembles $P2_1/a$. The S positions conform reasonably well to this subcell, exhibiting deviations of about 0.09 Å from centrosymmetrically related positions and about 0.15 Å from screw-related positions. Due to the variation in conformation over the four molecules, however, C and O atoms deviate from the hypersymmetric arrangement by as much as 0.7 Å about the local center and 1.1 Å about the approximate screw. The hypersymmetry did not cause difficulty in the refinement, with maximum correlation coefficient 66%.

The hypersymmetry is reflected in the intensity statistics. The mean value of $E^2 - 1$ is 0.95, near the ideal centrosymmetric value. The average F^2 of the l even reflections is 2.3 times that of the l odd reflections, as a result of the approximate $c/2$ translation.

At higher temperatures, the approximate symmetry becomes exact, and the structure converts to a centrosymmetric ($P2_1/a$) polymorph with c halved and $Z' = 1$. Cell dimensions at 150 K are $a = 9.460(2)$, $b = 11.145(3)$, $c = 10.448(2)$ Å, $\beta = 114.07(2)°$, consistent with the reported low-temperature structure. By 180 K, a phase transition has occurred, and cell dimensions are $a = 9.521(3)$, $b = 11.155(3)$, $c = 5.246(2)$ Å, $\beta = 114.33(2)°$. Upon cooling through the phase transition
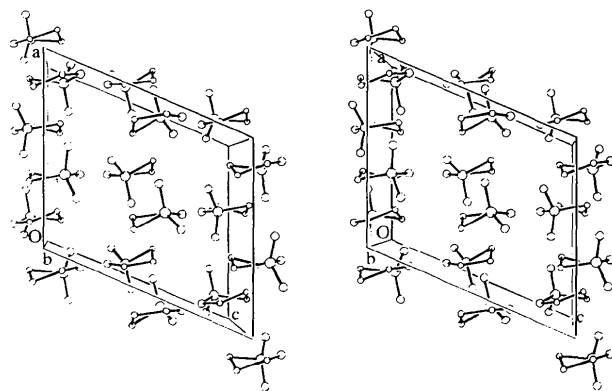
Fig. 2. Stereoview of the unit cell of the title compound. H atoms are not shown.

at a rate of $6.0\,\mathrm{K\,min^{-1}}$, the $P2_1/a$ polymorph converts to the $P2_1$ polymorph as a single crystal. Upon warming through the transition at the same rate, the single crystal becomes powder.

All angles and bonds compare well over the four molecules and agree within experimental error with similar structures (Brown *et al.*, 1983, 1987; Tafeenko *et al.*, 1987). The S=O bonds range from 1.424(2) Å (S4=O10) to 1.436(2) Å (S2=O4). S—O bonds in the ring range from 1.587(2) to 1.582(2) Å (S3—O9 and S4—O12, respectively), while these bonds compare closely with those in similar structures (Tafeenko *et al.*, 1987), but are longer than those in other previously reported structures (Brown *et al.*, 1983, 1987; Aslanov *et al.*, 1989). The C—S bonds, ranging from 1.776(3) Å (S3—C9) to 1.760(3) Å (S2—C6), are all significantly shorter than those in some previously reported structures (Tafeenko *et al.*, 1987; Aslanov *et al.*, 1989).

The four molecules differ somewhat in conformation. Molecule 1 (containing S1) is intermediate between

a C3 envelope and a C1 half-chair, with puckering parameters (Cremer & Pople, 1975) $q = 0.413\,(2)$ Å and $\varphi = 156.1\,(4)°$. Molecule 2 is a C4 half-chair with puckering parameters $q = 0.432\,(2)$ Å and $\varphi = 338.6\,(4)°$. Molecules 3 and 4 both have conformations near envelopes, with C8 and C12 at the flap positions. Puckering parameters are $q = 0.371\,(2)$ Å and $\varphi = 106.7\,(4)°$ for molecule 3, and $q = 0.407\,(3)$ Å and $\varphi = 139.6\,(4)°$ for molecule 4. The flap atoms lie out of the best planes of the other four ring atoms by $0.551\,(5)$ Å for C8 and $0.636\,(4)$ Å for C12. Similar structures in the literature show a preference for the envelope conformation (Tafeenko et al., 1987; Aslanov et al., 1989).

Experimental

The title compound was purchased from Acros Organics and used in an attempted reaction with 5-aminonaphthalene-dicarbonitrile. Excess starting material was isolated from the reaction mixture as an impure brown crystalline material. This compound was recrystallized by warming a vial containing the sample with the fingers until melting occurred, followed by slow cooling to room temperature (298 K). A single-crystal fragment was obtained from the solidified mass and cooled to 100 K over 45 min using an Oxford Cryosystems Cryostream cooler.

Crystal data

$C_3H_6O_3S$	Mo $K\alpha$ radiation
$M_r = 122.14$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 25
$P2_1$	reflections
$a = 9.272\,(2)$ Å	$\theta = 9.3-18.2°$
$b = 11.134\,(8)$ Å	$\mu = 0.542$ mm^{-1}
$c = 10.434\,(5)$ Å	$T = 100$ K
$\beta = 113.86\,(2)°$	Fragment
$V = 985.2\,(9)$ Å^3	$0.50 \times 0.30 \times 0.15$ mm
$Z = 8$	Brown
$D_x = 1.647$ Mg m^{-3}	
D_m not measured	

Data collection

Enraf–Nonius CAD-4	4537 reflections with
diffractometer	$I > 2\sigma(I)$
ω–2θ scans	$R_{int} = 0.019$
Absorption correction:	$\theta_{max} = 32.0°$
ψ scan (North et al.,	$h = -12 \to 12$
1968)	$k = -14 \to 16$
$T_{min} = 0.72$, $T_{max} = 0.92$	$l = -15 \to 0$
5592 measured reflections	3 standard reflections
3187 independent reflections	frequency: 60 min
(plus 1961 Friedel-related	intensity decay: 7.5%
reflections)	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.02$
$R[F^2 > 2\sigma(F^2)] = 0.039$	$\Delta\rho_{max} = 0.60$ e Å^{-3}
$wR(F^2) = 0.110$	$\Delta\rho_{min} = -0.41$ e Å^{-3}
$S = 1.042$	Extinction correction: none
5148 reflections	Scattering factors from
254 parameters	*International Tables for*
H-atom parameters	*Crystallography* (Vol. C)
constrained	Absolute structure:
$w = 1/[\sigma^2(F_o^2) + (0.0633P)^2 + 0.3979P]$	Flack (1983)
where $P = (F_o^2 + 2F_c^2)/3$	Flack parameter = 0.44 (8)

Table 1. *Selected geometric parameters (Å, °)*

S1—O1	1.427 (2)	S3—O8	1.424 (2)
S1—O2	1.429 (2)	S3—O7	1.426 (2)
S1—O3	1.585 (2)	S3—O9	1.587 (2)
S1—C3	1.767 (3)	S3—C9	1.776 (3)
S2—O5	1.431 (2)	S4—O10	1.424 (2)
S2—O4	1.436 (2)	S4—O11	1.434 (2)
S2—O6	1.583 (2)	S4—O12	1.582 (2)
S2—C6	1.760 (3)	S4—C12	1.764 (3)
O1—S1—O2	117.83 (15)	O8—S3—O7	117.58 (15)
O3—S1—C3	95.61 (13)	O9—S3—C9	97.41 (13)
O5—S2—O4	117.73 (16)	O10—S4—O11	117.58 (15)
O6—S2—C6	95.54 (13)	O12—S4—C12	96.35 (14)
C3—S1—O3—C1	28.4 (2)	C4—C5—C6—S2	−34.9 (3)
C6—S2—O6—C4	−30.9 (2)	O6—S2—C6—C5	38.9 (2)
C9—S3—O9—C7	−3.5 (2)	S3—O9—C7—C8	25.8 (3)
C12—S4—O12—C10	18.6 (2)	O9—C7—C8—C9	−39.1 (3)
S1—O3—C1—C2	−9.8 (3)	C7—C8—C9—S3	35.4 (3)
O3—C1—C2—C3	−17.8 (3)	O9—S3—C9—C8	−19.2 (2)
C1—C2—C3—S1	34.4 (3)	S4—O12—C10—C11	3.6 (3)
O3—S1—C3—C2	−37.0 (2)	O12—C10—C11—C12	−28.6 (3)
S2—O6—C4—C5	12.1 (3)	C10—C11—C12—S4	38.8 (3)
O6—C4—C5—C6	16.8 (3)	O12—S4—C12—C11	−34.2 (2)

The highest residual peak was 0.81 Å from S2, and the deepest residual hole was 1.03 Å from S1. Refinement of the Flack (1983) parameter was inconclusive and suggestive of a racemic twin. Refinement with averaged Friedel pairs led to marginally higher uncertainties and no shift of any parameter in the reported model by more than 1.5σ.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1993). Cell refinement: *CAD-4 EXPRESS*. Data reduction: *XCAD4* (Harms & Wocadlo, 1996). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL* (Bruker, 1998). Software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 1997).

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Taraxerol acetate at 100 K

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Abstract

The title triterpene, *D*-friedoolean-14-en-3β-yl acetate, $C_{32}H_{52}O_2$, was isolated from dichloromethane extracts of the roots of common ragweed *Ambrosia artemisiifolia*. The skeleton contains five fused six-membered rings with an average Csp^3—Csp^3 bond distance of 1.549 (6) Å and one double bond of length 1.348 (6) Å. The *D* and *E* rings are *cis*-fused. The compound also contains a β-oriented acetate group with a C—O distance 1.461 (5) Å.

Comment

In the course of our search for biologically active natural products, the dichloromethane extract of roots

of common ragweed, *Ambrosia artemisiifolia*, showed activity in a radiorespirometric assay (Franzblau & Collins, 1997) against *Mycobacterium tuberculosis* $H_{37}Rv$ (Cantrell *et al.*, 1998). The crude extract was chromatographed by standard vacuum liquid chromatography procedures (Cantrell *et al.*, 1996) using silica gel with solvent mixtures of increasing polarity. From nonpolar fractions, taraxerol acetate, (I), was isolated, but showed no antimycobacterial activity. We determined the crystal structure in order to confirm the identity of the compound and ascertain the ring conformations.

(I)
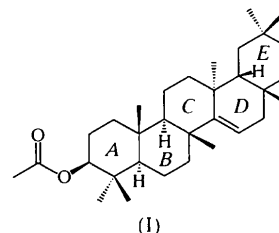
The structure contains five fused six-membered rings with only the *D* and *E* rings *cis*-fused. The average Csp^3—Csp^3 bond in the rings is 1.549 (6) Å, comparable to the equivalent distance of 1.539 (17) Å recently reported in taraxerone (Parvez *et al.*, 1999), as well as other similar triterpenes in the literature (Chakravarty *et al.*, 1989; Tinant *et al.*, 1982). The solitary Csp^2—Csp^2 bond (C14=C15) has length 1.348 (6) Å, comparable with 1.338 (3) Å reported for taraxerone. The conformations of the rings in the title compound are similar to the reported conformations of taraxerone (Parvez *et al.*, 1999). Rings *A* and *B* adopt chair conformations with puckering parameters $Q = 0.566$ (3) and 0.595 (3) Å, $\varphi = 63.85$ (5) and 347.03 (3)°, and $\theta = 4.4$ (1) and 8.3 (2)° (Cremer & Pople, 1975). Ring *C* has a twist-boat conformation [$Q = 0.709$ (2) Å, $\varphi = 20.83$ (2)°, $\theta = 87.1$ (3)°], while the conformations of rings *D* and *E* resemble twist
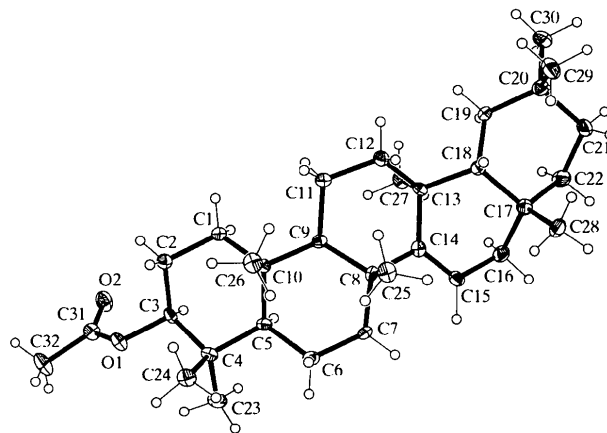

Fig. 1. Numbering scheme and ellipsoids at the 50% level. H atoms are represented by circles of arbitrary radius.