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A Sultone Derived from Racemic Camphene

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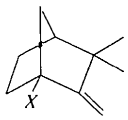
Abstract

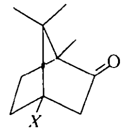
A controversy about the structures of five-membered ring sultones obtained by treatment of camphenes with acetic and concentrated sulfuric acids has been resolved by X-ray analysis of the sultone obtained from racemic camphene, namely, *endo*-3*H*-10,10-dimethyl-4-oxa-5-thiatricyclo[5.2.1.$0^{3,7}$]decane *S*,*S*-dioxide, (also known as 10-bornanesulfonic acid 2-hydroxy-γ-sultone), $C_{10}H_{16}O_3S$. Five-membered saturated sultone rings are shown to be conformationally flexible.

Comment

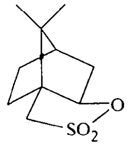
1-Substituted camphenes, (1), are convenient starting materials for the synthesis of 4-substituted camphors, (2) (Berson, 1963). However, this transformation, which involves treatment of (1) with acetic acid dissolved in concentrated sulfuric acid, on occasion gives rise to such large quantities of sultone by-product as to require the development of an alternative synthetic route (Morris & Murray, 1975). The sultone arising from unsubstituted camphene, (1*a*), was assigned structure (3) by Lipp & Holl (1929). Subsequently, a systematic investigation of the reaction led to the revised structure, (4); the configuration at the C atoms common to the sultone and norbornane residues was not specified, and could be either both *exo*, as shown, or both *endo* (Asahina & Kawahata, 1939; Asahina *et al.*, 1938).



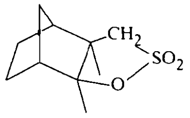
(1*a*) $X = H$
(1*b*) $X = NO_2$
(1*c*) $X = CO_2H$



(2)



(3)



(4)

We have, therefore, subjected the sultone formed from camphene, (1*a*), to single-crystal X-ray analysis. Racemic (1*a*) was used as the starting material because a racemization step, which is not always complete, is almost certainly involved in the formation of the sultone. The molecule (Fig. 1) has structure (3), as proposed by Lipp & Holl (1929). It seems likely that substituted camphenes, such as (1*b*) or (1*c*), also give rise to sultones like (3), rather than (4), and that the suggestions of Asahina (Asahina & Kawahata, 1939; Asahina *et al.*, 1938) should be disregarded.

Bond lengths in (3) (Table 1) show deviations of up to 0.03 Å from standard values. Thus, the staggered conformation across C1—C7 [1.556 (2) Å] leads to a

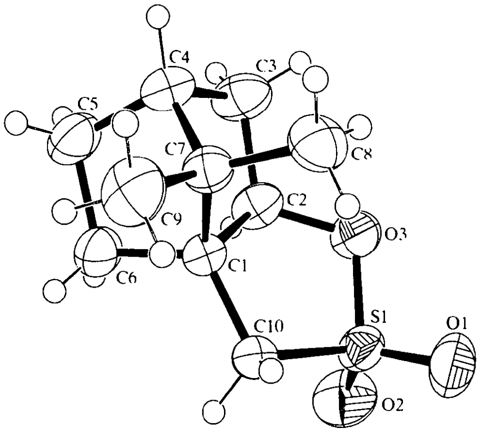


Fig. 1. A view of the title sultone molecule, (3), showing 50% probability ellipsoids. H atoms are shown as spheres of arbitrary radii.

bond which is slightly shorter than the mean of 1.588 Å proposed for $C_3C—CC_3$ bonds by Orpen *et al.* (1992; hereafter O92). The eclipsed conformation across C5—C6 [1.554 (2) Å] stretches the bond slightly (*cf.* 1.524 Å in O92). In the sultone ring, S1—O3 [1.590 (1) Å] and S1—C10 [1.787 (1) Å] are slightly longer than the O92 values of 1.577 and 1.745 Å, respectively; the S1—C10 distance is, however, typical of values in saturated five-membered SOC_3 sultone rings [mean 1.795 Å for nine such rings the Cambridge Structural Database (CSD) (Allen & Kennard, 1993); refcodes for SOC_3 sultone rings are CERPEU, FINLOO, FINLUJ, FORGUO, KUGDIZ, PHOXTL, WIKFOL and ZIZTOR (twice)]. Many of the 72 cyclic and acyclic sultones in the CSD contain terminal $S—CH_3$ bonds, which may be subject to appreciable librational shrinkage, and they give rise to a mean $S—C_{sp^3}$ distance of 1.760 Å, which is shorter than the value typical of cyclic sultones.

For the nine five-membered saturated sultone rings in the CSD, the Cremer & Pople (1975) puckering parameters are Q = 0.37–0.50 Å and φ = 17–72°, indicating considerable conformational flexibility. In (3), this ring is slightly less puckered than usual [Q = 0.372 (1) Å and φ = 51.8 (2)°], indicating a near-perfect half-chair (φ = 54°), with the pseudo-C_2 axis running through C10 and the centroid of C2—O3 (see Table 1 for the ring torsion angles).

The anomalously high rates of alkaline hydrolysis of five-membered rings containing a sulfur ester group have been explained, at least in part, in terms of repulsive interactions between the lone pairs of the ring O atom and the exocyclic S=O bonds (Boer & Flynn, 1969). Although some relief of these interactions in (3) is achieved by the deviation from zero of the endocyclic C—S—O—C torsion angle [−31.3 (1)°], the conformational flexibility of such rings in general is illustrated by corresponding torsion angles in the range 3–37° for the nine saturated SOC_3 sultone rings in the CSD (Allen & Kennard, 1993).

The title compound packs in the moderately unusual space group $P2/a$ (alternative setting of $P2/c$), with a mean atomic volume (ignoring H) of 19.0 Å³. Unsurprisingly, there are no unusually short intermolecular distances. The largest departures from the rigid-bond test of Hirshfeld (1976) relate to the *gem*-dimethyl group [ΔU = 0.0030 (12) Å² for the C7—C9 bond].

Experimental

Application of the procedure of Asahina & Kawahata (1939) to racemic (1*a*) produced a sultone, (3) (m.p. 406 K). Crystals suitable for X-ray analysis were grown from ethyl acetate. NMR spectra of solutions of (3) in $CDCl_3$ were measured on a Bruker AM-360 spectrometer. ^1H and ^{13}C chemical shifts in p.p.m. were referenced to chloroform at 7.25 and $CDCl_3$ at 77.00, respectively. ^1H NMR: 0.94 (3H, *s*), 1.12 (3H, *s*), 3.19 (1H), 3.26 (1H, *AB* quartet, J = 13.70 Hz), 4.39 (1H, *dd*, J = 7.92 and 3.52 Hz); ^{13}C NMR: 19.82 (CH_3), 19.90 (CH_3), 26.71 (CH_2), 29.07 (CH_2), 35.81 (CH_2), 44.38 (CH), 47.41 (C), 49.07 (CH_2), 55.49 (C), 87.90 (CH).

Crystal data

$C_{10}H_{16}O_3S$
M_r = 216.29
Monoclinic
$P2/a$
a = 10.5933 (6) Å
b = 8.8517 (7) Å
c = 11.3495 (6) Å
β = 91.606 (4)°
V = 1063.81 (12) Å³
Z = 4
D_x = 1.350 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 20.8–24.3°
μ = 0.284 mm^{-1}
T = 287 (2) K
Plate
0.38 × 0.38 × 0.10 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: Gaussian (Spek, 1997)
T_{min} = 0.889, T_{max} = 0.970
3997 measured reflections
3096 independent reflections
2321 reflections with $I > 2\sigma(I)$

R_{int} = 0.014
θ_{max} = 30°
$h = -14 \rightarrow 14$
$k = -12 \rightarrow 1$
$l = -15 \rightarrow 2$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.110
S = 1.008
3094 reflections
130 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0600P)^2 + 0.1639P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.26 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0034 (12)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

S1—O2	1.4211 (12)	C1—C7	1.556 (2)
S1—O1	1.4229 (12)	C2—C3	1.527 (2)
S1—O3	1.5903 (11)	C3—C4	1.533 (2)
S1—C10	1.7870 (13)	C4—C5	1.540 (2)
O3—C2	1.462 (2)	C4—C7	1.545 (2)
C1—C10	1.525 (2)	C5—C6	1.554 (2)
C1—C6	1.534 (2)	C7—C9	1.529 (2)
C1—C2	1.543 (2)	C7—C8	1.532 (2)
O2—S1—O1	118.09 (8)	O3—S1—C10	97.68 (6)
O2—S1—O3	109.26 (7)	C2—O3—S1	108.41 (8)
O1—S1—O3	106.03 (7)	C10—C1—C2	107.41 (10)
O2—S1—C10	109.72 (8)	C3—C2—C1	104.78 (11)
O1—S1—C10	113.91 (7)	C1—C10—S1	104.82 (9)
C10—S1—O3—C2	−31.32 (10)	C10—C1—C7—C4	169.28 (11)
S1—O3—C2—C1	41.66 (12)	C2—C1—C10—S1	11.42 (12)
C10—C1—C2—O3	−32.58 (14)	O3—S1—C10—C1	10.95 (10)
C4—C5—C6—C1	−2.6 (2)		

A single torsional parameter was refined for each methyl group. Otherwise, H atoms were placed in calculated positions, riding on their parent C atoms.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1992). Cell refinement: *CAD*-4 *EXPRESS*. Data reduction: *WINGX* (Farrugia, 1996). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1994). Molecular graphics: *ORTEP*3 (Farrugia, 1997). Software used to prepare material for publication: *WRITECIF* (Pauson & Muir, 1996).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1262). Services for accessing these data are described at the back of the journal.

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Gomisin N

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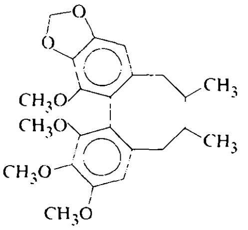
Abstract

The crystal structure of gomisin N (1,2,3,12-tetramethoxy-6,7-dimethyl-10,11-methylenedioxy-5,6,7,8-tetrahydrodibenzo[*a*,*c*]cyclooctene, $C_{23}H_{28}O_6$) has been determined. The cyclooctene ring of the molecule has a twisted boat–chair conformation. The angle between the two phenyl rings is 60.6 (11)°.

Comment

The title compound, (I), was originally isolated from the fruits of *Schisandra chinensis* Baill., a well known oriental medicinal plant (Ikeya *et al.*, 1979). Its structure was established by spectroscopic methods. Intense hepatoprotective action was found with gomisin N (Hikino *et al.*, 1984). In the course of our work on the biochemistry of natural lignans, we reisolated the title compound from the seeds of *Schisandra chinensis* (Lojková *et al.*, 1997; Slanina *et al.*, 1997).



(I)

The main part of the molecule is the cyclooctadiene ring, which possesses a twisted boat–chair conformation. The methyl group bonded to the cyclooctadiene ring at C7 is in a pseudo-axial position, while the methyl group bonded at C8 is in a pseudo-equatorial position. Two phenyl rings are connected to the eight-membered cycle. Both of these rings are relatively planar: the maximum deviations of best planes through atoms C10–C15, and C1–C5 and C16, are 0.01 (5) and 0.03 (2) Å, respectively (or 0.2 and 1.6, respectively, on a δ/σ scale). The angle between these planes is 60.6 (11)°. The