Discussion. A view of the molecule with the atom-labelling scheme is shown in Fig. 1. Bond lengths and selected valence and torsion angles are presented in Table 2. The results of the X-ray analysis confirm the assignment of Graziano, Iesce, Carotenuto & Scarpati (1977*a*). The only structural features worthy of discussion concern the dioxazole ring. The ring displays an envelope conformation with the peroxy O(2) atom displaced by 0.211 (3) Å out of the plane of the other intra-ring atoms, each of which deviates by no more than 0.007 (4) Å. The puckering of the ring can also be expressed by the dihedral angle formed by the plane defined by O(1), C(1), N and C(2) and the plane defined by O(1), O(2) and C(2). The value of this angle is 13.7 (8)° whereas that of the corresponding angle in the trioxolane ring (III), which has an identical conformation, is 45.2 (2)°. Why is there such a large difference? The answer is given by examination of the lengths of the bonds formed by the O atoms. While O(1)—O(2) and O(2)—C(2) are of typical single-bond length, O(1)—C(1) [1.352 (2) Å] is intermediate between the lengths of a single and a double bond, giving evidence of π-electron conjugation of O(1) with the fragment consisting of N, C(1) and the attached phenyl group. Two concomitant and interdependent effects reduce the puckering of the dioxazole ring: the O(1)—C(1) partial double bond pushes O(2) towards the ring plane and the π conjugation withdraws electron charge from the lone pairs of O(1) resulting in a smaller repulsion between the lone pairs on the two adjacent O atoms.

In conclusion, the valence state of the peroxy O atoms appears to be the major factor in determining the puckering of this heterocyclic ring. The crystal packing is presented in Fig. 2.

The author is grateful to Professor R. Scarpati and her research group for stimulating interest in this work and for providing the crystals. The work was financially supported by Progetto Finalizzato Chimica Fine e Secondaria 2 of CNR (Rome).

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Structure of Polymorph II of (1*R*,3*S*)-1,2,2-Trimethyl-3-(4-methylthiobenzoyl)-cyclopentanecarboxylic Acid

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Abstract. $C_{17}H_{22}O_3S$, $M_r = 306.407$, orthorhombic, $P2_12_12$, $a = 13.327$ (5), $b = 19.277$ (8), $c = 6.361$ (2) Å, $V = 1634$ (1) Å^3, $Z = 4$, $D_x = 1.245$ Mg m^{-3}, λ(Cu $K\alpha$) = 1.54178 Å, $\mu = 1.77$ mm^{-1}, $F(000) = 656$, $T = 293$ K, $R = 0.043$ for 2574 observed reflections. Two crystalline forms of the title compound have been obtained but only one (form II) has given suitable crystals for X-ray structure analysis. The five-membered ring has an envelope conformation with C(2) 0.60 (1) Å out of

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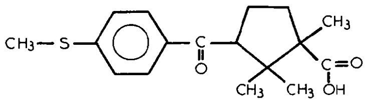
the plane defined by the other four atoms. The absolute configuration has been established and appears to be identical to that of camphoric acid used in the synthesis. Molecules form dimers around the twofold axis by means of hydrogen bonds between their carboxylic groups.

Introduction. The title compound (I) was prepared by Friedel–Crafts reaction from (1*R*,3*S*)-camphoric acid and *p*-methylthiobenzene (Chevallet & Orzalesi, 1984). Recrystallization of the compound gives two polymorphic forms with different melting points: 404 K for the polymorph I and 397 K for the polymorph II (Terol, Pauvert, Bouassab, Chevallet & Cassanas, 1992). The crystal structure determination was carried out to investigate the influence of the bulky φ-SCH_3 substituent on the overall conformation of the molecule and to compare the conformations of the two polymorphs. At this time only polymorph II has given suitable crystals for data collection. We present in this paper the crystallographic structure of polymorph II (m.p. 397 K).



(I)

Experimental. A colourless prismatic crystal of the title compound was obtained from recrystallization in a mixed benzene–heptane solution (1*v*/2*v*) at room temperature (293 K) under normal lighting conditions. A crystal of dimensions 0.18 × 0.20 × 0.41 mm was chosen for data collection. Lattice parameters were determined from 30 reflections in the range $16 \leq 2\theta \leq 50°$. Diffraction data, collected to $2\theta_{\max} = 135°$, were measured on a Huber four-circle diffractometer using an $\omega/2\theta$ scan and graphite-monochromated Cu $K\alpha$ radiation, with ranges of *hkl* −15 to 15, 0 to 23, 0 to 7, respectively. One standard reflection (251) was checked every 50 reflections and showed no significant deviation. Data were not corrected for absorption. 2954 independent reflections with $(\sin\theta/\lambda) \leq 0.599$ Å^{-1} were measured of which 2574 were observed with $I \geq 2.5\sigma(I)$. The structure was solved by direct methods with *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and refined by full-matrix least-squares calculations with *SHELX*76 (Sheldrick, 1976) using *F* magnitudes. Except for the hydroxyl proton, all H atoms were located from difference Fourier maps and refined with common isotropic thermal parameters $U = 0.07$ Å^2. The non-H atoms were refined anisotropically. Convergence gave $R = 0.043$ and $wR = 0.047$ with $w = 1/[\sigma^2(F) + 0.001883 \times F^2]$, $S = 1.11$ for 254 variables. Final maximum shift to e.s.d. was < 0.04 for non-H atoms and < 0.15 for H atoms. The maximum and minimum heights in the final difference Fourier synthesis were 0.26 and −0.35 e Å^{-3}. Atomic scattering factors and anomalous-dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). At the end of the refinement, 1051 Friedel pairs of reflections present in the data set were sorted according to $w^{1/2}||F_c(hkl)| - |F_c(\bar{h}\bar{k}\bar{l})||$ by decreasing magnitude. Among the first 200 pairs of reflections, the signs of 185 observed differences were consistent with the signs of the corresponding calculated differences establishing the correct absolute configuration.

Atomic parameters are given in Table 1, intramolecular bond distances and angles in Table 2.*

Discussion. X-ray analysis unequivocally establishes the molecular structure and absolute configuration of the title compound. A view of the molecule is given in Fig. 1 with the crystallographic numbering scheme (*PLUTO*; Motherwell & Clegg, 1978).

The bond distances of the cyclopentane ring are in good agreement with values found for camphoric acid (Barnes, Paton, Blyth & Howie, 1991). As shown in Table 2, the lengths of the C—O bonds in the carboxylic group are identical [1.265 (3) and 1.261 (4) Å] these values have been found in other studies [1.263/1.264 Å (Glusker, Zacharias & Carrell, 1975) and 1.263/1.270 Å (Fitzgerald, Gallucci & Gerkin, 1991)]. They are intermediate between the mean lengths for C=O double bonds (1.214 Å) and C—O single bonds (1.308 Å) observed in carboxylic acids (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987).

According to Leiserowitz (1976), the values for the C—O bonds we observed in the carboxylic group indicate disorder. The hydroxyl proton is delocalized; this explains its absence in the difference Fourier map.

The O···O distances between the refined molecule and its symmetrical partner with respect to the twofold axis along *z* are short: $O(2)\cdots O(2^i) = 2.688$ (6) and $O(3)\cdots O(3^i) = 2.651$ (5) Å [symmetry code: (i) $-x, -y, z$]. This fact indicates that these two molecules form hydrogen bonds of a cyclic-dimer type and that the hydroxyl protons can be centrally situated on a twofold axis or delocalized. Duchamp & Marsh (1969) estimate that the O···H···O bond cannot be symmetric when the distances are long

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, and bond distances and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55332 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL0533]

Table 1. *Atomic coordinates* (× 10⁴) *and equivalent isotropic temperature factors* (Å²)

$$B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
C(1)	1101 (2)	−1615 (1)	4009 (4)	4.32
C(2)	290 (2)	−2186 (1)	3404 (4)	3.73
C(3)	1001 (2)	−2809 (1)	2811 (4)	3.93
C(4)	1984 (2)	−2490 (2)	1968 (6)	5.09
C(5)	1893 (2)	−1705 (2)	2307 (5)	5.08
C(11)	627 (2)	−898 (1)	4000 (5)	5.03
C(12)	1559 (3)	−1754 (2)	6171 (5)	5.39
C(21)	−336 (2)	−1962 (2)	1496 (5)	5.14
C(22)	−421 (3)	−2347 (2)	5213 (5)	5.11
C(31)	531 (2)	−3311 (1)	1256 (4)	4.15
C(32)	−240 (2)	−3813 (1)	1958 (4)	3.97
C(33)	−369 (2)	−4040 (1)	4021 (4)	4.19
C(34)	−1076 (2)	−4536 (1)	4509 (4)	4.48
C(35)	−1681 (2)	−4829 (1)	2962 (4)	4.26
C(36)	−1574 (2)	−4590 (2)	916 (5)	5.30
C(37)	−861 (3)	−4098 (2)	425 (5)	5.19
C(38)	−3193 (3)	−5667 (2)	1405 (7)	7.24
S	−2526 (1)	−5473 (0)	3732 (1)	5.75
O(1)	766 (2)	−3292 (1)	−595 (3)	6.08
O(2)	605 (2)	−558 (1)	2300 (3)	7.10
O(3)	267 (2)	−662 (1)	5688 (3)	6.31

Table 2. *Interatomic distances* (Å) *and angles* (°)

C(2)—C(1)	1.590 (3)	O(3)—C(11)	1.261 (4)
C(5)—C(1)	1.522 (4)	C(32)—C(31)	1.480 (3)
C(11)—C(1)	1.520 (4)	O(1)—C(31)	1.219 (3)
C(12)—C(1)	1.528 (4)	C(33)—C(32)	1.394 (4)
C(3)—C(2)	1.574 (3)	C(37)—C(32)	1.392 (4)
C(21)—C(2)	1.536 (4)	C(34)—C(33)	1.378 (4)
C(22)—C(2)	1.523 (4)	C(35)—C(34)	1.393 (4)
C(4)—C(3)	1.543 (4)	C(36)—C(35)	1.388 (4)
C(31)—C(3)	1.519 (4)	S—C(35)	1.745 (3)
C(5)—C(4)	1.533 (4)	C(37)—C(36)	1.380 (4)
O(2)—C(11)	1.265 (3)	S—C(38)	1.767 (4)

C(5)—C(1)—C(2)	102.7 (2)	O(2)—C(11)—C(1)	119.0 (3)
C(11)—C(1)—C(2)	110.3 (2)	O(3)—C(11)—C(1)	118.8 (2)
C(11)—C(1)—C(5)	112.9 (2)	O(3)—C(11)—O(2)	122.2 (3)
C(12)—C(1)—C(2)	111.6 (2)	C(32)—C(31)—C(3)	120.4 (2)
C(12)—C(1)—C(5)	110.0 (3)	O(1)—C(31)—C(3)	120.3 (3)
C(12)—C(1)—C(11)	109.2 (2)	O(1)—C(31)—C(32)	119.3 (2)
C(3)—C(2)—C(1)	100.2 (2)	C(33)—C(32)—C(31)	125.1 (2)
C(21)—C(2)—C(1)	111.5 (2)	C(37)—C(32)—C(31)	117.3 (2)
C(21)—C(2)—C(3)	110.6 (2)	C(37)—C(32)—C(33)	117.5 (2)
C(22)—C(2)—C(1)	112.4 (2)	C(34)—C(33)—C(32)	121.0 (2)
C(22)—C(2)—C(3)	113.6 (2)	C(35)—C(34)—C(33)	121.2 (3)
C(22)—C(2)—C(21)	108.4 (2)	C(36)—C(35)—C(34)	117.9 (2)
C(4)—C(3)—C(2)	106.9 (2)	S—C(35)—C(34)	117.6 (2)
C(31)—C(3)—C(2)	113.2 (2)	S—C(35)—C(36)	124.5 (2)
C(31)—C(3)—C(4)	112.1 (2)	C(37)—C(36)—C(35)	120.8 (3)
C(5)—C(4)—C(3)	106.1 (2)	C(36)—C(37)—C(32)	121.5 (3)
C(4)—C(5)—C(1)	105.5 (2)	C(38)—S—C(35)	103.9 (2)

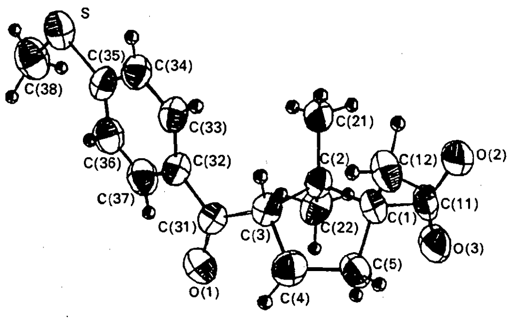

Fig. 1. *PLUTO* (Motherwell & Clegg, 1978) drawing of the title compound showing the numbering scheme.

(2.632 Å). Therefore, as in 1,3,5-trimesic acid (III) (Duchamp & March, 1969), the hydroxyl proton is probably partially disordered but not centrally situated in a symmetric O···H···O bond.

The carboxylic group is also involved in the cohesion of the crystal by two other lateral contacts: O(2)···C(38ⁱⁱ) [3.701 (7) Å] and O(3)···C(38ⁱⁱⁱ) [3.325 (7) Å] [symmetry code: (ii) −0.5 + x, −0.5

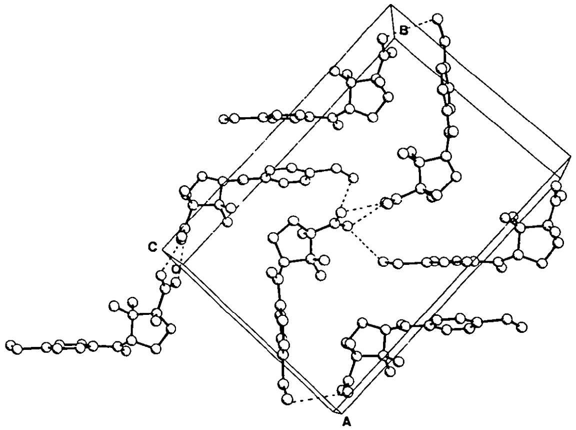

Fig. 2. Packing arrangement of the title compound with hydrogen bonds indicated by dashed lines.

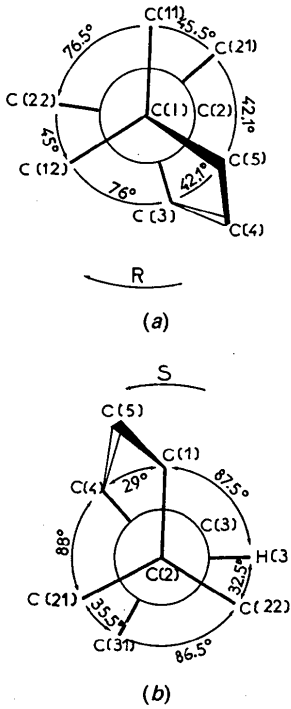

Fig. 3. Newman projections (*a*) along the C(1)—C(2) bond, and (*b*) along the C(2)—C(3) bond.

$-y, -z$; (iii) $-0.5-x, -0.5+y, 1-z$]. These contacts are longer but stabilize the crystal packing (Fig. 2).

Least-squares-planes calculations (*XANADU*; Roberts & Sheldrick, 1975) show that the five-membered ring has an envelope conformation with C(2) 0.60 (1) Å out of the plane defined by the other four atoms C(1), C(3), C(4) and C(5). The angle between the normals to the carboxylic group and to the planar part of the five-membered ring is 53 (1)°, slightly different from the value observed in camphoric acid [40.4 (4)°] (Barnes, Paton, Blyth & Howie, 1991).

The CH_3—S— substituted phenyl ring is planar to within experimental accuracy ($\sigma = 0.01$ Å) and is inclined 64 (1)° to the cyclopentane ring. It is on the same side as the carboxylic plane with respect to the five-membered ring.

The Newman projections along the C(1)—C(2) and C(2)—C(3) bonds show a staggered conformation and the (1*R*,3*S*) configuration (Fig. 3). The Friedel–Crafts reaction does not change the absolute configuration of native camphoric acid.

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Structures of Three Tricyclic γ-Lactams

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Abstract. Synthetic γ-lactams formed in acidic media: (I) (3aα,4α,8bα)-3,3a,4,8b-tetrahydro-4-methylindano[1,2-*b*]pyrrol-2(1*H*)-one, $C_{12}H_{13}NO$, $M_r = 187.24$, monoclinic, $P2_1/c$, $a = 14.589$ (2), $b = 8.330$ (3), $c = 8.186$ (4) Å, $\beta = 103.17$ (2)°, $V = 968.6$ (5) Å^3, $Z = 4$, $D_x = 1.284$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 0.764$ cm^{-1}, $F(000) = 400$, $T = 173$ K, final $R = 0.055$ for 1880 unique observations, $I \geq 3\sigma(I)$; (II) (3aα,4α,8bα)-1-benzyl-3,3a,4,8b-tetrahydro-4-methylindano[1,2-*b*]pyrrol-2(1*H*)-one, $C_{19}H_{19}NO$, $M_r = 277.37$, orthorhombic, $P2_12_12_1$, $a = 9.100$ (3), $b = 9.678$ (4), $c = 17.360$ (2) Å, $V = 1528.8$ (5) Å^3, $Z = 4$, $D_x = 1.205$ g cm^{-3}, λ(Cu $K\alpha$) = 1.5406 Å, $\mu = 5.416$ cm^{-1}, $F(000) = 592$, $T = 295$ K, final $R = 0.049$ for 729 observations, $I \geq 3\sigma(I)$; (III) (3aα,5α,9bα)-2,3,3a,4,5,9b-hexahydro-5-methylnaphtho[1,2-*b*]pyrrol-2(1*H*)-one, $C_{13}H_{15}NO$, $M_r = 201.27$, monoclinic, $P2_1/n$, $a = 8.121$ (5), $b = 16.257$ (4), $c = 8.686$ (2) Å, $\beta = 107.65$ (2)°, $V = 1092.7$ (7) Å^3, $Z = 4$, $D_x = 1.223$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 0.721$ cm^{-1}, $F(000) = 432$, $T = 295$ K, final $R = 0.046$ for 1522 unique observations,

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