Crystal Structure of Racemic *trans*-π-Camphanic Acid, 1α,5β-Dimethyl-2-oxo-3-oxabicyclo[3,3,0]octane-6β-carboxylic Acid, a γ-Lactone of Rare Type

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Summary *X*-Ray analysis has confirmed that the title compound contains a γ-lactone *trans*-fused to a cyclopentane ring and shows that both five-membered rings adopt the half-chair conformation such that the conformation in one ring is the mirror image of that in the other.

ALTHOUGH there exist many examples in which a γ-lactone is fused *cis* to a five-membered ring, the corresponding *trans*-fusion is unfavourable and rare. Recently[1] it was demonstrated from chemical and spectroscopic considerations that *trans*-π-camphanic acid[2] is one of those few γ-lactones with *trans*-fusion. Since such an arrangement may be expected to introduce considerable strain into the five-membered ring to which it is fused, and simultaneously be strained by that deformation, we have examined the crystal structure of (±)-*trans*-π-camphanic acid (I).

Crystal data: $C_{10}H_{14}O_4$, $M = 198{\cdot}2$, Monoclinic, $a = 12{\cdot}291(6)$, $b = 6{\cdot}290(4)$, $c = 12{\cdot}778(8)$ Å, $\beta = 99{\cdot}97(9)°$, $U = 973$ Å^3, space group $P2_1/c$ by systematic absences, $Z = 4$. The structure is based upon 1982 independent reflexions collected on a Hilger and Watts computer-controlled four-circle diffractometer.[3] 1145 intensities were greater than 3σ (counting statistics). Solution was by direct methods; R 6·7%.

Five-membered rings may be distorted from planarity into envelope or into half-chair forms.[4] These different forms are most conveniently distinguished by consideration of torsion angles. The envelope form has molecular symmetry C_s and thus one torsion angle has zero value and the signs of the remainder alternate round the ring whilst their magnitudes are related by the mirror plane. The largest torsion angles involve the 'flap' atom as a central atom. In contrast, in the half-chair form, where none has zero value, the torsion angles are related both in magnitude and sign by the C_2 axis and the largest value, which is unique in the ring, occurs about the bond through which the two-fold axis passes.

Examination of the torsion angles found for (I), see Figure, clearly shows that both rings have adopted the half-chair conformation. Further, roughly the same distortion is present in either ring and the molecule contains, as far as the two rings are concerned, an approximate plane of symmetry; this plane contains the bridgehead carbon atoms C(1) and C(5) and the methyl groups attached thereto.

These findings contrast with earlier determinations of simple lactones and those in which the lactone ring is *cis* fused; in these cases the conformation has been described as envelope.[5]

The considerable distortion from planarity reduces the

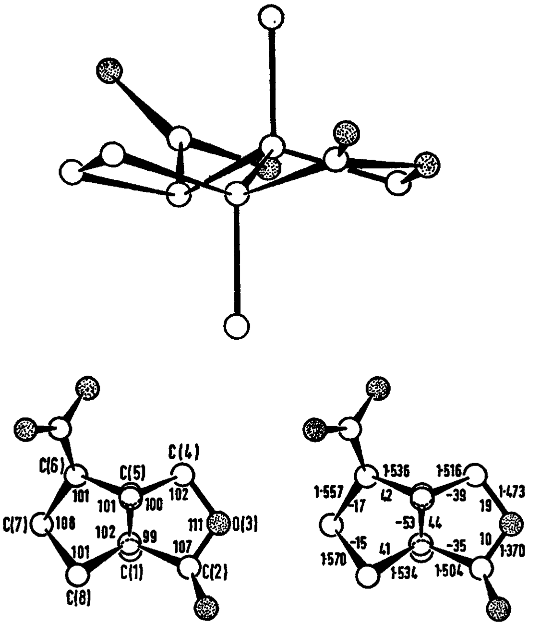
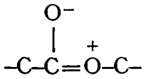


FIGURE. (*Top*) *Perspective view of both rings in half-chair conformation.* (*Lower left*) *Numbering scheme and bond angles and* (*lower right*) *bond lengths and torsion angles. The length* C(1)–C(5) *is* 1·538 Å. *The e.s.d. of a bond length is* ca. 0·008 Å.

mean bond angles in the five-membered rings from 108° to 102·5 and 103·7°, the lactone ring having the larger value. It is, however, still smaller than the averages (*ca.* 105—106°) previously quoted.[5] The largest individual angles are at C(7) and O(3) respectively. That at C(2) is larger than any of the other seven presumably because of the lower *p*-character associated with this atom. Even so, this angle is just smaller than that subtended at C(7). Of the four tetrahedral angles at each bridgehead carbon atom, three are near normal and hence almost the whole of the remaining angle deformation occurs at C(4)–C(5)–C(6) and at C(2)–C(1)–C(8), 125 and 128° respectively.

By comparison, the C_5 ring conforms to the half-chair form rather better than does the lactone ring. The observed bond shortening of C(2)–O(3) in comparison with C(4)–O(3), 1·37 *vs.* 1·47 Å, indicates some participation of the structure  $\overset{O^-}{\overset{|}{-C-C}}\overset{+}{=}O-C-$, which in the extreme would lead to a zero torsion angle about C(1)–C(2)–O(3)–C(4) and to the envelope form. In (I) coplanarity does not occur but, by comparison with the C_5 ring, it seems that participation is sufficient to reduce the torsion angle in the lactone ring by some 5°. Thus whilst the bond shortening is similar to that in earlier reported γ-lactones,[5] this effect, by itself, is insufficient to determine the conformation of the ring.

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