

## Atomic charges of cerbinal

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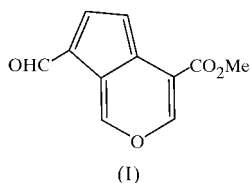
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The molecule of the title compound, methyl 1-formyl-6-oxa-6*H*-indene-4-carboxylate, C<sub>11</sub>H<sub>8</sub>O<sub>4</sub>, is planar. There are weak C—H···O intramolecular interactions and an intermolecular hydrogen bond in the structure, and these influence the crystal packing.

## Comment

Plants of the *Cerbera* species are distributed widely in the coastal areas of Southeast Asia and countries surrounding the Indian Ocean. Several research groups have previously isolated various groups of compounds from *Cerbera odollam* and *Cerbera manghas*, such as cardenolide glycosides, lignans and normonoterpenoids (Abe *et al.*, 1977, 1988*a,b*, 1989; Mahran *et al.*, 1972; Malathy & Krishnamoorthy, 1978; Li *et al.*, 1981; Rao, 1973; Rao *et al.*, 1974; Yamauchi *et al.*, 1987). Previously, cerbinal, a yellow compound having an iridoid skeleton, was reported as being isolated from the bark of *Cerbera manghas* (Abe *et al.*, 1977) and was identified by spectroscopic methods, but there is no information about its bioactivity. Recently, our group isolated cerbinal from the bark of *Cerbera odollam*. Preliminary testing against mycobacterium tuberculosis and breast-cancer cells exhibited moderate bioactivity.



The NMR spectrum and a resonance-theory prediction for the title compound, (I), suggested that the planarity of the molecule would allow electron delocalization from the ring O atom towards the five-membered ring. The planarity of the molecule was confirmed by the present structure determination. The electron delocalization was also confirmed by a theoretical calculation of the charge distribution using a PC

version of *MOPAC97* (Stewart, 1997), with an *AM1* set of parameters. Full optimization of the ground-state gas-phase structure gives the results presented in Fig. 1. The dipole is directed from C4 towards, but slightly below, C5. This molecule might be useful as a simple model for stereoselectivity studies and as a starting material in other syntheses.

The title compound (Fig. 2) has a planar aromatic structure, with a highly conjugated  $\pi$  system. The bond lengths and angles (Table 1) show normal values (Allen *et al.*, 1987); C1—C2 and C3—C4 show double-bond character. The fused five-membered and pyran rings are planar, with a maximum deviation for the C2 atom of 0.007 (3) Å. The mean plane through the fused five-membered ring forms a dihedral angle of 0.08 (16)° with the mean plane of the pyran ring. The methoxycarbonyl and formyl groups are coplanar with their attached rings [C4—C10—O4—C11 = 179.1 (3)° and C7—C8—C9—O1 = 179.5 (3)°]. Two weak intramolecular C—H···O interactions form O4—C10—C4—C3—H3A and O2—C10—C4—C5—C6—H6A closed rings. The O atoms of the methoxycarbonyl group are involved in these weak intramolecular interactions; C3—H3A···O4 (H3A···O4 = 2.33 Å and C3—H3A···O4 = 103°) and C6—H6A···O2 (H6A···O2 = 2.57 Å and C6—H6A···O2 = 109°), whereas the O atom of the formyl group is involved in an intermolecular hydrogen bond (Table 2). In addition, two intermolecular  $\pi$ — $\pi$  interactions between the centroids of the five- and six-membered rings, *i.e.* Cg1 and Cg2, respectively, were also observed; Cg1···Cg2<sup>ii</sup> =

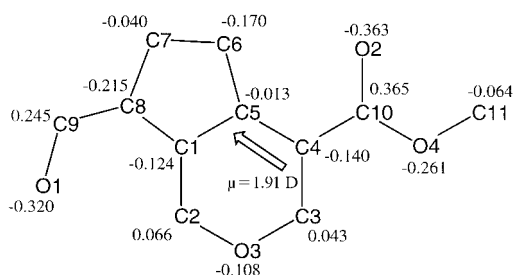


Figure 1

The *MOPAC97*-calculated (Stewart, 1997) charge distribution on the title compound. The direction of the calculated dipole moment (1.91 D) is indicated by the arrow.

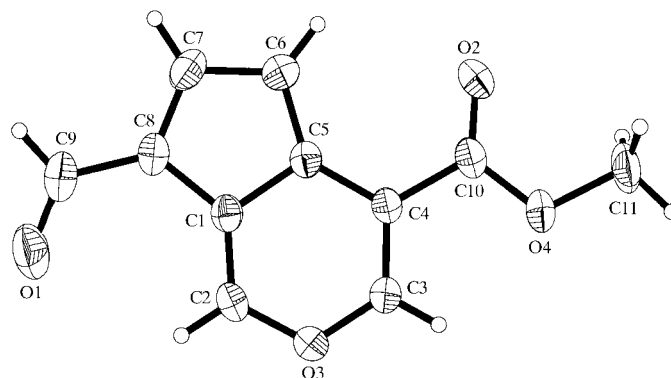
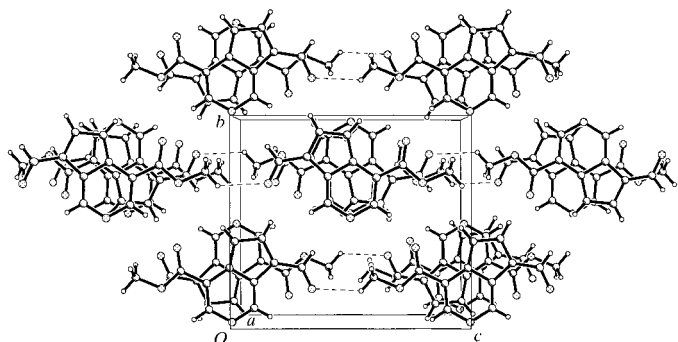


Figure 2

The structure of the title compound, showing 50% probability displacement ellipsoids and the atom-numbering scheme.

3.571 Å and  $Cg1 \cdots Cg2^{iii} = 3.575$  Å [symmetry codes: (ii)  $-1 - x, \frac{1}{2} + y, \frac{3}{2} - z$ ; (iii)  $-x, \frac{1}{2} + y, \frac{3}{2} - z$ ]. The existence of these  $\pi$ - $\pi$  interactions indicates that the title compound is a charge-transfer complex. The intermolecular C—H $\cdots$ O interactions interconnect the molecules into infinite molecular ribbons along the  $c$  axis and these ribbons are stacked along the  $a$  axis (Fig. 3). All these interactions, as well as van der Waals interactions, stabilize the molecular and non-centrosymmetric packing structure in the crystal.



**Figure 3**  
Packing diagram of the title compound viewed down the  $a$  axis. Hydrogen bonds are represented by dashed lines.

## Experimental

The air-dried bark of *Cerbera odollam* (1.50 kg) was ground and extracted by soaking it in hexane (25 l) for 5 d at room temperature. The mixture was filtered and concentrated under reduced pressure to give the crude extracts. Upon concentration under reduced pressure, the hexane extract yielded precipitates which were filtered off and recrystallized from  $CHCl_3$  to yield yellow needle-shaped crystals of compound (I) (m.p. 449–451 K).

### Crystal data

$C_{11}H_8O_4$	Mo $K\alpha$ radiation
$M_r = 204.17$	Cell parameters from 3144 reflections
Orthorhombic, $P2_12_12_1$	
$a = 6.8622$ (2) Å	$\theta = 2.5$ – $28.3^\circ$
$b = 10.8244$ (1) Å	$\mu = 0.11$ mm $^{-1}$
$c = 12.3446$ (3) Å	$T = 293$ (2) K
$V = 916.95$ (4) Å $^3$	Needle, yellow
$Z = 4$	$0.46 \times 0.16 \times 0.14$ mm
$D_x = 1.479$ Mg m $^{-3}$	

### Data collection

Siemens SMART CCD area-detector diffractometer	$R_{int} = 0.083$
$\omega$ scans	$\theta_{max} = 28.3^\circ$
6418 measured reflections	$h = -9 \rightarrow 8$
1323 independent reflections	$k = -13 \rightarrow 14$
900 reflections with $I > 2\sigma(I)$	$l = -16 \rightarrow 11$
	Intensity decay: none

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0799P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.056$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.145$	$(\Delta/\sigma)_{max} = 0.036$
$S = 1.01$	$\Delta\rho_{max} = 0.35$ e Å $^{-3}$
1323 reflections	$\Delta\rho_{min} = -0.45$ e Å $^{-3}$
138 parameters	Extinction correction: <i>SHELXL97</i>
H-atom parameters constrained	Extinction coefficient: 0.015 (5)

**Table 1**

Selected geometric parameters (Å, °).

O1—C9	1.217 (4)	O4—C10	1.336 (4)
O2—C10	1.210 (3)	O4—C11	1.457 (4)
O3—C2	1.359 (3)	C1—C2	1.344 (4)
O3—C3	1.361 (3)	C3—C4	1.359 (4)
C2—O3—C3	119.2 (2)	O1—C9—C8	125.1 (3)
C10—O4—C11	115.9 (2)		

**Table 2**

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C11—H11A $\cdots$ O1 <sup>i</sup>	0.96	2.57	3.262 (3)	130

Symmetry code: (i)  $x, y, 1 + z$ .

H atoms were treated as riding, with C—H distances of 0.93 and 0.96 Å.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1345). Services for accessing these data are described at the back of the journal.

## References

- Abe, F., Okaru, H. & Yamauchi, H. (1977). *Chem. Pharm. Bull.* **25**, 3422–3424.
- Abe, F., Yamauchi, T. & Wan, A. S. C. (1988a). *Phytochemistry*, **27**, 2627–2631.
- Abe, F., Yamauchi, T. & Wan, A. S. C. (1988b). *Chem. Pharm. Bull.* **36**, 795–759.
- Abe, F., Yamauchi, T. & Wan, A. S. C. (1989). *Chem. Pharm. Bull.* **37**, 2639–2642.
- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
- Li, R., Wang, Y. & Chen, Y. (1981). *Acta Pharm. Sin.* **16**, 361–365.
- Mahran, G. H., Abdel-Wahab, S. M. & Shoka, A. A. (1972). *Egypt. J. Pharm. Sci.* **13**, 309–319.
- Malathy, K. & Krishnamoorthy, A. J. (1978). *J. Chromatogr.* **152**, 592–594.
- Rao, E. V. (1973). *Indian J. Pharm.* **35**, 107–113.
- Rao, E. V., Sastry, B. S. & Narayanan, M. N. (1974). *Indian J. Pharm.* **36**, 75–76.
- Sheldrick, G. M. (1997). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
- Siemens (1996). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Spek, A. L. (1990). *Acta Cryst.* **A46**, C-34.
- Stewart, J. J. P. (1997). *MOPAC97*. Fujitsu Ltd, Japan.
- Yamauchi, T., Abe, F. & Wan, A. S. C. (1987). *Chem. Pharm. Bull.* **35**, 2744–2749.