

used to solve structure: *SHELXTL* (Sheldrick, 1996). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*, *PARST* (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HA1221). Services for accessing these data are described at the back of the journal.

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## Fibleucin from *Fibraurea chloroleuca* Miers

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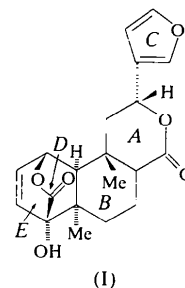
## Abstract

In the title compound, 9-(3-furyl)-1,4,4a,5,9,10,10a,10b-octahydro-4-hydroxy-4a,10a-dimethyl-1,4-etheno-3*H*,7*H*-benzo[1,2-*c*:3,4-*c'*]dipyran-3,7-dione, C<sub>20</sub>H<sub>20</sub>O<sub>6</sub>, the pyran ring adopts a conformation intermediate between sofa and half-chair. All other six-membered rings are in the boat conformation. The furan ring is planar and is

equatorially attached. The crystal structure is stabilized by O—H···O and C—H···O intermolecular hydrogen bonds.

## Comment

The title compound, (I), was first isolated from the plant *Fibraurea chloroleuca* Miers and identified by Ito & Furukawa (1969). It had been located in a crude methanol extract a few years earlier and it was found to possess antitumour and antifungal activity (Nakanishi *et al.*, 1965). The present X-ray structure determination was carried out in order to elucidate the molecular conformation.



Most of the bond lengths and angles in the structure agree with those observed in the epoxy derivative of this compound, (–)-fibrarin (Dampawan *et al.*, 1986). The fused rings, A and B, and the six-membered rings, D and E, formed by the lactone bridge, all adopt the boat conformation. Ring C is in a conformation which is intermediate between half-chair and sofa,

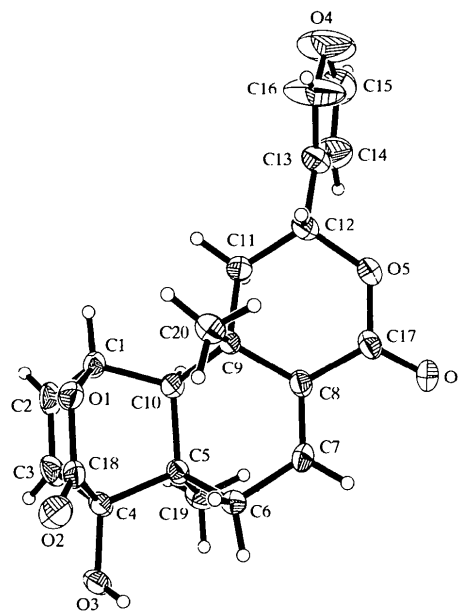


Fig. 1. The structure of the title compound, showing 30% probability displacement ellipsoids and the atom-numbering scheme.

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with asymmetry parameters  $\Delta C_5(\text{C11}) = 0.062(2)$  and  $\Delta C_2(\text{C8—C17}) = 0.062(2)$  (Nardelli, 1983). The A/B ring junction is *cis*. The furan ring is planar and is attached equatorially to ring C. The furan plane is twisted by 74.6(2) Å from the mean plane through ring C. The angles between the plane of the four-atom bridge C1—O1—C18—C4 and each of the four-atom planes of the boat-shaped six-membered rings (C1—C2—C3—C4 and C1—C10—C5—C4) are 58.3(2) and 61.8(2), respectively. The hydroxyl group is involved in an O—H···O inter-molecular hydrogen bond with the lactone bridge O atom. The crystal structure is stabilized by this, and by C—H···O intermolecular hydrogen bonds (Table 2).

## Experimental

Dried roots (4 kg) of *Fibraurea chloroleuca* Miers, collected from the vicinity of the Marine Research Station, Universiti Sains Malaysia, were extracted with benzene for 9 h. Crude crystals were obtained after concentration of the benzene extract. Recrystallization from methanol gave a mixture of fibleucin and the epoxidized derivative, fibraurin, which were separated by gradient column chromatography on silica gel with a mixture of chloroform and methanol. Recrystallization of the separated (–)-fibleucin,  $[\alpha]_D^{20} -11^\circ$  (c 0.2 pyridine) from ethyl acetate gave the crystals used in this X-ray study (m.p. 456–458 K). (–)-Fibraurin was obtained pure by further recrystallization from methanol.

### Crystal data

C <sub>20</sub> H <sub>20</sub> O <sub>6</sub>	Mo K $\alpha$ radiation
$M_r = 356.36$	$\lambda = 0.71073 \text{ \AA}$
Orthorhombic	Cell parameters from 40 reflections
$P2_12_12_1$	$\theta = 5.41\text{--}12.53^\circ$
$a = 7.2694(11) \text{ \AA}$	$\mu = 0.100 \text{ mm}^{-1}$
$b = 9.649(2) \text{ \AA}$	$T = 293(2) \text{ K}$
$c = 25.045(4) \text{ \AA}$	Block
$V = 1756.7(5) \text{ \AA}^3$	$0.58 \times 0.36 \times 0.30 \text{ mm}$
$Z = 4$	Colourless
$D_x = 1.347 \text{ Mg m}^{-3}$	
$D_m$ not measured	

### Data collection

Siemens P4 diffractometer	$\theta_{\max} = 27.49^\circ$
$\theta/2\theta$ scans	$h = -1 \rightarrow 9$
Absorption correction: none	$k = -1 \rightarrow 12$
3068 measured reflections	$l = -1 \rightarrow 32$
2854 independent reflections	3 standard reflections
1720 reflections with $I > 2\sigma(I)$	every 97 reflections
$R_{\text{int}} = 0.026$	intensity decay: < 3%

### Refinement

Refinement on $F^2$	$\Delta\rho_{\max} = 0.618 \text{ e \AA}^{-3}$
$R[F^2 > 2\sigma(F^2)] = 0.053$	$\Delta\rho_{\min} = -0.213 \text{ e \AA}^{-3}$
$wR(F^2) = 0.142$	Extinction correction:
$S = 0.912$	<i>SHELXL93</i>
2854 reflections	Extinction coefficient:
238 parameters	0.0052(18)

H atoms: see text  
 $w = 1/[\sigma^2(F_o^2) + (0.0791P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$

Scattering factors from  
*International Tables for  
 Crystallography* (Vol. C)

Table 1. Selected bond lengths (Å)

O1—C18	1.358(4)	C5—C19	1.525(5)
O1—C1	1.489(4)	C5—C6	1.538(5)
O2—C18	1.203(4)	C5—C10	1.566(5)
O3—C4	1.402(4)	C6—C7	1.498(5)
O4—C15	1.341(8)	C7—C8	1.327(5)
O4—C16	1.363(8)	C8—C17	1.492(4)
O5—C17	1.341(4)	C8—C9	1.520(5)
O5—C12	1.469(4)	C9—C11	1.531(5)
O6—C17	1.214(4)	C9—C20	1.550(5)
C1—C2	1.486(6)	C9—C10	1.554(5)
C1—C10	1.542(5)	C11—C12	1.512(5)
C2—C3	1.335(6)	C12—C13	1.499(5)
C3—C4	1.517(5)	C13—C16	1.326(7)
C4—C18	1.512(5)	C13—C14	1.371(6)
C4—C5	1.579(4)	C14—C15	1.329(7)

Table 2. Hydrogen-bonding geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3A···O1 <sup>i</sup>	0.820(4)	2.095(4)	2.885(4)	161.7(3)
C2—H2A···O3 <sup>ii</sup>	0.931(6)	2.485(6)	3.279(6)	143.4(5)

Symmetry codes: (i)  $2 - x, \frac{1}{2} + y, \frac{3}{2} - z$ ; (ii)  $1 - x, y - \frac{1}{2}, \frac{3}{2} - z$ .

The structure was solved by direct methods and refined by full-matrix least-squares techniques. Though the H atoms were located from a difference Fourier map, they were fixed and allowed to ride on the atoms to which they are attached. Since the absolute structure cannot be determined reliably, a configuration similar to that of (–)-fibraurin was used for the refinement. Both fibleucin and fibraurin were isolated from the same plant and the absolute configuration of fibraurin has already been established by Dampawan *et al.* (1986). The postulated biogenetic relationship between fibleucin and fibraurin suggests that the absolute configuration may be that depicted here.

Data collection: XSCANS (Siemens, 1994). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXTL/PC (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: SHELXTL/PC. Software used to prepare material for publication: SHELXL93 and PARST (Nardelli, 1995).

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### (±)-*cis*-10-Carboxymethyl-2-decalone: Catemeric Hydrogen Bonding in an $\epsilon$ -Keto Acid

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#### Abstract

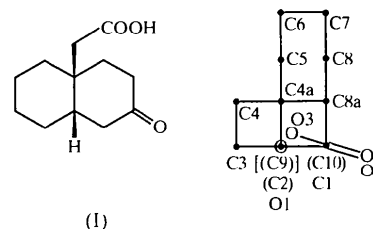
The crystal structure of the title compound, (±)-*cis*-2-oxoperhydronaphthalene-4a-acetic acid, C<sub>12</sub>H<sub>18</sub>O<sub>3</sub>, involves hydrogen-bonding catemers. Hydrogen bonds progress from the carboxyl group of one molecule to the ketone group of a translationally related neighbor [O...O 2.715 (3) Å]. Eight parallel hydrogen-bonding chains proceed in the *a* direction through the chosen cell. Two C=O...H—C close contacts were found, involving the acid carbonyl group.

#### Comment

Our continuing interest in the crystal structures of keto carboxylic acids lies in the elucidation of their hydrogen-bonding behavior, which is more elaborate than in unadorned acids. Most often, the ketone fails to participate in the hydrogen bonding, giving typical carboxyl dimers, but less commonly, intermolecular carboxyl-to-ketone hydrogen bonds occur, yielding a catemer. A third, rare arrangement has an internal hydrogen bond, and instances are known of acid-to-ketone dimerization and acid-to-acid catemerization, while several cases are known of hydrates with more complex hydrogen-bonding patterns. We have previously referenced and discussed numerous examples of these hydrogen-bonding modes (Thompson *et al.*, 1992, 1998; Coté *et al.*, 1996; Lalancette *et al.*, 1998). To denote the handed-

ness of the intrachain units, we have further categorized such catemers as either hetero- or homochiral, and the latter grouping contains subcategories for screw-related and translational types. Most of the previously reported keto-acid catemers have screw-related components, but a sizable minority are translational. In addition to these necessarily homochiral catemer types, a small minority display a glide relationship between adjacent members and are thus heterochiral (Thompson *et al.*, 1998).

The title compound, (I), is an  $\epsilon$ -keto acid, a category that includes dimers and at least one instance each of an internal hydrogen bond and a carboxyl-to-ketone catemer [refcodes KENROK (Abell *et al.*, 1990) and FAXWOQ (Vanderhoff *et al.*, 1986), respectively; Cambridge Structural Database, 1998]. Compound (I) was of interest to us as a one-carbon homolog of a dimerically hydrogen-bonded keto acid whose structure and hydrogen-bonding behavior we had previously reported (Lalancette *et al.*, 1991). Our experience has led us often to anticipate similar hydrogen-bonding behavior among structurally similar compounds, especially in certain small cyclic or polycyclic systems with specific skeletal features, including some present in (I). We report here that (I), rather than dimerizing, forms carboxyl-to-ketone catemers.



The asymmetric unit of (I) with its numbering is shown in Fig. 1. The decalone system crystallizes in the 'non-steroidal' conformation, in which the angular substituent is axial to the ketone ring, as has been found in some similar angularly substituted decalone acids [refcodes VILZIZ (Lalancette *et al.*, 1991) and OCBDCX (Chadwick & Dunitz, 1979); Cambridge Structural Database, 1998]. The only options available for full rotation in (I) involve bonds C4a—C9 and C9—C10. The former adopts a staggered arrangement, with C9—C10 *anti* to C4—C4a, while the carboxyl is rotated about C9—C10 so that it lies in a plane close to that of the ketone [dihedral angle C1/C2/C3/O1 *versus* C9/C10/O2/O3 is 16.7 (1)°], with the carboxyl C=O aimed toward the ketone. The result is a linear-opposed arrangement of ketone O=C and carboxyl C—O or O—H, of the sort that often allows the formation of translational catemers (Lalancette *et al.*, 1997; Brunskill *et al.*, 1997). This spatial arrangement is shown formally in the 'octant-rule' depiction of the conformation (Moffitt *et al.*, 1961), alongside the usual schematic structure for (I). An alignment normal to *c*,