

H atoms treated by a mixture of independent and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.0449P)^2 + 0.2161P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$

Scattering factors from *International Tables for Crystallography* (Vol. C)  
 Absolute structure: Flack (1983)  
 Flack parameter = 0.3 (6)

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## $\Delta^{8,9}$ -Decarboxyfibleucin from *Fibraurea chloroleuca* Miers

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The data collection nominally covered a sphere of reciprocal space by a combination of seven sets of exposures; each set had a different  $\varphi$  angle for the crystal and each exposure covered 0.3° in  $\omega$ . The crystal-to-detector distance was 4.5 cm. Coverage of the unique set is 100% complete to at least 28° in  $\theta$ . Crystal decay was monitored by repeating the initial frames at the end of data collection and analysing the duplicate reflections. H atoms were located by difference Fourier synthesis and refined with fixed individual displacement parameters [ $U(H) = 1.2U_{\text{eq}}(C)$ ] using a riding model with C—H(tertiary) = 1.00, C—H(secondary) = 0.99 or  $Csp^2$ —H = 0.95 Å. The structure contains only C, H and O atoms and since Mo  $K\alpha$  radiation was used, the absolute structure could not be determined.

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SMART*. Data reduction: *SAINT* (Siemens, 1995). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *XP (SHELXTL-Plus)*; Sheldrick, 1991).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: HA1235). Services for accessing these data are described at the back of the journal.

### Abstract

In the title compound, 2-(3-furyl)-1,4,6,6a,7,10,10a,10b-octahydro-6a,10b-dimethyl-2*H*-naphtho[2,1-*c*]pyran-7,4-dione, C<sub>19</sub>H<sub>20</sub>O<sub>4</sub>, one of the fused cyclohexane rings adopts a half-chair conformation and the other a sofa conformation. The conformation of the pyran ring is intermediate between sofa and half-chair. Screw-related molecules along the *c* axis form an infinite one-dimensional chain.

### Comment

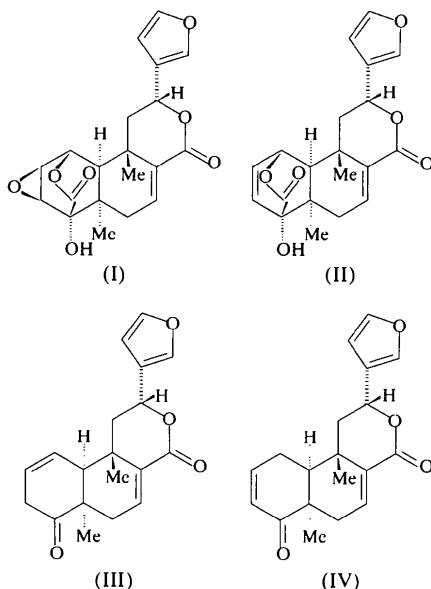
The compounds fibraurin, (I), and fibleucin, (II), isolated from the medicinal plant *Fibraurea chloroleuca* Miers (Ito & Furukawa, 1969), have been found to possess antitumour and antifungal activities (Nakanishi *et al.*, 1965). We wished to prepare derivatives from both of them, which might be more water soluble and exhibit enhanced antifungal activity. Opening either of the lactone rings in these compounds seemed like a reasonable option. However, attempted transesterification of the mixture with titanium tetraisopropoxide as the catalyst (Seebach *et al.*, 1982) indicated that fibleucin alone was slowly and poorly transformed into two products. Preliminary gas chromatography–mass spectrometry studies indicated that both these products were decarboxylated fibleucin. Currently, there is only one report in the literature of decarboxylation of a similar compound, namely, columbin to decarboxycolumbin (Barton & Elad, 1956). Decarboxylation of fibleucin, but not of fibraurin, was subsequently found to proceed smoothly and completely in boiling xylene. This reaction allowed the facile separation of fibraurin from a mixture of fibraurin and fibleucin. The products were easily isolated by thin layer chromatography. The major product from the decarboxylation of fibleucin was shown by spectroscopic studies to be  $\Delta^{9,10}$ -decarboxy-

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fibleucin, (III). The minor compound, (IV), is the subject of this paper.



The majority of the bond lengths and angles in the structure of (IV) are comparable with those observed in (–)-fibraurin [(I); Dampawan *et al.*, 1986] and fibleucin [(II); Bakhari *et al.*, 1998]. However, ring A (C1–C5 and C10) adopts a half-chair conformation in (IV), instead of the boat conformation observed in fibraurin and fibleucin, which have the lactone bridge. Ring B (C5–C10) adopts a sofa conformation, whereas ring C (C8, C9, C11, C12, O3 and C17) is in a conformation which is intermediate between sofa and half-chair, with asymmetry parameters  $\Delta C_1(C11) = 0.051(1)$  and  $\Delta C_2(C11-C9) = 0.068(1)$  (Nardelli, 1983). The planar

furan ring is attached equatorially to ring C and is twisted  $44.65(10)^\circ$  from the mean plane through ring C. The mean plane through ring B forms dihedral angles of  $55.18(8)$  and  $11.80(8)^\circ$  with those through rings A and C, respectively. The A/B ring junction is *cis*. Along the *c* axis, the screw-related molecules are linked by C—H...O intermolecular hydrogen bonds to form an infinite one-dimensional chain (Table 2).

## Experimental

A mixture of fibleucin and its epoxidized derivative, fibraurin, obtained from benzene extracts of the roots and stems of *Fibraurea chloroleuca* Miers (240 mg) was refluxed under nitrogen in dry *o*-xylene for 12 h. At the end of the reflux, the solvent was removed under reduced pressure. The residue was separated by preparative thin layer chromatography on silica gel with a chloroform/ethanol mixture (99:1), to give the major product and less polar component ( $R_f = 0.7$ ),  $\Delta^{8,9,10}$ -decarboxyfibleucin, the minor product,  $\Delta^{8,9}$ -decarboxyfibleucin ( $R_f = 0.6$ ) and unchanged fibraurin. Recrystallization of the minor product from methanol yielded the sample crystal.

### Crystal data

$C_{19}H_{20}O_4$   
 $M_r = 312.35$   
 Orthorhombic  
 $P2_12_12_1$   
 $a = 6.1925(1) \text{ \AA}$   
 $b = 10.2272(3) \text{ \AA}$   
 $c = 24.8189(6) \text{ \AA}$   
 $V = 1571.83(6) \text{ \AA}^3$   
 $Z = 4$   
 $D_x = 1.316 \text{ Mg m}^{-3}$   
 $D_m$  not measured

Mo  $K\alpha$  radiation  
 $\lambda = 0.71073 \text{ \AA}$   
 Cell parameters from 4074 reflections  
 $\theta = 3.17\text{--}27.49^\circ$   
 $\mu = 0.092 \text{ mm}^{-1}$   
 $T = 293(2) \text{ K}$   
 Plate  
 $0.54 \times 0.32 \times 0.20 \text{ mm}$   
 Colourless

### Data collection

Siemens SMART CCD area-detector diffractometer  
 $\omega$  scans  
 Absorption correction: none  
 10 434 measured reflections  
 3601 independent reflections

2504 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.034$   
 $\theta_{\text{max}} = 27.49^\circ$   
 $h = -8 \rightarrow 8$   
 $k = 0 \rightarrow 13$   
 $l = 0 \rightarrow 32$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.054$   
 $wR(F^2) = 0.113$   
 $S = 1.086$   
 3601 reflections  
 209 parameters  
 H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0322P)^2 + 0.2915P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$

$\Delta\rho_{\text{max}} = 0.167 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.121 \text{ e \AA}^{-3}$   
 Extinction correction: SHELXTL (Sheldrick, 1996)  
 Extinction coefficient: 0.0031(10)  
 Scattering factors from *International Tables for Crystallography* (Vol. C)

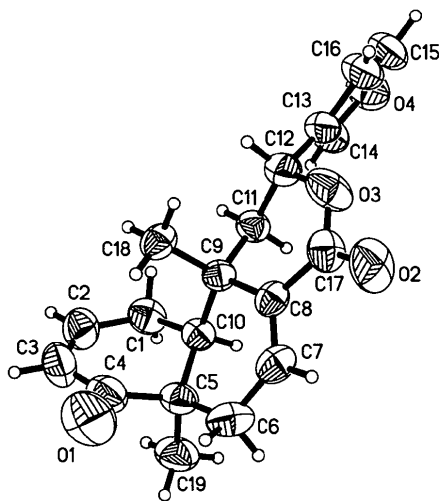


Fig. 1. The structure of the title compound, showing 50% probability displacement ellipsoids and the atom-numbering scheme.

Table 1. Selected bond lengths (Å)

O1—C4	1.214 (3)	C2—C3	1.348 (4)
O2—C17	1.208 (3)	C3—C4	1.455 (4)
O3—C17	1.339 (3)	C4—C5	1.527 (4)
O3—C12	1.459 (3)	C6—C7	1.472 (3)
O4—C15	1.360 (4)	C7—C8	1.329 (3)
O4—C14	1.366 (3)	C13—C14	1.345 (4)
C1—C2	1.457 (4)	C13—C16	1.428 (4)
C1—C10	1.534 (3)	C15—C16	1.319 (5)

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

D—H...A	D—H	H...A	D...A	D—H...A
C15—H...O1 <sup>1</sup>	0.93	2.45	3.226 (4)	141

Symmetry code: (i)  $-\frac{1}{2} - x, -y, \frac{1}{2} + z$ .

The data collection covered over a hemisphere of reciprocal space by a combination of three sets of exposures; each set had a different  $\varphi$  angle (0, 88 and 180°) for the crystal and each exposure of 30 s covered 0.3° in  $\omega$ . The crystal-to-detector distance was 4 cm and the detector swing angle was -35°. Coverage of the unique set is over 99% complete. Crystal decay was monitored by repeating thirty initial frames at the end of data collection and analysing the duplicate reflections, and was found to be negligible. The structure was solved by direct methods and refined by full-matrix least-squares techniques. Though all H atoms were located from a difference Fourier map, due to the low ratio of reflections to parameters they were fixed and allowed to ride on the atoms to which they are attached. Since the absolute structure cannot be reliably determined, a configuration similar to fibraurin was used for the refinement. Fibraurin was isolated from the same plant and its absolute configuration was established by Dampawan *et al.* (1986). The postulated biogenetic relationship suggests that the absolute configuration may be that depicted here.

Data collection: SMART (Siemens, 1996). Cell refinement: SAINT (Siemens, 1996). Data reduction: SAINT. Program(s) 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 and PARST (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HA1236). Services for accessing these data are described at the back of the journal.

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## 1,4-Bis[4-(1-pyridinium)styryl]benzene ditosylate

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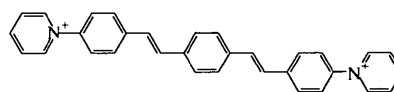
(Received 26 May 1998; accepted 28 September 1998)

## Abstract

The crystal structure of the title compound {alternative name: 1,1'-[*p*-phenylenebis(4-styryl)]dipyridinium ditosylate}, C<sub>32</sub>H<sub>26</sub>N<sub>2</sub><sup>2+</sup>·2C<sub>7</sub>H<sub>7</sub>O<sub>3</sub>S<sup>-</sup>, provides an energy-minimum conformation which can be related to its DNA-binding properties.

## Comment

The title cation (Auckland Cancer Laboratory synthesis number SN 18071) has been shown in assays to bind weakly in the minor groove of DNA, being totally released from the groove by competitive netropsin binding (Luck *et al.*, 1987). It has been shown to stabilize triplex DNA (Fortsch *et al.*, 1996) and also to inhibit the action of restriction endonucleases by binding in specific four or six base-pair DNA sequences (Kittler *et al.*, 1996).



SN 18071

Cocrystallization experiments of SN 18071 with DNA oligonucleotides were undertaken to characterize the minor-groove binding. These experiments showed the binding to be weak and disordered (Clark & Squire,