

Lists of structure factors, anisotropic thermal parameters and H-atom coordinates, together with a packing diagram, have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55171 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL1009]

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Methyl 1,2,4,5,6,10b-Hexahydro-8,9-methylenedioxy-2-oxobenzo[d]cyclopenta[b]azepine-4-carboxylate

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Abstract

The title compound contains the tetracyclic *A-B-C-E* ring system of *cephalotaxus* alkaloids. Unexpectedly, the five-membered-ring plane is twisted 67.2° from the aromatic ring plane and, like *cephalotaxine*, the seven-membered ring is oriented in a boat form with the nitrogen at the prow.

Comment

The title compound was synthesized as a key intermediate in studies of the total synthesis of the antileukemic agents harringtonine and homoharringtonine (Powell, Weisleder & Smith, 1972), the natural esters of *cephalotaxine*. Structures of the related alkaloid (Arora, Bates, Grady, Ger-

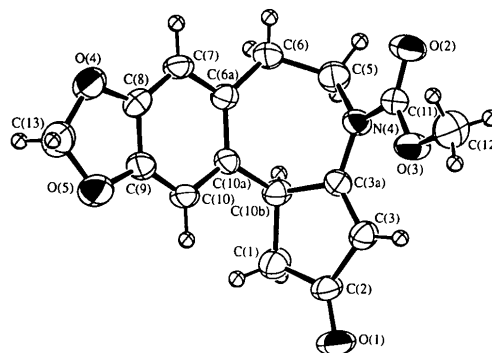


Fig. 1. Molecular configuration and atom-numbering scheme with thermal ellipsoids at the 50% probability level. H atoms are shown as unlabeled isotropic spheres with B values of 1.0 \AA^2 .

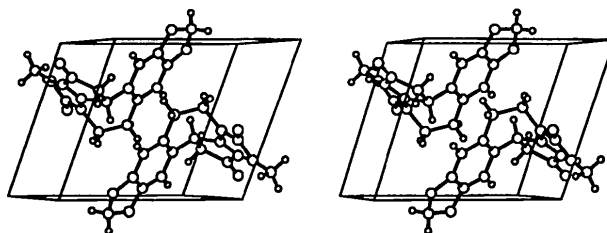
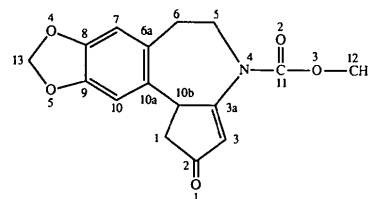


Fig. 2. Stereoscopic illustration of the molecular packing. The origin is at the lower-left-back corner, a is vertical, c is horizontal and b is out of the plane of the paper.

main, Declercq & Powell, 1976), its *p*-bromobenzoate (Arora, Bates, Grady & Powell, 1974) and its methiodide (Abraham, Rosenstein & McGandy, 1969) have been reported. The present study firmly establishes the structure of the synthetic compound and identifies the boat conformation of the seven-membered ring, a salient feature of the *cephalotaxus* alkaloids.

The title compound (1) was synthesized from the cyclization of methyl *N*-[2-(2-iodo-4,5-methylenedioxyphenyl)ethyl]-*N*-(3-oxo-1-cyclopentyl)carbamate [palladium acetate (catalytic amount), tri-*o*-tolylphosphine and triethylamine in acetonitrile (Hong, 1991)] followed by regioselective dehydrogenation [benzeneselenenyl chloride in ethyl acetate (Sharpless, Lauer & Teranishi, 1973)] and oxidation (hydrogen peroxide in tetrahydrofuran). M.p. 451–453 K (recrystallized from ether-hexane).



Experimental

Crystal data

$C_{16}H_{15}NO_5$
 $M_r = 301.30$

$D_x = 1.481 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation

Triclinic	$\lambda = 0.71069 \text{ \AA}$
$P\bar{1}$	Cell parameters from 17 reflections
$a = 8.810 (2) \text{ \AA}$	$\theta = 13.5\text{--}19^\circ$
$b = 9.231 (3) \text{ \AA}$	$\mu = 1.04 \text{ cm}^{-1}$
$c = 9.340 (2) \text{ \AA}$	$T = 296 \text{ K}$
$\alpha = 84.48 (2)^\circ$	Multifaceted
$\beta = 75.88 (2)^\circ$	$0.25 \times 0.16 \times 0.11 \text{ mm}$
$\gamma = 66.49 (2)^\circ$	Yellow
$V = 675.5 (7) \text{ \AA}^3$	
$Z = 2$	
Data collection	
Rigaku AFC5S diffractometer	$R_{\text{int}} = 0.021$
$\omega/2\theta$ scans	$\theta_{\text{max}} = 25^\circ$
Absorption correction: none	$h = -9 \rightarrow 10$
2533 measured reflections	$k = 0 \rightarrow 10$
2371 independent reflections	$l = -11 \rightarrow 11$
1139 observed reflections [$I > 2\sigma(I)$]	3 standard reflections monitored every 100 reflections
	intensity variation: -0.1%

Refinement

Refinement on F	$\Delta\rho_{\text{min}} = -0.19 \text{ e \AA}^{-3}$
Final $R = 0.049$	Extinction correction: Zachariassen type 2 Gaussian isotropic
$wR = 0.047$	Extinction coefficient: $0.1 (4) \times 10^{-6}$
$S = 1.32$	Atomic scattering factors from <i>International Tables for X-ray Crystallography</i> (1974, Vol. IV, Table 2.3.1)
1139 reflections	
200 parameters	
H-atom parameters not refined	
$w = 4F_o/\sigma^2(F_o^2)$	
$(\Delta/\sigma)_{\text{max}} = 0.0007$	
$\Delta\rho_{\text{max}} = 0.20 \text{ e \AA}^{-3}$	

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN LS*. Molecular graphics: *TEXSAN ORTEP* (Johnson, 1965). Software used to prepare material for publication: *TEXSAN FINISH*.

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2)

$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$				
	x	y	z	U_{eq}
O(1)	0.1417 (4)	0.4821 (4)	1.1106 (3)	0.066 (1)
O(2)	0.4353 (4)	1.0342 (4)	0.8239 (3)	0.061 (1)
O(3)	0.2453 (4)	0.9665 (3)	0.9915 (3)	0.054 (1)
O(4)	0.0407 (4)	0.8815 (4)	0.3167 (3)	0.057 (1)
O(5)	-0.0814 (4)	0.7364 (4)	0.4862 (4)	0.066 (1)
C(1)	0.3109 (6)	0.4453 (5)	0.8599 (5)	0.051 (1)
C(2)	0.2282 (6)	0.5265 (5)	1.0077 (5)	0.044 (1)
C(3)	0.2706 (6)	0.6631 (5)	1.0058 (4)	0.042 (1)
C(3a)	0.3623 (5)	0.6775 (5)	0.8719 (5)	0.035 (1)
N(4)	0.4315 (4)	0.7899 (4)	0.8195 (4)	0.040 (1)
C(5)	0.5773 (6)	0.7436 (6)	0.6905 (5)	0.050 (1)
C(6)	0.5318 (6)	0.7490 (5)	0.5423 (5)	0.047 (1)
C(6a)	0.3677 (5)	0.7362 (5)	0.5391 (4)	0.035 (1)
C(7)	0.2877 (6)	0.8195 (5)	0.4254 (5)	0.042 (1)
C(8)	0.1403 (6)	0.8090 (5)	0.4167 (5)	0.040 (1)
C(9)	0.0691 (6)	0.7222 (5)	0.5172 (5)	0.044 (1)

C(10)	0.1402 (6)	0.6418 (5)	0.6283 (5)	0.041 (1)
C(10a)	0.2953 (5)	0.6455 (5)	0.6393 (4)	0.035 (1)
C(10b)	0.3828 (6)	0.5573 (5)	0.7618 (5)	0.041 (1)
C(11)	0.3749 (6)	0.9400 (5)	0.8764 (5)	0.040 (1)
C(12)	0.1740 (7)	1.1204 (6)	1.0581 (5)	0.063 (1)
C(13)	-0.0905 (6)	0.8212 (6)	0.3498 (6)	0.061 (1)

Table 2. Geometric parameters (\AA , $^\circ$)

O(1)—C(2)	1.220 (5)	C(3a)—C(10b)	1.514 (6)
O(2)—C(11)	1.201 (5)	N(4)—C(5)	1.480 (5)
O(3)—C(11)	1.322 (5)	N(4)—C(11)	1.383 (5)
O(3)—C(12)	1.438 (5)	C(5)—C(6)	1.523 (6)
O(4)—C(8)	1.379 (5)	C(6)—C(6a)	1.504 (6)
O(4)—C(13)	1.431 (5)	C(6a)—C(7)	1.411 (6)
O(5)—C(9)	1.379 (5)	C(6a)—C(10a)	1.403 (5)
O(5)—C(13)	1.432 (5)	C(7)—C(8)	1.362 (6)
C(1)—C(2)	1.508 (6)	C(8)—C(9)	1.373 (6)
C(1)—C(10b)	1.538 (5)	C(9)—C(10)	1.348 (6)
C(2)—C(3)	1.448 (5)	C(10)—C(10a)	1.409 (6)
C(3)—C(3a)	1.340 (5)	C(10a)—C(10b)	1.522 (6)
C(3a)—N(4)	1.396 (5)		
C(11)—O(3)—C(12)	116.5 (4)	C(6a)—C(7)—C(8)	118.3 (4)
C(8)—O(4)—C(13)	104.9 (4)	O(4)—C(8)—C(7)	128.0 (4)
C(9)—O(5)—C(13)	105.9 (3)	O(4)—C(8)—C(9)	110.9 (4)
C(2)—C(1)—C(10b)	105.4 (3)	C(7)—C(8)—C(9)	121.1 (4)
O(1)—C(2)—C(1)	125.0 (4)	O(5)—C(9)—C(8)	109.1 (4)
O(1)—C(2)—C(3)	126.6 (4)	O(5)—C(9)—C(10)	128.2 (4)
C(1)—C(2)—C(3)	108.4 (4)	C(8)—C(9)—C(10)	122.7 (5)
C(2)—C(3)—C(3a)	109.5 (4)	C(9)—C(10)—C(10a)	118.2 (4)
C(3)—C(3a)—N(4)	129.8 (4)	C(6a)—C(10a)—C(10)	119.7 (4)
C(3)—C(3a)—C(10b)	113.2 (4)	C(6a)—C(10a)—C(10b)	119.3 (4)
N(4)—C(3a)—C(10b)	117.0 (3)	C(10)—C(10a)—C(10b)	121.0 (4)
C(3a)—N(4)—C(5)	116.6 (3)	C(1)—C(10b)—C(3a)	102.4 (3)
C(3a)—N(4)—C(11)	125.8 (3)	C(1)—C(10b)—C(10a)	118.0 (4)
C(5)—N(4)—C(11)	117.6 (3)	C(3a)—C(10b)—C(10a)	108.2 (3)
N(4)—C(5)—C(6)	115.2 (4)	O(2)—C(11)—O(3)	125.1 (4)
C(5)—C(6)—C(6a)	119.0 (4)	O(2)—C(11)—N(4)	123.1 (4)
C(6)—C(6a)—C(7)	116.3 (4)	O(3)—C(11)—N(4)	111.8 (4)
C(6)—C(6a)—C(10a)	123.7 (4)	O(4)—C(13)—O(5)	108.1 (4)
C(7)—C(6a)—C(10a)	120.0 (4)		

The scan rate was 3° min^{-1} (in ω). Weak reflections [$I < 10 \sigma(I)$] were rescanned (maximum of two rescans) and the counts accumulated to improve accuracy. During the final stages of refinement all H atoms were placed at assumed positions (C—H = 0.95 \AA , $U = 1.2 \times U_{\text{eq}}$ of associated C atom) and fixed. The methyl-group rotational orientation was determined from a difference Fourier synthesis.

Financial support from the National Institutes of Health is acknowledged.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55150 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR1010]

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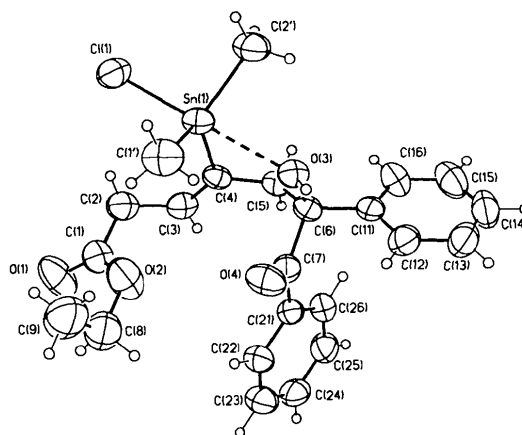


Fig. 1. General view (*SHELXTL-Plus* graphic) of the molecule, showing the atom-numbering scheme. Anisotropic ellipsoids represent 50% probability boundaries. H atoms are represented as spheres of arbitrary radii.

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Structure of Ethyl (Z)-4-(Chlorodimethylstannyl)-6-hydroxy-7-oxo-6,7-diphenyl-3-heptenoate

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Abstract

The atoms bound to Sn form a distorted trigonal bipyramid with the three C atoms in the equatorial [Sn—C 2.113(6), 2.122(5), 2.144(4) Å; C—Sn—C 116.8(2), 116.4(2), 118.0(2)°] and Cl and O in the apical positions [Sn—Cl 2.460(2), Sn—O 2.575(3) Å; Cl—Sn—O 172.53(9)°]. The remaining bond angles around Sn are in the range 70.7(2)–102.8(1)°.

Comment

The structure determination of the title compound was undertaken to confirm the presence of an intramolecular coordination between the Sn atom and the hydroxy group indicated by multinuclear NMR measurements. The Sn centre has a distorted trigonal bipyramidal environment. A similar coordination in the liquid phase has been demonstrated for other lone-pair-possessing nuclei (Jastrzebski, 1991) such as nitrogen (Jurkschat, Tzschach, Meunier-Piret & Van Meerssche, 1985; van Koten, Jastrzebski, Noltes, Verhoeckx, Spek & Kroon, 1980) and oxygen (Abbas & Poller, 1974; Kuivila, Dixon, Maxfield, Scarpa, Topka, Tsai & Wursthorn, 1975).

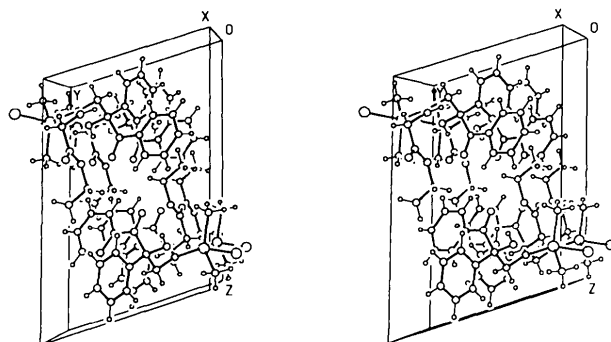


Fig. 2. Stereoscopic view (*SHELXTL-Plus* graphic) of the unit cell.

Experimental

Crystal data

$C_{23}H_{27}ClO_4Sn$

$M_r = 521.61$

Triclinic

$P\bar{1}$

$a = 8.321(3)$ Å

$b = 10.271(3)$ Å

$c = 15.313(4)$ Å

$\alpha = 71.59(2)^\circ$

$\beta = 84.88(2)^\circ$

$\gamma = 73.50(2)^\circ$

$V = 1190.6(7)$ Å³

$Z = 2$

$D_x = 1.455$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 24 reflections

$\theta = 8.1-14.6^\circ$

$\mu = 1.21$ mm⁻¹

$T = 293(1)$ K

$0.36 \times 0.22 \times 0.12$ mm

Colourless

Data collection

Nicolet $R3m/V$ diffractometer

$\theta/2\theta$ scans

Absorption correction:

empirical

$T_{min} = 1.00$, $T_{max} = 0.94$

6405 measured reflections

3124 independent reflections

2573 observed reflections

$[F > 4.0 \sigma(F)]$

$R_{int} = 0.035$

$\theta_{max} = 22.5^\circ$

$h = -9 \rightarrow 9$

$k = -12 \rightarrow 12$

$l = 0 \rightarrow 17$