

C(7)—C(8)	1.347 (8)	C(7)—C(9)	1.491 (8)
C(8)—N(1)	1.362 (8)	C(9)—C(10)	1.533 (7)
C(10)—C(11)	1.524 (7)	C(10)—N(4)	1.452 (6)
C(11)—O(3)	1.365 (6)	C(11)—O(4)	1.189 (6)
C(12)—C(13)	1.513 (9)	C(12)—O(3)	1.452 (7)
C(13)—N(2)	1.463 (8)	C(14)—O(2)	1.205 (8)
C(14)—N(2)	1.369 (8)	C(14)—N(3)	1.411 (8)
C(15)—C(16)	1.459 (9)	C(15)—O(1)	1.228 (8)
C(15)—N(3)	1.394 (8)	C(16)—C(17)	1.334 (8)
C(16)—C(18)	1.485 (9)	C(17)—N(2)	1.380 (8)
C(19)—O(5)	1.205 (6)	C(19)—O(6)	1.347 (6)
C(19)—N(4)	1.347 (6)	C(20)—C(21)	1.516 (9)
C(20)—C(22)	1.546 (11)	C(20)—C(23)	1.471 (10)
C(20)—O(6)	1.491 (7)	N(4)...O(1 ⁱ)	2.938 (6)
N(3')...O(4)	3.302 (6)	N(1)...O(5 ⁱⁱ)	2.890 (6)
C(2)—C(1)—C(6)	117.3 (6)	C(1)—C(2)—C(3)	121.0 (7)
C(2)—C(3)—C(4)	121.7 (7)	C(3)—C(4)—C(5)	118.6 (7)
C(4)—C(5)—C(6)	121.7 (5)	C(4)—C(5)—N(1)	131.3 (6)
C(6)—C(5)—N(1)	107.0 (5)	C(1)—C(6)—C(5)	119.8 (5)
C(1)—C(6)—C(7)	134.2 (5)	C(5)—C(6)—C(7)	106.0 (4)
C(6)—C(7)—C(8)	107.2 (5)	C(6)—C(7)—C(9)	124.7 (5)
C(8)—C(7)—C(9)	128.1 (5)	C(7)—C(8)—N(1)	110.3 (5)
C(7)—C(9)—C(10)	114.1 (4)	C(9)—C(10)—C(11)	108.3 (4)
C(9)—C(10)—N(4)	108.7 (4)	C(11)—C(10)—N(4)	110.0 (4)
C(10)—C(11)—O(3)	107.6 (4)	C(10)—C(11)—O(4)	126.9 (5)
O(3)—C(11)—O(4)	125.5 (5)	C(13)—C(12)—O(3)	110.8 (5)
C(12)—C(13)—N(2)	112.1 (5)	O(2)—C(14)—N(2)	125.1 (6)
O(2)—C(14)—N(3)	121.5 (6)	N(2)—C(14)—N(3)	113.4 (5)
C(16)—C(15)—O(1)	124.8 (6)	C(16)—C(15)—N(3)	115.0 (5)
O(1)—C(15)—N(3)	120.2 (6)	C(15)—C(16)—C(17)	117.6 (5)
C(15)—C(16)—C(18)	118.9 (5)	C(17)—C(16)—C(18)	123.5 (6)
C(16)—C(17)—N(2)	124.7 (5)	O(5)—C(19)—O(6)	126.6 (4)
O(5)—C(19)—N(4)	124.8 (4)	O(6)—C(19)—N(4)	108.7 (4)
C(21)—C(20)—C(22)	109.1 (6)	C(21)—C(20)—C(23)	114.0 (6)
C(21)—C(20)—O(6)	109.3 (5)	C(22)—C(20)—C(23)	112.4 (6)
C(22)—C(20)—O(6)	100.7 (5)	C(23)—C(20)—O(6)	110.5 (5)
C(11)—O(3)—C(12)	119.4 (4)	C(19)—O(6)—C(20)	120.4 (4)
C(5)—N(1)—C(8)	109.5 (5)	C(13)—N(2)—C(14)	117.6 (5)
C(13)—N(2)—C(17)	120.2 (5)	C(14)—N(2)—C(17)	122.1 (5)
C(14)—N(3)—C(15)	127.0 (5)	C(10)—N(4)—C(19)	119.6 (4)
N(4)...O(1 ⁱ)—C(15 ⁱ)	108.0 (4)	N(3')...O(4)—C(11)	125.4 (3)
N(1)...O(5 ⁱⁱ)—C(19 ⁱⁱ)	134.9 (3)		

Symmetry codes: (i) $x, 1 + y, z$; (ii) $x, y, 1 + z$.

Data were corrected for Lorentz and polarization effects. The structure was solved by direct methods using *MULTAN78* (Main *et al.*, 1978) followed by successive Fourier syntheses. The positional and anisotropic displacement parameters were refined by the block-diagonal least-squares method (Ashida, 1973). The H-atom positions were located from a $\Delta\rho$ synthesis and refined with isotropic displacement parameters.

We thank Drs Teruo Matsuura, Isao Saito and Hiroshi Sugiyama, Department of Synthetic Chemistry, Kyoto University, for supplying the crystals.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: OH1049). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1994). **C50**, 1269–1271

An Isocoumarin Derivative from *Paepalanthus bromelioides*

KOYCHI TOMITA* AND WAGNER VILEGAS

Instituto de Quimica-UNESP, CP 355, 14800-900, Araraquara, SP, Brazil

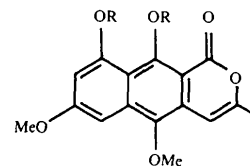
(Received 13 July 1993; accepted 10 December 1993)

Abstract

The structure of 5,7,9,10-tetramethoxy-3-methyl-1*H*-naphtho[2,3-*c*]pyran-1-one, $C_{18}H_{18}O_6$, a derivative of a natural isocoumarin isolated from *Paepalanthus bromelioides*, was determined by X-ray analysis, which unequivocally confirmed the previously assigned structure. Small deviations from the standard angles, resulting from steric hindrance between the methoxyl and carbonyl groups, were observed.

Comment

Isocoumarins have a wide range of biological properties (Hill, 1986). They are mainly formed through the acetate-malonate pathway that can lead to linear, as well as to angular-polycyclic aromatic natural products. The title compound, (2), was first prepared by methylation of a natural product, (1), isolated from the capitula of *P.bromelioides* (*Eriocaulaceae*) (Vilegas, Roque, Salatino, Giesbrecht & Davino, 1990).



(1) R = H

(2) R = CH₃

To clarify the bonding of the C atoms and the location of the oxygenation sites, ^{13}C — 1H long-

range COSY experiments have been used. Since good crystals of (1) could not be obtained, we carried out an X-ray crystallographic analysis of (2), which unequivocally confirmed the previously assigned structure. The values of bond distances and bond angles are in good agreement with accepted values.

$wR = 0.031$

$S = 3.21$

1471 reflections

217 parameters

H-atom parameters not refined

$\Delta\rho_{\max} = 0.14 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.20 \text{ e } \text{\AA}^{-3}$

Atomic scattering factors
from NRCVAX (Gabe,
Le Page, Charland, Lee &
White, 1989)

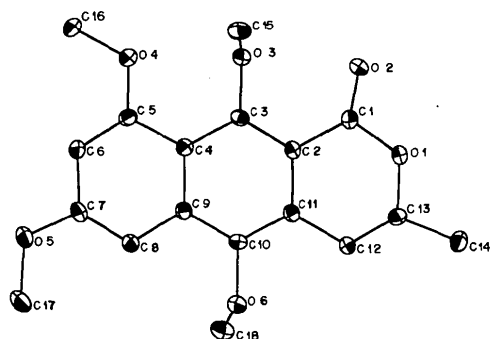


Fig. 1. View of the molecule with atomic numbering scheme.

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

$$B_{\text{eq}} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq}
O(1)	0.3326 (3)	0.1970 (2)	0.0179 (2)	3.7 (2)
O(2)	0.2495 (4)	0.2082 (3)	-0.1623 (2)	5.9 (2)
O(3)	0.0390 (3)	-0.0353 (2)	-0.3414 (2)	3.4 (1)
O(4)	-0.1568 (3)	-0.2841 (3)	-0.5005 (2)	4.1 (2)
O(5)	-0.3021 (3)	-0.7165 (3)	-0.3961 (2)	4.0 (2)
O(6)	0.1226 (3)	-0.3375 (3)	-0.0089 (2)	3.6 (2)
C(1)	0.2441 (5)	0.1271 (4)	-0.1030 (3)	3.6 (2)
C(2)	0.1582 (5)	-0.0343 (4)	-0.1417 (3)	2.8 (2)
C(3)	0.0587 (5)	-0.1115 (4)	-0.2605 (3)	2.9 (2)
C(4)	-0.0297 (5)	-0.2666 (4)	-0.2973 (3)	2.8 (2)
C(5)	-0.1424 (5)	-0.3547 (4)	-0.4178 (3)	3.1 (2)
C(6)	-0.2292 (5)	-0.5005 (4)	-0.4437 (3)	3.2 (2)
C(7)	-0.2063 (5)	-0.5696 (4)	-0.3546 (3)	3.2 (2)
C(8)	-0.0990 (5)	-0.4960 (4)	-0.2408 (3)	3.0 (2)
C(9)	-0.0097 (5)	-0.3431 (4)	-0.2108 (3)	2.7 (2)
C(10)	0.1010 (5)	-0.2621 (4)	-0.0925 (3)	2.8 (2)
C(11)	0.1797 (5)	-0.1110 (4)	-0.0561 (3)	2.8 (2)
C(12)	0.2830 (5)	-0.0267 (4)	0.0668 (3)	3.0 (2)
C(13)	0.3517 (5)	0.1194 (4)	0.0995 (3)	3.2 (2)
C(14)	0.4573 (5)	0.2250 (4)	0.2201 (3)	3.6 (2)
C(15)	0.1892 (5)	-0.0387 (4)	-0.3934 (3)	4.2 (2)
C(16)	-0.2580 (5)	-0.3714 (4)	-0.6208 (3)	3.9 (2)
C(17)	-0.2794 (5)	-0.8007 (4)	-0.3150 (3)	4.7 (3)
C(18)	0.2719 (5)	-0.4273 (4)	-0.0072 (3)	4.3 (2)

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

O(1)—C(1)	1.390 (4)	C(2)—C(11)	1.421 (5)
O(1)—C(13)	1.386 (4)	C(3)—C(4)	1.424 (5)
O(2)—C(1)	1.199 (5)	O(4)—C(5)	1.450 (5)
O(3)—C(3)	1.369 (4)	C(4)—C(9)	1.430 (5)
O(3)—C(15)	1.434 (4)	C(5)—C(6)	1.361 (5)
O(4)—C(5)	1.353 (4)	C(6)—C(7)	1.407 (5)
O(4)—C(16)	1.428 (4)	C(7)—C(8)	1.354 (5)
O(5)—C(7)	1.370 (4)	C(8)—C(9)	1.418 (5)
O(5)—C(17)	1.426 (4)	C(9)—C(10)	1.413 (5)
O(6)—C(10)	1.391 (4)	C(10)—C(11)	1.372 (5)
O(6)—C(18)	1.450 (4)	C(11)—C(12)	1.450 (5)
C(1)—C(2)	1.469 (5)	C(12)—C(13)	1.317 (5)
C(2)—C(3)	1.392 (5)	C(13)—C(14)	1.485 (5)
C(1)—O(1)—C(13)	123.1 (3)	C(4)—C(5)—C(6)	120.5 (3)
C(3)—O(3)—C(15)	113.79 (25)	C(5)—C(6)—C(7)	120.5 (3)
C(5)—O(4)—C(16)	117.5 (3)	O(5)—C(7)—C(6)	112.9 (3)
C(7)—O(5)—C(17)	117.7 (3)	O(5)—C(7)—C(8)	124.8 (3)
C(10)—O(6)—C(18)	113.48 (25)	C(6)—C(7)—C(8)	122.4 (3)
O(1)—C(1)—O(2)	114.7 (3)	C(7)—C(8)—C(9)	118.3 (3)
O(1)—C(1)—C(2)	116.8 (3)	C(4)—C(9)—C(8)	121.7 (3)
O(2)—C(1)—C(2)	128.5 (3)	C(10)—C(11)—C(12)	122.2 (3)
C(1)—C(2)—C(3)	120.7 (3)	C(11)—C(12)—C(13)	120.8 (3)
C(1)—C(2)—C(11)	118.9 (3)	O(1)—C(13)—C(12)	121.5 (3)
C(3)—C(2)—C(11)	120.4 (3)	O(1)—C(13)—C(14)	109.8 (3)
O(3)—C(3)—C(2)	119.5 (3)	C(12)—C(13)—C(14)	128.8 (3)
O(3)—C(3)—C(4)	119.9 (3)	C(4)—C(9)—C(10)	118.4 (3)
C(2)—C(3)—C(4)	120.6 (3)	C(8)—C(9)—C(10)	119.8 (3)
C(3)—C(4)—C(5)	124.7 (3)	O(6)—C(10)—C(9)	118.3 (3)
C(3)—C(4)—C(9)	118.8 (3)	O(6)—C(10)—C(11)	119.0 (3)
C(5)—C(4)—C(9)	116.5 (3)	C(9)—C(10)—C(11)	122.7 (3)
O(4)—C(5)—C(4)	116.7 (3)	C(2)—C(11)—C(10)	118.9 (3)
O(4)—C(5)—C(6)	122.8 (3)	C(2)—C(11)—C(12)	118.9 (3)

Experimental

The compound was obtained according to the procedure described by Vilegas, Roque, Salatino, Giesbrecht & Davino (1990).

Crystal data

C₁₈H₁₈O₆

$M_r = 330.33$

Triclinic

$P\bar{1}$

$a = 7.437 (1) \text{ \AA}$

$b = 9.336 (1) \text{ \AA}$

$c = 12.402 (2) \text{ \AA}$

$\alpha = 106.32 (1)^\circ$

$\beta = 106.07 (1)^\circ$

$\gamma = 95.21 (1)^\circ$

$V = 780.7 (2) \text{ \AA}^3$

$Z = 2$

$D_x = 1.405 \text{ Mg m}^{-3}$

$D_m = 1.41 (4) \text{ Mg m}^{-3}$

D_m measured by flotation in
CHBr₃/CH₃OH

Mo $K\alpha$ radiation

$\lambda = 0.71069 \text{ \AA}$

Cell parameters from 19
reflections

$\theta = 7-19^\circ$

$\mu = 0.099 \text{ mm}^{-1}$

Room temperature

Plate-like

$0.3 \times 0.3 \times 0.2 \text{ mm}$

Pale yellow

Data collection

Enraf–Nonius CAD-4
diffractometer

$\omega-2\theta$ scans

Absorption correction:
none

2329 measured reflections

2169 independent reflections

1471 observed reflections

$[I > 2.5\sigma(I)]$

$R_{\text{int}} = 0.010$

$\theta_{\text{max}} = 22.9^\circ$

$h = -8 \rightarrow 8$

$k = 0 \rightarrow 10$

$l = -13 \rightarrow 13$

1 standard reflection

frequency: 60 min

intensity variation: none

Refinement

Refinement on F

$R = 0.044$

$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{\text{max}} < 0.001$

Data reduction: *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). Structure solution: *SHELXS86* (Sheldrick, 1985). Structure refinement: *NRCVAX*. Molecular graphics: *ORTEP* (Johnson, 1965).

We thank the Instituto de Física e Química de São Carlos da Universidade de São Paulo, Brazil, for the use of the diffractometer and CNPq for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1106). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1994). **C50**, 1271–1273

2(*RS*)-*r*-2-[(*RS*)-1-(4-Chlorobenzoyloxy)-ethyl]-2-ethyl-1,3-dioxolan-*c*-4-ylmethyl 4-Chlorobenzoate

ULRICH BERENS AND GERHARD RAABE*

*Institut für Organische Chemie,
 Rheinisch-Westfälische Technische Hochschule Aachen,
 Professor-Pirlet-Straße 1, D-52056 Aachen, Germany*

(Received 20 August 1993; accepted 16 December 1993)

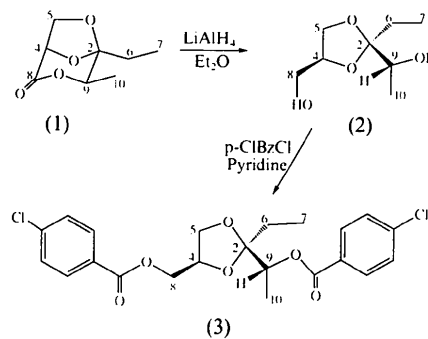
Abstract

X-ray structure analysis of the title compound, $C_{22}H_{22}Cl_2O_6$, (3), was carried out in order to determine the relative configuration at the substituent atoms C(6) and C(10) of its precursor (\pm)-5-ethyl-4-*endo*-methyl-3,6,8-trioxabicyclo[3.2.1]octan-2-one (1). This configuration is expected not to change during the series of reactions linking these two molecules. The solid-state structure of (3) is characterized by a contact between the bulky side chains which are both on the same side of the

five-membered ring. The shortest distance between these substituents involving non-H atoms (O...C) is 3.335 (3) Å. This striking structural characteristic of the title compound is realized in at least one local minimum on the hypersurface of the free molecule since a quantum-chemical calculation employing the semi-empirical AM1 method and starting from the solid-state structure of (3) resulted in a relative minimum with a similar distance between corresponding atoms.

Comment

(\pm)-5-Ethyl-4-*endo*-methyl-3,6,8-trioxabicyclo[3.2.1]octan-2-one, (1), was obtained as the lower-boiling isomer from a mixture of the *endo/exo*-methyl diastereomers of (1) in the course of a new β -multistriatin synthesis. Compound (1) is similar to the multistriatins whose pheromonic activity strongly depends on the relative stereochemistry of their methyl groups. Therefore, knowledge of the relative orientation of atoms C(10) and C(6) in (1) is of interest, since it allows estimation of possible pheromonic activity of this species. 1H NMR spectroscopic results obtained in solution turned out to be inconclusive in this regard. Moreover, it was not possible to obtain (1) in the form of single crystals suitable for X-ray structure determination. Thus, we prepared the title compound (3) as a crystalline derivative of (1) and determined its solid-state structure by means of X-ray crystallography.



The information regarding the relative configuration of C(10) and C(6) is retained during the reactions linking (1) and (3). Thus determination of the configuration about the C(2)—C(9) bond in (3) yields the relative orientation of the corresponding substituents in (1).

It is not difficult to see that if methyl group C(10) in (1) was in an axial position, the relative configuration at C(2) of the dioxolane system and at C(9) of its side chain in (3) would be different. Since the result of our solid-state structure determination of (3) shows that the absolute configuration at both