S1—C2—N3	111.8 (4)	C6′—C5′—C3,5′	122.1 (5)
N1′—C2′—N3′	125.8 (5)	N1′—C6′—C5′	124.5 (5)
N1′—C2′—C2α′	117.6 (5)	O22—C20—O23	118.9 (5)
N3′—C2′—C2α′	116.5 (5)	O22—C20—C21	121.7 (6)
N3—C4—C5	111.5 (5)	O23—C20—C21	119.5 (5)
N3—C4—C4α	120.5 (5)	N3—C3,5′—C5′	113.0 (4)
C5—C4—C4α	128.1 (5)	C5—C5α—C5β	114.5 (5)
N3′—C4′—N4α′	117.3 (5)	O5γ—C5β—C5α	109.6 (5)
N3′—C4′—C5′	120.7 (5)		

Table 3. *Hydrogen bonds and other interatomic close contacts* (Å, °)

Hydrogen bonds

D	H	*A*	*D*···*A*
O5γ	H5γ	N1′^{i}	2.976 (7)
N4α′	H4α′1	O23^{ii}	3.050 (8)
N4α′	H4α′1	N3′^{iii}	3.014 (7)
C2	H2	O22	2.972 (7)

Close contacts around S1

C	S	O	C—S	S···O	C—S···O	C···O
C2	S1	O22	1.671 (6)	2.995 (5)	73.0 (2)	2.972 (7)
C5	S1	O22	1.711 (6)		164.7 (2)	>4
C2	S1	O5γ^{iv}		3.253 (5)	163.4 (2)	>4
C5	S1	O5γ^{iv}			98.4 (2)	3.890 (7)

Miscellaneous contacts

C	H	O	C···O
C3,5′	H3,5′2	O22^{v}	3.809 (7)
C3,5′	H3,5′2	O22^{v}	3.188 (8)

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

The structure was solved by direct methods and subsequent difference Fourier methods. Anisotropic displacement parameters were refined for all non-H atoms. H-atoms were included in the structure-factor calculations, but not refined. Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Data reduction: *SDP-VAX*, Version 3.0 (1986) (Frenz, 1978). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SDP-VAX*. Molecular graphics: *ORTEP*II (Johnson, 1971).

We thank the Xunta de Galicia (XUGA81502188) for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry, least-squares-planes data and torsion angles have been deposited with the IUCr (Reference: HA1060). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Aoki, K., Yamazaki, H. & Adeyemo, A. (1991). *Inorg. Chim. Acta*, **180**, 117–124.
Blank, G., Rodrigues, M., Pletcher, J. & Sax, M. (1976). *Acta Cryst.* B**32**, 2970–2975.
Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Frenz, B. A. (1978). *The Enraf–Nonius CAD-4 SDP – a Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Solution. Computing in Crystallography*, edited by H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld & G. C. Bassi, pp. 64–71. Delft Univ. Press.
Hu, N. (1991). *Inorg. Chim. Acta*, **186**, 209–214.
Ishida, T., Tanaka, A. & Inoue, M. (1984). *Acta Cryst.* C**40**, 437–439.
Jin, Z., Liu, P., Wei, G. & Wang, W. (1990). *Chin. Sci. Bull.* **35**, 383–387.
Johnson, C. K. (1971). *ORTEP*II. Report ORNL-3794, 2nd Revision. Oak Ridge National Laboratory, Tennessee, USA.
Krampitz, L. O. (1969). *Annu. Rev. Biochem.* **38**, 213–240.
Kraut, J. & Reed, J. (1962). *Acta Cryst.* **15**, 747–757.
Louloudi, M., Hadjiliadis, N., Feng, J.-A., Sukumar, S. & Bau, R. (1990). *J. Am. Chem. Soc.* **112**, 7233–7238.
Pletcher, J., Sax, M., Sengupta, S., Chu, J. & Yoo, C. S. (1972). *Acta Cryst.* B**28**, 2928–2935.
Sheldrick, G. M. (1985). *SHELXS*86. *Program for the Solution of Crystal Structures*. Univ. of Göttingen, Germany.
Shin, W., Pletcher, J., Blank, G. & Sax, M. (1977). *J. Am. Chem. Soc.* **99**, 3491–3499.
Turano, A., Pletcher, J., Furey, W. & Sax, M. (1982). *Ann. New York Acad. Sci.* pp. 91–106.
Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.
Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.

Acta Cryst. (1994). C**50**, 1267–1269

2-Thymin-1-ylethyl Ester of *N-tert*-Butoxycarbonyl-L-tryptophan, $C_{23}H_{28}N_4O_6$

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Abstract

The dihedral angle between the indole and thymine rings is 31°, and little stacking interaction between these rings is observed in the crystalline state. The molecules are linked by three N—H···O hydrogen bonds.

Comment

The title compound, (I), was prepared in order to study the nature of the stacking interaction between nucleic acid bases and tryptophan (Sugiyama, 1984). The absorption and fluorescence spectra of both (I) and 5′-uridylyl-L-tryptophaniate in solution indicated strong stacking interactions between the indole and thymine rings (Sugiyama, 1984). The crystal structure determination of 5′-uridylyl-L-tryptophaniate hydrochloride revealed that the indole ring is stacked on the uracil group of a

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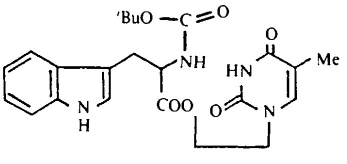
molecule related by a 2_1 screw axis (Saito, Sugiyama, Matsuura & Fukuyama, 1985).



(I)

The crystal structure analysis of (I) revealed that little stacking between the indole and thymine rings occurs in the crystalline state. The planes of the indole and thymine rings make an angle of 31°. The φ and ψ angles for the tryptophan residue are −62.3 (4) and 154.7 (4)°, respectively. The molecules lying along the b axis are linked by two hydrogen bonds, N(4)—H···O(1) [H···O(1) 2.04 Å] and N(3)—H···O(4) [H···O(4) 2.20 Å], while those along the c axis are linked by N(1)—H···O(5) hydrogen bonds [H···O(5) 1.99 Å].

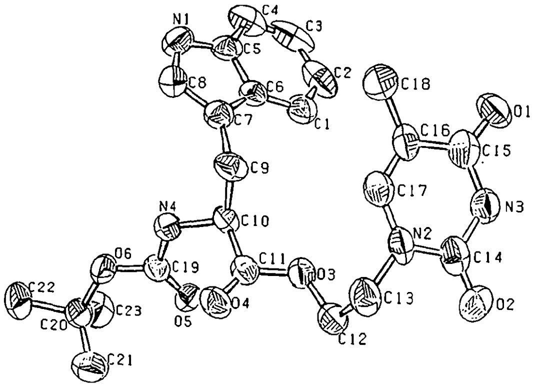


Fig. 1. *ORTEP*II (Johnson, 1976) drawing showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The direction of view is along the normal to the thymine ring.

Experimental

The compound was synthesized as described by Sugiyama (1984).

Crystal data

$C_{23}H_{28}N_4O_6$
$M_r = 456.5$
Orthorhombic
$P2_12_12_1$
$a = 27.414$ (5) Å
$b = 9.676$ (3) Å
$c = 8.843$ (3) Å
$V = 2346$ (1) Å^3
$Z = 4$
$D_x = 1.29$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 16 reflections
$\theta = 12.5$–15°
$\mu = 0.75$ mm^{-1}
$T = 293$ K
Plate-like
0.4 × 0.3 × 0.1 mm
Colourless

Data collection

Rigaku four-circle diffractometer
ω–2θ scans
Absorption correction: none
2011 measured reflections
1817 independent reflections
1817 observed reflections [$F_o > 2\sigma(F_o)$]

$\theta_{\max} = 60°$
$h = 0 \rightarrow 30$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 9$
2 standard reflections monitored every 100 reflections
intensity variation: ±1.2%

Refinement

Refinement on F
$R = 0.057$
$wR = 0.073$
$S = 0.88$
1817 reflections
411 parameters
All H-atom parameters refined
$w = 1$ for $F_o \leq 18$ and $w = 1/[1 + 0.25(F_o - 18)]$ for $F_o > 18$

$(\Delta/\sigma)_{\max} = 0.58$
$\Delta\rho_{\max} = 0.18$ e Å^{-3}
$\Delta\rho_{\min} = -0.20$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	B_{eq}
C(1)	0.6729 (2)	−0.0606 (6)	0.8840 (6)	5.1
C(2)	0.7086 (2)	−0.1326 (7)	0.9642 (9)	7.2
C(3)	0.7261 (2)	−0.0829 (8)	1.1053 (9)	7.3
C(4)	0.7083 (2)	0.0303 (7)	1.1683 (7)	6.3
C(5)	0.6730 (2)	0.1039 (6)	1.0913 (6)	4.7
C(6)	0.6551 (2)	0.0598 (5)	0.9483 (5)	3.8
C(7)	0.6198 (2)	0.1618 (5)	0.9025 (6)	4.2
C(8)	0.6176 (2)	0.2573 (6)	1.0132 (6)	5.2
C(9)	0.5924 (2)	0.1589 (6)	0.7570 (6)	4.6
C(10)	0.6234 (2)	0.1924 (5)	0.6177 (6)	3.8
C(11)	0.5920 (2)	0.1720 (5)	0.4773 (6)	4.0
C(12)	0.5655 (2)	−0.0149 (6)	0.3126 (7)	5.6
C(13)	0.5195 (2)	−0.0863 (6)	0.3663 (7)	5.4
C(14)	0.5407 (2)	−0.3247 (5)	0.4193 (7)	5.1
C(15)	0.5536 (2)	−0.3999 (6)	0.6881 (7)	5.2
C(16)	0.5433 (2)	−0.2583 (5)	0.7352 (7)	4.9
C(17)	0.5311 (2)	−0.1676 (5)	0.6281 (6)	4.5
C(18)	0.5457 (3)	−0.2233 (6)	0.8986 (7)	6.5
C(19)	0.6676 (2)	0.3885 (5)	0.5174 (5)	3.7
C(20)	0.6981 (2)	0.6140 (5)	0.4287 (6)	5.1
C(21)	0.6711 (3)	0.6045 (7)	0.2793 (7)	6.5
C(22)	0.6895 (3)	0.7586 (6)	0.4981 (9)	7.5
C(23)	0.7501 (2)	0.5787 (7)	0.4188 (9)	7.0
O(1)	0.5641 (2)	−0.4949 (4)	0.7742 (6)	6.3
O(2)	0.5415 (2)	−0.3549 (4)	0.2871 (5)	6.6
O(3)	0.5938 (1)	0.0352 (3)	0.4399 (4)	4.8
O(4)	0.5687 (1)	0.2575 (4)	0.4134 (4)	5.0
O(5)	0.6849 (1)	0.3229 (3)	0.4147 (4)	4.6
O(6)	0.6732 (1)	0.5249 (3)	0.5426 (4)	4.9
N(1)	0.6494 (2)	0.2248 (5)	1.1262 (5)	5.8
N(2)	0.5300 (2)	−0.1963 (4)	0.4752 (6)	4.7
N(3)	0.5508 (2)	−0.4231 (4)	0.5328 (5)	5.1
N(4)	0.6392 (1)	0.3354 (4)	0.6274 (5)	4.1

Table 2. *Selected geometric parameters* (Å, °)

C(1)—C(2)	1.394 (10)	C(1)—C(6)	1.385 (7)
C(2)—C(3)	1.421 (11)	C(3)—C(4)	1.322 (11)
C(4)—C(5)	1.382 (9)	C(5)—C(6)	1.422 (7)
C(5)—N(1)	1.372 (8)	C(6)—C(7)	1.440 (7)

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^{i})···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^{i})···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 *MULTAN*78 (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.

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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.

References

Ashida, T. (1973). *HBLS*IV. *The Universal Crystallographic Computing System – Osaka*, pp. 55–61. The Computation Center, Osaka University, Japan.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Main, P., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Saito, I., Sugiyama, H., Matsuura, T. & Fukuyama, K. (1985). *Tetrahedron Lett.* **26**, 4467–4470.

Sugiyama, H. (1984). PhD thesis, Kyoto Univ., Japan.

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An Isocoumarin Derivative from *Paepalanthus bromelioides*

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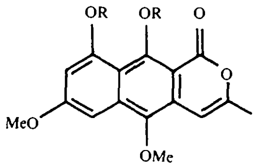
Abstract

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 = CH_3

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