Table 3. *Hydrogen-bonding geometry* (Å, °)

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
C38—H38*A*···O7	0.96 (2)	2.36 (1)	2.84 (1)	110 (1)
C39—H39*B*···O1	0.96 (2)	2.27 (1)	2.70 (1)	106.1 (9)
C41—H41*C*···O9	0.96 (1)	2.21 (1)	2.86 (1)	123.9 (9)
O1···O1*W*	2.829 (13)	O2···O5^{ii}		2.814 (8)
O1···O4^{i}	3.032 (10)	O4···O1Me^{iii}		2.759 (11)
O2···O1Me	2.780 (11)	O7···O1*W*^{iv}		3.002 (14)

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

The decay of the crystal was allowed for during data reduction by applying a correction during the scaling of the data. The structure was solved by direct methods using *SIR*92 (Burla *et al.* 1992) and refined by full-matrix least-squares methods using *SHELXTL-Plus* (Sheldrick, 1990). Attempts to locate H atoms in the difference Fourier map were only partially successful. The H atoms of the O2, O4 and O5 hydroxyl groups and those of the methanol and water solvent molecules were not included in the refinement. The final cycles of refinement were carried out with H atoms riding on the corresponding C atoms with $U_{iso} = 0.08$ Å^2. Data collection and cell refinement: Siemens *R3m/V* software. Data reduction: *SHELXTL-Plus*. Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *PARST* (Nardelli, 1983) and *PARSTCIF* (Nardelli, 1993).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1096). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–19.

Balerna, M., Keller-Schierlein, W., Martins, C., Wolf, H. & Zähner, H. (1969). *Arch. Mikrobiol.* **65**, 303–317.

Brufani, M., Cellai, L. & Keller-Schierlein, W. (1979). *J. Antibiot.* **32**, 167–168.

Burla, M. C., Camalli, M., Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1992). *Fourteenth European Crystallographic Meeting*, Enschede, The Netherlands, 2–7 August, Abstract 519.

Cellai, L., Polcaro, C. M., Rossi, W. & Brufani, M. (1982). *J. Chromatogr.* **234**, 509–512.

Hambley, T. W., Parthasarathi, V., Rickards, R. W. & Robertson, G. B. (1991). *Aust. J. Chem.* **4**, 655–665.

Keller-Schierlein, W., Meyer, M., Cellai, L., Cerrini, S., Lamba, D., Segre, A., Fedeli, W. & Brufani, M. (1984). *J. Antibiot.* **37**, 1357–1361.

Meyer, M., Keller-Schierlein, W., Megahed, S., Zähner, H. & Segre, A. L. (1986). *Helv. Chim. Acta*, **69**, 1356–1364.

Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.

Nardelli, M. (1993). *PARSTCIF. Program for the Creation of a CIF from the Output of PARST.* Univ. of Parma, Italy.

Okabe, T., Yuan, B. D., Isono, F., Sato, I., Fukazawa, H., Nishimura, T. & Tanaka, N. (1985). *J. Antibiot.* **38**, 230–235.

Sheldrick, G. M. (1990). *SHELXTL-Plus*. Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Williams, T. H. (1975). *J. Antibiot.* **28**, 85–86.

Acta Cryst. (1994). C**50**, 2064–2067

Madurahydroxylactone

E. F. Paulus

Hoechst AG, D-65926 Frankfurt/Main, Germany

K. Dornberger and W. Werner

Hans-Knöll-Institut für Naturstoff-Forschung eV,
D-07745 Jena, Beutenbergstrasse 11, Germany

D. Fenske

Institut für Anorganische Chemie der Universität,
D-76131 Karlsruhe, Germany

(*Received* 25 *October* 1993; *accepted* 23 *March* 1994)

Abstract

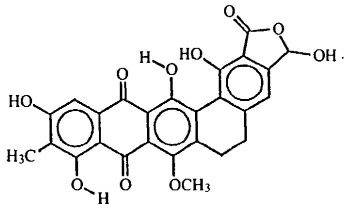
The data acquisition for the title compound, 3,9,11,14,15-pentahydroxy-7-methoxy-10-methyl-1,3,5,6,8,13-hexahydronaphthaceno[1,2-*f*]isobenzofuran-1,8,13-trione acetonitrile solvate, $C_{26}H_{18}O_{10}.C_2H_3N$, was carried out using an image-plate detector [$T = 293$ K, $R = 0.149$, $wR = 0.120$ for 4211 unique image-plate data with $|F| > 1\sigma(F)$] and also using a scintillation detector [$T = 193$ K, $R = 0.132$, $wR = 0.121$ for 1910 unique data $> 1\sigma(F)$]. It was not possible to solve the phase problem with the scintillation detector data set, the average I/σ being too small. The structure analysis corrects the molecular structure of madurahydroxylactone suggested ambiguously by spectroscopic methods. Three of the five hydroxy groups are involved in intramolecular hydrogen bonding.

Comment

Madurahydroxylactone and homologues were isolated from the culture broth of *Actinomadura rubra* by extraction, precipitation and high-performance liquid chromatography (HPLC) methods (Fleck, Strauss, Meyer & Porstendorfer, 1978). Four compounds were initially found which differed only by the type of alkoxy group at the hydroxylactone function of the natural basic molecule. These compounds were identified as methoxy, ethoxy, propoxy and butoxy derivatives of 'maduranic acid' (Strauss & Fleck, 1990; Strauss *et al.*, 1990) and they have strong antimicrobial activity against Gram-positive bacteria. Two possible structures were suggested from spectroscopic methods (Strauss & Fleck, 1990; Miosga, Römer & Hesse, 1985). Because a high degree of ambiguity remained, we decided to carry out an X-ray structure analysis of 'maduranic acid'. Figs. 1 and 2 show the results of the structure analysis. The hydroxylactone form is obtained when the carboxyl and

Acta Crystallographica Section C
ISSN 0108-2701 ©1994

o-formyl groups of the acid cyclize. The revised structural formula of the title compound (I) is given below.



(I)

One molecule of acetonitrile is connected to the hydroxyl group of the lactone ring through a hydrogen bond [2.852 (6) Å]. The backbone of the molecule is the tetrahydronaphthaceno[*a*]benzenedione ring system. The angle between the anthraquinone moiety and the phenyl ring is 40.4 (9)°, that between the two phenyl rings of the biphenyl segment is 35.8 (9)° and the angle between the two planar groups of the cyclohexadiene ring is 29.7 (8)°. In unsubstituted biphenyl, the phenyl rings are coplanar (Charbonneau & de Lugeard, 1977), whereas α-substituted derivatives of biphenyl have relatively high angles between the phenyl rings, for example, in 1-(biphenyl-2-yl)-5-methoxy-3-tosylbenzo[*c*]-thio-phene (Saito *et al.*, 1991) the angle is 55.5°. In unsubstituted cyclohexadiene, the angle between the planes of the two double bonds is 18° (Oberhammer & Bauer, 1969). All these comparisons suggest that the twist in the centre of the molecule is relatively small. The system of intramolecular hydrogen bonds could be one of the reasons for this. There are three intramolecular hydrogen bonds [O(02)—H···O(03) 2.530 (6), O(06)—H···O(04) 2.510 (6) and O(07)—H···O(06) 2.656 (5) Å] and one intermolecular hydrogen bond [O(01)—H···O(10) 2.714 (5) Å].

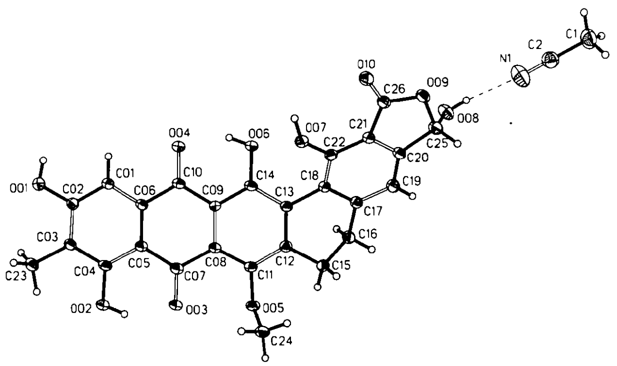


Fig. 1. The molecular structure of the title compound showing 30% probability displacement ellipsoids for the non-H atoms and the atom-numbering scheme.

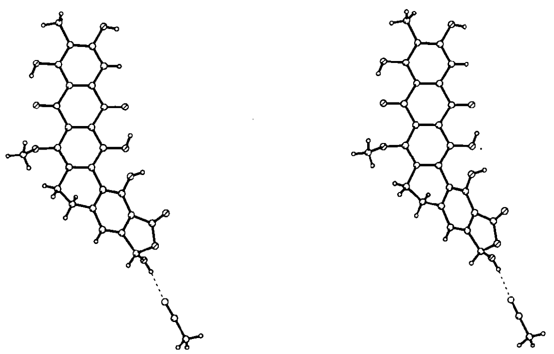


Fig. 2. Stereoscopic view of the title molecule.

Fig. 3 is a packing diagram of the structure projected parallel to the *y* axis. It can be seen that the molecules are lying in piles connected through the O(01)—H···O(10) intermolecular hydrogen bond. Neighbouring molecules within the piles are antiparallel. In this way, each molecule is linked to two other molecules of two piles in both directions along the *z* axis. It can also be seen that the O(03) atom is situated in the neighbourhood of atoms O(06) [3.134 (6) Å] and O(07) [2.926 (7) Å] in a position suitable for hydrogen bonding, suggesting that at least O(07) is involved in an intermolecular, but not an intramolecular, hydrogen bond. This contradicts the peak in the difference Fourier synthesis for the H atoms on atoms O(06) and O(07), favouring an intramolecular hydrogen bond, but one can assume, with a certain probability, that the H atoms can occupy both positions and that there is a tautomeric equilibrium in operation. Every molecule within a pile would then be connected by hydrogen bonds to four molecules of the two neighbouring piles. The piles are fitted into parallel $(\bar{1}\bar{1}1)$ layers which are separated by acetonitrile molecules.

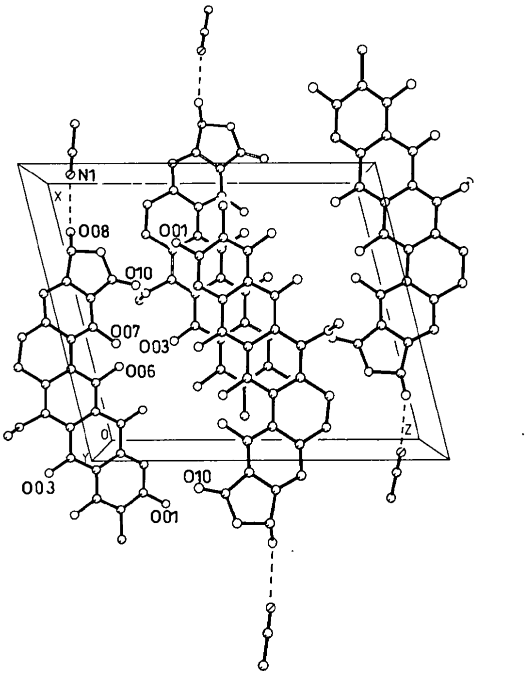


Fig. 3. The crystal structure of the title molecule viewed parallel to the *y* axis.

Experimental

Crystal data

$C_{26}H_{18}O_{10}.C_2H_3N$
$M_r = 531.48$
Monoclinic
$P2_1/n$
$a = 12.849$ (3) Å
$b = 12.675$ (3) Å
$c = 15.076$ (3) Å
$\beta = 103.95$ (5)°
$V = 2382.9$ Å^3
$Z = 4$
$D_x = 1.482$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 2.3–12.3°$
$\mu = 0.114$ mm^{-1}
$T = 293$ K
Needle
0.7 × 0.08 × 0.07 mm
Red
Crystal source: recrystallized from acetonitrile

Data collection

One-circle Stoe diffractometer with image plate
Absorption correction: none
31 701 measured reflections
4211 independent reflections
4201 observed reflections $[F > 1\sigma(F)]$

$R_{\rm int} = 0.148$
$\theta_{\rm max} = 25.8°$
$h = -15 \rightarrow 15$
$k = -15 \rightarrow 15$
$l = -18 \rightarrow 18$
No standard reflections

Refinement

Refinement on F
$R = 0.149$
$wR = 0.120$
$S = 2.22$
4207 reflections
364 parameters
H-atom parameters not refined

Unit weights applied
$(\Delta/\sigma)_{\rm max} = 0.004$
$\Delta\rho_{\rm max} = 0.37$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.43$ 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)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
C(01)	0.4095 (5)	0.4237 (5)	0.5894 (4)	0.047 (2)
C(02)	0.2996 (5)	0.4482 (5)	0.5630 (4)	0.047 (2)
C(03)	0.2363 (5)	0.4241 (5)	0.4774 (4)	0.049 (2)
C(04)	0.2852 (5)	0.3756 (5)	0.4142 (4)	0.047 (2)
C(05)	0.3970 (5)	0.3526 (5)	0.4362 (4)	0.046 (2)
C(06)	0.4573 (4)	0.3764 (5)	0.5257 (4)	0.042 (2)
C(07)	0.4453 (5)	0.3062 (5)	0.3679 (5)	0.053 (2)
C(08)	0.5633 (5)	0.2851 (5)	0.3930 (4)	0.045 (2)
C(09)	0.6233 (4)	0.3041 (5)	0.4843 (4)	0.042 (2)
C(10)	0.5735 (5)	0.3518 (5)	0.5521 (4)	0.047 (2)
C(11)	0.6185 (5)	0.2504 (5)	0.3286 (4)	0.043 (2)
C(12)	0.7299 (5)	0.2301 (4)	0.3542 (4)	0.041 (2)
C(13)	0.7862 (5)	0.2344 (5)	0.4462 (4)	0.042 (2)
C(14)	0.7333 (5)	0.2794 (5)	0.5101 (4)	0.045 (2)
C(15)	0.7923 (5)	0.2083 (5)	0.2838 (4)	0.046 (2)
C(16)	0.9061 (5)	0.2550 (5)	0.3138 (4)	0.050 (2)
C(17)	0.9596 (5)	0.2075 (5)	0.4060 (4)	0.048 (2)
C(18)	0.8984 (4)	0.1962 (5)	0.4707 (4)	0.042 (2)
C(19)	1.0670 (5)	0.1747 (5)	0.4242 (4)	0.052 (2)
C(20)	1.1108 (5)	0.1290 (5)	0.5072 (4)	0.047 (2)
C(21)	1.0513 (4)	0.1127 (5)	0.5711 (4)	0.043 (2)
C(22)	0.9425 (5)	0.1435 (5)	0.5527 (4)	0.043 (2)
C(23)	0.1184 (5)	0.4508 (6)	0.4539 (5)	0.058 (2)
C(24)	0.5432 (5)	0.1342 (5)	0.2080 (5)	0.057 (2)
C(25)	1.2237 (5)	0.0892 (6)	0.5485 (4)	0.054 (2)
C(26)	1.1163 (5)	0.0627 (5)	0.6534 (5)	0.052 (2)
O(01)	0.2505 (3)	0.4977 (3)	0.6227 (3)	0.034 (1)
O(02)	0.2223 (3)	0.3527 (4)	0.3304 (3)	0.038 (1)
O(03)	0.3905 (3)	0.2857 (5)	0.2899 (3)	0.053 (2)
O(04)	0.6249 (3)	0.3723 (4)	0.6316 (3)	0.040 (2)
O(05)	0.5688 (3)	0.2409 (3)	0.2375 (3)	0.032 (1)
O(06)	0.7929 (3)	0.3047 (3)	0.5940 (3)	0.036 (1)
O(07)	0.8838 (3)	0.1151 (3)	0.6133 (3)	0.032 (1)
O(08)	1.2966 (3)	0.1681 (4)	0.5553 (3)	0.050 (2)
O(09)	1.2180 (3)	0.0516 (3)	0.6406 (3)	0.036 (1)
O(10)	1.0950 (3)	0.0351 (3)	0.7227 (3)	0.036 (1)
C(1)	1.6818 (8)	−0.0303 (9)	0.6638 (8)	0.091 (4)
C(2)	1.5862 (8)	0.0308 (9)	0.6321 (7)	0.095 (4)
N(1)	1.5058 (8)	0.0774 (9)	0.6042 (7)	0.166 (5)

Table 2. *Bond lengths* (Å) *and angles* (°)

C(01)—C(02)	1.406 (8)	C(13)—C(14)	1.424 (9)
C(01)—C(06)	1.394 (9)	C(13)—C(18)	1.480 (8)
C(02)—C(03)	1.383 (8)	C(14)—O(06)	1.350 (6)
C(02)—O(01)	1.370 (8)	C(15)—C(16)	1.540 (8)
C(03)—C(04)	1.402 (9)	C(16)—C(17)	1.519 (8)
C(03)—C(23)	1.510 (8)	C(17)—C(18)	1.400 (9)
C(04)—C(05)	1.425 (8)	C(17)—C(19)	1.403 (9)
C(04)—O(02)	1.357 (7)	C(18)—C(22)	1.398 (8)
C(05)—C(06)	1.417 (7)	C(19)—C(20)	1.370 (8)
C(05)—C(07)	1.448 (10)	C(20)—C(21)	1.383 (9)
C(06)—C(10)	1.483 (8)	C(20)—C(25)	1.521 (8)
C(07)—C(08)	1.496 (8)	C(21)—C(22)	1.414 (8)
C(07)—O(03)	1.245 (7)	C(21)—C(26)	1.462 (8)
C(08)—C(09)	1.427 (7)	C(22)—O(07)	1.365 (8)
C(08)—C(11)	1.404 (9)	C(24)—O(05)	1.437 (8)
C(09)—C(10)	1.461 (9)	C(25)—O(08)	1.357 (8)
C(09)—C(14)	1.408 (8)	C(25)—O(09)	1.487 (8)
C(10)—O(04)	1.248 (7)	C(26)—O(09)	1.373 (8)
C(11)—C(12)	1.414 (8)	C(26)—O(10)	1.195 (9)
C(11)—O(05)	1.373 (6)	C(1)—C(2)	1.433 (14)
C(12)—C(13)	1.402 (7)	C(2)—N(1)	1.177 (14)
C(12)—C(15)	1.503 (9)		

C(02)—C(01)—C(06)	118.6 (5)	C(12)—C(13)—C(14)	117.9 (5)
C(01)—C(02)—C(03)	122.6 (6)	C(12)—C(13)—C(18)	118.2 (5)
C(01)—C(02)—O(01)	120.3 (5)	C(14)—C(13)—C(18)	123.8 (5)
C(03)—C(02)—O(01)	117.1 (5)	C(09)—C(14)—C(13)	120.9 (5)
C(02)—C(03)—C(04)	118.2 (5)	C(09)—C(14)—O(06)	120.7 (6)
C(02)—C(03)—C(23)	120.0 (6)	C(13)—C(14)—O(06)	118.3 (5)
C(04)—C(03)—C(23)	121.8 (5)	C(12)—C(15)—C(16)	110.6 (5)
C(03)—C(04)—C(05)	121.6 (5)	C(15)—C(16)—C(17)	107.7 (5)
C(03)—C(04)—O(02)	117.6 (5)	C(16)—C(17)—C(18)	118.2 (5)
C(05)—C(04)—O(02)	120.8 (6)	C(16)—C(17)—C(19)	120.2 (6)
C(04)—C(05)—C(06)	117.8 (6)	C(18)—C(17)—C(19)	121.7 (5)
C(04)—C(05)—C(07)	119.9 (5)	C(13)—C(18)—C(17)	117.9 (5)
C(06)—C(05)—C(07)	122.3 (5)	C(13)—C(18)—C(22)	122.7 (6)
C(01)—C(06)—C(05)	121.1 (5)	C(17)—C(18)—C(22)	119.2 (5)
C(01)—C(06)—C(10)	119.2 (5)	C(17)—C(19)—C(20)	118.1 (6)
C(05)—C(06)—C(10)	119.6 (5)	C(19)—C(20)—C(21)	121.7 (6)
C(05)—C(07)—C(08)	118.4 (5)	C(19)—C(20)—C(25)	131.0 (6)
C(05)—C(07)—O(03)	121.0 (6)	C(21)—C(20)—C(25)	107.3 (5)
C(08)—C(07)—O(03)	120.6 (6)	C(20)—C(21)—C(22)	120.5 (5)
C(07)—C(08)—C(09)	119.5 (6)	C(20)—C(21)—C(26)	111.0 (5)
C(07)—C(08)—C(11)	122.1 (5)	C(22)—C(21)—C(26)	128.5 (6)
C(09)—C(08)—C(11)	118.4 (5)	C(18)—C(22)—C(21)	118.5 (6)
C(08)—C(09)—C(10)	121.3 (5)	C(18)—C(22)—O(07)	123.0 (5)
C(08)—C(09)—C(14)	120.1 (6)	C(21)—C(22)—O(07)	118.4 (5)
C(10)—C(09)—C14)	118.6 (5)	C(20)—C(25)—O(08)	111.1 (5)
C(06)—C(10)—C(09)	118.8 (5)	C(20)—C(25)—O(09)	103.4 (5)
C(06)—C(10)—O(04)	118.7 (6)	O(08)—C(25)—O(09)	110.8 (5)
C(09)—C(10)—O(04)	122.5 (5)	C(21)—C(26)—O(09)	107.1 (6)
C(08)—C(11)—C(12)	121.0 (5)	C(21)—C(26)—O(10)	131.6 (6)
C(08)—C(11)—O(05)	121.9 (5)	O(09)—C(26)—O(10)	121.3 (5)
C(12)—C(11)—O(05)	117.0 (5)	C(11)—O(05)—C(24)	114.1 (4)
C(11)—C(12)—C(13)	120.7 (6)	C(25)—O(09)—C(26)	111.2 (4)
C(11)—C(12)—C(15)	121.2 (5)	C(1)—C(2)—N(1)	177.3 (11)
C(13)—C(12)—C(15)	118.1 (5)		

Quite a few crystals were studied before finding one with an acceptable diffracting power. For the actual measurements the chosen crystal was sealed in a Lindemann glass capillary.

The crystal was of extremely low diffracting power (very high R values). Scintillation detector data were collected over 30 d but the structure could not be solved because the ratio of intensity to standard deviation was too small. Data from the same crystal, measured over 12 h using an image-plate detector, solved the structure immediately by a routine input.

H atoms were refined as a riding model with fixed isotropic U values. The relatively high R values are the result of the low crystal quality. All calculations were carried out on a MicroVAX II computer using the *SHELXTL-Plus* programs (Sheldrick, 1990).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SE1045). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Charbonneau, G.-P. & de Lugeard, Y. (1977). *Acta Cryst.* B**33**, 1586–1588.

Fleck, W. F., Strauss, D. G., Meyer, J. & Porstendorfer, G. (1978). *Z. Allg. Mikrobiol.* **18**, 389–398.

Miosga, N., Römer, W. & Hesse, G. (1985). *Z. Chem.* **25**, 146–147.

Oberhammer, H. & Bauer, S. H. (1969). *J. Am. Chem. Soc.* **91**, 10–16.

Saito, T., Ayukawa, H., Sumizawa, N., Shizuta, T., Motoki, S. & Kobayashi, K. (1991). *J. Chem. Soc. Perkin Trans.* 1, pp. 1405–1410.

Sheldrick, G. M. (1990). *SHELXTL-Plus*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Strauss, D. G. & Fleck, W. F. (1990). *Proceedings of the International Symposium on Advances in Bioactive Natural Product Chemistry.* Seoul, Korea.

Strauss, D., Fleck, W. F., Tresselt, D., Kochmann, W., Richter, H. P., Müller, S., Keil, A., Till, H.-J., Scharfenberg, P. & Weiher, B. (1990). Patent No. DD 285614 A5 (22-09/19-12-90).

Acta Cryst. (1994). C**50**, 2067–2069

(−)-Norcocaine

Naijue Zhu, Mark Reynolds and Cheryl L. Klein

Department of Chemistry, Xavier University
of Louisiana, New Orleans, Louisiana 70125, USA

Mark Trudell

Department of Chemistry, University of New Orleans,
New Orleans, Louisiana 70148, USA

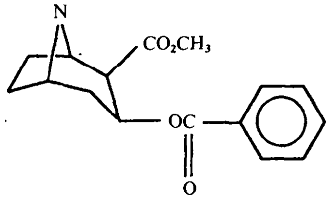
(*Received* 1 *November* 1993; *accepted* 28 *March* 1994)

Abstract

The title compound, [2*R*,3*S*-(2β,3β)]-methyl 3-(benzoyloxy)-8-azabicyclo[3.2.1]octane-2-carboxylate, $C_{16}H_{19}NO_4$, is a metabolite of the tropane alkaloid cocaine. The molecule crystallized as the free base with the piperidine ring in a chair conformation. The tropane ring system and its methoxycarbonyl and benzoyl groups are rigid; only rotational flexibility is allowed in the conformation of the substituents.

Comment

Cocaine is a tropane alkaloid that has been widely abused as a recreational drug. It causes a variety of pharmacological effects on the central nervous, cardiovascular and sympathetic nervous systems. When inhaled through the nose or injected intravenously, cocaine causes euphoria and an increase in heart rate and blood pressure (Byke & Vandyke, 1977). The title compound (I), which is the demethylated metabolite of cocaine, shows approximately one-third the pharmacological activity of cocaine. We have begun to study the three-dimensional structures of some cocaine derivatives and report here the structure of the free-base form of norcocaine.



(I)

The title compound crystallizes as the free base with one molecule in the asymmetric unit. The fractional coordinates were defined in accordance with the known absolute configuration of (−)-norcocaine. The X-ray crystal structure of norcocaine hydrobromide has been reported (Kelly, Knox, Lazer, Nieforth & Hite, 1977) and, like the title compound, it has the piperidine ring in a chair conformation. The tropane rings show very similar internal torsion angles in all of the crystal structures reported for cocaine (Hrynchuk, Barton & Robertson, 1983) and its derivatives, cocaine hydrochloride (Gabe & Barnes, 1963), cocaine methiodide (Shen, Ruble & Hite, 1975) and norcocaine hydrobromide (Kelly *et al.*, 1977). In addition, in all four of these structures and in the free base of norcocaine reported here, the methoxycarbonyl group is bonded axially to the tropane ring at C2 and the benzoyl group is bonded equatorially to the tropane ring at C3. This substituent orientation corresponds to the stereoisomer (*R*)-cocaine which occurs naturally in *Erythroxylon coca* leaves and which shows the highest pharmacological activity of the eight possible stereoisomers.

The bridgehead N atom has an axial H atom that is intramolecularly hydrogen bonded to the carbonyl O atom (O3) of the methoxycarbonyl group [HN···O3 2.306 (2) Å]. This hydrogen bond is weaker than the comparable one in norcocaine hydrobromide (HN···O,