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(−)-Thebaine

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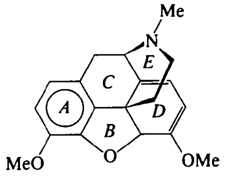
Abstract

The structure of the opioid thebaine, 6,7,8,14-tetradehydro-4,5-epoxy-3,6-dimethoxy-17-methylmorphinan, $C_{19}H_{21}NO_3$, has been determined by single-crystal X-ray diffraction techniques at low temperature. The thebaine molecule adopts the same T-shaped conformation of the five fused rings as found in closely related rigid opioids. The geometry of the double bond at the bridgehead C atom is significantly distorted from planarity.

Comment

Thebaine (1) is a metabolite of morphine and is found in small quantities in opium extracts (Lentz, Evans, Walters & Hopfinger, 1986; Bentley, 1971). Thebaine has often been used as the starting point for the synthesis of opioid derivatives. We have determined the structure of thebaine as part of a study of its reactivity with metals to form useful organometallic intermediates.



(1)

Compared with other members of the opioid family, the distinctive structural feature of thebaine is the presence of two double bonds in ring *D*. The general conformation of the molecule is similar to morphine (Bye, 1976; Gylbert, 1973) and codeine (Kartha, Ahmed & Barnes, 1962), which have one double bond, and to naloxone (Karle, 1974; Klein, Majeste & Stevens, 1987), which has no double bonds. Significant differences are observed in the bond distances and angles in ring *D*, as expected from the placement of the double bonds. The C6—C7 and C8—C14 bond lengths [1.339 (3) and 1.338 (2) Å, respectively] confirm the location of the double bonds, and the C7—C8 single-bond length [1.456 (3) Å], which is intermediate between the C7═C8 double-bond distance of 1.313 (6) Å in morphine (Bye, 1976) and the C7—C8 single-bond distance of 1.501 (1) Å in naloxone (Klein, Majeste & Stevens, 1987), suggests conjugation of the double bonds. The C6—C7—C8—C14 torsion angle is −1.4 (3)°. Compared with the other opioids, the other bonds to C6 and C9 are shorter in thebaine as a result of the change in hybridization at those C atoms. The

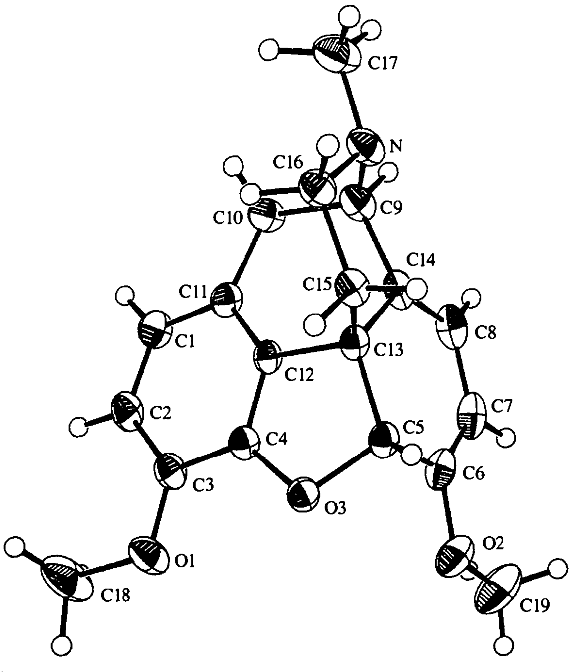


Fig. 1. *ORTEP*II (Johnson, 1976) plot of the thebaine molecule. Displacement ellipsoids are drawn at the 50% probability level.

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rings impose a distortion of the double-bond geometry at C14, the bridgehead carbon end. The C14 atom is displaced by 0.099 (2) Å from the plane defined by the C8, C9 and C13 atoms.

Experimental

A sample of thebaine was obtained from the National Institutes of Health and recrystallized from a solution of dichloromethane and heptane by slow cooling.

Crystal data

$C_{19}H_{21}NO_3$
$M_r = 311.38$
Orthorhombic
$P2_12_12_1$
$a = 7.939 (2)$ Å
$b = 7.713 (3)$ Å
$c = 25.291 (6)$ Å
$V = 1548.7 (8)$ Å^3
$Z = 4$
$D_x = 1.336$ Mg m^{-3}
D_m not measured

Mo–$K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 16$–$25°$
$\mu = 0.080$ mm^{-1}
$T = 100$ K
Rectangular
$0.40 \times 0.30 \times 0.30$ mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical, ψ scan (North, Phillips & Mathews, 1968)
    $T_{\min} = 0.968$, $T_{\max} = 0.999$
3072 measured reflections

3072 independent reflections
2262 observed reflections [$I > 3\sigma(I)$]
$\theta_{\max} = 31.95°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 22$
$l = 0 \rightarrow 37$
3 standard reflections
    frequency: 120 min
    intensity decay: 1.03%

Refinement

Refinement on F
$R = 0.042$
$wR = 0.054$
$S = 1.874$
2262 reflections
293 parameters
H atoms refined isotropically
$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0016F_o^4]$
$(\Delta/\sigma)_{\max} = 0.005$

$\Delta\rho_{\max} = 0.201$ e Å^{-3}
$\Delta\rho_{\min} = -0.219$ e Å^{-3}
Extinction correction: isotropic (Zachariasen, 1963)
Extinction coefficient: 0.36×10^{-6}
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	$U_{\rm eq}$
O1	0.7754 (2)	1.1075 (2)	0.98179 (5)	0.0436 (7)
O2	1.2744 (2)	1.0597 (2)	0.87142 (6)	0.0454 (8)
O3	0.9327 (2)	1.0329 (2)	0.88383 (5)	0.0334 (6)
N	0.8053 (3)	0.4488 (2)	0.78554 (6)	0.0308 (7)
C1	0.6893 (3)	0.6372 (3)	0.96218 (7)	0.0331 (9)
C2	0.6885 (3)	0.8019 (3)	0.98561 (7)	0.0318 (9)
C3	0.7662 (3)	0.9436 (3)	0.96176 (7)	0.0288 (8)
C4	0.8410 (2)	0.9155 (2)	0.91273 (7)	0.0245 (7)
C5	1.0229 (2)	0.9303 (2)	0.84350 (7)	0.0243 (7)
C6	1.2013 (3)	0.9037 (3)	0.86073 (7)	0.0298 (8)
C7	1.2756 (2)	0.7479 (3)	0.86190 (8)	0.0332 (9)
C8	1.1835 (3)	0.5899 (3)	0.84959 (8)	0.0337 (8)
C9	0.9014 (3)	0.4410 (2)	0.83587 (8)	0.0302 (8)
C10	0.7876 (3)	0.4363 (2)	0.88670 (7)	0.0308 (8)
C11	0.7630 (2)	0.6111 (2)	0.91279 (7)	0.0272 (7)
C12	0.8296 (2)	0.7560 (2)	0.88876 (6)	0.0229 (7)
C13	0.9231 (2)	0.7610 (2)	0.83692 (7)	0.0234 (7)
C14	1.0193 (3)	0.5927 (2)	0.83763 (7)	0.0277 (7)
C15	0.8076 (2)	0.7671 (2)	0.78817 (7)	0.0256 (7)
C16	0.7015 (3)	0.6052 (3)	0.78253 (7)	0.0302 (8)
C17	0.7052 (4)	0.2950 (3)	0.77706 (8)	0.042 (1)
C18	0.6722 (5)	1.1434 (4)	1.02665 (9)	0.055 (1)
C19	1.4411 (3)	1.0517 (4)	0.8928 (1)	0.056 (1)

Table 2. *Geometric parameters (Å, °)*

O1—C3	1.364 (2)	C5—C6	1.496 (2)
O1—C18	1.427 (3)	C5—C13	1.537 (2)
O2—C6	1.363 (2)	C6—C7	1.339 (3)
O2—C19	1.431 (3)	C7—C8	1.456 (3)
O3—C4	1.373 (2)	C8—C14	1.338 (2)
O3—C5	1.477 (2)	C9—C10	1.572 (2)
N—C9	1.485 (2)	C9—C14	1.499 (2)
N—C16	1.462 (2)	C10—C11	1.514 (2)
N—C17	1.444 (2)	C11—C12	1.377 (2)
C1—C2	1.401 (2)	C12—C13	1.507 (2)
C1—C11	1.394 (2)	C13—C14	1.506 (2)
C2—C3	1.392 (2)	C13—C15	1.537 (2)
C3—C4	1.392 (2)	C15—C16	1.513 (2)
C4—C12	1.375 (2)		

C3—O1—C18	116.4 (2)	N—C9—C10	114.0 (1)
C6—O2—C19	115.5 (2)	N—C9—C14	108.3 (1)
C4—O3—C5	105.8 (1)	C10—C9—C14	110.7 (1)
C9—N—C16	111.6 (1)	C9—C10—C11	114.2 (1)
C9—N—C17	112.1 (1)	C1—C11—C10	125.0 (1)
C16—N—C17	111.1 (2)	C1—C11—C12	116.1 (1)
C2—C1—C11	120.8 (1)	C10—C11—C12	118.7 (1)
C1—C2—C3	121.7 (1)	C4—C12—C11	123.8 (1)
O1—C3—C2	126.2 (1)	C4—C12—C13	109.2 (1)
O1—C3—C4	116.9 (1)	C11—C12—C13	126.4 (1)
C2—C3—C4	116.9 (1)	C5—C13—C12	100.5 (1)
O3—C4—C3	126.7 (1)	C5—C13—C14	118.0 (1)
O3—C4—C12	113.0 (1)	C5—C13—C15	111.6 (1)
C3—C4—C12	120.3 (1)	C12—C13—C14	102.6 (1)
O3—C5—C6	109.3 (1)	C12—C13—C15	113.9 (1)
O3—C5—C13	106.3 (1)	C14—C13—C15	109.8 (1)
C6—C5—C13	113.8 (1)	C8—C14—C9	127.0 (2)
O2—C6—C5	109.9 (1)	C8—C14—C13	120.7 (2)
O2—C6—C7	126.9 (1)	C9—C14—C13	110.8 (1)
C5—C6—C7	123.1 (2)	C13—C15—C16	112.5 (1)
C6—C7—C8	121.7 (1)	N—C16—C15	111.2 (1)
C7—C8—C14	121.6 (2)		

The structure was solved using direct-methods analysis and refined by full-matrix least-squares methods. The absolute configuration of thebaine was chosen to agree with that of morphine (Mackay & Hodgkin, 1955; Gylbert, 1973). The atomic coordinates given in Table 1 correspond to the known absolute configuration.

Data collection: *CAD*-4 (Enraf–Nonius, 1977). Cell refinement: *CAD*-4. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *MULTAN*80 (Main *et al.*, 1980). Program(s) used to refine structure: *LSFM MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *BTABLE PTABLE CIF* in *MolEN*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1169). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(*Z*)-*N*-Formylnornuciferin Isolated from *Piper argyrophylum*

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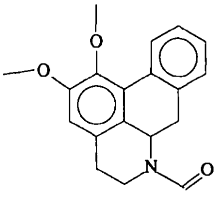
Abstract

The title compound (systematic name: 4,5,6a,7-tetrahydro-1,2-dimethoxy-6*H*-dibenzo[*de*,*g*]quinoline-6-carboxaldehyde), $C_{19}H_{19}NO_3$, was isolated as a minor component from the methanol extract of stems of *P. argyrophylum Miq.* The molecules are non-planar and the two benzene ring planes are at an angle of 21.9 (1)°. The *N*-formyl group and the two neighbouring C atoms constitute a planar fragment. The C—O—C planes of the two methoxy groups are nearly perpendicular to each other.

Comment

In a phytochemical investigation of the methanol extract of stems from *P. argyrophylum Miq.*, 25 compounds were isolated (Singh, Prasad, Olsen, Jha, Jain, Parmar & Wengel, 1996). One of the isolated compounds was the title compound (I) which could not be identified immediately from spectroscopic data and so a structure determination by X-ray diffraction was undertaken. The identity of (I) was confirmed further by NMR spectroscopy (Pachaly, Adnan & Will, 1992). Compound (I) has three planar domains, the two benzene rings (C1–C4, C16, C17 and C5–C10) and the *N*-formyl group with the two neighbouring atoms (O20, C20, N13, C12, C14). The Csp^3 atoms C11, C12, C14 and C15 force the molecule to be non-planar; this is reflected in the torsion angles [C10—C11—C12—C17 59.1 (4), C12—N13—C14—C15 −58.9 (4)°] and in the angle of 21.9 (1)° between the least-squares planes of the benzene rings. The C—O—C planes of the two methoxy groups are nearly perpendicular to each other, with torsion angles



(I)

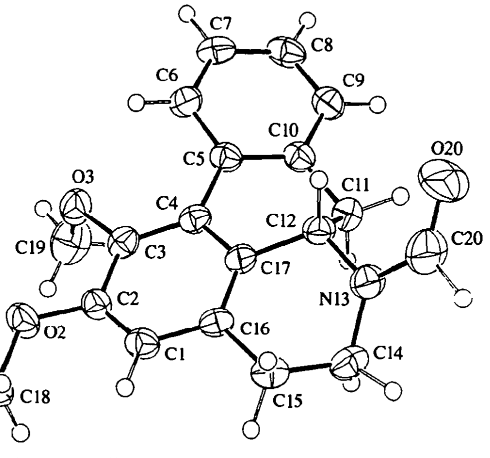


Fig. 1. Displacement-ellipsoid plot of (I) with ellipsoids drawn at the 50% probability level. H atoms are drawn as spheres of an arbitrary radius.