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Key indicators

Single-crystal X-ray study
T = 290 K
Mean σ(C–C) = 0.006 Å
R factor = 0.049
wR factor = 0.126
Data-to-parameter ratio = 8.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

6-*O*-Acetylcodeine

The title compound (systematic name: 6α-acetoxy-4,5α-epoxy-3-methoxy-17-methyl-morphin-7-ene), $C_{20}H_{23}NO_4$, crystallizes with one molecule in the asymmetric unit. The molecular structure exhibits features typical of morphine derivatives with a T configuration. The three-dimensional packing is stabilized by intermolecular C—H···N and C—H···π interactions.

Comment

6-*O*-Acetylcodeine, (I), was synthesized as a part of our study on opium alkaloids. The transformation of morphine derivatives into different metabolites is a matter of practical interest for detecting opiates in blood or urine. Although the studied compound has long been known as a urinary marker to detect the use of street heroin, its crystal structure has not been reported in the literature until now.

(I)
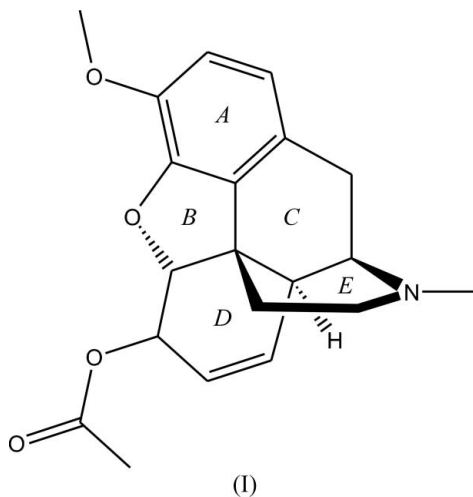
The molecule of (I) has the characteristic T-shape of classical opiates, with a dihedral angle between the mean planes of the *A*/*B*/*C* and *D*/*E* rings (see scheme) of 80.56 (8)°; the rings are denoted following commonly used nomenclature for opiates. The main structural features of the molecule are very close to those of codeine, heroin and morphine (Canfield *et al.*, 1979, 1987; Gylbert, 1973). The ring fusions and conformations are similar to those previously reported for morphine derivatives (Gelders & de Ranter, 1979; Petrickova *et al.*, 2002; Moody *et al.*, 1997). Aromatic ring *A* is planar, *B* is close to an envelope, *C* and *D* assume half-chair conformations and *E* assumes a chair form (Table 1). The conformation about the single C—C bonds within the rings is staggered, except for those along the C5—C6 bond which is eclipsed, with an O2—C5—C6—O3 torsion angle of 0.8 (5)° (Moss, 1996).

The three-dimensional arrangement of the molecules is shown in Fig. 2. Two distinct types of weak interactions are observed (Table 2); C5—H5···N1 contacts connect molecules along the *a* axis to form chains, while C—H$_A$···π contacts link the chains along the *b* axis. The angle between the normal to the plane of the aromatic unit and the line linking C20 and the centroid of the ring (Cg1) is 7.35 (15)°.

An independent structure determination of 6-*O*-acetyl-codeine is reported in the preceding paper (Sonar *et al.*, 2005).

Experimental

Compound (I) was synthesized according to Huang *et al.* (1999). Crystals suitable for X-ray diffraction were obtained by slow evaporation of an ethyl acetate solution at room temperature.

Figure 1
The molecular structure of (I), showing the atom-numbering scheme and 50% probability displacement ellipsoids.

Crystal data

$C_{20}H_{23}NO_4$	Mo $K\alpha$ radiation
$M_r = 341.39$	Cell parameters from 22
Orthorhombic, $P2_12_12_1$	reflections
$a = 8.628$ (2) Å	$\theta = 18.3–19.7°$
$b = 12.727$ (2) Å	$\mu = 0.09$ mm^{-1}
$c = 15.4842$ (19) Å	$T = 290$ (2) K
$V = 1700.3$ (5) Å^3	Prism, colorless
$Z = 4$	$0.25 \times 0.25 \times 0.25$ mm
$D_x = 1.334$ Mg m^{-3}	

Data collection

Enraf–Nonius CAD-4	$\theta_{max} = 26.0°$
diffractometer	$h = 0 \rightarrow 10$
Non–profiled $\omega/2\theta$ scans	$k = 0 \rightarrow 15$
4181 measured reflections	$l = -19 \rightarrow 19$
1928 independent reflections	3 standard reflections
1093 reflections with $I > 2\sigma(I)$	frequency: 120 min
$R_{int} = 0.077$	intensity decay: 5%

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.049$	$w = 1/[\sigma^2(F_o^2) + (0.0562P)^2]$
$wR(F^2) = 0.126$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.98$	$(\Delta/\sigma)_{max} < 0.001$
1928 reflections	$\Delta\rho_{max} = 0.20$ e Å^{-3}
226 parameters	$\Delta\rho_{min} = -0.19$ e Å^{-3}

Table 1
Selected torsion angles (°).

O2—C4—C12—C13	−4.3 (5)	C10—C11—C12—C13	6.8 (7)
C13—C5—O2—C4	32.5 (4)	C4—C12—C13—C5	23.3 (5)
C13—C5—C6—C7	4.8 (5)	C11—C12—C13—C15	86.5 (5)
C5—C6—O3—C19	−76.4 (5)	C15—C13—C14—C9	−64.5 (4)
C6—C7—C8—C14	−1.0 (8)	C13—C15—C16—N1	−51.2 (5)
C7—C8—C14—C13	−24.8 (6)	O4—C19—O3—C6	−11.8 (7)
C14—C9—N1—C16	−62.5 (4)	C20—C19—O3—C6	166.1 (4)
C14—C9—C10—C11	37.8 (6)		

Figure 2
The packing of the 6-*O*-acetylcodeine molecules. The dotted lines indicate C—H···N interactions. [Symmetry codes: (i) $\frac{1}{2} + x, 1 - y, 1 - z$; (ii) $2 - x, \frac{1}{2} + y, \frac{1}{2} - z$.]

H atoms were placed in idealized positions (C—H = 0.93–0.98 Å) and constrained to ride on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$. In the absence of significant anomalous scattering effects, Friedel pairs were merged.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3 for Windows* (Farrugia, 1997) and *MERCURY* (Version 1.3; Bruno *et al.*, 2002); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C5—H5···N1^i	0.98	2.42	3.363 (5)	163
C20—H20C···Cg1^{ii}	0.96	2.52	3.421 (2)	157

Symmetry codes: (i) $x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (ii) $-x + 2, y + \frac{1}{2}, -z + \frac{1}{2}$. Cg1 is the centroid of ring A
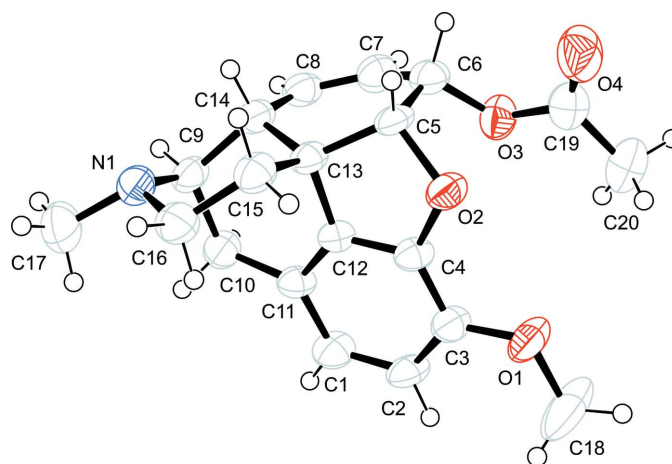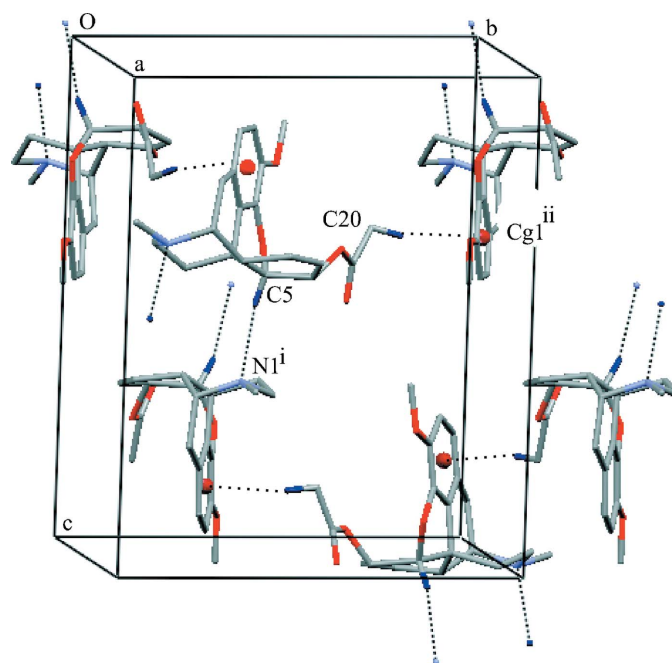
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