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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1003). Services for accessing these data are described at the back of the journal.

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## (7*R*,8*S*,10*bR*)-7,8-Dihydroxy-1,5,6,7,8,9,10,10*b*-octahydro-3*H*-1,3-oxazolo[4,3-*a*]isoquinolin-3-one

KHALIL A. ABBOUD, GABOR BUTORA, STEPHEN P. FEARNLEY, ANDREW G. GUM, MICHELE R. STABILE AND TOMAS HUDLICKY

Department of Chemistry, University of Florida, PO Box 117200, Gainesville, Florida 32611-7200, USA. E-mail: [abboud@chem.ufl.edu](mailto:abboud@chem.ufl.edu)

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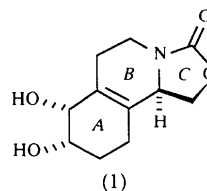
## Abstract

The title compound, C<sub>11</sub>H<sub>15</sub>NO<sub>4</sub>, was synthesized as an intermediate in a synthesis of the morphine skeleton. The two six-membered rings adopt <sup>4</sup>H<sub>3</sub> half-chair conformations. The five-membered ring is in an envelope (*E*) conformation. Chains of the molecules hydro-

gen bonded through the allylic hydroxyl and carbonyl groups extend along the *b* axis. These chains are cross-linked along the [101] direction by hydrogen bonds between the adjacent secondary OH group and the allylic O atom [allylic O···O(*x*, 1 + *y*, *z*) 2.836 (2) Å, O—H···O 133 (2)<sup>o</sup>; secondary hydroxyl O···O( $\frac{1}{2} + x$ ,  $\frac{3}{2} - y$ , 1 - *z*) 2.751 (2) Å, O—H···O 174 (2)<sup>o</sup>].

## Comment

In the past 40 years, numerous total syntheses of morphine have been published [for a recent review see Hudlicky *et al.* (1996), and references therein]. We recently reported a chemo-enzymatic synthesis of the morphine skeleton in which the title compound, (1), was synthesized in one of the intermediate steps (Butora *et al.*, 1996). Attempts have been made to relate the absolute stereochemistry at C10*b* to either C7 or C8 using standard spectroscopic techniques. Careful coupling-constant analysis (<sup>1</sup>H NMR, various solvents) suggested the absolute stereochemistry shown below. Although nuclear Overhauser enhancement experiments seemed to support these conclusions, final proof was sought from a single-crystal X-ray structure determination. As the absolute stereochemistry at C7 and C8 is set enzymatically (Stabile *et al.*, 1995), this also provided proof of the absolute stereochemistry of (1) as shown.



The bond lengths and angles in (1) are in good agreement with counterparts observed in other organic compounds (Allen *et al.*, 1987). The molecules of (1) have two six-membered rings fused through the C6a=C10a double bond, which has the only zero-value endocyclic torsion angle in either ring. The planar geometry around the double bond forces the ring conformations to deviate from a more stable chair conformation. Consequently, rings A and B adopt half-chair conformations which may be described as <sup>4</sup>H<sub>3</sub> according to Boeyens (1978) terminology. Ring A has C8 and C9 at distances of -0.465 (3) and 0.294 (3) Å, respectively, from the plane of C6a, C7, C10a and C10, while N4 and C5 are at distances of -0.340 (3) and 0.303 (4) Å, respectively, from the plane of C6, C6a, C10a and C10*b*. Ring C adopts an envelope conformation with C10*b* occupying the flap position at a distance of 0.382 (3) Å from the plane of C1, O2, C3 and N4.

Each molecule of (1) is involved in two intermolecular hydrogen bonds. One hydrogen bond between O7—H7 and O1 results in a chain of molecules extending

along the *b* axis. The second hydrogen bond, between O8—H8 and O7, cross-links the chains along the [101] direction.

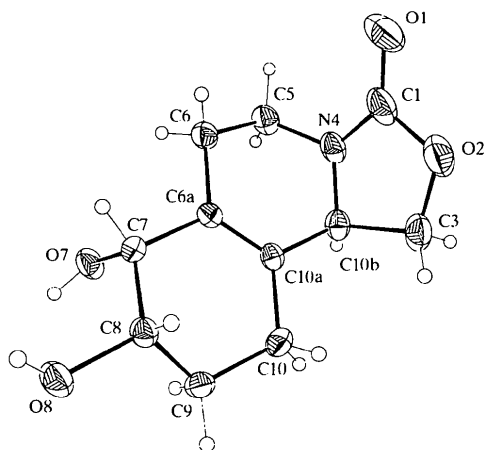


Fig. 1. The molecular structure of (1) showing the atom-numbering scheme. Displacement ellipsoids are at the 50% probability level.

## Experimental

The synthesis of (1) has been reported previously (Butora *et al.*, 1996). Colorless blocks of (1) were obtained by slow evaporation of an ethyl acetate solution.

### Crystal data

$C_{11}H_{15}NO_4$   
 $M_r = 225.24$   
 Orthorhombic  
 $P2_12_12_1$   
 $a = 8.519(2) \text{ \AA}$   
 $b = 9.315(2) \text{ \AA}$   
 $c = 13.429(3) \text{ \AA}$   
 $V = 1065.7(4) \text{ \AA}^3$   
 $Z = 4$   
 $D_x = 1.404 \text{ Mg m}^{-3}$   
 $D_m$  not measured

### Data collection

Siemens P3/PC diffractometer  
 $\omega$  scans  
 Absorption correction:  
 by integration based on measured crystal faces (SHELXTLS; Sheldrick, 1995)  
 $T_{\min} = 0.963$ ,  $T_{\max} = 0.972$   
 2745 measured reflections  
 1224 independent reflections

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.038$   
 $wR(F^2) = 0.078$

Mo  $K\alpha$  radiation  
 $\lambda = 0.71073 \text{ \AA}$   
 Cell parameters from 32 reflections  
 $\theta = 10\text{--}11^\circ$   
 $\mu = 0.107 \text{ mm}^{-1}$   
 $T = 298(2) \text{ K}$   
 Block  
 $0.38 \times 0.34 \times 0.31 \text{ mm}$   
 Colorless

1115 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.017$   
 $\theta_{\text{max}} = 27.5^\circ$   
 $h = -11 \rightarrow 11$   
 $k = 0 \rightarrow 12$   
 $l = 0 \rightarrow 17$   
 4 standard reflections every 100 reflections  
 intensity decay: <1%

$(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 0.20 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.16 \text{ e \AA}^{-3}$

$S = 1.06$   
 2447 reflections  
 154 parameters  
 H atoms: see below  
 $w = 1/[\sigma^2(F_o^2) + (0.0183P)^2 + 0.4538P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

Extinction correction:  
 SHELXTLS  
 Extinction coefficient:  
 0.034(2)  
 Scattering factors from  
 International Tables for  
 Crystallography (Vol. C)

Table 1. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

O1—C1	1.209(3)	N4—C10b	1.453(2)
C1—O2	1.351(3)	N4—C5	1.457(2)
C1—N4	1.352(3)	C7—O7	1.442(2)
O2—C3	1.440(3)	C8—O8	1.426(2)
O1—C1—O2	122.5(2)	C1—N4—C10b	110.8(2)
O1—C1—N4	127.8(2)	C1—N4—C5	121.1(2)
O2—C1—N4	109.7(2)	C10b—N4—C5	117.36(14)
C1—O2—C3	109.0(2)		

Table 2. Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ )

D—H...A	D—H	H...A	D...A	D—H...A
O7—H7...O1'	0.81(3)	2.22(3)	2.836(2)	133(2)
O8—H8...O7 <sup>n</sup>	0.83(2)	1.93(2)	2.751(2)	174(2)

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

Friedel pairs were used in an attempt to determine the absolute configuration, but refinement of the Flack (1983) parameter was inconclusive. The hydroxyl H atoms were refined without constraints, while the rest of the H atoms were placed in idealized positions and were refined riding on their parent atoms. C—H distances of 0.98 and 0.97  $\text{\AA}$  were used for tertiary and secondary C atoms, respectively. The displacement parameters of the H atoms were set at  $1.2U_{\text{eq}}$  of the parent C.

Data collection: P3/PC (Siemens, 1993). Cell refinement: P3/PC. Data reduction: SHELXTL-Plus (Sheldrick, 1990). Program(s) used to solve structure: SHELXTLS (Sheldrick, 1995). Program(s) used to refine structure: SHELXTLS. Molecular graphics: SHELXTLS. Software used to prepare material for publication: SHELXTLS.

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