O(3)	0.22743 (58)	0.54841 (38)	0.73892 (18)	2.4 (1)
O(4)	0.53024 (51)	0.59677 (38)	0.66478 (16)	2.1 (1)
O(5)	0.90428 (55)	0.41161 (34)	0.64285 (19)	2.2 (1)
N(4)	0.38349 (58)	0.66905 (31)	0.88055 (19)	1.1 (1)
C(2)	0.58974 (73)	0.46024 (47)	0.94414 (22)	1.6 (1)
C(3)	0.36450 (72)	0.51658 (42)	0.91911 (22)	1.1 (1)
C(5)	0.52170 (69)	0.68028 (44)	0.80361 (22)	1.2 (1)
C(6)	0.75560 (71)	0.63222 (45)	0.82274 (24)	1.5 (1)
C(7)	0.20916 (68)	0.53081 (43)	0.99395 (22)	1.2 (1)
C(8)	0.41309 (69)	0.59969 (43)	0.73035 (24)	1.3 (1)

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

S(1)—C(2)	1.807 (4)	C(3)—C(7)	1.536 (5)
S(1)—C(6)	1.813 (4)	O(1)—C(7)	1.281 (5)
C(2)—C(3)	1.518 (6)	O(2)—C(7)	1.219 (5)
C(5)—C(6)	1.522 (6)	C(5)—C(8)	1.531 (5)
N(4)—C(3)	1.501 (5)	O(3)—C(8)	1.230 (5)
N(4)—C(5)	1.500 (4)	O(4)—C(8)	1.273 (5)
C(6)—S(1)—C(2)	95.6 (2)	C(3)—C(7)—O(1)	112.9 (3)
S(1)—C(2)—C(3)	111.9 (3)	C(3)—C(7)—O(2)	120.2 (3)
C(2)—C(3)—N(4)	109.9 (3)	O(1)—C(7)—O(2)	126.9 (3)
C(3)—N(4)—C(5)	116.4 (3)	C(6)—C(5)—C(8)	115.4 (3)
N(4)—C(5)—C(6)	110.0 (3)	N(4)—C(5)—C(8)	111.0 (3)
C(5)—C(6)—S(1)	111.6 (3)	C(5)—C(8)—O(3)	119.2 (3)
C(2)—C(3)—C(7)	112.3 (3)	C(5)—C(8)—O(4)	113.7 (4)
N(4)—C(3)—C(7)	107.2 (3)	O(3)—C(8)—O(4)	127.0 (4)

Density was measured by flotation in a $CHCl_3/CHBr_3$ mixture. Data were corrected for Lorentz and polarization effects but not for absorption. The structure was solved by direct methods with *SIR*88 (Burla *et al.*, 1989) and refined by anisotropic full-matrix least squares on F. At this stage the water molecule and all the H atoms were clearly located through difference syntheses. In the final refinement the H atoms were modeled at ideal geometry with isotropic thermal parameters fixed to the corresponding value of the non-H atoms to which they are linked, and fixed bond lengths (X—H = 1.03 Å with X = C, N, O). Calculations were carried out on the Data General Eclipse MV/8000 II of the CNR Area (Roma) using mainly *SIRCAOS* (Camalli *et al.*, 1986). Some of the final calculations were performed with *PARST* (Nardelli, 1983). The scattering factors were those of Cromer & Mann (1968) for the non-H atoms and those of Hanson, Herman, Lea & Skillman (1964) for the H atoms.

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Structure of Sinoacutine

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Abstract

In the title alkaloid, $(9\alpha,13\alpha)$-5,6,8,14-tetradehydro-4-hydroxy-3,6-dimethoxy-17-methylmorphinan-7-one, the mean value of three C—N—C angles is 111.0 (4)° indicating sp^3 hybridization of the N atom. The interplanar angle between the aromatic ring A and planar ring D [maximum deviation 0.051 (5) Å at C14] is 53.8 (1)°. The absolute configuration has been assigned to agree with the known chirality at C3 (*S*) [Southon & Buckingham, (1989). *Dictionary of Alkaloids*, p. 974. London: Chapman and Hall].

Comment

Sinoacutine is an enantiomer of salutaridine. In nature it occurs both in optically active and racemic

forms (Stuart, 1971). Sinoacutine contains a sequence isosteric with γ-aminobutyric acid (GABA) and according to *in vitro* measurements (Kardos, Blaskó, Simonyi & Szántay, 1984) it can be considered as a partial agonist of the GABA/benzodiazepine receptor complex. Sinoacutine plays an important role as biosynthetic intermediate in the formation of morphine (Barton & Cohen, 1957).

The title alkaloid of morphinandienone-type was isolated from the aerial parts of the species *Corydalis ochroleuca*. The extraction of dried plant material was carried out according to Preininger, Vesely, Gašić, Šimanek & Dolejš (1975) and it was isolated as described by Gašić, Popović & Dragutinović (1985). Total synthesis of sinoacutine has been described by Ludwig & Schaefer (1986).

From the puckering parameters (Cremer & Pople, 1975) of ring B [$Q = 0.530$ (6) Å, $\varphi = 18.2$ (8)^c, $\theta = 52.6$ (6)$^\circ$] it can be seen that it is a transition form between half-chair and envelope shape, whereas ring C [$Q = 0.556$ (6) Å, $\varphi = 305$ (4)$^\circ$, $\theta = 8.6$ (6)$^\circ$], forming a bridge between C11 and the chiral atom C3, adopts an almost perfect chair conformation. H3′ participates in a symmetrical three-centered hydrogen-bond interaction (Jeffrey, 1978). The intramolecular component of the three-centered hydrogen bond with the parameters O3—H3′ = 0.93 (5), O3···O2 = 2.623 (5) Å, H3′···O2 = 2.16 (6) Å, O3—H3′···O2 = 110 (4)$^\circ$ is the cause of the small C9—C8—O2 bond angle of 114.3 (4)$^\circ$. The molecules are bound together by the intermolecular component of a three-centered hydrogen bond with the parameters O3···N^i = 2.884 (5), H3′···N^i = 2.04 (5) Å, O3—H3′···N^i = 150 (5)$^\circ$ [symmetry code: (i) $\frac{1}{2} - x$, $1 - y$, $z - \frac{1}{2}$]. The O2···H3′···N^i angle is 101 (2)$^\circ$ and H3′ lies exactly in the plane formed by atoms O3, O2 and N^i. The O4—C18 bond is nearly

in the plane of ring D, while the O2—C17 bond deviates from the plane of the phenyl ring A as indicated by the corresponding torsion angles.

Experimental

Crystal data

$C_{19}H_{21}NO_4$	Cell parameters from 22
$M_r = 327.38$	reflections
Orthorhombic	$\theta = 6.0$– 13.5°
$P2_12_12_1$	$\mu = 0.09$ mm^{-1}
$a = 10.745$ (5) Å	$T = 293$ K
$b = 11.435$ (5) Å	Irregular shape
$c = 13.003$ (6) Å	$0.28 \times 0.25 \times 0.20$ mm
$V = 1598$ (1) Å^3	Citrine
$Z = 4$	Crystal source: alkaloid from
$D_x = 1.361$ Mg m^{-3}	*Corydalis ochroleuca*
Mo $K\alpha$ radiation	
$\lambda = 0.7107$ Å	

Data collection

CAD-4 diffractometer	$h = 0 \rightarrow 12$
$\omega/2\theta$ scans	$k = 0 \rightarrow 13$
2785 measured reflections	$l = 0 \rightarrow 14$
1453 independent reflections	1 standard reflection
1389 observed reflections	frequency: 200 min
[$I > 3.5\sigma(I)$]	intensity variation: none
$\theta_{max} = 24^\circ$	

Refinement

Refinement on F	$(\Delta/\sigma)_{max} = 0.020$
Final $R = 0.057$	$\Delta\rho_{max} = 0.21$ e Å^{-3}
$S = 0.968$	$\Delta\rho_{min} = 0.20$ e Å^{-3}
1389 reflections	
222 parameters	Atomic scattering factors
$w = 1$	from *SHELX*76

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

$$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$$

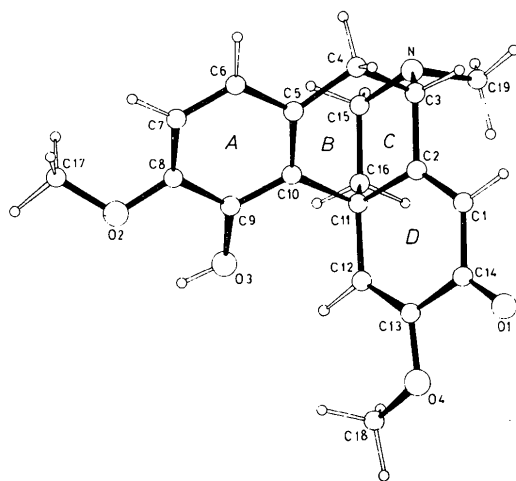|	x	y	z	U_{eq}
C1	0.6561 (5)	0.4773 (5)	0.7858 (4)	0.045 (1)
C2	0.5440 (4)	0.4929 (5)	0.8228 (4)	0.034 (1)
C3	0.5167 (4)	0.4963 (4)	0.9361 (4)	0.038 (1)
C4	0.4460 (5)	0.3855 (4)	0.9615 (4)	0.041 (1)
C5	0.3488 (5)	0.3508 (4)	0.8823 (4)	0.037 (1)
C6	0.2671 (5)	0.2620 (5)	0.9092 (4)	0.044 (1)
C7	0.1724 (5)	0.2299 (5)	0.8457 (4)	0.040 (1)
C8	0.1540 (4)	0.2901 (5)	0.7557 (4)	0.038 (1)
C9	0.2355 (4)	0.3794 (4)	0.7252 (3)	0.033 (1)
C10	0.3371 (4)	0.4069 (4)	0.7864 (4)	0.032 (1)
C11	0.4300 (4)	0.5050 (4)	0.7572 (3)	0.032 (1)
C12	0.4604 (4)	0.5067 (4)	0.6440 (3)	0.035 (1)
C13	0.5750 (4)	0.4926 (5)	0.6079 (4)	0.040 (1)
C14	0.6818 (5)	0.4692 (5)	0.6767 (4)	0.043 (1)
C15	0.3442 (5)	0.6302 (5)	0.9012 (4)	0.038 (1)
C16	0.3712 (5)	0.6248 (4)	0.7865 (4)	0.036 (1)
C17	−0.0478 (5)	0.2154 (6)	0.7294 (5)	0.059 (2)
C18	0.5152 (6)	0.5290 (6)	0.4377 (4)	0.059 (2)
C19	0.5407 (5)	0.7029 (5)	0.9661 (4)	0.050 (1)
N	0.4524 (4)	0.6048 (4)	0.9668 (3)	0.036 (1)
O1	0.7846 (3)	0.4478 (4)	0.6428 (3)	0.064 (1)
O2	0.0582 (3)	0.2706 (4)	0.6892 (3)	0.058 (1)
O3	0.2109 (3)	0.4400 (3)	0.6383 (2)	0.045 (1)
O4	0.6090 (3)	0.4957 (4)	0.5063 (2)	0.049 (1)

Fig. 1. Perspective view of the sinoacutine molecule showing atomic numbering. The H atoms are shown but not labelled.

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

C1—C2	1.309 (7)	C9—O3	1.352 (5)
C1—C14	1.448 (7)	C10—C11	1.549 (6)
C2—C3	1.503 (7)	C11—C12	1.508 (6)
C2—C11	1.499 (6)	C11—C16	1.556 (7)
C3—C4	1.514 (7)	C12—C13	1.328 (6)
C3—N	1.475 (7)	C13—C14	1.479 (7)
C4—C5	1.520 (7)	C13—O4	1.371 (6)
C5—C6	1.387 (7)	C14—O1	1.214 (6)
C5—C10	1.408 (7)	C15—C16	1.521 (7)
C6—C7	1.361 (8)	C15—N	1.471 (7)
C7—C8	1.372 (8)	C17—O2	1.403 (7)
C8—C9	1.402 (7)	C18—O4	1.399 (7)
C8—O2	1.363 (6)	C19—N	1.469 (7)
C9—C10	1.387 (6)		
C2—C1—C14	123.0 (5)	C9—C10—C11	122.1 (4)
C1—C2—C3	122.9 (5)	C2—C11—C10	108.7 (4)
C1—C2—C11	123.7 (5)	C2—C11—C12	112.3 (4)
C3—C2—C11	113.3 (4)	C2—C11—C16	105.9 (4)
C2—C3—C4	106.9 (4)	C10—C11—C12	112.8 (4)
C2—C3—N	112.2 (4)	C10—C11—C16	108.4 (4)
C4—C3—N	114.2 (4)	C12—C11—C16	108.4 (4)
C3—C4—C5	114.6 (4)	C11—C12—C13	123.0 (4)
C4—C5—C6	117.1 (5)	C12—C13—C14	121.8 (5)
C4—C5—C10	122.9 (4)	C12—C13—O4	125.8 (5)
C6—C5—C10	120.0 (5)	C14—C13—O4	112.4 (4)
C5—C6—C7	121.2 (5)	C1—C14—C13	115.7 (5)
C6—C7—C8	119.3 (5)	C1—C14—O1	122.8 (5)
C7—C8—C9	121.1 (5)	C13—C14—O1	121.5 (5)
C7—C8—O2	124.6 (5)	C16—C15—N	114.2 (4)
C9—C8—O2	114.3 (4)	C11—C16—C15	110.7 (4)
C8—C9—C10	119.6 (4)	C3—N—C15	112.3 (4)
C8—C9—O3	119.2 (4)	C3—N—C19	109.8 (4)
C10—C9—O3	121.2 (4)	C15—N—C19	110.9 (4)
C5—C10—C9	118.4 (4)	C8—O2—C17	116.8 (4)
C5—C10—C11	119.3 (4)	C13—O4—C18	115.4 (4)

Data were corrected for Lorentz and polarization factors. A value for R_{int} is missing since a unique data set was collected. The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1985) and refined using *SHELX*76 (Sheldrick, 1976). The positions of H atoms were generated from assumed geometry except that of H3' which was calculated using the program *MMX* (Allinger, Schäfer, Siam, Klimkowski & van Alsenoy, 1985) and refined isotropically. The positions of H atoms in CH_3 groups were checked on a $\Delta\rho$ map. Non-H atoms were refined anisotropically. Several weighting schemes were tested and the best results were obtained with the unit weight. The overall isotropic temperature factor for H atoms was $U_1 = 0.0575$ (50) Å^2 and for the methyl H atoms $U_2 = 0.0868$ (73) Å^2. Software used to prepare material for publication: *CSU* (Vicković, 1988). All calculations were carried out on a PC/AT computer.

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3-[1-(Ethylamino)ethylidene]-6-methyl-3*H*-pyran-2,4-dione

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Abstract

The structural results clearly indicate that 3-[1-(ethylamino)ethylidene]-6-methyl-3*H*-pyran-2,4-dione exists as a keto-enamine tautomer in the solid state. The H atom bonded to N(9) refines with a normal temperature factor and the bond distance of the keto group [C(4)—O(13)] of 1.263 (1) Å is elongated due to resonance. This resonance is also indicated by an averaging of the single bonds [C(2)—C(3), C(3)—C(4), C(4)—C(5) and C(8)—N(9)] and double bonds [C(3)—C(8) and C(4)—O(13)] in the crystal structure and by the fact that not only is the pyran ring planar [r.m.s. deviation 0.0212 (9) Å] but also there is