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Acta Cryst. (1979). **B35**, 986–988

N-Cyano-1-hydroxy-1,2-seconarcotine

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(Received 16 October 1978; accepted 1 December 1978)

Abstract. $C_{23}H_{24}N_2O_8$, orthorhombic, $P2_12_12_1$, $a = 8.477$ (3), $b = 10.914$ (3), $c = 23.552$ (5) Å, $V = 2179.0$ Å³, $M_r = 456.5$, $D_x = 1.391$, $D_m = 1.38$ Mg m⁻³, $\mu(\text{Mo } K\alpha, \lambda = 0.71069 \text{ Å}) = 0.114$ mm⁻¹, $Z = 4$. The structure was solved by direct methods and refined to $R = 0.092$. The two asymmetric C atoms have an *S* configuration.

Introduction. Reaction of compounds which have a 2-methyl-1,2,3,4-tetrahydroisoquinoline skeleton with BrCN (in aprotic solvents) results in the opening of the tetrahydroisoquinoline ring but not in *N*-demethylation (von Braun, 1916). When the reaction of (–)- α -narcotine (1*R*:9*S*) with BrCN was completed in benzene, the product could not be isolated as a homogeneous compound (Gaal, Kerekes & Bognár, 1971). Boiling the crude intermediate product with acid one obtains (+)- β -narcotine (1*S*:9*S*), due to the inversion of the configuration of C(1).

When these reactions are carried out in aqueous tetrahydrofuran (in the presence of base) the product of the ring opening can be isolated in high yield (Albright & Goldman, 1969; Rönsch, 1972). By use of this method, the same ring-opened product (*N*-cyano-1-

hydroxy-1,2-seconarcotine) is obtained from two of four possible narcotine isomers: either from (–)- α -narcotine (1*R*:9*S*) or (+)- β -narcotine (1*S*:9*S*). Elucidation of the stereochemistry of the reaction requires knowledge of the relative configuration and conformation of the seco compound; thus the crystal structure determination of the product obtained from (+)- β -narcotine was carried out.

The intensities of 2071 independent reflections were collected on a Syntex $P2_1$ automatic four-circle diffractometer with monochromated Mo $K\alpha$ radiation. The structure was solved by direct methods using the *MULTAN 77* program (Main, Woolfson, Lessinger, Germain & Declercq, 1977).

The molecular scattering factors of atomic groups with suspected conformations were used for the calculation of E values (Main, 1976). Phase determination was performed with 260 reflections ($E \geq 1.44$) and 5000 phase relationships. The E map calculated with the sign set of the highest combined figure of merit revealed the positions of all non-hydrogen atoms ($R = 0.22$).

The atomic positions of the heavy atoms were refined by an anisotropic least-squares procedure using the program *SHELX 77* (Sheldrick, 1977). The positions of the H atoms were calculated from assumed geometries (all non-methylene hydrogens were also located in a difference map), and were refined in an isotropic mode. The final $R = 0.092$ for all reflections.

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Table 1. Final fractional coordinates ($\times 10^4$) for the non-hydrogen atoms

Estimated standard deviations are in parentheses.

	x	y	z
C(1)	2008 (11)	7949 (8)	2957 (3)
C(2)	926 (13)	8196 (12)	2454 (4)
C(3)	717 (13)	9574 (11)	2353 (5)
N(4)	-169 (10)	9840 (10)	1811 (4)
C(5)	677 (19)	9653 (20)	1287 (6)
C(6)	-1648 (11)	9603 (9)	1815 (4)
N(7)	-3054 (10)	9385 (8)	1802 (4)
C(8)	1363 (11)	8070 (10)	3496 (4)
C(9)	2277 (13)	7773 (9)	3948 (4)
O(10)	1896 (11)	7805 (8)	4515 (3)
C(11)	3265 (19)	7431 (13)	4812 (4)
O(12)	4451 (10)	7055 (8)	4408 (3)
C(13)	3784 (13)	7365 (9)	3881 (4)
C(14)	4459 (11)	7223 (9)	3358 (4)
O(15)	5944 (9)	6771 (7)	3298 (3)
C(16)	7157 (17)	7565 (19)	3543 (9)
C(17)	3580 (10)	7550 (8)	2884 (3)
C(18)	4434 (12)	7455 (9)	2317 (4)
O(19)	3953 (8)	8358 (6)	1922 (3)
C(20)	4323 (11)	6160 (8)	2064 (4)
O(21)	2741 (8)	5891 (6)	1876 (3)
C(22)	2660 (11)	5690 (9)	1300 (4)
O(23)	1449 (8)	5479 (9)	1079 (4)
C(24)	4324 (10)	5790 (9)	1083 (4)
C(25)	4891 (10)	5592 (9)	538 (4)
O(26)	3966 (9)	5208 (7)	95 (3)
C(27)	2941 (15)	6058 (15)	-144 (6)
C(28)	6527 (10)	5721 (9)	456 (4)
O(29)	7033 (8)	5534 (8)	-90 (3)
C(30)	8639 (13)	5515 (14)	-189 (6)
C(31)	7501 (10)	5953 (10)	910 (4)
C(32)	6892 (10)	6146 (9)	1453 (4)
C(33)	5308 (11)	6042 (9)	1524 (4)

The final atomic coordinates are listed in Tables 1 and 2.*

Discussion. A perspective view of the molecule with the atomic numbering used (different from that applied in chemistry) is shown in Fig. 1. Bond lengths and angles are given in Tables 3 and 4.

The trunk of the molecule is composed of two fused fairly coplanar ring-pairs, the planes of which are inclined at an angle of 29.7° (Table 5).

The configuration of the two asymmetric C(18) and C(20) atoms [C(1) and C(9) according to chemical numbering] compares to that in (+)- β -narcotine, *i.e.* (1*S*:9*S*) (Fig. 2). Although the absolute configuration has not yet been determined, on the basis of the experimental derivation of the molecule the configuration can be taken as absolute.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34120 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Final fractional coordinates ($\times 10^3$) of the hydrogen atoms

Estimated standard deviations are in parentheses.

	x	y	z
H(21)	36 (18)	767 (13)	241 (6)
H(22)	136 (11)	777 (8)	208 (4)
H(3a)	161 (10)	990 (8)	232 (4)
H(3b)	14 (11)	1008 (9)	271 (4)
H(51)	161 (19)	943 (17)	140 (7)
H(52)	32 (16)	1008 (14)	96 (6)
H(53)	34 (11)	876 (8)	114 (4)
H(8)	33 (12)	841 (9)	359 (4)
H(111)	395 (17)	818 (13)	504 (6)
H(112)	293 (13)	674 (10)	513 (4)
H(161)	833 (9)	741 (7)	347 (3)
H(162)	739 (9)	700 (7)	387 (3)
H(163)	674 (10)	847 (7)	332 (3)
H(18)	557 (12)	762 (9)	240 (4)
H(19)	439 (8)	915 (6)	207 (3)
H(20)	469 (12)	560 (8)	237 (4)
H(271)	261 (15)	563 (11)	-47 (5)
H(272)	428 (15)	649 (11)	-37 (5)
H(273)	229 (10)	651 (7)	10 (3)
H(301)	881 (19)	543 (16)	-69 (7)
H(302)	922 (11)	465 (8)	-3 (4)
H(303)	931 (15)	640 (11)	-9 (5)
H(31)	877 (9)	606 (6)	83 (3)
H(32)	791 (13)	649 (9)	173 (4)

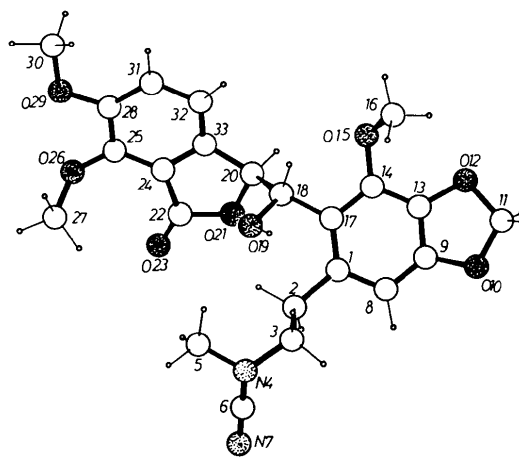


Fig. 1. Perspective view of the molecule with the atomic numbering. Bare numbers represent carbon atoms.

Bond lengths and angles are generally normal. However, a remarkably long C—O bond is found in one of the methoxy groups [C(16)—O(15), 1.46 (2) Å]. The C(6)—N(7) triple bond is also somewhat longer than usual [1.22 (1) Å]. Relevant torsion angles are shown in Table 6.

The molecules maintain no hydrogen bonds. A projection of the unit cell is depicted in Fig. 3.

Table 3. Bond lengths (Å)

E.s.d.'s are 0.01 Å (0.02 Å for distances with asterisks).

C(1)—C(2)	1.52	C(17)—C(18)	1.52
C(1)—C(8)	1.39	C(18)—O(19)	1.42
C(1)—C(17)	1.41	C(18)—C(20)	1.54
C(2)—C(3)	1.53*	C(20)—O(21)	1.44
C(3)—N(4)	1.51	C(20)—C(33)	1.53
N(4)—C(5)	1.44*	O(21)—C(22)	1.38
N(4)—C(6)	1.28	C(22)—O(23)	1.17
C(6)—N(7)	1.22	C(22)—C(24)	1.50
C(8)—C(9)	1.36	C(24)—C(33)	1.36
C(9)—O(10)	1.37	C(24)—C(25)	1.39
C(9)—C(13)	1.36*	C(25)—O(26)	1.37
O(10)—C(11)	1.42*	C(25)—C(28)	1.41
C(11)—O(12)	1.44*	O(26)—C(27)	1.39*
O(12)—C(13)	1.41	C(28)—O(29)	1.37
C(13)—C(14)	1.37	C(28)—C(31)	1.37
C(14)—O(15)	1.36	C(29)—C(30)	1.38
C(14)—C(17)	1.39	C(31)—C(32)	1.40
O(15)—C(16)	1.46*	C(32)—C(33)	1.36

Table 4. Bond angles (°) with their estimated standard deviations in parentheses

C(2)—C(1)—C(8)	117.2 (9)	C(17)—C(18)—O(19)	113.1 (7)
C(17)—C(1)—C(2)	121.9 (8)	C(17)—C(18)—C(20)	111.9 (8)
C(17)—C(1)—C(8)	120.8 (8)	O(19)—C(18)—C(20)	111.6 (7)
C(1)—C(2)—C(3)	111.4 (9)	C(18)—C(20)—O(21)	111.3 (7)
C(2)—C(3)—N(4)	112.2 (9)	C(18)—C(20)—C(33)	111.5 (8)
C(3)—N(4)—C(5)	116.7 (10)	O(21)—C(20)—C(33)	103.6 (7)
C(3)—N(4)—C(6)	116.3 (9)	C(20)—O(21)—C(22)	112.4 (7)
C(5)—N(4)—C(6)	117.7 (10)	O(21)—C(22)—O(23)	120.8 (9)
N(4)—C(6)—N(7)	178.1 (11)	O(21)—C(22)—C(24)	106.0 (8)
C(1)—C(8)—C(9)	118.0 (9)	O(23)—C(22)—C(24)	133.1 (10)
C(8)—C(9)—C(10)	128.5 (10)	C(22)—C(24)—C(33)	109.3 (8)
C(8)—C(9)—C(13)	121.6 (9)	C(22)—C(24)—C(25)	128.9 (8)
O(10)—C(9)—C(13)	110.0 (9)	C(25)—C(24)—C(33)	121.7 (8)
C(9)—O(10)—C(11)	106.3 (9)	C(24)—C(25)—O(26)	123.6 (8)
O(10)—C(11)—O(12)	109.1 (8)	C(24)—C(25)—C(28)	116.9 (8)
C(11)—O(12)—C(13)	103.5 (8)	O(26)—C(25)—C(28)	119.3 (8)
O(12)—C(13)—C(9)	110.7 (8)	C(25)—O(26)—C(27)	117.5 (9)
O(12)—C(13)—C(14)	126.9 (9)	C(25)—C(28)—C(31)	120.2 (8)
C(9)—C(13)—C(14)	122.3 (9)	C(25)—C(28)—O(29)	115.0 (8)
C(13)—C(14)—O(15)	121.5 (9)	O(29)—C(28)—C(31)	124.7 (8)
C(13)—C(14)—C(17)	118.0 (9)	C(28)—O(29)—C(30)	118.0 (8)
O(15)—C(14)—C(17)	120.4 (8)	C(28)—C(31)—C(32)	121.2 (8)
C(14)—O(15)—C(16)	113.2 (10)	C(31)—C(32)—C(33)	117.8 (8)
C(14)—C(17)—C(1)	119.2 (8)	C(32)—C(33)—C(24)	122.0 (9)
C(14)—C(17)—C(18)	115.6 (8)	C(32)—C(33)—C(20)	129.5 (8)
C(1)—C(17)—C(18)	125.2 (7)	C(24)—C(33)—C(20)	108.5 (8)

Table 5. Atomic least-squares planes of the molecule with their r.m.s.d. from the planes and dihedral angles of planes

Plane	Atoms	r.m.s.d. (Å)
1	C(1), C(8), C(9), C(13), C(14), C(17)	0.01
2	C(9), O(10), C(11), O(12), C(13)	0.03
3	C(1), C(8), C(9), C(13), C(14), C(17), O(10), C(11), O(12)	0.02
4	C(24), C(25), C(28), C(31), C(32), C(33)	0.01
5	C(20), O(21), C(22), C(24), C(33)	0.01
6	C(24), C(25), C(28), C(31), C(32), C(33) C(20), O(21), C(22)	0.02

Dihedral angles (°)					
1-2	1-2	3-6	29.7	4-5	2.4

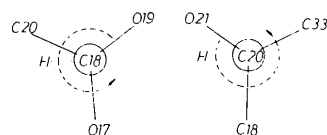


Fig. 2. The Newman projections of the [O(19), C(20), O(17)]-C(18)—H and [O(21), C(18), C(33)]C(20)—H groups.

Table 6. Relevant torsion angles (°)

C(13) C(14) O(15) C(16)	-64.7	C(1)—C(17)—C(18)—C(20)	-94.4
C(17) C(1) C(2) C(3)	-104.7	C(17)—C(18)—C(20)—O(21)	70.1
C(1) C(2) C(3) N(4)	172.3	O(19) C(18) C(20) O(21)	-57.8
C(2) C(3) N(4) C(5)	73.6	C(18)—C(20) C(33)—C(24)	-117.2
C(2) C(3) N(4) C(6)	72.3	C(24) C(25) O(26) C(27)	74.2
C(1) C(17) C(18) O(19)	32.7	C(25) C(28) O(29) C(30)	173.1

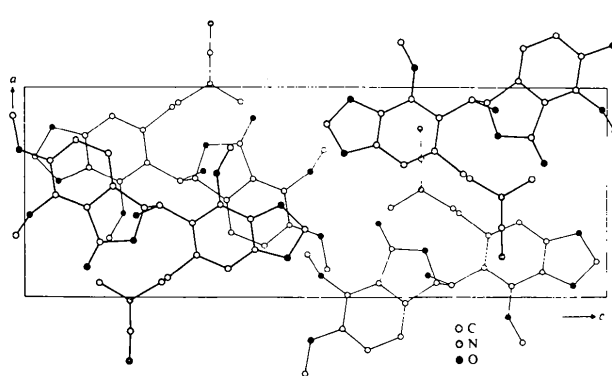


Fig. 3. The orthogonal projection of the non-hydrogen contents of the unit cell on (010).

We are indebted to the Science Research Council for a Fellowship and express thanks to Professor M. M. Woolfson for his generous hospitality, facilitating the work of crystal structure determination, and to Dr P. Main for the helpful discussions concerning the proper use of the latest version of the *MULTAN* program.

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