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## Structures of Novel Dehydroxycycloleuconolam Alkaloid Derivatives

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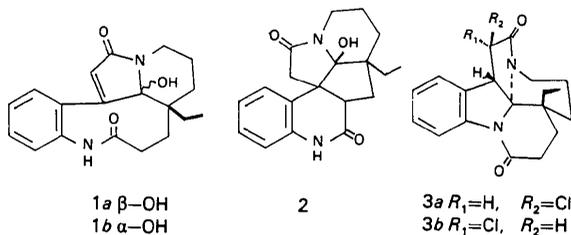
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**Abstract.** C<sub>19</sub>H<sub>21</sub>ClN<sub>2</sub>O<sub>2</sub>,  $M_r = 344.84$ , monoclinic,  $P2_1$ ,  $a = 9.903$  (2),  $b = 7.513$  (1),  $c = 11.399$  (3) Å,  $\beta = 106.08$  (2)°,  $V = 814.9$  (2) Å<sup>3</sup>,  $Z = 2$ ,  $D_m = 1.41$  (by flotation in KI/H<sub>2</sub>O),  $D_x = 1.405$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 4.13$  cm<sup>-1</sup>,  $F(000) = 364$ ,  $T = 297$  K,  $R = 0.047$  based on 1446 observed [ $|F_o| > 2\sigma(|F_o|)$ ] reflections. The easy recyclization of the ring-opened indole alkaloid, leuconolam, with hydrochloric acid provides alkaloidal derivatives possessing a new pentacyclic diazaspiro-indole skeleton.

**Introduction.** Among several natural products from *Leuconotis* species is the structurally interesting ring-opened indole alkaloid leuconolam (1a) (Goh, Wei & Mohd. Ali, 1984; Wei, Mohd. Ali, Goh, Sinn & Butcher, 1986), and our continuing studies have led to the isolation of the isomer epileuconolam (1b) from acidic extracts. Under basic conditions leuconolam (1a) is transformed into a pentacyclic melodinus-type alkaloid (2), but acid (HCl) treatment of (1a) yielded two novel products, (3a) and (3b), for which unambiguous structural assignments could not be made based on spectroscopic (NMR, IR and UV) data alone. Accordingly the minor product (3b) was subjected to X-ray analysis, which revealed the presence of a novel dehydroxycycloleuconolam skeleton.



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**Experimental.** Colorless polyhedral crystal (0.24 × 0.24 × 0.16 mm) of (3b) mounted on Nicolet R3m diffractometer, graphite-monochromated Mo  $K\alpha$  radiation. Unit-cell parameters from least-squares fit to refined angles of 21 independent reflections.  $\omega$ - $2\theta$  scan mode at 2.02–8.37° min<sup>-1</sup> for  $2\theta_{\text{max}} = 50^\circ$ ; scan range 1° below  $K\alpha_1$  to 1° above  $K\alpha_2$ ; ranges of  $h, k, l$ : 0 to 11, 0 to 8, -13 to 13; two standard reflections used to monitor every 125 reflections; absorption correction not applied; 1546 unique data collected, 1446 with  $|F_o| > 2\sigma(|F_o|)$ , phase determination by direct methods. All non-hydrogen atoms, other than the ring carbon atoms, were refined anisotropically, H atoms generated geometrically (C–H 0.96 Å), assigned fixed isotropic thermal parameters and allowed to ride on their respective parent C atoms; methyl group was handled as rigid group with  $d(\text{C–H}) = 0.98$  Å and  $U_{\text{iso}} = 0.06$  Å<sup>2</sup>; blocked cascade least-squares refinement (Schilling, 1970) on  $F$  for 134 parameters converged at  $R = 0.047$  and  $wR = 0.064$ ,  $w = [\sigma^2(F_o) + 0.0015|F_o|^2]^{-1}$ ,  $S = 1.273$ ;  $(\Delta/\sigma)_{\text{max}} < 0.003$  in final cycle; residual extrema in final difference map 0.29 to -0.27 e Å<sup>-3</sup>; analytic expressions of neutral-atom scattering factors and anomalous-dispersion corrections taken from *International Tables for X-ray Crystallography* (1974); all computations performed on Data General Nova 3/12 minicomputer with *SHELXTL* program package (Sheldrick, 1982).†

**Discussion.** Table 1 lists the atomic coordinates and equivalent isotropic thermal parameters. Table 2

† Tables of hydrogen coordinates, anisotropic thermal parameters, and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 43051 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic temperature factors ( $\text{\AA}^2 \times 10^3$ )

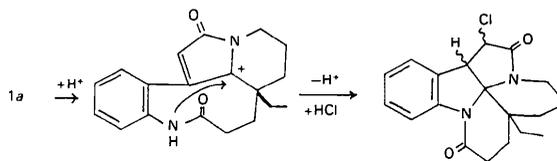
	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub> / <i>U</i>
Cl	6062 (1)	2605 (3)	3232 (1)	67 (1)*
O(2)	-280 (3)	-233 (5)	-772 (2)	44 (1)*
O(5)	5595 (3)	-1314 (5)	3919 (3)	56 (1)*
N(1)	1590 (3)	0	888 (3)	28 (1)*
N(4)	3379 (3)	-1106 (5)	2627 (3)	31 (1)*
C(2)	150 (4)	28 (6)	324 (3)	33 (1)
C(3)	3026 (4)	-2990 (6)	2641 (4)	35 (1)
C(5)	4600 (4)	-447 (6)	3349 (4)	37 (1)
C(6)	4483 (4)	1574 (6)	3343 (4)	37 (1)
C(7)	3145 (4)	1983 (6)	2299 (3)	31 (1)
C(8)	3345 (4)	2079 (6)	1034 (3)	31 (1)
C(9)	4166 (4)	3208 (6)	569 (4)	39 (1)
C(10)	4168 (4)	3051 (7)	-653 (4)	43 (1)
C(11)	3345 (4)	1794 (7)	-1392 (4)	42 (1)
C(12)	2490 (4)	653 (6)	-947 (4)	35 (1)
C(13)	2481 (4)	855 (6)	259 (3)	29 (1)
C(14)	1981 (4)	-3253 (7)	3396 (4)	39 (1)
C(15)	761 (4)	-1983 (6)	2943 (4)	37 (1)
C(16)	-839 (4)	470 (7)	1067 (4)	40 (1)
C(17)	-140 (4)	1112 (6)	2355 (4)	36 (1)
C(18)	942 (5)	211 (8)	5177 (4)	53 (2)
C(19)	1806 (4)	661 (6)	4290 (3)	38 (1)
C(20)	1161 (4)	3 (6)	2968 (3)	30 (1)
C(21)	2250 (4)	234 (5)	2223 (3)	27 (1)

\* *U*<sub>eq</sub> is calculated as one-third of the trace of the orthogonalized *U*<sub>*ij*</sub> matrix.

Table 2. Bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ )

Cl—C(6)	1.781 (5)	N(1)—C(2)	1.392 (5)
N(1)—C(13)	1.434 (5)	N(1)—C(21)	1.492 (4)
N(4)—C(3)	1.459 (6)	N(4)—C(5)	1.354 (5)
N(4)—C(21)	1.480 (5)	O(2)—C(2)	1.219 (4)
O(5)—C(5)	1.210 (5)	C(2)—C(16)	1.498 (7)
C(3)—C(14)	1.532 (7)	C(5)—C(6)	1.523 (7)
C(6)—C(7)	1.547 (5)	C(7)—C(8)	1.512 (6)
C(7)—C(21)	1.573 (6)	C(9)—C(10)	1.399 (6)
C(8)—C(9)	1.378 (6)	C(10)—C(11)	1.373 (6)
C(11)—C(12)	1.395 (7)	C(12)—C(13)	1.385 (6)
C(8)—C(13)	1.393 (5)	C(14)—C(15)	1.514 (6)
C(15)—C(20)	1.542 (6)	C(16)—C(17)	1.518 (5)
C(17)—C(20)	1.531 (5)	C(18)—C(19)	1.532 (7)
C(19)—C(20)	1.546 (5)	C(20)—C(21)	1.556 (6)
C(2)—N(1)—C(21)	125.0 (3)	C(2)—N(1)—C(13)	117.1 (3)
C(13)—N(1)—C(21)	107.5 (2)	C(3)—N(4)—C(5)	121.6 (3)
C(3)—N(4)—C(21)	120.1 (3)	C(5)—N(4)—C(21)	114.2 (3)
N(1)—C(2)—O(2)	119.5 (4)	N(1)—C(2)—C(16)	119.2 (3)
O(2)—C(2)—C(16)	121.2 (4)	N(4)—C(3)—C(14)	109.4 (4)
N(4)—C(3)—O(5)	125.9 (4)	N(4)—C(3)—C(14)	107.9 (3)
O(5)—C(3)—C(14)	126.1 (4)	Cl—C(6)—C(5)	111.5 (3)
Cl—C(6)—C(7)	116.2 (3)	C(5)—C(6)—C(7)	104.4 (3)
C(6)—C(7)—C(8)	115.6 (3)	C(6)—C(7)—C(21)	103.1 (3)
C(8)—C(7)—C(21)	102.0 (3)	C(8)—C(9)—C(10)	119.7 (4)
C(9)—C(10)—C(11)	120.3 (5)	C(10)—C(11)—C(12)	121.1 (4)
C(11)—C(12)—C(13)	117.7 (4)	N(1)—C(13)—C(12)	128.4 (3)
N(1)—C(13)—C(8)	109.5 (3)	C(8)—C(13)—C(12)	122.0 (4)
C(7)—C(8)—C(9)	130.1 (3)	C(7)—C(8)—C(13)	110.7 (4)
C(9)—C(8)—C(13)	119.1 (4)	C(3)—C(14)—C(15)	109.1 (4)
C(14)—C(15)—C(20)	115.3 (3)	C(16)—C(17)—C(20)	111.7 (4)
C(2)—C(16)—C(17)	115.0 (3)	C(18)—C(19)—C(20)	114.7 (4)
C(15)—C(20)—C(17)	109.8 (3)	C(15)—C(20)—C(19)	111.2 (3)
C(15)—C(20)—C(21)	108.2 (3)	C(17)—C(20)—C(19)	109.8 (3)
C(17)—C(20)—C(21)	108.2 (3)	C(19)—C(20)—C(21)	109.5 (3)
N(1)—C(21)—N(4)	108.5 (3)	N(1)—C(21)—C(7)	103.7 (3)
N(1)—C(21)—C(20)	111.6 (3)	N(4)—C(21)—C(7)	100.7 (3)
N(4)—C(21)—C(20)	109.4 (3)	C(7)—C(21)—C(20)	121.9 (3)

contains bond distances and angles. Fig. 1 shows a perspective view of molecule (3b) and Fig. 2 is the packing stereogram. In principle leuconolam (1a) on reaction with hydrochloric acid may undergo ring closure to give four possible stereoisomers with a *cisoid* disposition of the C(7)—C(8) and N(1)—C(21) bonds:



The relative configuration of the minor product (3b) was shown by the present X-ray diffraction study to possess a novel dehydroxycycloleuconolam skeleton (Fig. 1). With the determination of this structure the other product (3a) could be assigned based on the NMR spectral data. In particular, the vicinal protons on C(6)—C(7) have a large coupling constant (7 Hz) in (3b), but a negligible one (<0.2 Hz) in (3a) owing to

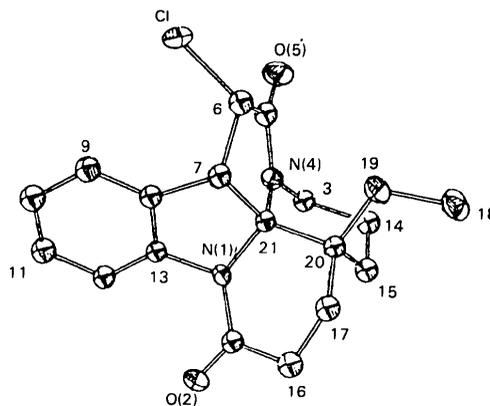
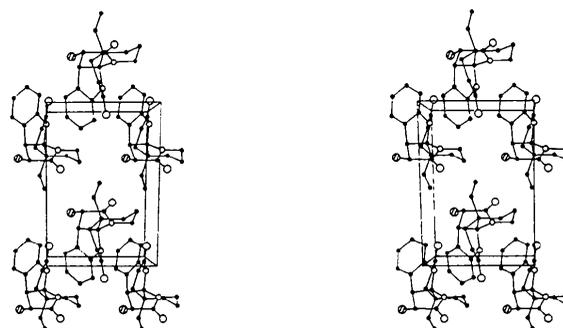


Fig. 1. ORTEP plot (Johnson, 1965) (35% thermal ellipsoids) with atom labelling of compound (3b).

Fig. 2. Stereogram showing the molecular packing (origin at lower left corner, with *a* pointing towards the reader, *b* from left to right, and *c* upwards).

differences in dihedral angles. These results indicate that isomers (3a) and (3b) are formed by a stereospecific transannular attack by N(1) on the incipient carbonium ion from leuconolam (1a) followed by a non-stereospecific anti-Markownikoff HCl addition at the  $\beta$  face of the molecule. The bond configuration about the quaternary carbon atom at the junction of four adjoining rings (two five-membered and two six-membered) manifests the effects of ring strain; the valence angles at C(21) range from 100.7 to 121.9° as compared with 101.3 to 115.0° in leuconolam before ring closure.

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### Structure of (4R)-4-Benzyl-3-dichloroacetyl-1,3-oxazolidine\*

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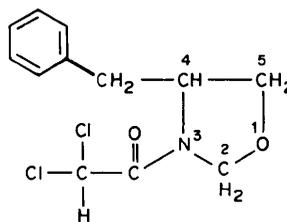
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**Abstract.**  $C_{12}H_{13}Cl_2NO_2$ ,  $M_r = 274.1$ , orthorhombic,  $P2_12_12_1$ ,  $a = 6.235$  (1),  $b = 8.219$  (1),  $c = 25.636$  (2) Å,  $V = 1313.7$  Å<sup>3</sup>,  $Z = 4$ ,  $D_m$  (floatation in KI solution) = 1.40,  $D_x = 1.39$  Mg m<sup>-3</sup>,  $\lambda$  (Mo  $K\alpha$ ) = 0.7107 Å,  $\mu = 4.84$  mm<sup>-1</sup>,  $F(000) = 568.0$ ,  $T = 293$  K,  $R = 0.047$  for 979 observed reflections. The absolute configuration determined confirms the title compound to be  $R(+)$ . The 1,3-oxazolidine ring adopts an envelope conformation with C(9) as flap. The bond lengths and angles of the oxazolidine ring are normal. The molecule has an extended conformation. The molecules are held together by van der Waals interactions.

**Introduction.** The title compound was prepared in connection with a scheme to synthesize biologically active aminoalcohols. This involves the conversion of phenylalanine to its methyl ester followed by reduction to phenylalaninol (Seki, Koga, Matsuo, Ohki, Matsuo & Yamada, 1965). This by interaction with formaline

gave the title compound (Kumar, Natu & Gogte, 1985, unpublished). The aim of the present investigation is to establish the absolute configuration unequivocally.



**Experimental.** Crystal approx. 0.3 × 0.37 × 0.7 mm, Nonius CAD-4F-11M diffractometer; graphite-monochromated Mo  $K\alpha$  radiation;  $\omega/2\theta$  scan mode, scan speed 1° min<sup>-1</sup>;  $\theta < 23.5^\circ$ ,  $h$  0 to 7,  $k$  0 to 9,  $l$  0 to 28. 1179 reflections collected, 979 judged significant ( $|F_o| > 3\sigma|F_o|$ ). Lattice parameters from 25 reflections ( $20 < 2\theta < 40^\circ$ ), three standard reflections (0,2,10, 1,2,13 and 307) every 1000 s, 3% variation in intensity. No correction for absorption. Structure solved by direct methods, program *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Full-matrix

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‡ Article dedicated to the memory of Dr V. N. Gogte.