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Dehydroretronecine,* $C_8H_{11}NO_2$

BY M. F. MACKAY AND P. MITRPRACHACHON

Department of Physical Chemistry, La Trobe University, Bundoora, Victoria 3083, Australia

AND C. C. J. CULVENOR

Division of Animal Health, CSIRO, Parkville, Victoria 3052, Australia

Abstract. $M_r = 153.2$, orthorhombic, $P2_12_12_1$, $a = 7.370$ (1), $b = 8.148$ (1), $c = 12.847$ (1) Å, $V = 771.5$ (1) Å^3, $Z = 4$, $D_x = 1.319$ Mg m^{-3}, λ(Cu $K\alpha$) $= 1.5418$ Å, $\mu = 0.69$ mm^{-1}, $F(000) = 328$, $T = 289$ (1) K. Final $R = 0.045$ for 685 observed reflections. The pyrrolizidine nucleus is planar within ± 0.04 (1) Å except for C(6) which lies on the opposite side of the plane from the C(7)-hydroxyl oxygen substituent; bond lengths in ring B indicate extensive electron delocalization. Hydrogen bonds involving only the hydroxyl substituents link the molecules into sheets perpendicular to the c axis.

Introduction. The nucleotoxic properties of the pyrrolizidine alkaloids are due to metabolic activation to the corresponding pyrrole derivatives or dehydroalkaloids (McLean, 1970; Huxtable, 1979, 1980). Dehydroretronecine (I), itself an active metabolite, is formed on hydrolysis of the dehydroalkaloids and has been prepared by oxidation of retronecine (Culvenor, Edgar, Smith & Tweeddale, 1970). This analysis was carried out so that the conformation of the pyrrolizidine

nucleus in the dehydroaminodiol could be compared with its conformation in two typical macrocyclic dehydroalkaloids, dehydrosenecionine and dehydromonocrotaline (Mackay, Sadek, Culvenor & Smith, 1983, 1984).

(I)
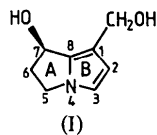
Experimental. Title compound, prepared by the method of Culvenor *et al.* (1970), formed colourless prisms from benzene. As the crystal proved unstable in air a crystal *ca* $0.52 \times 0.28 \times 0.20$ mm was sealed in a thin-walled Lindemann-glass tube for the data collection; 25 reflections used for measuring lattice parameters. Cu $K\alpha$ radiation (graphite-crystal monochromator), Rigaku-AFC four-circle diffractometer; of 782 non-equivalent reflections ($2\theta_{max} = 130°$, range of hkl: 0–8, 0–9, 0–15) recorded by an ω–2θ scan of 4° min^{-1} and with 10 s stationary background counts, 685 with $I_o > 2\sigma(I_o)$ used for structure refinement; three reference reflections monitored every 50 reflections

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* 1β-Hydroxy-2,3-dihydro-1H-pyrrolizine-7-methanol.

showed no significant variation in intensity during data collection; intensities not corrected for absorption or extinction but three large reflections apparently seriously affected by extinction (020, 021, 012) omitted from final refinement. Structure solved by direct methods with *SHELX*76 (Sheldrick, 1976). All H-atom sites located on difference maps. Refinement with anisotropic temperature factors given to the C, N and O atoms and isotropic factors given to the H atoms converged at $R = 0.045$ and $wR = 0.052$; function minimized was $\sum w(|F_o|-|F_c|)^2$, $w = (\sigma^2|F_o|+0.0005|F_o|^2)^{-1}$. Largest peaks on final difference map $+0.20$ and -0.29 e Å^{-3}; maximum parameter shift-to-error ratio at convergence 0.007:1. Scattering factors for O, N and C from Cromer & Mann (1968), for H from Stewart, Davidson & Simpson (1965); anomalous-dispersion corrections made for the non-H atoms with values of Cromer & Liberman (1970).

Discussion. Final atomic coordinates are given in Table 1.* The molecular conformation and numbering scheme are illustrated in the *ORTEP* plot (Johnson, 1965) given in Fig. 1. Bond lengths and angles are listed in Table 2. Apart from C(6), the N and C atoms in the molecule are coplanar within ±0.04 (1) Å so that C(9) lies within the plane of ring *B* [atoms coplanar within ±0.01 (1) Å]. The angle between the mean planes defined by the atoms C(1), C(2), N(4), C(8) and N(4), C(5), C(7), C(8) of 176.8 (4)° is similar to the values 178.6 (6) and 176.3 (4)° for this angle in dehydromonocrotaline and dehydrosenecionine respectively. Ring *A* is puckered with C(6) on the opposite side of the plane from O(11) as in other retronecine derivatives. The pucker angle of 26.7 (4)° lies midway between the values 11.1 (6)° in dehydromonocrotaline and 39.5 (7)° in dehydrosenecionine. The torsion angle, C(2)—C(1)—C(9)—O(10), of +47.4 (4)° in dehydroretronecine, compared with the respective values −125.6 (5) and −152.5 (4)° in the dehydroalkaloids, illustrates a substantial twist about the C(1)—C(9) bond relative to the latter. In each of the three molecules one H atom at C(9) lies closer to the plane of ring *B* than the other; in dehydroretronecine this is reflected in the torsion angles C(2)—C(1)—C(9)—H(9*A*) of +176 (3)° and C(2)—C(1)—C(9)—H(9*B*) of −73 (3)°.

As expected for a pyrrole system the bond lengths in ring *B* indicate extensive electron delocalization; the C—C bonds range from 1.376 (5) Å for C(1)—C(8) to 1.428 (5) Å for C(1)—C(2) and the C—N bonds are 1.357 (5) and 1.369 (5) Å. Similar values for these

bonds were noted in dehydromonocrotaline and dehydrosenecionine as well as a similar distortion of the exocyclic angles C(3)—N(4)—C(5) and C(1)—C(8)—C(7) from the standard trigonal value; these are 137.2 (3) and 142.1 (3)° respectively in dehydroretronecine. There is no intramolecular hydrogen bond in the molecule. The hydroxyl groups lie on opposite sides of the pyrrolizidine plane and are directed away from each other; torsion angles C(1)—C(9)—O(10)—H(10) and C(8)—C(7)—O(11)—H(11) are +71 (5) and −176 (5)° respectively.

Table 1. *Final atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors with e.s.d.'s in parentheses*

	x	y	z	$B^*_{eq}(\text{Å}^2)$
C(1)	849 (5)	4401 (4)	8156 (3)	2·6 (1)
C(2)	1820 (6)	5401 (4)	8879 (3)	3·1 (1)
C(3)	692 (6)	5720 (5)	9709 (3)	3·3 (1)
N(4)	−920 (4)	4972 (4)	9519 (2)	2·9 (1)
C(5)	−2676 (6)	4805 (6)	10041 (3)	4·0 (1)
C(6)	−3555 (6)	3419 (5)	9422 (3)	3·6 (1)
C(7)	−2672 (5)	3485 (4)	8344 (3)	2·7 (1)
C(8)	−850 (5)	4187 (4)	8578 (3)	2·5 (1)
C(9)	1465 (5)	3748 (5)	7128 (3)	3·1 (1)
O(10)	3237 (4)	3010 (3)	7168 (2)	3·5 (1)
O(11)	−3593 (4)	4593 (3)	7650 (2)	3·3 (1)

* Calculated from the refined anisotropic thermal parameters, $B_{eq} = 8\pi^2 U_{eq} = \frac{8}{3}\pi^2 \sum_i \sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i \cdot \mathbf{a}_j$.

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

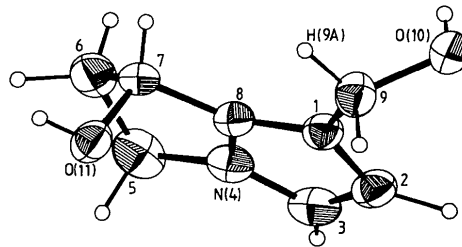|			
C(1)—C(2)	1·428 (5)	N(4)—C(8)	1·369 (5)
C(1)—C(8)	1·376 (5)	C(5)—C(6)	1·526 (6)
C(1)—C(9)	1·494 (5)	C(6)—C(7)	1·531 (6)
C(2)—C(3)	1·377 (6)	C(7)—C(8)	1·490 (5)
C(3)—N(4)	1·357 (5)	C(7)—O(11)	1·439 (5)
N(4)—C(5)	1·464 (6)	C(9)—O(10)	1·438 (5)
C(2)—C(1)—C(8)	105·8 (3)	N(4)—C(5)—C(6)	101·8 (3)
C(2)—C(1)—C(9)	128·7 (3)	C(5)—C(6)—C(7)	105·4 (3)
C(8)—C(1)—C(9)	125·4 (3)	C(6)—C(7)—C(8)	102·4 (3)
C(1)—C(2)—C(3)	108·0 (3)	C(6)—C(7)—O(11)	112·5 (3)
C(2)—C(3)—N(4)	107·7 (4)	C(8)—C(7)—O(11)	108·0 (3)
C(3)—N(4)—C(5)	137·2 (3)	C(1)—C(8)—C(7)	142·1 (3)
C(3)—N(4)—C(8)	109·6 (3)	N(4)—C(8)—C(7)	108·9 (3)
C(5)—N(4)—C(8)	113·2 (3)	C(1)—C(9)—O(10)	113·1 (3)

Fig. 1. A perspective view of the molecule with thermal ellipsoids at the 40% probability level.

* Lists of structure amplitudes, anisotropic temperature factors, H-atom parameters and intermolecular contacts have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42141 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
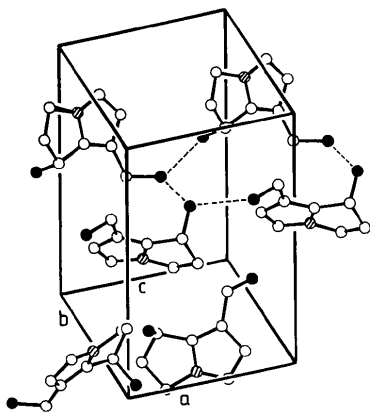
Fig. 2. The crystal packing.

The molecular packing is illustrated in Fig. 2. Two intermolecular hydrogen bonds in the crystal link the molecules into sheets parallel to the ab plane. The hydroxyl oxygen at C(7) acts as the donor in the interaction with the hydroxyl oxygen at C(9) of a molecule related by a cell translation along a; the O(11)$\cdots$O(10), H(11)$\cdots$O(10) and O(11)—H(11) distances are 2·739 (4), 1·93 (5) and 0·82 (7) Å, respectively, with the angle O(11)—H(11)$\cdots$O(10) 169 (5)°. In the other interaction, O(10) is the donor to O(11) of a molecule related by the screw axis along b ($x = 0$,

$z = \frac{3}{4}$); the O(10)$\cdots$O(11), O(10)$\cdots$H(11) and O(10)—H(10) distances have the respective values of 2·807 (4), 2·26 (5) and 0·64 (7) Å and the O(10)—H(10)$\cdots$O(11) angle is 145 (5)°. All other intermolecular contacts are normal.

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Chromotropisms of Imidazole Derivatives. II. Structure of 4,5-Bis(4-methoxyphenyl)-2-(4-nitrophenyl)imidazolium Acetate Dihydrate, $C_{23}H_{20}N_3O_4^+.C_2H_3O_2^-.2H_2O$

BY YOSHINOBU INOUYE*

Department of Chemistry, University of Tsukuba, Sakura-mura, Niihari-gun, Ibaraki 305, Japan

AND YOSHIKO SAKAINO

Department of Chemistry, Faculty of Education, Gunma University, Maebashi 371, Japan

Abstract. $M_r = 497·49$, monoclinic, $C2/c$, $a = 39·306$ (14), $b = 6·974$ (3), $c = 21·291$ (8) Å, $\beta = 121·83$ (3)°, $V = 4959$ (4) Å^3, $Z = 8$, $D_m = 1·33$ (2), $D_x = 1·33$ g cm^{-3}, $\lambda(\text{Cu }K\alpha) = 1·54178$ Å, $\mu = 8·51$ cm^{-1}, $F(000) = 2096$, room temperature, $R = 0·046$ for 1700 observed reflections. The imidazole ring is protonated and is in the same plane as the benzene ring containing the nitro group. Two imidazole rings related by the center of symmetry are linked to each
other through four water molecules at the H—N site. The molecules are packed in sheets parallel to the ac plane. The hydration or dehydration of the crystal structure is related to the color change of the crystal.

Introduction. Crystallization of 4,5-bis(4-methoxyphenyl)-2-(4-nitrophenyl)imidazole from acetic acid–water gave orange crystals with one molecule of acetic acid and two molecules of water. The crystal changed its color from yellow to dark red on drying, heating or trituration. Below 343 K, the phenomena were rever-

* To whom correspondence should be addressed.