SHORT STRUCTURAL PAPERS

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The Alkaloid Otosenine. Evidence of a Weak $\geq$N:···C$\leq$O Intra-Annular Bond

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Abstract. $C_{19}H_{27}O_7N$, orthorhombic, $P2_12_12_1$, a = 16·355 (7), b = 12·843 (2), c = 8·961 (1) Å, Z = 4, D_m = 1·34 g cm^{-3}. The alkaloid otosenine is a pyrrolizidine derivative isolated from a senecio plant. Some features observed in the pyrrolizidine ring suggest the presence of a N · · · C (2·18 Å) intra-annular 'one electron bond'. The macrocycle can be described in terms of pseudo twofold symmetry.

Introduction. A crystal of dimensions 0·30 × 0·20 × 0·16 mm was selected for recording intensity data on a fully automated diffractometer. Graphite-monochromated Mo $K\alpha$ radiation was used to collect the 1002 diffractometer-significant (no time was wasted for accidentally absent reflexions) independent reflexions up to θ = 25°. Of these, 848 were considered as observed according to the criterion $I > 2\sigma(I)$. The data were corrected for Lorentz and polarization effects, but no absorption correction was applied.

The structure was solved by direct methods using the *MULTAN* 74 system (Main, Woolfson, Lessinger, Germain & Declercq, 1974). An E map, generated from the best of 200 phase sets, located 23 of the 27 non-hydrogen atoms in the asymmetric unit. The rest of the structure, including the H atoms, was found from difference maps. Refinement was by full-matrix least

Table 1. *Final fractional coordinates* (×10^4) *for the heavy atoms, with standard deviations in parentheses*

	x	y	z
C(1)	3890 (4)	1359 (7)	888 (9)
C(2)	3538 (5)	470 (7)	571 (9)
C(3)	3629 (6)	459 (7)	1530 (11)
N(4)	4102 (4)	−121 (5)	2864 (8)
C(5)	4915 (5)	−567 (7)	3037 (10)
C(6)	5480 (5)	335 (7)	3437 (9)
C(7)	5316 (4)	1224 (6)	2344 (8)
C(8)	4407 (4)	1479 (6)	2272 (9)
C(9)	3708 (4)	2331 (7)	24 (8)
O(10)	4429 (3)	2700 (4)	−834 (5)
C(11)	4503 (4)	2397 (6)	−2254 (9)
C(12)	5241 (5)	2894 (6)	−2955 (9)
C(13)	6009 (4)	2510 (6)	−2109 (8)
C(14)	6050 (4)	1327 (6)	−2194 (9)
C(15)	6590 (4)	820 (6)	−989 (9)
C(16)	6387 (4)	1108 (6)	554 (8)
O(17)	5588 (3)	932 (4)	851 (6)
O(18)	4140 (3)	2062 (4)	3291 (6)
C(19)	3611 (6)	−17 (8)	4239 (12)
O(20)	3999 (3)	1872 (5)	−2874 (6)
C(21)	5150 (5)	4081 (6)	−2982 (9)
O(22)	5310 (3)	2524 (4)	−4456 (5)
C(23)	6792 (5)	3026 (7)	−2711 (9)
O(24)	7450 (3)	734 (4)	−1306 (5)
C(25)	6964 (5)	−204 (6)	−1300 (9)
C(26)	7163 (6)	−1001 (6)	−135 (10)
O(27)	6859 (3)	1500 (5)	1417 (6)

Table 2. *Fractional coordinates* (×10^3) *and isotropic thermal parameters for the hydrogen atoms*

	x	y	z	B (Å^2)
H(2)	315 (4)	35 (5)	−28 (7)	2 (2)
H(3*A*)	308 (4)	−58 (5)	193 (8)	3 (2)
H(3*B*)	389 (6)	−109 (8)	104 (11)	5 (2)
H(5*A*)	495 (4)	−115 (6)	374 (8)	7 (2)
H(5*B*)	509 (7)	−97 (9)	213 (14)	5 (3)
H(6*A*)	538 (6)	66 (8)	448 (11)	4 (3)
H(6*B*)	608 (4)	17 (5)	320 (7)	3 (1)
H(7)	554 (5)	180 (7)	260 (9)	5 (2)
H(9*A*)	324 (4)	216 (5)	−69 (7)	3 (2)
H(9*B*)	354 (5)	282 (6)	64 (9)	3 (2)
H(13)	598 (3)	273 (4)	−106 (7)	1 (1)
H(14*A*)	624 (4)	111 (5)	−303 (7)	2 (1)
H(14*B*)	550 (3)	97 (4)	−210 (6)	1 (1)
H(19*A*)	323 (6)	47 (8)	414 (11)	7 (3)
H(19*B*)	335 (8)	−72 (13)	448 (16)	9 (4)
H(19*C*)	391 (7)	22 (10)	−513 (12)	7 (3)
H(21*A*)	506 (4)	428 (5)	−204 (7)	3 (2)
H(21*B*)	564 (5)	440 (6)	−344 (9)	4 (4)
H(21*C*)	465 (5)	427 (6)	−358 (9)	3 (2)
H(22)	524 (7)	285 (9)	−523 (14)	9 (3)
H(23*A*)	723 (4)	273 (5)	−212 (8)	5 (2)
H(23*B*)	687 (3)	287 (4)	−379 (6)	2 (1)
H(23*C*)	681 (3)	388 (4)	−257 (6)	1 (1)
H(25)	687 (5)	−64 (6)	−232 (9)	3 (2)
H(26*A*)	719 (7)	−60 (9)	85 (13)	5 (3)
H(26*B*)	664 (5)	−142 (6)	20 (9)	6 (2)
H(26*C*)	752 (8)	−159 (11)	−42 (18)	8 (4)

Table 3. *Bond lengths* (Å)

The averaged least-squares standard deviation (l.s.s.d.) is 0·01 Å. For brevity atoms are represented by their identification numbers (Fig. 1).

1–2	1·31	4–19	1·48	9–10	1·50	12–22	1·43	15–25	1·44
1–8	1·51	5–6	1·52	10–11	1·34	13–14	1·52	16–17	1·35
1–9	1·50	6–7	1·53	11–12	1·50	13–23	1·54	16–27	1·20
2–3	1·48	7–8	1·52	11–20	1·20	14–15	1·54	24–25	1·44
3–4	1·49	7–17	1·46	12–13	1·55	15–16	1·47	25–26	1·50
4–5	1·46	8–18	1·26	12–21	1·53	15–24	1·48		

Table 4. *Bond angles* (°)

The averaged l.s.s.d. is 0·6°.

2–1–8	120·9	7–8–18	115·8	13–14–15	114·3
2–1–9	121·8	1–9–10	112·0	14–15–16	115·1
8–1–9	116·8	9–10–11	116·1	14–15–24	117·0
1–2–3	122·2	10–11–12	110·3	14–15–25	118·8
2–3–4	106·5	10–11–20	122·9	16–15–24	115·3
3–4–5	116·4	12–11–20	126·6	16–15–25	119·7
3–4–19	114·5	11–12–13	108·2	24–15–26	59·3
5–4–19	116·3	11–12–21	110·5	15–16–17	111·2
4–5–6	106·2	11–12–22	108·3	15–16–27	124·3
5–6–7	108·1	13–12–21	113·9	17–16–27	124·3
6–7–8	111·0	13–12–22	106·9	7–17–16	115·6
6–7–17	110·0	21–12–22	108·9	15–24–25	61·7
8–7–17	108·3	12–13–14	109·3	15–25–24	59·0
7–8–1	124·0	12–13–23	111·4	15–25–26	124·6
1–8–18	117·6	14–13–23	112·1	24–25–26	117·0

Table 5. *Torsional angles* (°) *for the two main rings*

The averaged l.s.s.d. is 0·8°.

8–1–2–3	−0·4	9–10–11–12	176·9
1–2–3–4	4·9	10–11–12–13	62·7
2–3–4–5	−113·7	11–12–13–14	58·4
3–4–5–6	134·4	12–13–14–15	−159·9
4–5–6–7	−48·1	13–14–15–16	54·2
5–6–7–8	51·8	14–15–16–17	53·8
6–7–8–1	−116·8	15–16–17–7	−178·1
7–8–1–2	87·0	16–17–7–8	153·0
8–1–9–10	74·5	17–7–8–1	4·2
1–9–10–11	93·8	7–8–1–9	−101·1

squares, anisotropic for non-hydrogen atoms and isotropic for H (Stewart, Kundell & Baldwin, 1970). A weighting scheme was used in order to diminish any trend of ΔF *versus* F_o or $\sin\theta/\lambda$ (Cano & Martínez-Ripoll, 1975). Final weighted and unweighted R values were 0·061 and 0·062 respectively. A final difference Fourier synthesis showed no residual electron density greater than 0·28 e Å^{-3}. Tables 1 and 2 give the refined atomic parameters.* Fig. 1 shows the X-ray molecular model and Tables 3 and 4 the bond lengths and angles for the non-hydrogen atoms. Table 5 shows the torsional angles for the two main rings.

Discussion. The title compound is the second major alkaloid isolated from the plant Bourg, a *Senecio auricola*. The 'otosenine' alkaloid which is present in *Senecio erucaefolius* has IR, NMR and mass spectra similar to but not identical with those of the present compound (Martin-Panizo & Rodriguez, 1974). It was thought that a different configuration at C(15) could be the reason for this discrepancy. Nevertheless, this work shows that the alkaloid from *S. auricola* has the same configuration as that proposed for the alkaloid from *S. erucaefolius*. However, the molecular conformation established by spectroscopic means is confirmed by the X-ray model.

An important feature of the pyrrolizidine alkaloids is their toxicity, which is strongly associated with the presence of the C(1)=C(2) double bond (Wodak, 1975). The folding of the ester linkage to C(7) frees the space around this double bond [the C(2)C(1)C(9)O(10) torsion angle is −114°] making it more accessible to chemical attack (*i.e.* more toxic).

The absolute configuration shown in Fig. 1 is that found by X-ray anomalous dispersion for retusamine (Wunderlich, 1967).

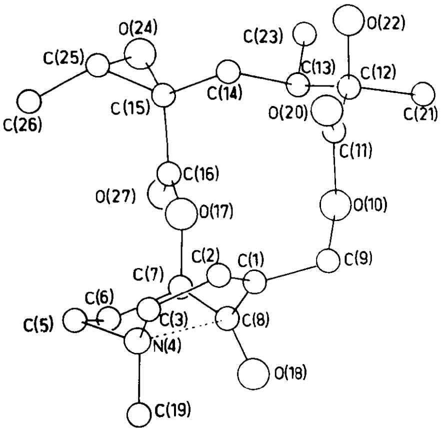

Fig. 1. A computer-generated view of the otosenine molecule.

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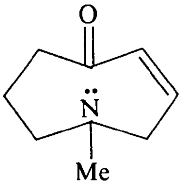
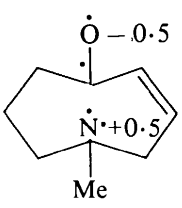
* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32815 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

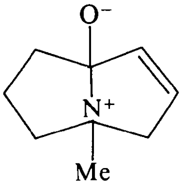
There are three main results: (i) There is a weak intermolecular hydrogen bond, O(22)–H···O′(18) [O(22)···O′(18) = 2·84 (1) Å and ∠OHO = 111 (1)°]. (ii) The macrocycle displays pseudo twofold symmetry, where the pseudo-axis goes from C(1)–C(8) to C(13)–C(14). This pseudosymmetry decreases when approaching the pyrrolizidine ring. Bond distances and angles generally agree with those found in retusamine (Wunderlich, 1967) and jacobine (Fridrichsons & Mathieson, 1963). (iii) Especially interesting is the short intra-annular distance of 2·18 (1) Å between N(4) and C(8). Some work has been done on N···C=O interactions by Bürgi, Dunitz & Shefter (1973); they found some relationships between the C···N distance and the geometry around both atoms. We find it useful to interpret our otosenine results with the electron-repulsion distribution theory (Linnett, 1966). This scheme shows models of the pyrrolizidine group for: (*a*) no N–C bond, (*b*) a one-electron N–C bond and (*c*) a two-electron N–C bond (single bond). Otosenine is better understood with model (*b*), which is also supported by some special features of the pyrrolizidine geometry: (1) a three-electron bond distance, C∸O = 1·26 Å, (2) a C(1)C(7)O(18) plane, with a 0·13 Å deviation of C(8) towards N, (3) an increased average value for the CNC angle of 115°, indicating that only one electron of the N pair repels the three N–C bonds, the other electron being shared between N(4) and C(8).



(*a*)



(*b*)



(*c*)

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Adamantylideneadamantane Peroxide. A Stable 1,2-Dioxetane

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Abstract. $C_{20}H_{28}O_2$, monoclinic, $P2_1/c$, $a = 18{\cdot}59$ (1), $b = 9{\cdot}89$ (1), $c = 13{\cdot}24$ (1) Å, $\beta = 105{\cdot}3$ (1)°, $D_m = 1{\cdot}27$, $D_x = 1{\cdot}28$ g cm^{-3}, $Z = 6$. The structure was solved by direct methods and refined to an R_w of 0·11 for 2164 reflections with $\sin\theta/\lambda \le 0{\cdot}6$ Å^{-1}. The molecule contains a four-membered ring in which a peroxide group is connected by two C atoms.

Introduction. Adamantylideneadamantane-1,2-dioxetane (I, Fig. 1) was synthesized by Wieringa, Strating, Wijnberg & Adam (1972). Although (I) is the most stable dioxetane known, it slowly decomposes into adamantanone at room temperature. The presence of the four-membered dioxetane ring makes the molecule interesting and it was decided to determine its geometry by X-ray diffraction.

Crystals were obtained by slow evaporation of the solute from a solution of (I) in acetone. The density was determined by flotation in K_2HgI_4 solutions. The symmetry relations between the reflections and the