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Grantaline, $C_{18}H_{25}NO_6$, a Pyrrolizidine Alkaloid

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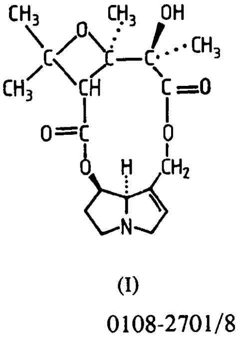
Abstract. M_r = 351·4, monoclinic, $P2_1$, a = 6·409 (1), b = 17·846 (2), c = 8·260 Å, β = 109·87 (1)°, U = 888·5 (2) Å^3, Z = 2, D_m = 1·316 (3), D_x = 1·314 Mg m^{-3}, $F(000)$ = 376, μ(Cu $K\alpha$) = 0·83 mm^{-1}, $\bar{\lambda}$(Cu $K\alpha$) = 1·5418 Å, room temperature. The structure was solved by direct methods with diffractometer data measured with Cu $K\alpha$ radiation, and full-matrix least-squares refinement converged at R = 0·036 for 1539 observed reflections. The carbonyl bonds of the ester functions are situated on the same side of the 11-membered macrocyclic ring and directed outwards from it resulting in an angle between the bonds of 93·9 (3)°. An intermolecular hydrogen bond between the hydroxyl substituent of the macrocyclic ring and the N atom links the molecules into helices extending along the b axis.

Introduction. The structure reported here provides part of a study of the conformational aspects of hepatotoxic pyrrolizidine alkaloids. Grantaline (I) is an alkaloid of *Crotalaria virgulata* subsp. *grantiana* (Harvey) Polhill (formerly known as *C. grantiana* Harvey). It was isolated from a sample of mixed alkaloid supplied by Professor Adams (*cf.* Adams & Gianturco, 1956) and has been described by Bull, Culvenor & Dick (1968) and Smith & Culvenor (1983). Grantaline hydrolyses to the aminodiol retronecine and a dicarboxylic acid named grantalinic acid. Structural assignments from spectral data led to tentative structures, but were not wholly conclusive as regards detail associated with the macroring fragment from C(12) to C(14) (Bull, Culvenor & Dick, 1968); structures based on both an 11- and a 12-membered macroring remained possible. The present X-ray analysis has defined the structure and conformational detail in crystals of the free alkaloid.



(I)

Experimental. Weissenberg photographs showed that the colourless prismatic crystals grown from ethanol are monoclinic and systematic extinctions indicated the space group $P2_1$. Cell parameters determined by least squares from 2θ values measured for 25 strong reflections with Cu $K\alpha$ radiation ($\bar{\lambda}$ = 1·5418 Å) on a diffractometer; crystal density determined by flotation; integrated intensities measured with Cu $K\alpha$ radiation (graphite-crystal monochromator, $\bar{\lambda}$ = 1·5418 Å) from a crystal *ca* 0·38 × 0·28 × 0·42 mm aligned on a Rigaku AFC four-circle diffractometer with the c axis approximately parallel to the diffractometer φ axis; ω–2θ scan, 2θ scan rate 2° min^{-1}, scan range ($\Delta\omega$) 1·2° + 0·5° tanθ, 10s stationary background counts; three reference reflections monitored every 50 reflections showed no significant variation in intensity during the data-collection period; of 1559 non-equivalent terms measured to a 2θ maximum of 130°, 1539 for which $|F| > 2\sigma|F_o|$ were used for the structure refinement; intensities not corrected for absorption; 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-hydrogen atoms with the values of Cromer & Liberman (1970).

Structure solved by direct methods with *SHELX76* (Sheldrick, 1976); an E map calculated with 283 phased terms, with $|E|$ greater than 1·20, revealed the sites of all non-hydrogen atoms; after full-matrix least-squares refinement with anisotropic temperature factors, the sites of the H atoms were located on the subsequent difference map; final refinement, in which positional coordinates and isotropic temperature factors of the H atoms were allowed to vary, converged at R = 0·036 and R_w = 0·048; the function minimized was $\sum w(|F_o| - |F_c|)^2$ with weights

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$(\sigma^2|F_o| + 5 \times 10^{-4}|F_o|^2)^{-1}$; mean parameter shift-to-error ratios at convergence were 0·02:1 for the H atoms and 0·003:1 for all other parameters; largest features on the final difference map were of heights +0·20 and −0·29 e Å^{-3}.

Discussion. Final atomic coordinates are given in Table 1;* Fig. 1 which contains the atom numbering and Fig. 2 have been prepared from the output of *ORTEP* (Johnson, 1965). The molecular conformation of grantaline is illustrated in Fig. 1, bond lengths and angles are given in Table 2 and torsional angles in Table 3. The molecule has an 11-membered macrocyclic diester system onto which an oxetane ring is fused at C(13), C(14), and the hydroxyl substituent is at C(12). The structure has the carbon skeleton and oxygenation pattern of the preferred structure of Bull, Culvenor & Dick (1968) which was an 11-membered macrocyclic ring with a 1,2-epoxide ring at C(12), C(13).

As observed for other retronecine alkaloids, the pyrrolizidine ring is *exo*-buckled at an angle of

Table 1. *Final atomic coordinates* (×10^4, *for* H ×10^3) *and isotropic temperature factors with e.s.d.'s in parentheses*

For non-hydrogen atoms $B_{\rm eq} = 8\pi^2 U_{\rm eq} = \frac{8}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	$B_{\rm eq}$ or $B_{\rm iso}$ ($\mathrm{\AA}^2$)
C(1)	5817 (4)	799 (2)	6464 (4)	2·33 (10)
C(2)	4022 (5)	819 (2)	6892 (4)	2·85 (11)
C(3)	2225 (5)	321 (2)	5797 (5)	3·11 (11)
N(4)	3127 (4)	0	4508 (3)	2·63 (9)
C(5)	1975 (5)	251 (2)	2727 (5)	3·51 (13)
C(6)	3751 (6)	199 (2)	1914 (4)	3·32 (13)
C(7)	5745 (5)	536 (2)	3302 (4)	2·62 (10)
C(8)	5500 (4)	253 (2)	4986 (4)	2·52 (10)
C(9)	7908 (5)	1220 (2)	7374 (3)	2·69 (11)
O(10)	7880 (4)	1915 (2)	6455 (3)	3·02 (8)
C(11)	9592 (4)	2374 (2)	7066 (3)	2·29 (9)
C(12)	9271 (4)	3088 (2)	5940 (3)	2·04 (9)
C(13)	9049 (4)	2866 (2)	4068 (3)	2·05 (9)
C(14)	6721 (4)	2546 (2)	2977 (3)	2·06 (9)
C(15)	6605 (4)	1741 (2)	2434 (3)	2·21 (9)
O(16)	5536 (3)	1340 (2)	3300 (3)	2·47 (7)
C(17)	11226 (5)	3615 (2)	6678 (4)	3·07 (13)
C(18)	11082 (5)	2448 (2)	3986 (4)	3·07 (11)
C(19)	6621 (5)	3202 (2)	1742 (3)	2·52 (10)
C(20)	6992 (7)	3036 (2)	63 (4)	3·44 (13)
C(21)	4626 (6)	3712 (2)	1485 (4)	3·30 (13)
O(22)	11183 (4)	2242 (2)	8310 (3)	3·52 (9)
O(23)	7277 (3)	3418 (2)	5995 (3)	2·47 (7)
O(24)	8626 (3)	3530 (2)	3002 (2)	2·50 (7)
O(25)	7390 (4)	1457 (2)	1447 (3)	3·22 (8)
H(2)†	383 (5)	111 (2)	785 (4)	2·4 (6)
H(3*a*)	85 (7)	62 (3)	511 (5)	4·1 (8)
H(3*b*)	181 (8)	−11 (3)	644 (6)	5·5 (10)
H(5*a*)	153 (6)	81 (3)	267 (5)	3·9 (8)
H(5*b*)	63 (8)	−9 (3)	209 (7)	5·8 (11)
H(6*a*)	337 (7)	42 (2)	71 (6)	4·2 (8)
H(6*b*)	413 (6)	−36 (3)	175 (5)	4·1 (8)
H(7)	722 (5)	42 (2)	321 (4)	2·5 (6)
H(8)	643 (6)	−18 (2)	539 (4)	3·0 (6)
H(9*a*)	930 (6)	93 (2)	748 (4)	2·8 (6)
H(9*b*)	805 (6)	137 (2)	855 (5)	3·2 (7)
H(14)	567 (4)	263 (2)	361 (4)	1·5 (5)
H(17*a*)	1101 (6)	402 (2)	584 (6)	3·9 (8)
H(17*b*)	1269 (9)	342 (3)	689 (7)	5·8 (11)
H(17*c*)	1133 (7)	380 (3)	777 (6)	4·1 (8)
H(18*a*)	1244 (9)	276 (3)	456 (7)	5·6 (10)
H(18*b*)	1137 (7)	198 (3)	485 (6)	5·3 (10)
H(18*c*)	1087 (7)	230 (3)	279 (6)	4·8 (9)
H(20*a*)	738 (8)	350 (3)	−34 (7)	5·7 (11)
H(20*b*)	841 (6)	270 (2)	26 (5)	3·6 (7)
H(20*c*)	573 (9)	283 (3)	−79 (8)	6·4 (12)
H(21*a*)	481 (7)	423 (3)	96 (6)	4·6 (9)
H(21*b*)	454 (7)	389 (3)	258 (6)	4·3 (8)
H(21*c*)	313 (9)	342 (3)	77 (8)	6·3 (12)
H(O23)	728 (6)	386 (3)	569 (5)	3·1 (7)

† H atoms have the same numbering as the atoms to which they are bonded.

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

C(1)—C(2)	1·314 (4)	C(11)—O(22)	1·199 (4)
C(1)—C(8)	1·521 (5)	C(12)—C(13)	1·553 (3)
C(1)—C(9)	1·497 (4)	C(12)—C(17)	1·519 (5)
C(2)—C(3)	1·492 (5)	C(12)—O(23)	1·422 (4)
C(3)—N(4)	1·488 (4)	C(13)—C(14)	1·565 (4)
N(4)—C(5)	1·474 (4)	C(13)—C(18)	1·523 (5)
N(4)—C(8)	1·505 (4)	C(13)—O(24)	1·446 (4)
C(5)—C(6)	1·508 (5)	C(14)—C(15)	1·499 (5)
C(6)—C(7)	1·521 (5)	C(14)—C(19)	1·540 (4)
C(7)—C(8)	1·537 (4)	C(15)—O(16)	1·351 (4)
C(7)—O(16)	1·441 (5)	C(15)—O(25)	1·206 (4)
C(9)—O(10)	1·451 (5)	C(19)—C(20)	1·514 (4)
O(10)—C(11)	1·324 (4)	C(19)—C(21)	1·524 (5)
C(11)—C(12)	1·549 (5)	C(19)—O(24)	1·472 (4)

C(2)—C(1)—C(8)	110·1 (3)	C(13)—C(12)—C(17)	109·9 (2)
C(2)—C(1)—C(9)	124·6 (3)	C(13)—C(12)—O(23)	110·0 (2)
C(8)—C(1)—C(9)	125·3 (3)	C(17)—C(12)—O(23)	110·0 (3)
C(1)—C(2)—C(3)	112·8 (3)	C(12)—C(13)—C(14)	114·4 (2)
C(2)—C(3)—N(4)	104·8 (3)	C(12)—C(13)—C(18)	112·2 (2)
C(3)—N(4)—C(5)	114·4 (2)	C(12)—C(13)—O(24)	109·4 (2)
C(3)—N(4)—C(8)	107·5 (2)	C(14)—C(13)—C(18)	117·3 (3)
C(5)—N(4)—C(8)	106·8 (2)	C(14)—C(13)—O(24)	90·2 (2)
N(4)—C(5)—C(6)	103·2 (3)	C(18)—C(13)—O(24)	111·1 (3)
C(5)—C(6)—C(7)	102·0 (3)	C(13)—C(14)—C(15)	117·5 (2)
C(6)—C(7)—C(8)	103·5 (3)	C(13)—C(14)—C(19)	85·5 (2)
C(6)—C(7)—O(16)	109·8 (3)	C(15)—C(14)—C(19)	122·9 (3)
C(8)—C(7)—O(16)	106·9 (3)	C(14)—C(15)—O(16)	109·4 (3)
C(1)—C(8)—N(4)	104·5 (2)	C(14)—C(15)—O(25)	128·0 (3)
C(1)—C(8)—C(7)	119·3 (3)	O(16)—C(15)—O(25)	122·6 (3)
N(4)—C(8)—C(7)	105·4 (2)	C(7)—O(16)—C(15)	117·7 (3)
C(1)—C(9)—O(10)	112·8 (3)	C(14)—C(19)—C(20)	118·3 (3)
C(9)—O(10)—C(11)	117·9 (3)	C(14)—C(19)—O(21)	113·0 (3)
O(10)—C(11)—C(12)	110·9 (3)	C(20)—C(19)—C(24)	90·2 (2)
O(10)—C(11)—O(22)	123·9 (3)	C(20)—C(19)—O(21)	112·0 (3)
C(12)—C(11)—O(22)	125·2 (3)	C(20)—C(19)—O(24)	110·8 (3)
C(11)—C(12)—C(13)	109·6 (2)	C(21)—C(19)—O(24)	110·0 (3)
C(11)—C(12)—C(17)	110·2 (2)	C(13)—O(24)—C(19)	92·4 (2)
C(11)—C(12)—O(23)	105·0 (2)		

Table 3. *Torsional angles* (°) *in the macroring*

E.s.d.'s are about 0·4°. Atoms are represented by their identification number. Corresponding values for incanine, monocrotaline, fulvine, axillarine and retusamine are included.

	Grantaline	Incanine	Monocrotaline	Fulvine	Axillarine	Retusamine
1–8–7–16	−18·4	−24·0	−27·8	−28·6	−19·1	32·4
1–9–10–11	179·6	−105·1	−157·4	−155·5	−104·2	−139·2
2–1–9–10	−96·0	−80·2	−66·4	−63·7	−88·2	−103·8
6–7–16–15	−96·9	−83·0	−137·2	−138·3	−92·5	−85·2
7–16–15–14	−164·4	−175·2	−177·7	−176·0	−177·0	176·5
8–1–9–10	87·8	101·4	111·8	112·1	93·8	85·8
8–7–16–15	151·4	167·2	113·2	110·6	152·6	155·0
9–1–8–7	−61·3	−64·0	−61·0	−60·6	−64·7	−84·9
9–10–11–12	−179·4	175·5	175·1	172·4	−174·2	163·3
10–11–12–13	−60·0	−127·8	−84·6	−87·0	−125·5	−102·1
11–12–13–14	77·4	63·2	53·5	54·9	53·6	98·9
11–12–13–24	176·8					
12–13–14–15	−114·1	−81·5	−73·9	−72·2	−75·4	−95·8
13–14–15–16	110·3	103·4	155·4	155·4	111·2	72·7
16–15–14–19	−146·3					

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* Lists of structure factors, anisotropic thermal parameters and intermolecular contacts have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38450 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

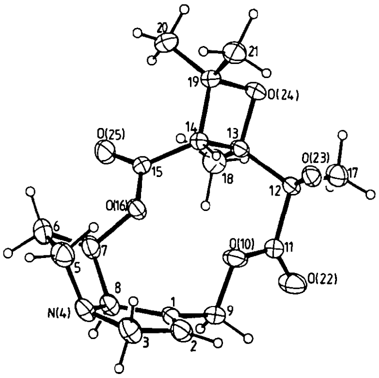

Fig. 1. A perspective view of the molecule with thermal ellipsoids scaled to 40% probability. The C atoms are denoted by numerals only.

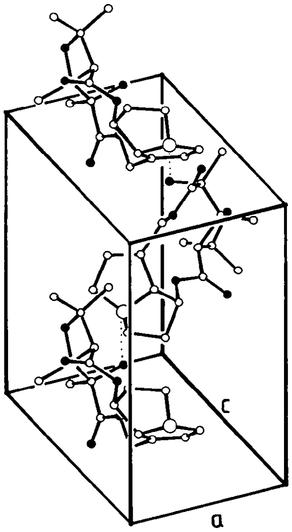

Fig. 2. The molecular packing in the crystal.

46·4 (4)°. The smaller values 41·8 (8) and 39·5 (7)° have recently been noted in crystals of incanine (Tashkhodzhaev, Telezhenetskaya & Yunusov, 1979) and monocrotaline (Wang, 1981) respectively. The angle between the mean planes defined by the atoms C(1), C(2), C(3), N(4), C(8) and C(5), N(4), C(8), C(7) is 124·3 (5)° compared with the values 125·4 (7)° in incanine and 124·3 (7)° in monocrotaline. The atoms in the unsaturated ring and C(9) are coplanar to within ±0·038 (4) Å, whereas in the 12-membered-ring alkaloids C(9) lies significantly from its associated ring plane; for example, in senecionine (Mackay & Culvenor, 1982) and jacobine (Pérez-Salazar, Cano & García-Blanco, 1978) C(9) lies 0·252 (5) and 0·247 (6) Å respectively from the ring plane.

The conformation of the 11-membered macrocyclic system is defined by the torsional angles given in Table 3. The corresponding values available for other 11-membered-ring alkaloids in the series, *viz* incanine, monocrotaline, fulvine (Sussman & Wodak, 1973), axillarine (Stoeckli-Evans & Crout, 1976) and retusamine (Wunderlich, 1967), have been included for comparison. It can be seen that the conformation in grantaline does not closely resemble the conformation in any of these alkaloids. The carbonyl bonds of the ester functions lie the same side of the plane of the macroring and are directed outwards from it resulting in an angle between the bonds of 93·9 (3)°. Although a similar orientation of the carbonyl bonds associated with the macrocycle is noted in retusamine (angle between the bonds being 89°), in incanine, fulvine, monocrotaline and axillarine they are *syn*-parallel whereas in trichodesmine (Tashkhodzhaev, Yagudaev & Yunusov, 1979) they are *anti*-parallel. The intramolecular O(16)···O(10) distance of 2·728 (6) Å in grantaline is similar to the value 2·71 Å for this length in retusamine, but significantly shorter than the values 3·00 (1) Å in incanine, 3·040 (8) Å in monocrotaline, 2·957 (5) Å in fulvine, 3·03 (2) Å in axillarine and 2·83 (1) Å in trichodesmine. The shorter distance observed in grantaline and retusamine no doubt arises from the orientation of the carbonyl bonds which results in the ring O atoms being directed more towards the centre of the macroring.

The atoms in the primary-ester group, C(9), O(10), C(11), C(12), O(22), are coplanar within ±0·008 (3) Å and the methyl carbon, C(17), at C(12) lies almost in the plane [torsional angle O(22)—C(11)—C(12)—C(17) −2·2 (4)°]. The C(9) methylene group is nearly bisected by the ester plane [torsional angle H(9*b*)—C(9)—O(10)—C(11) +58 (3)°] rather than having one hydrogen, H(9*b*), closer than the other to the ester plane as in senecionine [torsional angle H(9*b*)—C(9)—O(10)—C(11) −28 (3)°]. In this instance, therefore, the large difference in chemical shift of the H(9) atoms observed in the NMR spectra [ΔH(9) 1·10 p.p.m.; Smith & Culvenor (1983)] seems to be due to a differential influence of the ring double bond rather than the carbonyl group. The secondary-ester system at C(7), however, does not have the planar conformation preferred by a secondary ester (Culvenor, 1966). The twisting of the ester plane is relatively minor with torsional angles C(7)—O(16)—C(15)—C(14) and C(7)—O(16)—C(15)—O(25) having values −164·4 (4) and 12·8 (3)° respectively. However, the H atom H(7) is substantially out of the plane, with torsional angle H(7)—C(7)—O(16)—C(15) 30 (3)°. The non-planar conformation of the ester group may be due as much to its association with the 11-membered ring as to its association with the fused oxetane system. The latter is also twisted with an angle between the planes C(13), C(14), C(19) and C(13), O(24), C(19) of 166·3 (4)°. As trimethylene oxide itself has an essentially planar four-membered ring (Chan, Borgers, Russell, Strauss & Gwinn, 1966), the distortion of the oxetane ring from planarity in grantaline no doubt is imposed by its fusion to the macrocyclic system.

The bond lengths and angles are similar to those reported for related structures. The ring-fusion distance N(4)—C(8) of 1·505 (4) Å and the exocyclic angle C(3)—N(4)—C(5) with value 114·4 (2)° are similar to the respective values 1·486 (5) Å and 115·2 (4)° in jacobine and 1·491 (7) Å and 114·4 (2)° in monocrotaline. The oxetane ring angles are similar in value to those reported in comparable structures by Castellano & Hodder (1973) and Büldt, Debaerdemaeker & Friedrichsen (1980). The angle subtended at the C atom opposite to the O is significantly smaller in value than the angle at the O. In grantaline the difference is 6·9 (2)° while in the structures referred to above the difference is on average 9·5°. As expected, a number of the exocyclic angles associated with the oxetane ring also are severely distorted from the regular tetrahedral value. The largest distortion is at C(14) where the angles C(15)—C(14)—C(19) and C(15)—C(14)—C(13) have the respective values of 122·9 (3) and 117·5 (2)°.

In the crystal the molecules are linked into helices along the *b* axis by intermolecular hydrogen bonds involving the α-OH substituent and the N atom of an adjacent molecule related by the twofold screw axis. The O(23)···N(4), O(23)—H(23) and H(23)···N(4) distances are 2·853 (4), 0·83 (5) and 2·05 (5) Å respectively and the N(4)···H(23)—O(23) angle is 163°. Similar interactions have been observed in crystals of other pyrrolizidine alkaloids; for example, in jacobine and senecionine the comparable dimensions are 2·827 (4), 0·77 (5), 2·07 (5) Å, 167 (3)° and 2·928 (5), 0·71 (5), 2·23 (5) Å and 167 (7)° respectively.

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Dehydrosenecionine, $C_{18}H_{23}NO_5$: Active Metabolite of the Pyrrolizidine Alkaloid Senecionine

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Abstract. $M_r = 333·4$, orthorhombic, $P2_12_12_1$, $a = 6·796$ (1), $b = 14·842$ (2), $c = 16·917$ (1) Å from diffractometer measurements ($\bar{\lambda} = 1·5418$ Å), $U = 1706·4$ (4) Å^3, $D_x = 1·298$ Mg m^{-3}, $Z = 4$, $F(000) = 712$, $\mu(\text{Cu } K\alpha) = 0·69$ mm^{-1}, $T = 288$ K. The structure was solved by direct methods with diffractometer data measured with Cu *K*α radiation, and full-matrix least-squares refinement converged at $R = 0·047$ for 1540 observed reflections. Apart from the pyrrolizidine nucleus, the molecule has a conformation which closely resembles that of the parent alkaloid.

Introduction. The present analysis forms part of a structural study of hepatotoxic pyrrolizidine alkaloids. It is well established that the nucleotoxic properties of the alkaloids are due to metabolic activation to the

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