Table 5. *Selected torsion angles* (°)

C(1)–C(2)–C(3)–C(4)	−70·8	C(1)–C(2)–N–C(18)	165·5	C(3)–C(4)–C(12)–C(13)	116·0
C(2)–C(3)–C(4)–C(5)	47·2	C(3)–C(2)–N–C(18)	−71·7	C(3)–C(4)–C(12)–C(17)	−62·1
C(3)–C(4)–C(5)–C(10)	−12·6	C(1)–C(2)–N–C(19)	−68·9	C(5)–C(4)–C(12)–C(13)	−4·3
C(4)–C(5)–C(10)–C(1)	−0·8	C(3)–C(2)–N–C(19)	53·9	C(5)–C(4)–C(12)–C(17)	177·5
C(5)–C(10)–C(1)–C(2)	−19·9			C(11)–C(4)–C(12)–C(13)	−126·4
C(10)–C(1)–C(2)–C(3)	54·2			C(11)–C(4)–C(12)–C(17)	55·4

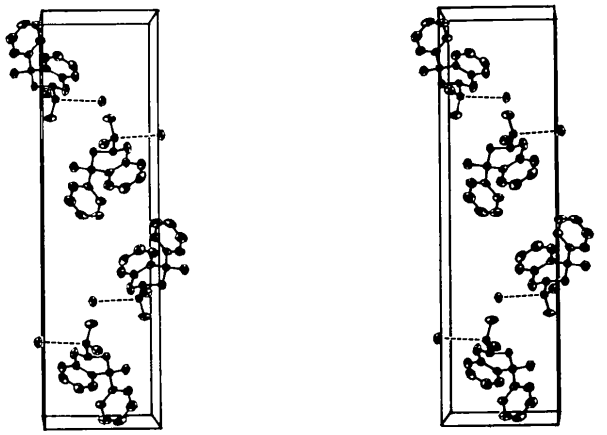

Fig. 2. Stereoscopic view of a unit cell in the *a* axis projection; the *b* axis is horizontal, and the *c* axis vertical.

Martin, 1973), was shown to be correct when it gave an *R* factor of 0·038 compared with 0·041 for the other enantiomer. As the other three stereoisomers have been unambiguously correlated with this one (Martin *et al.*, 1969; Kandeel & Martin, 1973), their configurations are also verified. The most potent analgetic of the four [(−)-(I*a*)] is thus the one most closely related to morphine in structure.

The cyclohexene-type ring is a typical half-chair, with the methyl and protonated dimethylamino groups pseudoequatorial. The protonated dimethylamino group adopts the staggered arrangement about the C(2)–N bond which puts H(N) and C(3) antiparallel [torsion angle H(N)–N–C(2)–C(3) is 169°]. H(N) is hydrogen bonded to the iodide ion [I–N distance 3·496 (6) Å]. The phenyl group is rotated to approximately bisect the C(3)–C(4)–C(11) angle, making the torsion angle C(5)–C(4)–C(12)–C(13) −4·3°. The angle between the aromatic rings, whose C atoms average 0·009 Å from the least-squares planes, is 106·0°.

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Monocrotaline: A Pyrrolizidine Alkaloid

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Abstract. $C_{16}H_{23}NO_6$, orthorhombic, $P2_12_12_1$, a = 10·16 (1), b = 11·44 (1), c = 13·63 (2) Å, D_m = 1·35, D_c = 1·363 Mg m^{-3}, μ(Cu $K\alpha$) = 0·78 mm^{-1}. Intensities were measured using the equi-inclination Weissenberg method; films were scanned with an automatic densitometer. The structure was refined to R = 0·0799. The ester carbonyl bonds are synparallel and directed below the plane of the 11-membered macroring.

Introduction. Monocrotaline, a pyrrolizidine alkaloid (PA) derived from retronecine, is commonly found in the plant family *Leguminosea* (genus *Crotalaria*) (Bull, Culvenor & Dick, 1968). The PA's are extremely toxic

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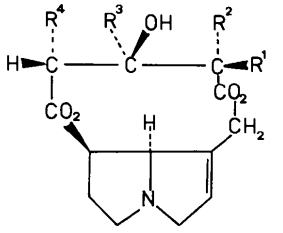
and important in the etiology of human and animal liver disease (McLean, 1970; Mattocks, 1972). Monocrotaline is isomorphous with fulvine (Sussman & Wodak, 1973) but it is only half as toxic (Schoental, 1968). The present analysis confirms the chemical structure and stereochemistry of monocrotaline proposed previously (Robins & Crout, 1969), and forms part of a structural study of PA's whose structure and/or toxicity are of particular interest (Stoeckli-Evans & Crout, 1976).



Monocrotaline $R^1 = OH, R^2 = R^3 = R^4 = CH_3$
Fulvine $R^1 = H, R^2 = R^3 = R^4 = CH_3$
Axillarine $R^1 = OH, R^2 = CH(OH)CH_3, R^3 = H, R^4 = CH(CH_3)_2$

Monocrotaline was isolated from *Crotalaria spectabilis* and crystals were grown from an acetone solution by evaporation. Using two crystals, layers 0–7*kl* and *hk*0–1 were recorded by the equi-inclination Weissenberg method using Ni-filtered Cu $K\alpha$ radiation on multiple-film packs. The films were scanned by the Science Research Council microdensitometer service, with an Optronics P-1000 photoscan. The intensities were corrected for Lorentz–polarization effects only.

Table 1. *Final positional parameters* ($\times 10^4$) *and their standard deviations*

	x	*y*	*z*
C(1)	−8545 (14)	−1401 (11)	−2886 (9)
C(2)	−8860 (15)	−833 (12)	−2124 (10)
C(3)	−9890 (15)	135 (13)	−2313 (9)
N(4)	−10109 (9)	−1 (8)	−3367 (7)
C(5)	−9859 (13)	1055 (12)	−3941 (11)
C(6)	−9320 (15)	629 (12)	−4918 (10)
C(7)	−8445 (12)	−436 (10)	−4598 (10)
C(8)	−9274 (12)	−982 (11)	−3771 (9)
C(9)	−7504 (11)	−2357 (11)	−2972 (10)
O(10)	−6234 (8)	−1776 (7)	−2740 (7)
C(11)	−5134 (12)	−2284 (10)	−3112 (8)
C(12)	−3934 (12)	−1546 (10)	−2942 (8)
C(13)	−3708 (12)	−595 (10)	−3719 (8)
C(14)	−4946 (11)	161 (9)	−3882 (8)
C(15)	−6062 (12)	−436 (11)	−4450 (10)
O(16)	−7229 (8)	77 (8)	−4167 (6)
O(17)	−6018 (8)	−1211 (8)	−5021 (7)
O(18)	−5159 (9)	−3226 (7)	−3505 (7)
C(19)	−2744 (14)	−2376 (13)	−2808 (11)
O(20)	−4154 (9)	−955 (8)	−1987 (6)
C(21)	−3143 (13)	−1141 (12)	−4691 (10)
O(22)	−2798 (8)	197 (8)	−3317 (6)
C(23)	−4676 (16)	1327 (12)	−4423 (12)

754 unique observed reflections were obtained after inter-layer scaling and merging of equivalent reflections. As monocrotaline and fulvine are isomorphous the coordinates of the skeleton atoms of the latter were used to calculate a difference Fourier synthesis, in which the remaining five substituents of monocrotaline were easily located. Initial isotropic full-matrix least-squares refinement and previous calculations were by *SHELX* (G. M. Sheldrick). Final anisotropic block-diagonal least-squares refinement was by *BLOK* (*X-ray ARC*, 1973) using atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Refinement was terminated at $R = 0{\cdot}0799$, $R' = 0{\cdot}1070$ (average parameter shift $\leq 0{\cdot}3$ e.s.d.). The weighting scheme was $\sqrt{w} = 1$ if $F_o \leq 18$, otherwise $\sqrt{w} = 18/F_o$. A final difference synthesis revealed no peaks higher than possible H atoms; no attempt was made to locate them. Final positional parameters are given in Table 1.*

Discussion. Bond distances and angles and their standard deviations are given in Table 2. A comparison

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33930 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond distances* (Å) *and bond angles* (°)

C(1)–C(2)	1·27 (2)	C(11)–C(12)	1·50 (2)
C(2)–C(3)	1·54 (2)	C(12)–C(13)	1·54 (2)
C(3)–N(4)	1·46 (2)	C(12)–C(19)	1·55 (2)
N(4)–C(5)	1·46 (2)	C(12)–O(20)	1·48 (1)
N(4)–C(8)	1·51 (2)	C(13)–C(14)	1·54 (2)
C(5)–C(6)	1·52 (2)	C(13)–C(21)	1·57 (2)
C(6)–C(7)	1·57 (2)	C(13)–O(22)	1·41 (1)
C(7)–C(8)	1·54 (2)	C(14)–C(15)	1·53 (2)
C(8)–C(1)	1·49 (2)	C(14)–C(23)	1·55 (2)
C(1)–C(9)	1·53 (2)	C(15)–O(16)	1·38 (1)
C(9)–O(10)	1·49 (1)	C(15)–O(17)	1·18 (2)
O(10)–C(11)	1·36 (1)	O(16)–C(7)	1·49 (2)
C(11)–O(18)	1·20 (2)	C(15)···O(10)	2·79
C(9)–C(1)–C(2)	127·3 (9)	O(18)–C(11)–C(12)	126·1 (8)
C(9)–C(1)–C(8)	120·8 (6)	C(11)–C(12)–C(13)	114·5 (5)
C(8)–C(1)–C(2)	111·9 (8)	C(11)–C(12)–C(19)	107·9 (5)
C(1)–C(2)–C(3)	113·7 (8)	C(11)–C(12)–O(20)	105·6 (5)
C(2)–C(3)–N(4)	101·0 (6)	C(19)–C(12)–O(20)	107·1 (5)
C(3)–N(4)–C(8)	110·6 (7)	C(19)–C(12)–C(13)	113·5 (6)
C(3)–N(4)–C(5)	114·4 (4)	O(20)–C(12)–C(13)	107·7 (4)
C(8)–N(4)–C(5)	108·7 (7)	C(12)–C(13)–C(14)	112·0 (6)
N(4)–C(5)–C(6)	105·5 (2)	C(12)–C(13)–C(21)	110·7 (4)
C(5)–C(6)–C(7)	102·1 (7)	C(12)–C(13)–O(22)	106·7 (5)
C(6)–C(7)–C(8)	102·0 (8)	C(21)–C(13)–O(22)	110·1 (6)
C(6)–C(7)–O(16)	105·9 (4)	C(21)–C(13)–C(14)	113·5 (6)
C(8)–C(7)–O(16)	109·0 (7)	O(22)–C(13)–C(14)	103·4 (3)
C(7)–C(8)–C(1)	116·7 (9)	C(13)–C(14)–C(15)	115·2 (3)
C(7)–C(8)–N(4)	105·8 (4)	C(13)–C(14)–C(23)	114·0 (7)
N(4)–C(8)–C(1)	102·8 (6)	C(23)–C(14)–C(15)	105·9 (6)
C(1)–C(9)–O(10)	105·4 (5)	C(14)–C(15)–O(16)	107·8 (5)
C(9)–O(10)–C(11)	116·4 (5)	C(14)–C(15)–O(17)	129·7 (9)
O(10)–C(11)–O(18)	122·2 (8)	O(17)–C(15)–O(16)	122·4 (8)
O(10)–C(11)–C(12)	111·7 (5)	C(15)–O(16)–C(7)	115·9 (5)

Table 3. *Torsion angles (°) in the macrocyclic ring; (A) average values for monocrotaline and fulvine, (B) values for axillarine*

	(A)	(B)
C(2)–C(1)–C(9)–O(10)	−63·3	−88·2
C(8)–C(1)–C(9)–O(10)	112·9	93·8
C(1)–C(9)–O(10)–C(11)	−155·9	−104·2
C(9)–O(10)–C(11)–C(12)	172·8	−174·2
O(10)–C(11)–C(12)–C(13)	−84·8	−125·5
C(11)–C(12)–C(13)–C(14)	51·6	53·6
C(12)–C(13)–C(14)–O(15)	−73·5	−75·4
C(13)–C(14)–C(15)–C(16)	153·3	111·2
C(14)–C(15)–O(16)–C(7)	−176·5	−177·0
C(15)–O(16)–C(7)–C(8)	115·5	152·6
O(16)–C(7)–C(8)–C(9)	−27·4	−19·1
C(7)–C(8)–C(1)–C(9)	−60·8	−64·7

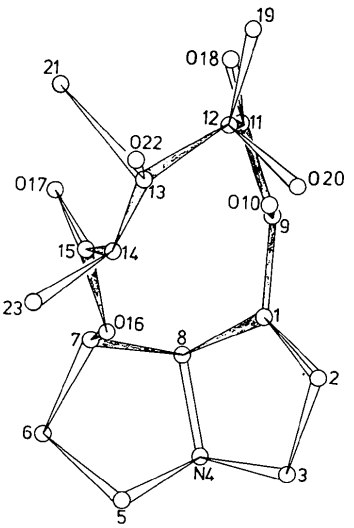


Fig. 1. A perspective view of the molecule showing the numbering scheme. The macrocyclic ring is shaded.

of the average torsion angles in the macrocyclic ring of monocrotaline and fulvine with axillarine is given in Table 3. Fig. 1 shows the atom-labelling scheme used. The absolute configuration of monocrotaline was assigned by comparison with that of jacobine (Fridrichsons, Mathieson & Sutor, 1963), as both are derived from the same pyrrolizidine nucleus, retronecine (Bull *et al.*, 1968). The geometry of monocrotaline is similar to that of fulvine (Sussman & Wodak, 1973) and axillarine (Stoeckli-Evans & Crout, 1976). All three PA's have an 11-membered macro-ring and are derived from retronecine. Structural features of interest are:

(*a*) The unsaturated five-membered ring and atom C(6) are on opposite sides of the plane defined by atoms N(4), C(5) and C(7). Hence the pyrrolizidine nucleus exists in the *exo*-puckered form with a puckering angle of 37° between the planes defined by atoms C(5), C(6), C(7) and C(5), N(4), C(8). In fulvine this angle is 46° and in axillarine 42°.

(*b*) Atoms C(1), C(2), C(3), N(4), C(8) and C(9) are coplanar within 0·03 Å.

(*c*) The angle between the least-squares planes defined by atoms C(1), C(2), C(3), N(4), C(8) and C(5), N(4), C(8), C(7) of the pyrrolizidine nucleus is 125°, compared to 126° in fulvine and 126° in axillarine.

(*d*) The pyrrolizidine-ring-fusion distance N(4)–C(8) is 1·51 (2) Å, compared to 1·49 Å in fulvine and 1·50 Å in axillarine.

(*e*) The orientation of the C(9) ester function is further proof of the general conformation of the 11-membered macro-ring in retronecine-derived PA's (see Fig. 1). The carbonyl bonds of the C(7) and C(9) ester functions are synparallel and directed below the plane of the macro-ring. In PA's with a 12-membered macro-ring, such as jacobine (Pérez-Salazer, Cano & García-Blanco, 1978), swazine (Laing & Sommerville, 1972) and retrorsine (Stoeckli-Evans, 1978), these carbonyl bonds are antiparallel, that of the C(9) ester function being directed above the plane of the macro-ring. This structural difference between the two groups of alkaloids is thought to be responsible for the corresponding observed difference in the chemical-shift-difference ($\Delta\delta$) values in the NMR spectra due to the non-equivalent C(9) protons (Stoeckli-Evans & Crout, 1976).

As in fulvine, the only hydrogen bond formed in the crystal is that between the C(13) hydroxyl substituent in one molecule and the N atom of the molecule translated one unit cell away in the *a* direction. The distance O(20) to N(4^{i}) is 2·7 Å. The distance between the centers of the carbonyl bonds is 3·08 Å compared to 3·07 Å in fulvine and 3·03 Å in axillarine. As in fulvine it is the transannular distance O(10)···C(15) which is the shorter, 2·79 Å in monocrotaline and 2·78 Å in fulvine, while in axillarine the distance O(16)···C(11) is the shorter, 2·88 Å. The C=O bonds are nearly parallel in all three PA's but the conformations of the macro-rings differ slightly, which accounts for the different transannular interactions. For example, torsion angle C(9)–O(10)–C(11)–C(12) is +173° in monocrotaline and fulvine but −174° in axillarine. The differences in torsion angles around the macro-ring appear to be due to crystal-packing considerations. Axillarine was studied as the hydrobromide ethanol solvate, and all the hydroxyl substituents are involved in hydrogen bonding, while monocrotaline and fulvine were studied as the free alkaloids.

It has been suggested that the toxicity of the PA's depends on the susceptibility of attack of the C(1)–C(2) double bond, the accessibility of which, in turn, depends on the dihedral angle between bonds C(1)–C(2) and C(9)–O(10) (Sussman & Wodak, 1973). This angle is 63° in monocrotaline, 64° in fulvine and

88° in axillarine. However, the toxicity decreases in the order fulvine : monocrotaline : axillarine ($1 : \frac{1}{2} : \frac{1}{7}$) (Schoental, 1976). Fulvine possesses only one hydroxyl substituent, monocrotaline two and axillarine three. Hence as suggested previously (Schoental, 1968), water solubility and hence increased rate of excretion of the alkaloids play an important role in the degree of toxicity.

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2-(*p*-Toluenesulfonyl)-3-(*p*-chlorophenyl)oxaziridine

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Abstract. $C_{14}H_{12}ClNO_3S$, $M_r = 309{\cdot}771$, triclinic, $P\bar{1}$, $a = 7{\cdot}504$ (3), $b = 8{\cdot}112$ (2), $c = 13{\cdot}041$ (3) Å, $\alpha = 105{\cdot}61$ (2), $\beta = 94{\cdot}52$ (2), $\gamma = 112{\cdot}33$ (2)°, $V = 692{\cdot}54$ (2) Å^3, $Z = 2$, $D_c = 1{\cdot}485$ Mg m^{-3}, $\mu = 3{\cdot}69$ mm^{-1}, λ(Cu $K\alpha$) = 1·54178 Å, $R = 0{\cdot}069$ for all 1885 observed reflections. The *p*-toluenesulfonyl and *p*-chlorophenyl groups are *trans* with respect to the oxaziridine ring.

Introduction. Oxaziridines are of considerable interest because of their unusual heterocyclic ring system (Davis, Nadir & Kluger, 1977; Davis & Nadir, 1977), and the *p*-toluenesulfonyl derivatives are of particular interest because of the conformation about the S–N bond. The three-membered heterocyclic ring makes it energetically unfavorable for the N atom to achieve a pseudo-planar conformation which would favor lone-pair–*d*-orbital interactions, and it is postulated that electron-repulsion interactions are more significant in the determination of the conformation (Chen, Watson, Davis, Lamendola & Nadir, 1978).

The title compound was synthesized and recrystallized from toluene at room temperature yielding a white crystalline material. A crystal of dimensions 0·3 × 0·4 × 0·5 mm was used to collect all data. The unit cell was found to be triclinic and room-temperature cell dimensions were obtained by a least-squares fit to 15 medium-angle reflections. There were no systematic absences and statistics indicated space group $P\bar{1}$. Intensity data for $2\theta < 120°$ were collected on a Syntex $P2_1$ diffractometer by the θ:2θ scan technique using graphite-monochromatized radiation and a variable scan speed. A periodically monitored reflection showed no significant crystal deterioration. Of the 1885 independent reflections measured, 1853 had intensities greater than $3\sigma(I)$ where $\sigma(I)$ was estimated from counting statistics. Negative measured intensities were assigned a value of zero. Lorentz and polarization corrections were applied but no absorption corrections were made.

The structure was solved by direct methods using *MULTAN* (Germain, Main & Woolfson, 1971) to

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