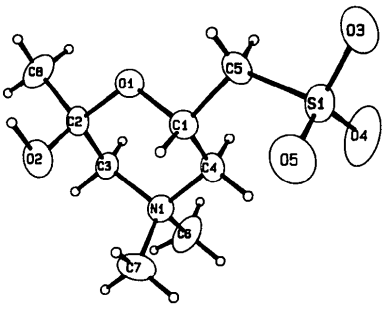

Fig. 1. View of the title compound, 50% thermal ellipsoids (Johnson, 1965).

transferase: Gandour, Colucci, Brady & Brady (1986), Colucci, Gandour, Fronczek, Brady & Brady (1987); as model enzyme-bound reaction intermediates: Colucci & Gandour (1988).

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(+)-7,9-*O*,*O*-Maleoylretronecine, $C_{12}H_{13}NO_4$: a Pyrrolizidine Alkaloid Analogue

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Abstract. (+)-7-Methyl-2,3,5,7a-tetrahydro-1*H*-pyrrolizine-1,8-diyl maleate, $M_r = 235{\cdot}2$, orthorhombic, $P2_12_12_1$, $a = 7{\cdot}826\ (2)$, $b = 10{\cdot}510\ (1)$, $c = 13{\cdot}566\ (1)$ Å, $V = 1115{\cdot}8$ Å^3, $Z = 4$, $D_x = 1{\cdot}40$ g cm^{-3}, λ(Mo $K\alpha$) $= 0{\cdot}71069$ Å, $\mu = 0{\cdot}99$ cm^{-1}, $F(000) = 496$, $T = 291$ K, final $R = 0{\cdot}037$ for 1816 observed reflections. The title compound is isomorphous with the previously reported ten-membered macrocyclic diester of (+)-7,9-*O*,*O*-succinoylretronecine [Burton, Freer & Robins (1985). *Acta Cryst.* C**41**, 944–946]. The pyrrolizidine nucleus adopts the familiar *exo–endo* conformation with ring *A* *exo*-buckled with a puckering angle of 41·7 (4)° whilst the *endo* ring, *B*, has a puckering angle of 179·0 (5)°. The dihedral angle of 127·6 (3)° between the planes defined by atoms C(1), C(8), N(4), C(3) and C(5), N(4), C(8), C(7) is similar to values found for other pyrrolizidine nuclei. The ester-group carbonyls lie on either side of the macrocycle in a nearly antiparallel orientation.

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Experimental. Colourless, plate-shaped crystals grown from hexane, crystal *ca* 0·5 × 0·4 × 0·1 mm used in data collection, CAD-4 diffractometer. Systematic absences from Weissenberg photographs indicated the crystals to be orthorhombic, $P2_12_12_1$. 3122 independent intensities, θ limit 28°, $\omega/2\theta$ scan. Two standard intensities ($0\bar{1}\bar{8}$ and $0\bar{5}\bar{5}$) were used to monitor variations in intensity data; <2% variation observed. Least-squares refinement on 25 reflections, $\theta > 12°$, used to determine lattice parameters. No absorption correction, h 0 to 10, k 0 to 13, l 0 to 17. Structure solution by direct methods with *MITHRIL* (Gilmore, 1984). Full-matrix least-squares refinement on F of coordinates and anisotropic thermal parameters for all non-H atoms converged to R and wR of 0·037 and 0·046 with $w = 1/\sigma^2(F_o)$. H-atom coordinates located from difference Fourier synthesis were included, but not refined, in the final cycles of least squares. 1816 reflections with $I \geq 3{\cdot}0\sigma_I$ used. $(\Delta/\sigma)_{max} = 0{\cdot}12$; max. and min. heights in final difference Fourier synthesis $= 0{\cdot}24$ and $-0{\cdot}18$ e Å^{-3}. Scattering factors from

Table 1. *Final positional parameters and equivalent isotropic thermal parameters* (Å²) *with e.s.d.'s in parentheses*

	x	*y*	*z*	U_{eq}
O(10)	0·60688 (18)	0·02899 (15)	0·11008 (12)	0·046
O(11)	0·6832 (3)	0·1225 (2)	−0·0322 (1)	0·065
O(14)	0·6318 (2)	0·1974 (2)	0·3393 (1)	0·062
O(15)	0·83275 (18)	0·15998 (13)	0·22316 (10)	0·038
N(4)	1·1508 (2)	−0·0277 (2)	0·1959 (1)	0·040
C(1)	0·8931 (3)	−0·0606 (2)	0·1074 (2)	0·039
C(2)	1·0166 (3)	−0·0504 (2)	0·0420 (2)	0·046
C(3)	1·1869 (3)	−0·0287 (3)	0·0892 (2)	0·049
C(5)	1·1947 (3)	0·0879 (2)	0·2488 (2)	0·050
C(6)	1·0661 (3)	0·0948 (2)	0·3307 (2)	0·048
C(7)	0·9006 (3)	0·0538 (2)	0·2811 (2)	0·039
C(8)	0·9633 (3)	−0·0506 (2)	0·2105 (2)	0·038
C(9)	0·7086 (3)	−0·0831 (2)	0·0844 (2)	0·047
C(11)	0·6236 (3)	0·1288 (2)	0·0491 (2)	0·047
C(12)	0·5602 (3)	0·2487 (2)	0·0931 (2)	0·051
C(13)	0·5958 (3)	0·2884 (2)	0·1823 (2)	0·048
C(14)	0·6878 (3)	0·2125 (2)	0·2573 (2)	0·043

$$U_{eq} = \tfrac{1}{3}\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

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

O(10)–C(9)	1·464 (3)	O(10)–C(11)	1·343 (3)
O(11)–C(11)	1·199 (4)	O(14)–C(14)	1·206 (3)
O(15)–C(7)	1·464 (3)	O(15)–C(14)	1·344 (3)
N(4)–C(3)	1·475 (4)	N(4)–C(5)	1·452 (3)
N(4)–C(8)	1·500 (3)	C(1)–C(2)	1·316 (4)
C(1)–C(8)	1·507 (4)	C(1)–C(9)	1·496 (4)
C(2)–C(3)	1·496 (4)	C(5)–C(6)	1·501 (4)
C(6)–C(7)	1·522 (4)	C(7)–C(8)	1·537 (3)
C(11)–C(12)	1·480 (4)	C(12)–C(13)	1·309 (4)
C(13)–C(14)	1·480 (4)		

C(9)–O(10)–C(11)	115·4 (2)	C(7)–O(15)–C(14)	115·7 (2)
C(3)–N(4)–C(5)	116·5 (2)	C(3)–N(4)–C(8)	108·4 (2)
C(5)–N(4)–C(8)	107·5 (2)	C(2)–C(1)–C(8)	110·6 (2)
C(2)–C(1)–C(9)	125·6 (3)	C(8)–C(1)–C(9)	123·8 (2)
C(1)–C(2)–C(3)	112·2 (3)	N(4)–C(3)–C(2)	104·5 (2)
N(4)–C(5)–C(6)	104·4 (2)	C(5)–C(6)–C(7)	103·3 (2)
O(15)–C(7)–C(6)	109·3 (2)	O(15)–C(7)–C(8)	109·0 (2)
C(6)–C(7)–C(8)	101·9 (2)	N(4)–C(8)–C(1)	104·2 (2)
N(4)–C(8)–C(7)	106·3 (2)	C(1)–C(8)–C(7)	120·8 (2)
O(10)–C(9)–C(1)	110·4 (2)	O(10)–C(11)–O(11)	124·1 (3)
O(10)–C(11)–C(12)	112·6 (3)	O(11)–C(11)–C(12)	123·3 (3)
C(11)–C(12)–C(13)	124·9 (3)	C(12)–C(13)–C(14)	124·5 (3)
O(14)–C(14)–O(15)	124·8 (3)	O(14)–C(14)–C(13)	121·9 (3)
O(15)–C(14)–C(13)	113·3 (2)		

International Tables for X-ray Crystallography (1974). All calculations on a Gould SEL 32/27 computer using Glasgow *GX* package (Mallinson & Muir, 1985). Final positional and equivalent isotropic thermal parameters are given in Table 1 while bond lengths and angles with their standard deviations are given in Table 2.* An *ORTEP* (Johnson, 1976) diagram, Fig. 1, illustrates the numbering scheme and absolute configuration for the molecule. The absolute configuration of (+)-retronecine has already been determined (Adams & Fleš, 1959) and natural (+)-retronecine was used in the synthesis of the (+)-7,9-*O,O*-maleoylretronecine (Burton & Robins, 1986).

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51150 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

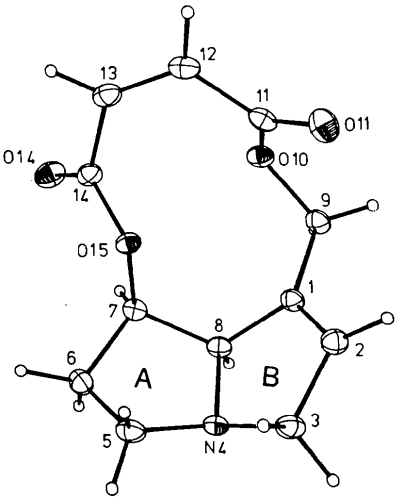

Fig. 1. A perspective view of the molecule showing the numbering scheme and vibrational ellipsoids (45% probability level).

Related literature. Pyrrolizidine alkaloids have a widespread distribution and many of them are hepatotoxic (Mattocks, 1986). The most toxic are macrocyclic diesters of (+)-retronecine. Pyrrolizidine alkaloids are known with ring sizes of 11, 12, 13 and 14 (Robins, 1982). No pyrrolizidine alkaloids containing ten-membered rings have so far been discovered, but a number have been made from (+)-retronecine and various succinate derivatives by two different methods (Burton & Robins, 1985, 1986). Knowledge of the conformation of these analogues is an important prerequisite in assessing their toxicity (Mattocks, Driver, Barbour & Robins, 1986).

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