conformations of (I)–(III) are ($\underline{ag}^+g^+$, g^+ag^-, $g^+g^-\underline{a}$)$_2$, ($\underline{g}^+ag^+$, ag^+g^+, $g^+a\underline{g}^+$)(g^+ag^-, $a\underline{g}^-g^-$, aag^+) and ($\underline{g}^+g^+a$, aag^+, $aa\underline{g}^-$)($\underline{a}g^-g^-$, $a\underline{g}^-g^-$, $g^+a\underline{g}^+$) (the g/a designations on either side of the commas give the C—S bond conformations). In an earlier paper (Ammon *et al.*, 1984) (III) had been reported to have four of eight *anti* C—S conformations, and we find three of eight examples of the *anti* conformation in (II). A major factor for the different ring shapes in (I) and (II) undoubtedly is the hybridization at N which is translated into different C—N conformations in the molecules. In (I), four of four C—N bond conformations are *anti*, whereas four of four in (II) and three of four in (III) are *gauche*. Two of the S atoms in (II) adopt the exodentate (point away from the ring center) position, whereas the other two S atoms as well as all four S atoms in (I) are neither exo- nor endodentate (*i.e.* the C—S—C triangle is more or less perpendicular to the macrocycle plane).

There are no short intermolecular contacts in either (I) or (II). This seemed a bit unusual in the case of (I) since the N—H groups could function as both hydrogen-bond donors and acceptors. Moreover, the position of the amino H atom (see Fig. 1), which points toward the center of the macrocycle, was difficult to rationalize in the absence of an intermolecular effect which favored the inside over the outside position. The explanation for the inside location, however, can be obtained by considering an intramolecular interaction between the amino H and its nearest two S atom neighbors, S(4) and S(7'). The observed H···S(4) and H···S(7') distances of 2·7 (1) and 2·8 (1) Å respectively [2·6 (1) and 2·7 (1) Å with the N—H bond stretched to 1·0 Å] are close to the van der Waals distance (2·85 Å) for this interaction (Pauling, 1960).

We further note that if the H atom pointed outside, the N atom's nonbonded electron pair would point inside toward the S atoms' nonbonded electrons, resulting in an unfavorable interaction. We cannot, of course, determine from the structural data which of these two effects is the more important.

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References

AMMON, H. L., BHATTACHARJEE, S. K., SHINKAI. S. & HONDA. Y. (1984). *J. Am. Chem. Soc.* **106**, 262–263.
CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**. 321–324.
DALE, J. (1980). *Isr. J. Chem.* **20**, 3–11.
DUNITZ, J. D., DOBLER, M., SEILER, P. & PHIZACKERLEY. R. P. (1974). *Acta Cryst.* B**30**, 2733–2738.
HARTMAN, J. R., WOLF, R. E., FOXMAN, B. M. & COOPER. S. R. (1983). *J. Am. Chem. Soc.* **105**, 131–132.
JOHNSON, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.
MAIN. P., FISKE, S. J., HULL, S. E., LESSINGER. L., GERMAIN. G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN*80. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
MAVERICK, E., SEILER, P., SCHWEIZER, W. B. & DUNITZ, J. D. (1980). *Acta Cryst.* B**36**, 615–620.
PAULING, L. (1960). *The Nature of the Chemical Bond*, 2nd ed., p. 260. Ithaca: Cornell Univ. Press.
STEWART, J. M., MACHIN. P. A., DICKINSON. C. W., AMMON, H. L., HECK, H. & FLACK, H. (1976). The *XRAY*76 system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland. College Park, Maryland.
STEWART, R. F., DAVIDSON. E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
WATSON, W. H., GALLOY, J., GROSSIE. D. A., VÖGTLE, R. & MÜLLER, W. M. (1984). *J. Org. Chem.* **49**, 347–353.

α- and β-Epoxides from Monocrotaline, a Pyrrolizidine Alkaloid: 1,2-Dihydro-1α,2α-epoxymonocrotaline, $C_{16}H_{23}NO_7$, and 1,2-Dihydro-1β,2β-epoxymonocrotaline Monohydrate, $C_{16}H_{23}NO_7.H_2O$

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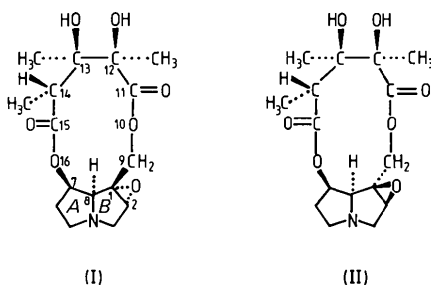
Abstract. 1,2-Dihydro-1α,2α-epoxymonocrotaline: $M_r = 341.4$, orthorhombic, $P2_12_12_1$, $a = 10.140$ (1), $b = 11.691$ (1), $c = 13.681$ (1) Å, $U = 1621.8$ (2) Å^3, $Z = 4$, $D_x = 1.398$ Mg m^{-3}, λ(Cu $K\alpha$) = 1.5418 Å, μ $= 0.83$ mm^{-1}, $F(000) = 728$, $T = 290$ (1) K. 1,2-Dihydro-1β,2β-epoxymonocrotaline monohydrate: $M_r = 359.4$, orthorhombic, $P2_12_12_1$, $a = 9.621$ (1), $b = 12.416$ (1), $c = 14.174$ (1) Å, $U = 1693.1$ (2) Å^3, Z

= 4, $D_x = 1.410$ Mg m^{-3}, $\bar{\lambda}$(Cu $K\alpha$) = 1.5418 Å, μ = 0.86 mm^{-1}, $F(000) = 768$, $T = 290$ (1) K. Final R = 0.059 and 0.037 for 1303 and 1602 unique observed reflections for the α-epoxide and the β-epoxide monohydrate respectively. The absolute molecular structures of the epoxides, formed by oxidations at the 1,2-double bond of monocrotaline, have been assigned by comparison with that of retronecine. Apart from the pyrrolizidine nucleus, both epoxide molecules have conformations that closely resemble that of monocrotaline and other pyrrolizidine alkaloids containing the 11-membered macrocycle.

Introduction. The 1,2-epoxides of the hepatotoxic pyrrolizidine alkaloid, monocrotaline, are formed by the oxidation at the 1,2-double bond of the alkaloid (Culvenor, O'Donovan, Sawhney & Smith, 1970). The α-epoxide (I) was formed as the major product (52% yield), only an 8% yield of the β-isomer (II) being obtained. The crystallographic analyses were carried out to assess the extent of conformational change that occurs when the parent alkaloid is converted into the 1,2-epoxides.

(I)   (II)

Experimental. Colourless prisms of 1,2-dihydro-1α,2α-epoxymonocrotaline and colourless plates of 1,2-dihydro-1β,2β-epoxymonocrotaline monohydrate were grown from ethanol; crystals ca 0.11 × 0.15 × 0.25 mm (α-epoxide) and ca 0.19 × 0.29 × 0.46 mm (β-epoxide monohydrate). Rigaku-AFC diffractometer, Cu $K\alpha$ radiation, graphite-crystal monochromator. Cell parameters determined by least squares from 2θ values measured for 25 strong reflections. Integrated intensities recorded by an ω–2θ scan, 2θ scan rate 2° min^{-1}, scan range ($\Delta\omega$) 1.2° + 0.5° tanθ, 10 s stationary background counts. Three reference reflections monitored every 50 reflections showed no significant variation in intensity during data collection; $2\theta_{max} = 130°$; terms for which $I_o > \sigma I_o$ used for structure refinements to give 1303 of a total 1521 non-equivalent terms, h 0–11, k 0–14, l 0–16, for the α-epoxide; for the β-epoxide, 1602 terms of a total 1689, h 0–11, k 0–14, l 0–16 and h $\bar{11}$–$\bar{6}$, k 1–6, l 1–14 ($2\theta_{min} = 70°$) resulted. No correction for absorption or extinction. Structures solved by direct methods with $SHELX76$ (Sheldrick, 1976). All H-atom sites located

on difference maps. Full-matrix least-squares refinement with anisotropic temperature factors for C, N and O atoms and isotropic for H atoms converged at $R = 0.059$, $R_w = 0.065$ for the α-epoxide and $R = 0.037$, $R_w = 0.040$ for the β-epoxide structure; $\sum w(|F_o| - |F_c|)^2$ minimized with weights $(\sigma^2|F_o| + m|F_o|^2)^{-1}$ for which values of m were 5×10^{-4} and 5×10^{-5} for the α- and β-epoxide structures respectively. At convergence mean parameter shift-to-error ratios 0.10:1 for H atoms, 0.05:1 for all other parameters (α-epoxide); values for β-epoxide monohydrate 0.008:1 and 0.003:1. Largest peaks on final difference map +0.28 and −0.27 e Å^{-3} (α-epoxide), +0.19 and −0.20 e Å^{-3} (β-epoxide). Scattering factors for O, N and C from Cromer & Mann (1968), for H from Stewart, Davidson & Simpson (1965); anomalous-dispersion corrections made with values of Cromer & Liberman (1970).

Discussion. Final atomic coordinates of the non-H atoms are given in Tables 1 and 2,* and the molecular conformations and numbering schemes are illustrated in the $ORTEP$ plots (Johnson, 1965) in Fig. 1. Bond lengths and angles are given in Table 3 and selected torsional angles in Table 4.

The absolute molecular structures have been assigned by comparison with that of retronecine; that of 1,2-dihydro-1α,2α-epoxymonocrotaline (1R,2R) is illustrated in Fig. 1(a) and that of 1,2-dihydro-1β,2β-epoxymonocrotaline (1S,2S) in Fig. 1(b). As expected, the oxidation of the 1,2-double bond of monocrotaline has resulted in some conformational change in the pyrrolizidine nucleus. Although the usual exo-buckling of retronecine alkaloids is observed in both epoxides, the pucker angle of 25.8 (8)° in the α-epoxide is considerably smaller than the respective values of 35.4 (4) and 39.5 (7)° in the β-epoxide and monocrotaline† (Stoeckli-Evans, 1979; Wang, 1981). Atoms N(4), C(5), C(7), C(8) of ring A in the β-epoxide and in monocrotaline are coplanar within experimental error. However, this is not so for the α-epoxide molecule in which the atoms have an r.m.s. deviation from the mean plane of 0.07 (1) Å with N(4) having the largest deviation of 0.09 (1) Å. In both epoxides, atoms C(1), C(2), C(3), C(8) of ring B are coplanar within experimental error with C(9) and N(4) lying on opposite sides of the plane, C(9) at +0.56 (1) and +0.69 (1) Å in the α- and β-epoxides respectively and N(4) at −0.30 (1) and −0.10 (1) Å. The angle between

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* Lists of structure amplitudes, anisotropic temperature factors, H-atom parameters and short intermolecular contact distances have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39552 (36 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† All numerical values refer to the more recent analysis by Wang (1981).

Table 1. *Final atomic coordinates of the non-H atoms* ($\times 10^4$) *and equivalent isotropic temperature factors for* 1,2-*dihydro-*1α,2α-*epoxymonocrotaline*

E.s.d.'s are given in parentheses.

	x	y	z	B_{eq}*(Å^2)
C(1)	6360 (6)	−1520 (5)	7030 (5)	3·0 (3)
C(2)	6134 (6)	−745 (6)	7848 (5)	3·9 (3)
C(3)	5419 (8)	290 (6)	7494 (5)	3·8 (3)
N(4)	4923 (5)	−10 (4)	6506 (3)	2·9 (2)
C(5)	5097 (9)	940 (6)	5794 (6)	4·5 (4)
C(6)	5881 (9)	444 (8)	4951 (5)	4·8 (4)
C(7)	6664 (6)	−510 (6)	5382 (5)	3·0 (3)
C(8)	5723 (6)	−997 (5)	6142 (4)	2·6 (2)
C(9)	7464 (6)	−2368 (6)	6962 (6)	3·6 (3)
O(10)	8669 (4)	−1794 (3)	7233 (3)	3·2 (2)
C(11)	9769 (6)	−2210 (5)	6866 (4)	3·2 (3)
C(12)	10981 (6)	−1505 (5)	7125 (4)	3·0 (3)
C(13)	11326 (6)	−589 (5)	6321 (4)	2·8 (2)
C(14)	10133 (6)	192 (5)	6094 (4)	2·7 (2)
C(15)	9004 (6)	−384 (5)	5542 (4)	2·7 (3)
O(16)	7840 (4)	−58 (3)	5866 (3)	3·1 (2)
C(17)	12138 (6)	−2326 (6)	7310 (6)	4·6 (4)
C(18)	11932 (6)	−1129 (5)	5404 (5)	3·5 (3)
C(19)	10493 (9)	1271 (6)	5502 (6)	4·5 (3)
O(20)	9826 (5)	−3082 (4)	6396 (4)	5·6 (3)
O(21)	10696 (5)	−900 (4)	8011 (3)	3·8 (2)
O(22)	12256 (4)	164 (4)	6778 (3)	3·2 (2)
O(23)	9131 (5)	−1032 (5)	4857 (4)	4·9 (2)
O(24)	5357 (4)	−1780 (4)	7765 (3)	4·3 (2)

* Calculated from the refined anisotropic thermal parameters (deposited), $B_{eq} = 8\pi^2 U_{eq}$.

Table 2. *Final atomic coordinates of the non-H atoms* ($\times 10^4$) *and equivalent isotropic temperature factors for* 1,2-*dihydro-*1β,2β-*epoxymonocrotaline monohydrate*

E.s.d.'s are given in parentheses.

	x	y	z	B_{eq}*(Å^2)
C(1)	−3354 (3)	−773 (2)	−1308 (2)	2·5 (1)
C(2)	−4253 (3)	−1537 (3)	−1814 (2)	2·8 (1)
C(3)	−5554 (3)	−1711 (3)	−1270 (2)	2·9 (1)
N(4)	−5393 (2)	−1110 (2)	−370 (2)	2·5 (1)
C(5)	−5362 (3)	−1769 (3)	504 (2)	3·3 (1)
C(6)	−3868 (3)	−1845 (3)	800 (2)	2·6 (1)
C(7)	−3331 (3)	−733 (3)	530 (2)	2·3 (1)
C(8)	−4087 (3)	−461 (2)	−399 (2)	3·3 (1)
C(9)	−2434 (3)	−32 (4)	−1841 (2)	2·9 (2)
O(10)	−1052 (2)	−6 (2)	−1425 (1)	2·6 (1)
C(11)	−360 (3)	927 (2)	−1432 (2)	2·4 (1)
C(12)	1151 (3)	786 (2)	−1128 (2)	2·2 (1)
C(13)	1326 (3)	816 (2)	−16 (2)	2·1 (1)
C(14)	428 (3)	−80 (2)	454 (2)	2·4 (1)
C(15)	−1118 (3)	145 (2)	503 (2)	2·6 (1)
O(16)	−1839 (2)	−787 (1)	429 (1)	3·7 (2)
C(17)	2019 (4)	1657 (3)	−1604 (2)	3·1 (1)
C(18)	1084 (4)	1935 (2)	376 (2)	3·1 (1)
C(19)	902 (4)	−329 (3)	1471 (2)	4·3 (1)
O(20)	−871 (3)	1759 (2)	−1685 (2)	2·9 (1)
O(21)	1649 (2)	−254 (2)	−1392 (2)	2·6 (1)
O(22)	2754 (2)	573 (2)	166 (1)	3·8 (1)
O(23)	−1668 (2)	987 (2)	634 (2)	3·0 (1)
O(24)	−3015 (2)	−1906 (2)	−1336 (1)	3·9 (1)
O(*W*)	753 (3)	−908 (2)	−3161 (2)	3·9 (1)

* Calculated from the refined anisotropic thermal parameters (deposited), $B_{eq} = 8\pi^2 U_{eq}$.

the epoxide ring and the plane of the four ring *B* atoms is 104·5 (8)° in the α-epoxide and 106·2 (4)° in the β-epoxide.

The conformation of the macrocycle from C(1) to C(7) in both epoxide molecules is similar to that observed in monocrotaline – see Table 4. The angles between the synparallel carbonyl bonds of the ester functions are 19·1 (7) and 26·4 (3)° in the α- and β-epoxides respectively compared with the value 15·2 (5)° in monocrotaline. The intramolecular O(16)···O(10) distances of 2·885 (5) Å in the α-epoxide and 2·901 (2) Å in the β-epoxide are slightly shorter than the value 3·040 (8) Å in monocrotaline but closer in value to the distances of 2·957 (5) and 2·921 (6) Å observed in fulvine (Sussman & Wodak, 1973) and crispatine (Mackay, Sadek & Culvenor, 1984) respectively. The transannular distance, O(10)···C(15), is 2·861 (7) Å in the α-epoxide and 2·740 (3) Å in the β-epoxide compared with the values 2·741 (9) Å in monocrotaline, 2·765 (7) Å in fulvine and 2·647 (7) Å in crispatine.

Atoms in the primary ester group, C(9), O(10), C(11), C(12), O(20), are coplanar within ±0·04 (1) Å in the α-epoxide and within ±0·08 (1) Å in the β-epoxide. The methylene H atoms at C(9) are asymmetrically orientated about the ester plane as reflected in the torsional angles H(9a)—C(9)—O(10)—C(11) and H(9b)—C(9)—O(10)—C(11) of 97 (5), 94 (3)° and −46 (5), −23 (3)° in the α- and β-epoxides respectively. However, in monocrotaline they are fairly symmetrically placed [*cf.* torsional angles 74 (5) and −60 (5)°]. The secondary ester system at C(7) has the atoms C(7), O(16), C(15), C(14), O(23) coplanar within ±0·02 (1) Å in the α-epoxide and within ±0·03 (1) Å in the β-epoxide. In the former, H(7) lies within the ester plane whereas in the latter it is substantially out-of-plane, the torsional angle C(7)—H(7)—O(16)—C(15) being −34 (3)° [*cf.* values −22 (5)° in crispatine and −13 (5)° in monocrotaline].
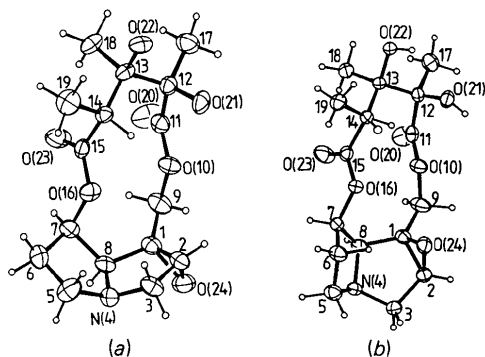

Fig. 1. Perspective views of the molecules with thermal ellipsoids scaled to 40% probability. The C atoms are denoted by numerals only. (*a*) 1,2-Dihydro-1α,2α-epoxymonocrotaline. (*b*) 1,2-Dihydro-1β,2β-epoxymonocrotaline.

Table 3. Bond lengths (Å) and angles (°) with e.s.d.'s in parentheses

	α-Epoxide	β-Epoxide		α-Epoxide	β-Epoxide		α-Epoxide	β-Epoxide
C(1)–C(2)	1·458 (9)	1·470 (4)	C(5)–C(6)	1·516 (11)	1·500 (4)	C(12)–C(17)	1·537 (10)	1·524 (4)
C(1)–C(8)	1·506 (9)	1·519 (4)	C(6)–C(7)	1·491 (11)	1·523 (5)	C(12)–O(21)	1·433 (7)	1·427 (4)
C(1)–C(9)	1·498 (9)	1·483 (5)	C(7)–C(8)	1·522 (9)	1·541 (4)	C(13)–C(14)	1·547 (8)	1·558 (4)
C(1)–O(24)	1·462 (8)	1·444 (4)	C(7)–O(16)	1·463 (8)	1·444 (3)	C(13)–C(18)	1·533 (9)	1·514 (4)
C(2)–C(3)	1·491 (10)	1·485 (4)	C(9)–O(10)	1·442 (8)	1·454 (3)	C(13)–O(22)	1·434 (7)	1·430 (3)
C(2)–O(24)	1·448 (8)	1·444 (4)	O(10)–C(11)	1·316 (8)	1·336 (4)	C(14)–C(15)	1·528 (8)	1·514 (4)
C(3)–N(4)	1·484 (8)	1·486 (4)	C(11)–C(12)	1·522 (9)	1·526 (4)	C(14)–C(19)	1·543 (9)	1·543 (4)
N(4)–C(5)	1·488 (9)	1·485 (4)	C(11)–O(20)	1·207 (8)	1·199 (4)	C(15)–O(16)	1·317 (7)	1·353 (3)
N(4)–C(8)	1·496 (8)	1·493 (3)	C(12)–C(13)	1·575 (8)	1·585 (4)	C(15)–O(23)	1·212 (8)	1·186 (4)
C(2)–C(1)–C(8)	107·4 (5)	107·8 (2)	C(6)–C(7)–O(16)	110·1 (6)	108·7 (2)	C(17)–C(12)–O(21)	108·8 (5)	110·0 (2)
C(2)–C(1)–C(9)	125·2 (6)	120·2 (3)	C(8)–C(7)–O(16)	109·7 (5)	113·2 (2)	C(12)–C(13)–C(14)	111·6 (5)	110·5 (2)
C(2)–C(1)–O(24)	59·5 (4)	59·4 (2)	C(1)–C(8)–N(4)	106·1 (5)	106·0 (2)	C(12)–C(13)–C(18)	112·4 (5)	111·7 (2)
C(8)–C(1)–C(9)	122·6 (6)	123·4 (3)	C(1)–C(8)–C(7)	115·7 (5)	116·7 (2)	C(12)–C(13)–O(22)	105·0 (4)	106·0 (2)
C(8)–C(1)–O(24)	109·9 (5)	112·1 (2)	N(4)–C(8)–C(7)	106·2 (5)	104·8 (2)	C(14)–C(13)–C(18)	113·1 (5)	114·4 (2)
C(9)–C(1)–O(24)	115·1 (5)	117·1 (3)	C(1)–C(9)–O(10)	108·0 (6)	110·6 (3)	C(14)–C(13)–O(22)	103·9 (5)	107·7 (2)
C(1)–C(2)–C(3)	109·4 (6)	109·6 (3)	C(9)–O(10)–C(11)	116·6 (5)	118·1 (2)	C(18)–C(13)–O(22)	110·3 (5)	106·0 (2)
C(1)–C(2)–O(24)	60·4 (4)	59·4 (2)	O(10)–C(11)–C(12)	113·3 (5)	111·9 (2)	C(13)–C(14)–C(15)	115·2 (5)	115·6 (2)
C(3)–C(2)–O(24)	112·8 (3)	113·9 (3)	O(10)–C(11)–O(20)	123·8 (6)	123·0 (3)	C(13)–C(14)–C(19)	113·8 (5)	112·3 (2)
C(2)–C(3)–N(4)	105·6 (6)	106·5 (3)	C(12)–C(11)–O(20)	122·9 (6)	125·0 (3)	C(15)–C(14)–C(19)	106·2 (5)	106·5 (2)
C(3)–N(4)–C(5)	112·3 (5)	116·2 (2)	C(11)–C(12)–C(13)	112·7 (5)	112·3 (2)	C(14)–C(15)–O(16)	112·2 (5)	110·0 (2)
C(3)–N(4)–C(8)	107·6 (5)	109·6 (2)	C(11)–C(12)–C(17)	108·5 (5)	108·4 (2)	C(14)–C(15)–O(23)	125·3 (6)	127·4 (3)
C(5)–N(4)–C(8)	107·1 (5)	107·7 (2)	C(11)–C(12)–O(21)	107·6 (5)	110·4 (2)	O(16)–C(15)–O(23)	122·4 (6)	122·5 (3)
C(5)–C(6)–C(7)	105·3 (7)	101·4 (3)	C(13)–C(12)–C(17)	111·7 (5)	111·4 (2)	C(7)–O(16)–C(15)	118·3 (5)	117·5 (2)
C(6)–C(7)–C(8)	102·5 (6)	104·7 (2)	C(13)–C(12)–O(21)	107·5 (5)	104·3 (2)			

Table 4. Torsional angles (°) in the macroring

E.s.d.'s for the α-epoxide are about 0·8° and for the β-epoxide about 0·4°. Values for monocrotaline (Wang, 1981) are included. Atoms are represented by their identification number.

	α-Epoxide	β-Epoxide	Monocrotaline
1—9—10—11	−153·8	−144·6	−157·4
9—10—11—12	175·7	−170·3	175·1
10—11—12—13	−93·5	−85·0	−84·6
11—12—13—14	54·3	58·1	53·5
12—13—14—15	−70·8	−75·9	−73·9
13—14—15—16	140·1	147·4	155·4
14—15—16—7	177·9	175·7	−177·7
15—16—7—8	129·2	85·7	113·2
16—7—8—1	−32·6	26·5	−27·8
7—8—1—9	−49·0	−93·2	−61·0
8—1—9—10	105·6	81·2	111·8
2—1—9—10	−46·9	−135·0	−66·4
6—7—16—15	−118·8	−158·5	−88·4

The bond lengths and angles are similar to those reported for comparable structures. In the α-epoxide molecule, the O atom of the hydroxyl substituent at C(12) acts as a donor in an intramolecular hydrogen-bonding interaction with the adjacent O atom at C(13), the O(21)···O(22), H(21)···O(22) and O(21)—H(21) distances being 2·626 (6), 1·86 (5) and 1·02 (6) Å respectively with the angle subtended at H(21) 129 (5)°. A similar intramolecular interaction was noted in dehydromonocrotaline (Mackay, Sadek, Culvenor & Smith, 1984) but there are no intramolecular hydrogen bonds in the β-epoxide and monocrotaline.

The molecular packing in the two crystals is illustrated in Fig. 2. In both there is an intermolecular hydrogen bond between the N atom of one molecule and the hydroxyl substituent at C(13) of the adjacent molecule related by a unit-cell translation along **a**. The
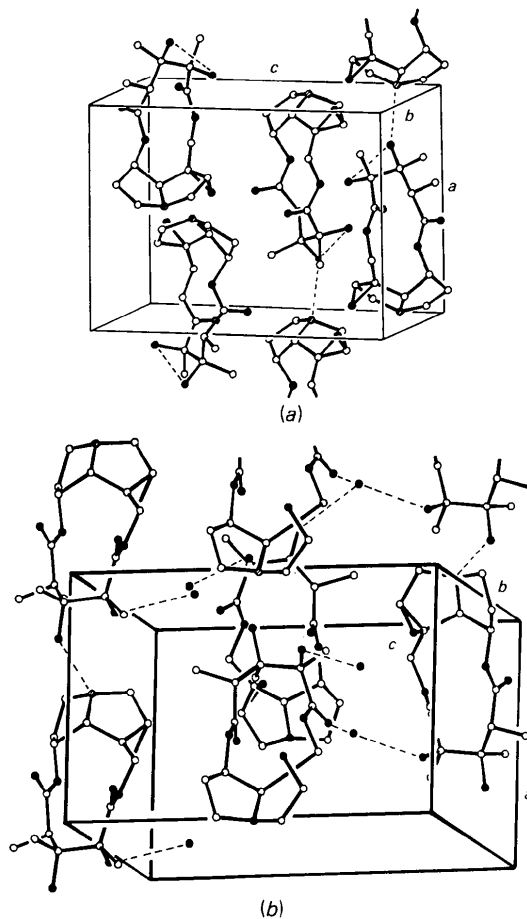

(a)

(b)

Fig. 2. The crystal packing. (a) 1,2-Dihydro-1α,2α-epoxymonocrotaline. (b) 1,2-Dihydro-1β,2β-epoxymonocrotaline monohydrate.

O(22)···N(4), H(22)···N(4) and O(22)–H(22) distances in the α-epoxide are 2·737 (6), 1·83 (5) and 0·97 (7) Å respectively and the angle subtended at H(22) is 154 (4)°; the corresponding values in the β-epoxide are 2·849 (3), 2·01 (3) and 0·90 (4) Å and 155 (2)°. This interaction links the alkaloid molecules into chains in the α-epoxide crystal similar to the packing mode observed in the monocrotaline crystal. However, the additional hydrogen bonding in the β-epoxide monohydrate structure, in which each water links three alkaloid molecules, results in a three-dimensional network of hydrogen bonding. The water oxygen is the acceptor in the hydrogen bond with O(21); O(21)···O(W), H(21)···O(W), O(21)–H(21) distances are 2·773 (4), 1·94 (4) and 0·85 (5) Å respectively and the angle at H(21) is 166 (3)°. In the two other interactions the water oxygen is the donor atom; for the interaction with the carbonyl oxygen of the primary ester moiety the O(W)···O(20), H(1W)···O(20) and O(W)–H(1W) distances have the respective values 2·907 (4), 2·09 (4) and 0·87 (5) Å and the angle at H(1W) is 156 (3)°. For the interaction with the hydroxyl oxygen at C(13), the O(W)···O(22), H(2W)···O(20) and O(W)–H(2W) distances are

2·803 (3), 1·79 (5) and 1·04 (8) Å respectively and the angle at H(2W) is 164 (4)°.

References

CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.
CULVENOR, C. C. J., O'DONOVAN, G. M., SAWHNEY, R. S. & SMITH, L. W. (1970). *Aust. J. Chem.* **23**, 347–352.
JOHNSON, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
MACKAY, M. F., SADEK, M. & CULVENOR, C. C. J. (1984). *Acta Cryst.* C**40**, 470–472.
MACKAY, M. F., SADEK, M., CULVENOR, C. C. J. & SMITH, L. W. (1984). *Acta Cryst.* C**40**, 473–476.
SHELDRICK, G. M. (1976). *SHELX76.* A program for crystal structure determination. Univ. of Cambridge, England.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
STOECKLI-EVANS, H. (1979). *Acta Cryst.* B**35**, 231–234.
SUSSMAN, J. L. & WODAK, S. J. (1973). *Acta Cryst.* B**29**, 2918–2926.
WANG, S. (1981). *Sci. Sin.* **24**, 497–507.

Structure of (−)-Epicatechin: (2R,3R)-2-(3,4-Dihydroxyphenyl)-3,4-dihydro-2H-1-benzopyran-3,5,7-triol, $C_{15}H_{14}O_6$

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Abstract. $M_r = 290·28$, orthorhombic, $P2_12_12_1$, $a = 6·702$ (1), $b = 13·273$ (1), $c = 14·227$ (2) Å, $U = 1265·6$ (3) Å^3, $Z = 4$, $D_x = 1·523$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0·71069$ Å, $\mu = 0·74$ cm^{-1}, $F(000) = 608$, $T = 295$ K, $R = 0·052$ for 623 reflexions [$I > 1·5\sigma(I)$]. The heterocyclic ring is in a half-chair conformation. All oxygen atoms are involved in hydrogen bonds. Interaction between the OH groups of dihydroxyphenyl and 3,5,7-trihydroxybenzopyran residues, O(5)–H···O(4), connects molecules along **b** to form infinite chains. Parallel chains related by 2_1 axes along **b** are connected through O(3)–H···O(2) bonds between 3,5,7-trihydroxybenzopyran residues and O(2)–H···O(5) bonds in the *ab* plane. The O(2) hydroxyl group also exhibits an intramolecular contact to the heterocyclic O(1) forming a bifurcated hydrogen bond with O(5) as does O(5)–H with O(6) (both of the 3,4-dihydroxyphenyl residue). A weak interaction, O(6)–H···O(1), completes this bonding in a three-dimensional network.

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