in the direction of the crystallographic axis, with a Cl(1)···Cl(11) separation of 3·643 (2) Å.

The molecular thickness is 3·05 Å in 1 and 3·30 Å in 2, *i.e.* close to that of *B*, making a partial intercalation inside duplex DNA possible in principle as in *B*. In this connection 3-chloro-4-dimethylaminothioangelicin shows an evident affinity towards DNA in the dark, forming a molecular complex with the macromolecule as shown by the classic Scathchard plot reported in Fig. 3. In fact, the *K* value ($7070\ M^{-1}$) correlated to the affinity of the ligand towards DNA is much higher than that of the parent compound angelicin ($K = 560\ M^{-1}$) (Dall'Acqua, Vedaldi, Guiotto, Rodighiero, Carlassare, Baccichetti & Bordin, 1981).

The substitution of oxygen in *B* by sulfur, in addition to the crystal-packing changes, seems to affect the electronic arrangement of the chromophore at the excited state probably reducing the DNA photobinding. In fact the antiproliferative activity, which is correlated with the DNA photobinding, is poor (Mosti, Schenone, Menozzi, Romussi, Baccichetti, Carlassare & Bordin, 1983).

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Echinatine, $C_{15}H_{25}NO_5$, a Pyrrolizidine Alkaloid

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Abstract. $M_r = 299{\cdot}4$, monoclinic, $P2_1$, $a = 7{\cdot}214$ (1), $b = 13{\cdot}577$ (1), $c = 9{\cdot}005$ (1) Å, $\beta = 111{\cdot}58$ (1)°, $V = 820{\cdot}2$ (1) Å^3, $Z = 2$, D_m (flotation) = 1·21 (1), $D_x = 1{\cdot}213$ Mg m^{-3}, $\lambda(\mathrm{Cu}\,K\alpha) = 1{\cdot}5418$ Å, $\mu = 0{\cdot}66$ mm^{-1}, $F(000) = 324$, $T = 288$ (1) K, final $R = 0{\cdot}052$ for 1364 observed reflections. Echinatine, a heliotridine alkaloid, is a diastereoisomer of lycopsamine, a retronecine ester with the same esterifying acid. The pyrrolizidine nucleus in echinatine is *exo*-puckered in contrast to the *endo*-puckering in crystals of two other heliotridine alkaloids, heliotrine and lasiocarpine. As observed in the other monoester alkaloids the esterifying acid moiety, in this case (−)-viridifloric acid, adopts an extended conformation. Hydrogen bonding in the crystal links the molecules into layers parallel to the *bc* plane.

Introduction. Echinatine (I), a monoester of the aminoalcohol heliotridine with (−)-viridifloric acid, is a pyrrolizidine alkaloid which has been isolated from

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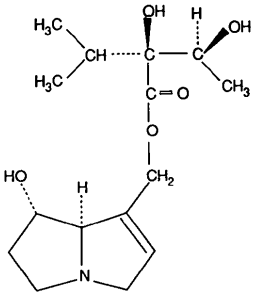
Heliotropium supinum L. (Crowley & Culvenor, 1959) and other species of the family Boraginaceae (Bull, Culvenor & Dick, 1968). The alkaloid is hepatotoxic and has been shown to be mutagenic in *Drosophila melanogaster* (Clark, 1960). Echinatine is a diastereoisomer of the retronecine alkaloid lycopsamine,* the two alkaloids having the same esterifying acid. The crystallographic analysis reported here has defined the conformational detail in echinatine crystals, and forms part of a study of the conformational aspects of the hepatotoxic pyrrolizidine alkaloids currently being undertaken by us.



(I)

Experimental. Colourless plates were grown from acetone. A crystal *ca* 0·55 × 0·45 × 0·29 mm was aligned on a Rigaku-AFC diffractometer; cell parameters determined by least squares from 2θ values for 25 strong reflections ($42 < 2\theta < 60°$); Cu $K\alpha$ radiation (graphite-crystal monochromator); ω–2θ scan, 2θ scan rate 2° min^{-1}, scan range ($\Delta\omega$) 1·2° + 0·5°tanθ, 10 s stationary background counts; three standard reflections, no significant intensity variation; 1406 unique data to $2\theta_{max} = 130°$ (h −7 to 7, k 0 to 15, l 0 to 10), R_{int} 0·009 for 118 merged data; 1364 data [$I_o \geq 2\sigma(I_o)$] for refinement; no correction for extinction, but four large terms (111, 100, $\bar{1}0\bar{1}$, 021) apparently seriously affected by extinction omitted from final refinement; corrections for Lorentz and polarization factors and for absorption (transmission factors 0·844–0·696). Structure solved by direct methods with *SHELX*76 (Sheldrick, 1976). Methyl H atoms and those on C(6) and C(9) included at idealized positions (C–H 1·08 Å) as sites not clearly resolved on difference maps; all other H-atom sites located. Full-matrix least-squares refinement with anisotropic temperature factors given to the C, N and O atoms and isotropic for the H atoms converged at $R = 0·052$, $wR = 0·069$, $S = 2·71$ (238 parameters varied); function minimized $\sum w(|F_o| - |F_c|)^2$, with weights $(\sigma^2|F_o| + 0·0006|F_o|^2)^{-1}$. At convergence $(\Delta/\sigma)_{max}$ 0·19:1 [x coordinate of H(15)]; $(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ = 0·24, −0·30 e Å^{-3}. Atomic scattering factors (Table 2.2*B*) and anomalous-dispersion factors (Table 2.31) from *International Tables for X-ray Crystallography* (1974). Figures were prepared from the output of *ORTEP*II (Johnson, 1976). All calculations were performed on a VAX 11/780 computer.

* The structural representation of lycopsamine and intermedine given as (I) in Mackay, Sadek & Culvenor (1983) is in error. The C(12)–OH bond should be β and not α.

Table 1. *Final atomic coordinates of the non-*H *atoms* (× 10^4) *and equivalent isotropic temperature factors with e.s.d.'s in parentheses*

$B_{eq} = \frac{8}{3}\pi^2 \sum_i \sum_j a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$

	x	y	z	B_{eq}(Å^2)
C(1)	1287 (5)	1127	1393 (4)	2·79 (5)
C(2)	−253 (5)	536 (4)	1123 (4)	3·66 (6)
C(3)	100 (6)	−444 (4)	534 (5)	3·96 (6)
N(4)	2077 (4)	−355 (3)	374 (3)	3·03 (4)
C(5)	2031 (9)	−423 (4)	−1276 (5)	4·77 (8)
C(6)	3619 (8)	241 (4)	−1326 (5)	5·54 (9)
C(7)	3467 (5)	1123 (4)	−317 (4)	3·37 (6)
C(8)	2908 (4)	634 (3)	1000 (3)	2·50 (5)
C(9)	1473 (6)	2175 (4)	1908 (4)	3·71 (6)
O(10)	3042 (4)	2233 (3)	3519 (3)	3·35 (4)
C(11)	4066 (6)	3073 (4)	3886 (4)	3·42 (6)
C(12)	5578 (5)	3083 (4)	5569 (4)	3·21 (5)
C(13)	4507 (6)	2971 (4)	6747 (4)	4·05 (7)
C(14)	2925 (6)	3740 (5)	6541 (6)	5·77 (9)
C(15)	7256 (6)	2316 (4)	5817 (5)	4·15 (7)
C(16)	6648 (9)	1254 (4)	6039 (6)	5·79 (9)
C(17)	8061 (6)	2369 (5)	4458 (6)	6·07 (10)
O(18)	3807 (6)	3764 (3)	2986 (3)	5·53 (6)
O(19)	6514 (4)	4028 (3)	5833 (3)	4·35 (5)
O(20)	5935 (5)	2952 (3)	8347 (3)	4·86 (5)
O(21)	5262 (4)	1657 (3)	418 (3)	4·72 (5)

Discussion. Final atomic coordinates are given in Table 1.* The molecular conformation and numbering scheme are illustrated in Fig. 1, and the molecular geometry is given in Table 2.

The absolute molecular structure has been assigned by comparison with that of heliotridine, so that the absolute configuration of echinatine is (7*S*,12*S*,13*S*). The alkaloid is a diastereoisomer of the retronecine alkaloid lycopsamine, both having the same esterifying acid, (−)-viridifloric acid, whose absolute structure (Kochetkov, Likhosherstov & Kulakov, 1969) is in accord with that assigned to echinatine.

The pucker of the pyrrolizidine nucleus is *exo* as is generally observed in crystals of retronecine alkaloids. The *exo* pucker, however, contrasts with the *endo* pucker observed in crystals of two other heliotridine alkaloids, lasiocarpine (Hay, Mackay & Culvenor, 1982) and heliotrine (Wodak, 1975). In echinatine the pucker angle is 39·8 (4)° and the angle between the mean planes defined by the atoms

* Lists of structure amplitudes, anisotropic temperature factors, H-atom coordinates, torsion angles and intermolecular contacts have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44965 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths* (Å), *bond angles* (°) *and selected torsion angles* (°)

E.s.d.'s for torsion angles are *ca* 0·4°.

C(1)–C(2)	1·319 (5)	C(9)–O(10)	1·478 (4)	C(1)–C(8)–C(7)–O(21)	102·3	−21·8*
C(1)–C(8)	1·498 (5)	O(10)–C(11)	1·333 (6)	C(1)–C(9)–O(10)–C(11)	149·9	176·9
C(1)–C(9)	1·487 (6)	C(11)–C(12)	1·507 (4)	C(2)–C(1)–C(8)–C(7)	118·8	118·3
C(2)–C(3)	1·489 (7)	C(11)–O(18)	1·208 (6)	C(2)–C(1)–C(9)–O(10)	114·8	−142·1
C(3)–N(4)	1·489 (6)	C(12)–C(13)	1·532 (6)	C(9)–O(10)–C(11)–C(12)	177·8	177·5
N(4)–C(5)	1·477 (6)	C(12)–C(15)	1·549 (7)	C(9)–O(10)–C(11)–O(18)	−1·2	−2·3
N(4)–C(8)	1·494 (5)	C(12)–O(19)	1·428 (6)	O(10)–C(11)–C(12)–C(13)	−61·3	127·7
C(5)–C(6)	1·471 (9)	C(13)–C(14)	1·507 (8)	O(10)–C(11)–C(12)–C(15)	65·6	−108·9
C(6)–C(7)	1·531 (7)	C(13)–O(20)	1·431 (4)	O(10)–C(11)–C(12)–O(19)	−177·8	9·7
C(7)–C(8)	1·537 (6)	C(15)–C(16)	1·542 (8)	C(11)–C(12)–C(13)–C(14)	−55·9	−58·9
C(7)–O(21)	1·418 (5)	C(15)–C(17)	1·537 (8)	C(11)–C(12)–C(13)–O(20)	178·4	−177·3
				C(11)–C(12)–C(15)–C(16)	−78·8	−70·1
C(2)–C(1)–C(8)	111·2 (2)	C(9)–O(10)–C(11)	116·3 (3)	C(11)–C(12)–C(15)–C(17)	47·0	55·8
C(2)–C(1)–C(9)	127·8 (3)	O(10)–C(11)–C(12)	112·8 (3)	C(13)–C(12)–C(11)–O(18)	117·6	−52·5
C(8)–C(1)–C(9)	120·8 (3)	O(10)–C(11)–O(18)	124·3 (3)	C(14)–C(13)–C(12)–C(15)	178·0	−179·8
C(1)–C(2)–C(3)	111·5 (3)	C(12)–C(11)–O(18)	123·0 (3)	C(15)–C(12)–C(11)–O(18)	−115·4	70·9
C(2)–C(3)–N(4)	104·9 (3)	C(11)–C(12)–C(13)	109·5 (3)	O(19)–C(12)–C(11)–O(18)	1·1	−170·5
C(3)–N(4)–C(5)	115·1 (3)	C(11)–C(12)–C(15)	112·1 (3)	O(19)–C(12)–C(13)–O(20)	−65·3	−60·6
C(3)–N(4)–C(8)	107·6 (3)	C(11)–C(12)–O(19)	107·4 (3)			
C(5)–N(4)–C(8)	107·1 (3)	C(13)–C(12)–C(15)	113·6 (3)			
N(4)–C(5)–C(6)	105·2 (4)	C(13)–C(12)–O(19)	107·6 (3)			
C(5)–C(6)–C(7)	103·6 (4)	C(15)–C(12)–O(19)	106·5 (3)			
C(6)–C(7)–C(8)	102·5 (3)	C(12)–C(13)–C(14)	113·4 (3)			
C(6)–C(7)–O(21)	115·1 (3)	C(12)–C(13)–O(20)	109·8 (3)			
C(8)–C(7)–O(21)	108·3 (3)	C(14)–C(13)–O(20)	111·7 (3)			
C(1)–C(8)–N(4)	104·5 (2)	C(12)–C(15)–C(16)	113·8 (4)			
C(1)–C(8)–C(7)	116·0 (3)	C(12)–C(15)–C(17)	111·0 (4)			
N(4)–C(8)–C(7)	106·3 (2)	C(16)–C(15)–C(17)	110·9 (4)			
C(1)–C(9)–O(10)	107·8 (3)					

* Torsion angles for lycopsamine included for comparison in the second column.

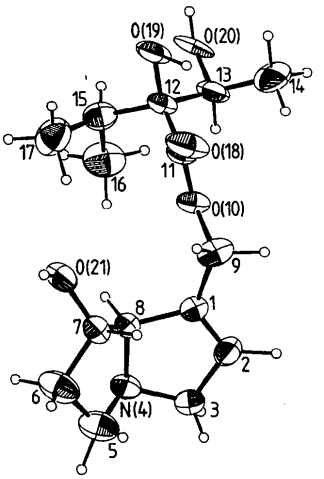


Fig. 1. Perspective view of the molecule with thermal ellipsoids scaled to 50% probability.

C(1),C(2),C(3),N(4),C(8) and C(5),N(4),C(8),C(7) is 123·0 (3)°. These values are similar to the respective values 40·2 (4) and 125·4 (3)° for these angles in lycopsamine (Mackay, Sadek & Culvenor, 1983). In the unsaturated ring the atoms are coplanar within ±0·03 (1) Å with C(9) lying 0·10 (1) Å from the plane [*cf.* C(9) lies 0·14 (1) Å from the ring plane in lycopsamine]. The torsion angle C(2)–C(1)–C(9)–O(10) is 114·7 (4)° [*cf.* 142·1 (4)° in lycopsamine] so that one H atom at C(9), H(9*b*), lies close to the plane of the unsaturated ring [torsion angle C(2)–C(1)–C(9)–H(9*b*) −5·1 (6)°, *cf.* −22 (3)° in lycopsamine].

As in lycopsamine the viridifloric acid moiety at C(9) adopts an extended conformation with the atoms C(1), C(9), O(10), C(11), C(12), O(18) and O(19) nearly coplanar [see torsion angles C(1)–C(9)–O(10)–C(11), C(9)–O(10)–C(11)–C(12) and O(19)–C(12)–C(11)–O(18), Table 2]. The monoprotic esterifying acid moieties, lasiocarpic acid in lasiocarpine, heliotric acid in heliotrine and heleurine (Mackay, Mitrprachachon, Oliver & Culvenor, 1985) and trachelanthic acid in intermedine (Mackay, Sadek & Culvenor, 1983) all adopt an extended conformation. The five atoms of the ester group in echinatine, C(9), O(10), C(11), C(12) and O(18), are coplanar within ±0·03 (1) Å. However, the relative orientation of the viridifloric acid moiety with respect to the pyrrolizidine nucleus is different to that observed in lycopsamine; in the latter, the O–H bond of the hydroxyl substituent at C(12) is directed away from the carbonyl O(18) atom, the carbonyl bond being *syn*-parallel with the C(8)–H bond. In echinatine, the C(12) hydroxyl and O(18) lie on the same side of the extended chain, and the carbonyl bond is antiparallel with the C(8)–H bond as observed in both supinine and heleurine. This conformation allows intramolecular hydrogen bonding in which the hydroxyl O atoms at C(12) and C(13) are the donor atoms in interactions with O(18) and O(19) respectively. The

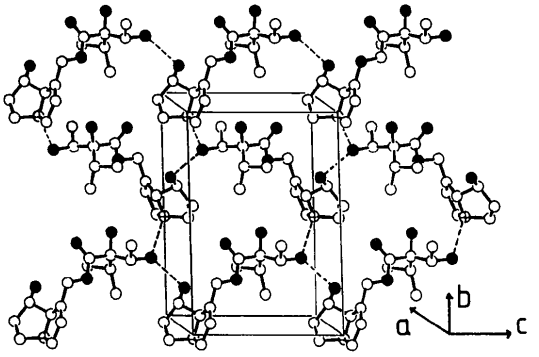


Fig. 2. The crystal packing.

interaction involving O(20) is bifurcated, this atom also being involved in an intermolecular hydrogen bond; the O(20)···O(19), H(20)···O(19) and O(20)–H(20) distances are 2·852 (5), 2·57 (7) and 0·93 (7) Å respectively, with the angle O(20)–H(20)···O(19) 98(5)°. For the other interaction, the O(19)···O(18), H(19)··· O(18), O(19)–H(19) distances are 2·613 (5), 1·89 (7) and 1·17 (7) Å, with the angle O(19)–H(19)··· O(18) 115(5)°.

The crystal packing is illustrated in Fig. 2. There are two unique intermolecular hydrogen-bonding interactions which link the molecules into a two-dimensional network, each molecule being bonded to four others. One interaction between molecules related by the twofold screw axis (bifurcated, see above) links the molecules into infinite spirals along the crystal *b* axis; the O(20)···N(4) $(1-x, \frac{1}{2}+y, 1-z)$, H(20)···N(4) distances are 2·730 (5) and 1·82 (7) Å respectively with the O(20)–H(2)···N(4) angle 166 (5)°. The other interaction between the hydroxyl substituent on the pyrrolizidine nucleus at C(7) and O(20) links the molecules along the *c* axis; O(21)···O(20), H(21)··· O(20) and O(21)–H(21) have the respective values 2·733 (5), 1·77 and 0·98 Å, with the O(21)–H(21)··· O(20) angle 167°. The molecular layers which are orientated parallel to the *bc* plane are held together in the crystal by van der Waals interactions.

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1-Oxo-2,3,7,7a-tetraphenyl-5-[α-(triphenylphosphonio)benzylidene]-1,7a-dihydro-5*H*-pyrrolizin-1-olate, $C_{56}H_{40}NO_2P$ (I), and 2,3,5,6,8-Pentaphenyl-1,7-indolizinedione, $C_{38}H_{25}NO_2$ (II)

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Abstract. (I) $C_{56}H_{40}NO_2P$, $M_r = 789{\cdot}9$, monoclinic, $P2_1/c$, $a = 21{\cdot}857\ (6)$, $b = 10{\cdot}349\ (5)$, $c = 19{\cdot}294\ (6)$ Å, $\beta = 102{\cdot}53\ (9)°$, $V = 4260\ (3)$ Å^3, $Z = 4$, $D_x = 1{\cdot}232$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0{\cdot}10$ mm^{-1}, $F(000) = 1656$, $T = 291\ (1)$ K, final $R = 0{\cdot}116$ for 3201 unique observed $[F \geq 2{\cdot}0\sigma(F)]$ diffractometer data. (II) $C_{38}H_{25}NO_2$, $M_r = 527{\cdot}65$, orthorhombic, *Pbca*, $a = 11{\cdot}906\ (7)$, $b = 23{\cdot}706\ (9)$, $c =$

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