formation of clonazepam. Accordingly, the coordinates reported herein are those of the R isomer.

In conclusion, the molecular conformation of suriclone is found to be similar to that of its congener, zopiclone, and the R isomer of suriclone matches the active conformation of the agonist 1,4-benzodiazepines. The greater potency of suriclone over zopiclone is attributed to a larger hydrophobic group, formed by the coplanar rings (A) and (B), which can bind to a site on the benzodiazepine receptor that distinguishes ligands by the size of the group bound to the receptor at this point.

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Jacoline and Ethanol Solvate of Jaconine Hydrochloride. Pyrrolizidine Alkaloids

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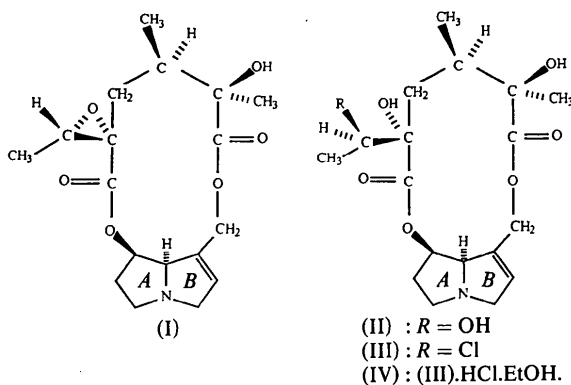*Division of Animal Health, CSIRO, Parkville, Victoria* 3052, *Australia*

Abstract. $T = 288$ (1) K, Cu $K\alpha$, $\lambda = 1.5418$ Å. Jacoline (II): $C_{18}H_{27}NO_7$, $M_r = 369.4$, monoclinic, $P2_1$, $a = 16.585$ (2), $b = 12.124$ (1), $c = 9.430$ (1) Å, $\beta = 90.72$ (2)°, $U = 1896.0$ (5) Å^3, D_m (flotation) = 1.29 (1), $D_x = 1.294$ Mg m^{-3}, $Z = 4$, $F(000) = 792$, μ(Cu $K\alpha$) = 0.74 mm^{-1}. Final $R = 0.030$ for 3403 observed data. Ethanol solvate of jaconine hydrochloride (IV): $C_{18}H_{27}ClNO_6^+.Cl^-.C_2H_6O$, $M_r = 470.4$, orthorhombic, $P2_12_12_1$, $a = 11.330$ (1), $b = 14.746$ (1), $c = 14.021$ (1) Å, $U = 2342.5$ (5) Å^3, D_m (flotation) = 1.33 (1), $D_x = 1.334$ Mg m^{-3}, $Z = 4$, $F(000) = 1000$, μ(Cu $K\alpha$) = 2.71 mm^{-1}. Final $R = 0.055$ for 1853 observed data. Jacoline and jaconine are closely related to jacobine as glycol–chlorohydrin–epoxide. The two independent molecules of (II) have very similar conformations. The conformations adopted by the 12-membered macrocyclic rings in these three alkaloids are very similar.

Introduction. The hepatotoxic alkaloids jacoline and jaconine have been isolated from the plant *Senecio jacobaea* L. (commonly known as ragwort) along with the closely related retronecine alkaloid jacobine (Bradbury & Culvenor, 1954). The molecular structures of jacobine, jaconine and jacoline were deduced by Geissman (1959) and Bradbury & Masamune (1959) from the chemical and spectral evidence, the three alkaloids being shown to be related as epoxide–chlorohydrin–glycol. An X-ray analysis of jacobine bromohydrin by Fridrichsons, Mathieson & Sutor

(1960, 1963) confirmed the structures and defined the absolute stereochemistry of jacobine as (I), jacoline (II) and jaconine (III). More recent X-ray analyses of crystals of jacobine (Pérez-Salazar, Cano & Garcia-Blanco, 1978) and jacobine methanol solvate (Rohrer, Karchesy & Deinzer, 1984) have defined accurate conformational detail for the jacobine molecule. The present report on jacoline and jaconine hydrochloride forms part of a study of the conformational aspects of the hepatotoxic pyrrolizidine alkaloids currently being undertaken by us.

CH3 H C OH CH2 C CH3 CH3 C C C=O O=C O O CH2 H A B N (I)

CH3 H C OH CH2 C CH3 R OH C C C=O CH3 C O=C O O CH2 H A B N

(II) : R = OH
(III) : R = Cl
(IV) : (III).HCl.EtOH.

Experimental. Colourless plate-like crystals of jacoline (II) from acetone; needle crystals of jaconine hydrochloride ethanol solvate (IV) from ethanol; crystals ca $0.11 \times 0.37 \times 0.46$ (II), $0.26 \times 0.34 \times 0.52$ mm (IV) sealed in a Lindemann-glass tube, 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 $2° \text{min}^{-1}$, scan range ($\Delta\omega$) $1.2° + 0.5°\tan\theta$, $2\theta_{max}$ $= 130°$, 10 s stationary background counts; three standard reflections for (II) and (IV) showed a gradual ~3% decrease in intensities and data scaled accordingly; 3377 non-equivalent terms for (II), h −19 to 19, k 0 to 14, l 0 to 11, 3043 having $I > 2\sigma(I)$ were used for structure refinement; 2232 non-equivalent terms for (IV), h −13 to 0, k 0 to 17, l 0 to 16, 1853 with $I > 2\sigma(I)$; intensities corrected for Lorentz and polarization effects and for absorption, transmission factors 0.761 to 0.924 (II) and 0.400 to 0.527 (IV); for (II) isotropic extinction correction of form $F = F_c \times$ $(1 - 1.07 \times 10^{-6} F^2/\sin\theta)$ applied to calculated structure amplitudes; four low-angle terms (020, 101, 011, 021) apparently seriously affected by extinction omitted from final refinement of (IV). Structures solved by direct methods with SHELX76 (Sheldrick, 1976). H-atom sites located on difference maps and H coordinates refined for (II). For (IV), H atoms at C(3), C(5), C(9), C(25), C(26) included at idealized positions, H atom at N(4) located but not refined and

those of ethanol omitted; remaining H atoms located and coordinates refined. Refinement with anisotropic temperature factors given to C, N, O, Cl atoms of alkaloid moieties, isotropic for H and C, O of ethanol; at convergence $R = 0.030$, $wR = 0.035$, $S = 1.16$ (685 parameters varied) for (II); $R = 0.055$, $wR = 0.073$, $S = 1.52$ (326 parameters varied) for (IV); function minimized $\sum w(|\Delta F|)^2$ with $w = [\sigma^2(|F_o|) + m|F_o|^2]^{-1}$ for which $m = 0.0005$ (II) and 0.0015 (IV). Parameters refined in two blocks (II), each block containing parameters for one molecule; full-matrix refinement for (IV); $(\Delta/\sigma)_{max}$ 0.11 [y coordinate of O(56)] and 0.04 [z coordinate of one C(14) methyl H atom] for (II) and (IV) respectively; $(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ = 0.14, −0.16 (II) and 0.69, −0.53 e Å^{-3} (IV). Atomic scattering factors and anomalous-dispersion factors from *International Tables for X-ray Crystallography* (1974). Figures were prepared from the output of ORTEPII (Johnson, 1976). Calculations performed on a VAX11/780 computer.

Discussion. Final atomic coordinates of the non-hydrogen atoms for structures (II) and (IV) are given in Table 1.* The molecular conformations for the two structures are illustrated in Fig. 1, which also includes the atom numbering, while bond lengths and angles and selected torsion angles are given in Table 2.

The two independent jacoline molecules (IIa) and (IIb) have essentially identical conformations with only small variations in torsion angles. The absolute molecular structures of jacoline (12R, 13R, 15S, 25R) and the jaconine cation (12R, 13R, 15R, 25R) illustrated in Fig. 1 have been assigned by comparison with that of retronecine. The pyrrolizidine nuclei have the usual exo-buckling observed in retronecine alkaloids. The pucker angles of 35.7 (3) (IIa), 37.3 (3) (IIb) and 40.6 (7)° (IV) are similar to the value 36.9 (4)° in jacobine (Pérez-Salazar, Cano & García-Blanco, 1978). The angles between the mean planes defined by ring B atoms and C(5), N(4), C(8), C(7) of ring A are 127.1 (3) (IIa), 125.4 (3) (IIb) and 126.2 (7)° (IV) compared with 127.3 (5)° in jacobine. Ring B atoms are coplanar to within ±0.052 (5) (IIa), ±0.064 (5) (IIb) and ±0.01 (1) Å (IV) with C(9) lying 0.105 (5) (IIa), 0.161 (5) (IIb) and 0.14 (1) Å (IV) from the ring planes. In jacobine C(9) lies 0.25 (1) Å from its ring plane as in the two retronecine alkaloids senecionine (Mackay & Culvenor, 1982) at 0.252 (5) Å and retrorsine (Coleman, Coucourakis & Pretorius, 1980) at 0.24 (1) Å.

Table 1. *Final atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors with e.s.d.'s in parentheses*

	x	y	z	$B_{eq}{}^*(\text{Å}^2)$
(a) Jacoline: Molecule (II*a*) atoms 1 to 27, molecule (II*b*) atoms 31 to 57				
C(1)	4620 (1)	4728	5214 (2)	2·66 (4)
C(2)	4881 (2)	4063 (2)	6226 (3)	3·37 (5)
C(3)	5753 (2)	4188 (3)	6536 (3)	3·82 (5)
N(4)	5997 (1)	5132 (2)	5662 (2)	2·91 (4)
C(5)	6720 (2)	4973 (3)	4782 (3)	3·64 (5)
C(6)	6502 (2)	5525 (3)	3373 (3)	3·39 (5)
C(7)	5618 (1)	5262 (2)	3203 (3)	2·76 (4)
C(8)	5309 (1)	5425 (2)	4709 (2)	2·61 (4)
C(9)	3778 (2)	4842 (3)	4667 (3)	3·27 (5)
O(10)	3649 (1)	4250 (1)	3328 (2)	3·03 (3)
C(11)	3531 (1)	3157 (2)	3468 (3)	2·57 (4)
C(12)	3355 (1)	2597 (2)	2054 (2)	2·58 (4)
C(13)	4089 (1)	2718 (2)	1060 (2)	2·36 (4)
C(14)	4836 (1)	2124 (2)	1675 (2)	2·40 (4)
C(15)	5643 (1)	2609 (2)	1203 (2)	2·39 (4)
C(16)	5654 (1)	3848 (2)	1474 (2)	2·46 (4)
O(17)	5534 (1)	4095 (1)	2835 (2)	2·60 (3)
O(20)	3546 (1)	2690 (2)	4595 (2)	3·39 (3)
C(21)	2591 (2)	3119 (3)	1410 (3)	3·66 (5)
O(22)	3178 (1)	1476 (2)	2296 (2)	3·22 (3)
C(23)	3881 (2)	2293 (3)	−427 (3)	3·60 (5)
O(24)	5750 (1)	2464 (2)	−287 (2)	2·95 (3)
O(24A)	7070 (1)	2781 (2)	1767 (2)	3·49 (3)
C(25)	6379 (1)	2102 (2)	1986 (2)	2·82 (4)
C(26)	6541 (2)	918 (3)	1571 (4)	4·18 (6)
O(27)	5746 (1)	4517 (2)	550 (2)	3·66 (3)
C(31)	882 (2)	8668 (2)	608 (3)	3·44 (5)
C(32)	1390 (2)	9456 (3)	930 (3)	4·46 (6)
C(33)	2221 (2)	9051 (3)	1229 (4)	4·85 (6)
N(34)	2179 (1)	7857 (2)	864 (2)	3·57 (4)
C(35)	2511 (2)	7103 (3)	1960 (3)	4·65 (6)
C(36)	1913 (2)	6166 (3)	2005 (4)	4·71 (6)
C(37)	1117 (2)	6754 (2)	1812 (3)	3·19 (4)
C(38)	1308 (1)	7578 (2)	630 (3)	3·11 (4)
C(39)	20 (2)	8777 (4)	169 (3)	4·75 (6)
O(40)	−521 (1)	8399 (2)	1288 (2)	3·99 (4)
C(41)	−838 (1)	9171 (3)	2126 (3)	3·49 (5)
C(42)	−1372 (1)	8654 (2)	3262 (3)	3·31 (4)
C(43)	−861 (1)	7857 (2)	4191 (3)	3·17 (4)
C(44)	−153 (1)	8475 (2)	4908 (3)	2·87 (4)
C(45)	560 (1)	7759 (2)	5395 (2)	2·82 (4)
C(46)	731 (1)	6918 (2)	4242 (3)	2·90 (4)
O(47)	943 (1)	7422 (1)	3047 (1)	2·70 (3)
O(50)	−728 (2)	10137 (2)	1993 (2)	5·61 (5)
C(51)	−2076 (2)	8078 (3)	2524 (4)	4·67 (6)
O(52)	−1728 (1)	9500 (2)	4076 (2)	4·61 (4)
O(53)	−1369 (2)	7239 (4)	5257 (4)	5·75 (8)
O(54)	346 (1)	7221 (2)	6665 (2)	4·36 (4)
O(54A)	1982 (1)	7690 (2)	5799 (2)	5·17 (4)
C(55)	1332 (1)	8443 (3)	5622 (3)	3·26 (5)
C(56)	1266 (2)	9248 (3)	6830 (3)	4·28 (6)
O(57)	664 (1)	5933 (2)	4361 (2)	4·23 (4)

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

Table 1 (*cont.*)

	x	y	z	$B_{eq}(\text{Å}^2)$
(b) Jaconine hydrochloride ethanol solvate				
C(1)	3598 (6)	4358 (5)	−515 (5)	3·72 (13)
C(2)	3600 (7)	3497 (6)	−764 (6)	4·91 (16)
C(3)	2529 (8)	2988 (5)	−485 (8)	6·00 (19)
N(4)	1790 (5)	3702 (4)	−7 (4)	4·77 (10)
C(5)	1420 (9)	3520 (7)	981 (6)	6·42 (20)
C(6)	1420 (8)	4444 (8)	1458 (7)	5·89 (20)
C(7)	2526 (7)	4847 (5)	1044 (5)	3·70 (13)
C(8)	2468 (6)	4588 (4)	3 (5)	3·08 (11)
C(9)	4488 (7)	5052 (6)	−768 (6)	5·28 (16)
O(10)	5335 (4)	5202 (3)	8 (4)	4·14 (9)
C(11)	6215 (5)	4590 (5)	59 (4)	3·15 (11)
C(12)	7121 (6)	4859 (4)	826 (5)	3·10 (11)
C(13)	6556 (8)	4932 (6)	1811 (6)	3·23 (13)
C(14)	5920 (6)	4051 (4)	2075 (5)	2·95 (12)
C(15)	4837 (5)	4114 (4)	2761 (4)	2·81 (10)
C(16)	3898 (6)	4714 (4)	2324 (4)	2·94 (11)
O(17)	3547 (4)	4405 (3)	1469 (3)	3·24 (8)
O(20)	6304 (4)	3936 (4)	−446 (3)	4·50 (10)
C(21)	7721 (7)	5749 (5)	496 (6)	4·30 (15)
O(22)	7965 (4)	4156 (3)	909 (4)	3·60 (9)
C(23)	7431 (9)	5234 (8)	2566 (6)	4·89 (18)
O(24)	5145 (4)	4449 (4)	3676 (3)	3·19 (8)
Cl(24A)	2955 (2)	3209 (1)	3534 (1)	4·87 (4)
C(25)	4353 (6)	3147 (5)	2896 (5)	3·61 (12)
C(26)	5192 (8)	2514 (5)	3461 (7)	5·52 (17)
O(27)	3501 (4)	5387 (3)	2703 (3)	3·94 (9)
Cl(1)	−582 (1)	3468 (1)	−910 (1)	3·55 (3)
O(Et)	9255 (8)	3202 (7)	2398 (7)	10·4 (2)†
C1(Et)	8732 (14)	2706 (11)	3194 (12)	10·7 (4)†
C2(Et)	9600 (17)	2201 (13)	3683 (14)	12·7 (5)†

† Isotropic temperature factor.

The 12-membered macrocyclic rings adopt conformations very similar to that of jacobine (see Table 2*c*). As so far observed in all the alkaloids containing the 12-membered macrocycle, the carbonyl bonds are antiparallel, the angles between them being 162·9 (2) (II*a*), 168·1 (2) (II*b*) and 161·3 (5)° (IV) − comparable to values of 161·7 (3)° in jacobine, 163·2 (3)° in senecionine and 162·8 (7)° in retrorsine. The O(10)⋯ O(17) trans-annular distances of 3·172 (3) (II*a*), 3·154 (3) (II*b*) and 3·111 (7) Å (IV) are significantly shorter than the values of 3·255 (4) Å in jacobine, 3·293 (3) Å in senecionine and 3·28 (1) Å in retrorsine: other close contacts within the macrocycle are C(11)⋯C(14) of 3·034 (4) (II*a*), 2·968 (4) (II*b*) and 2·955 (9) Å (IV) and C(1)⋯O(17) of 2·829 (4) (II*a*), 2·753 (4) (II*b*) and 2·783 (7) Å (IV).

The conformations about the primary-ester groupings at C(9) [see torsion angles C(2)−C(1)−C(9)− O(10), C(1)−C(9)−O(10)−C(11) and C(9)−O(10)− C(11)−O(20) in Table 2] are such than one H atom at C(9) lies close to the plane of the unsaturated ring *B* [torsion angle H(9*b*)−C(9)−C(1)−C(2) 23 (2) (II*a*), 12 (2) (II*b*) and 21° (IV)]. The α-OH at C(12), which lies nearly in the plane of the ester carbonyl group and *cis* to it [torsion angle O(20)−C(11)−C(12)−O(22) 2·8 (3) (II*a*), 2·1 (4) (II*b*) and −7·4 (9)° (IV)], forms an intramolecular hydrogen bond with the carbonyl oxygen (see Table 2*d*). The allylic ester carbonyl is approximately parallel to the C(2)−H(2) bond, and atoms in the ester group C(9), O(10), C(11), O(20), C(12) are coplanar within ±0·022 (5) (II*a*), ±0·015 (5)
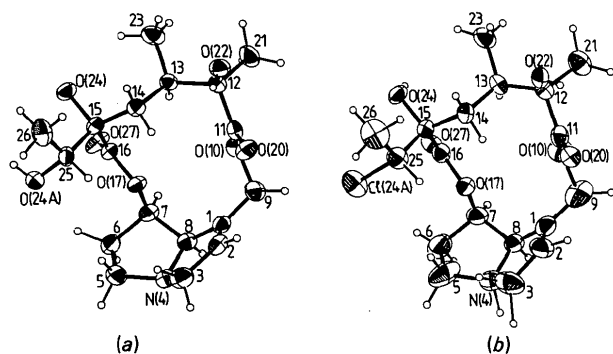

Fig. 1. Perspective views with thermal ellipsoids scaled to 50% probability. The C atoms are denoted by numerals only. (*a*) Jacoline (molecule II*a*). (*b*) Jaconine cation (IV).

(IIb) and ±0·04 (1) Å (IV). The relative positions of the H atoms at C(9), the primary-ester carbonyl and the ring double bond are similar to those in jacobine, senecionine and retrorsine. A discussion of these features in relation to NMR spectral data by Stoeckli-

Evans & Crout (1976) suggests that the alkaloids have the same conformation in the crystal as in solution.

As already noted for senecionine, the secondary-ester system at C(7) has a substantial twist imposed on the preferred conformation (Culvenor, 1966) in which the

Table 2. Molecular geometry (e.s.d.'s in parentheses)

	Jacoline		Jaconine		Jacoline		Jaconine
	(IIa)	(IIb)	cation		(IIa)	(IIb)	cation
(a) Bond lengths (Å)							
C(1)–C(2)	1·318 (3)	1·307 (4)	1·317 (11)	C(11)–O(20)	1·204 (3)	1·192 (4)	1·201 (9)
C(1)–C(8)	1·503 (2)	1·499 (3)	1·511 (10)	C(12)–C(13)	1·553 (2)	1·549 (3)	1·526 (11)
C(1)–C(9)	1·489 (4)	1·489 (5)	1·480 (11)	C(12)–C(21)	1·535 (4)	1·521 (4)	1·549 (10)
C(2)–C(3)	1·480 (5)	1·487 (5)	1·479 (12)	C(12)–O(22)	1·410 (3)	1·415 (3)	1·415 (8)
C(3)–N(4)	1·470 (4)	1·489 (4)	1·503 (11)	C(13)–C(14)	1·540 (3)	1·542 (3)	1·531 (11)
N(4)–C(5)	1·479 (4)	1·481 (4)	1·472 (10)	C(13)–C(23)	1·529 (4)	1·518 (5)	1·517 (13)
N(4)–C(8)	1·487 (3)	1·497 (2)	1·516 (8)	C(14)–C(15)	1·533 (3)	1·533 (3)	1·562 (9)
C(5)–C(6)	1·527 (4)	1·509 (5)	1·518 (15)	C(15)–C(16)	1·524 (3)	1·520 (3)	1·513 (9)
C(6)–C(7)	1·507 (4)	1·509 (5)	1·503 (12)	C(15)–O(24)	1·429 (3)	1·413 (3)	1·418 (7)
C(7)–C(8)	1·529 (3)	1·533 (4)	1·510 (10)	C(15)–C(25)	1·546 (3)	1·538 (3)	1·539 (9)
C(7)–O(17)	1·463 (3)	1·450 (3)	1·455 (9)	C(16)–O(17)	1·335 (3)	1·333 (3)	1·343 (7)
C(9)–O(10)	1·466 (4)	1·467 (4)	1·468 (10)	C(16)–O(27)	1·202 (3)	1·205 (3)	1·212 (7)
O(10)–C(11)	1·346 (3)	1·337 (4)	1·347 (8)	O(24A)*–C(25)	1·428 (3)	1·421 (3)	1·821 (7)
C(11)–C(12)	1·521 (3)	1·533 (4)	1·539 (9)	C(25)–C(26)	1·513 (4)	1·505 (5)	1·550 (11)
(b) Valence angles (°)							
C(2)–C(1)–C(8)	109·2 (1)	109·8 (2)	110·2 (5)	C(11)–C(12)–C(21)	108·1 (2)	108·4 (2)	107·6 (5)
C(2)–C(1)–C(9)	127·3 (2)	127·8 (2)	127·0 (6)	C(11)–C(12)–O(22)	109·1 (2)	109·4 (2)	108·6 (4)
C(8)–C(1)–C(9)	123·5 (2)	122·2 (2)	122·5 (5)	C(13)–C(12)–C(21)	111·8 (2)	112·6 (2)	113·2 (5)
C(1)–C(2)–C(3)	113·1 (2)	113·3 (2)	114·7 (6)	C(13)–C(12)–O(22)	110·8 (1)	112·0 (2)	105·1 (5)
C(2)–C(3)–N(4)	104·1 (2)	103·7 (2)	102·7 (6)	C(21)–C(12)–O(22)	106·8 (2)	104·9 (2)	110·4 (5)
C(3)–N(4)–C(5)	116·3 (2)	115·0 (2)	116·8 (6)	C(12)–C(13)–C(14)	111·2 (1)	110·7 (2)	110·9 (6)
C(3)–N(4)–C(8)	108·1 (2)	107·2 (2)	109·0 (5)	C(12)–C(13)–C(23)	110·6 (2)	112·2 (2)	112·2 (6)
C(5)–N(4)–C(8)	108·3 (2)	108·2 (2)	107·0 (5)	C(14)–C(13)–C(23)	111·0 (2)	112·1 (2)	112·8 (6)
N(4)–C(5)–C(6)	104·3 (2)	104·2 (2)	104·5 (6)	C(13)–C(14)–C(15)	114·4 (1)	115·9 (2)	117·9 (5)
C(5)–C(6)–C(7)	102·7 (2)	102·4 (2)	100·6 (7)	C(14)–C(15)–C(16)	109·8 (1)	108·4 (2)	109·7 (4)
C(6)–C(7)–C(8)	102·2 (2)	102·0 (2)	103·7 (6)	C(14)–C(15)–O(24)	111·0 (1)	108·3 (2)	112·6 (4)
C(6)–C(7)–O(17)	108·6 (2)	110·5 (2)	109·1 (5)	C(14)–C(15)–C(25)	113·3 (1)	112·0 (2)	107·5 (4)
C(8)–C(7)–O(17)	108·3 (2)	105·4 (2)	108·5 (5)	C(16)–C(15)–O(24)	106·5 (1)	110·4 (2)	109·6 (4)
C(1)–C(8)–N(4)	104·8 (1)	104·9 (2)	103·4 (5)	C(16)–C(15)–C(25)	107·7 (1)	107·4 (2)	109·9 (4)
C(1)–C(8)–C(7)	119·1 (2)	118·9 (2)	119·0 (5)	C(25)–C(15)–O(24)	108·3 (1)	110·4 (2)	107·4 (4)
N(4)–C(8)–C(7)	105·5 (2)	104·4 (2)	104·4 (5)	C(15)–C(16)–O(17)	112·4 (1)	110·5 (2)	111·8 (4)
C(1)–C(9)–O(10)	112·3 (2)	111·5 (2)	111·8 (5)	C(15)–C(16)–O(27)	123·0 (2)	125·5 (2)	124·2 (4)
C(9)–O(10)–C(11)	114·7 (2)	117·1 (2)	115·0 (4)	O(17)–C(16)–O(27)	124·6 (1)	124·0 (2)	124·0 (4)
O(10)–C(11)–C(12)	112·3 (2)	111·2 (2)	111·0 (4)	C(7)–O(17)–C(16)	115·5 (1)	118·7 (1)	116·7 (4)
O(10)–C(11)–O(20)	123·2 (2)	124·3 (2)	124·7 (4)	C(15)–C(25)–O(24A)*	109·4 (1)	107·4 (2)	108·9 (4)
C(12)–C(11)–O(20)	124·4 (2)	124·5 (2)	124·3 (5)	C(15)–C(25)–C(26)	113·3 (2)	112·7 (2)	113·7 (5)
C(11)–C(12)–C(13)	110·1 (2)	109·5 (2)	111·8 (5)	O(24A)*–C(25)–C(26)	111·4 (2)	113·0 (2)	108·2 (5)

* Replace O(24A) with Cl(24A) for the jaconine cation.

(c) Selected torsion angles (°), with e.s.d.'s in parentheses. Atoms are represented by their identification number. Corresponding values for jacobine (Pérez-Salazar, Cano & Garcia-Blanco, 1978) and jacobine methanol solvate (Rohrer, Karchesy & Deinzer, 1984) are included for comparison. E.s.d.'s are about 0·4 and 0·2° respectively for the latter two structures

	Jacoline		Jaconine		Jacobine
	(IIa)	(IIb)	cation	Jacobine	solvate
2–1–9–10	−100·8 (3)	−108·6 (4)	−99·1 (9)	−106·2	−106·2
1–9–10–11	80·0 (3)	97·9 (3)	81·2 (8)	88·4	86·7
9–10–11–12	176·9 (2)	−178·6 (2)	174·2 (6)	179·2	179·1
10–11–12–13	62·7 (2)	60·0 (3)	59·3 (7)	51·8	54·9
11–12–13–14	63·5 (2)	59·1 (3)	55·1 (8)	63·3	64·4
12–13–14–15	−152·9 (2)	−158·5 (2)	−151·3 (6)	−159·3	−159·2
13–14–15–16	51·9 (2)	42·5 (3)	59·6 (7)	59·8	58·1
14–15–16–17	57·9 (2)	62·3 (2)	58·0 (6)	50·7	49·3
7–17–16–15	174·0 (2)	−178·9 (2)	171·1 (5)	−175·8	−176·2
8–7–17–16	169·5 (2)	178·1 (2)	165·2 (5)	167·2	168·6
1–8–7–17	−33·6 (2)	−33·0 (3)	−28·2 (8)	−29·4	−30·1
7–8–1–9	−69·6 (3)	−74·0 (4)	−71·6 (9)	−75·3	−73·8
6–7–17–16	−80·3 (2)	−72·5 (3)	−82·5 (7)	−82·4	−80·6
8–1–9–10	82·3 (3)	76·2 (4)	87·4 (8)	85·6	82·3
9–10–11–20	−1·5 (3)	2·3 (4)	−3·6 (9)	0·4	−0·7
10–11–12–21	−59·8 (3)	−63·1 (3)	−65·6 (7)	−71·1	−68·7
10–11–12–22	−175·5 (2)	−177·0 (2)	174·8 (5)	174·3	176·6
11–12–13–23	−172·6 (2)	−175·0 (2)	−177·7 (7)	−172·4	−169·3
13–14–15–24	−65·6 (2)	−77·3 (2)	−62·8 (7)		
13–14–15–25	172·3 (2)	160·7 (2)	179·1 (6)		
14–15–16–27	−120·8 (2)	−115·6 (3)	−122·7 (6)	−129·6	−130·5
14–15–25–24A	−165·0 (2)	−169·0 (2)	−171·0 (4)		
14–15–25–26	70·1 (2)	66·0 (3)	68·2 (7)		
20–11–12–21	118·6 (3)	115·9 (3)	122·2 (7)	107·6	111·0
20–11–12–22	2·8 (3)	2·1 (4)	−7·4 (9)	−7·0	−3·6

Table 2 (cont.)

(d) Hydrogen-bonding dimensions. Distances (Å) and angles (°), with e.s.d.'s in parentheses. Transformations of the coordinates (x, y, z) are denoted by superscripts

Jaconine (II)

X—H···Y	X···Y	H···Y	X—H	X—H···Y
O(22)—H(22)···O(20)*	2·684 (3)	2·35 (4)	0·85 (4)	135 (3)
O(24)—H(24)···O(27)*	2·611 (3)	2·09 (4)	0·76 (4)	151 (3)
O(52)—H(52)···O(50)*	2·700 (3)	2·42 (4)	0·80 (4)	135 (3)
O(54)—H(54)···O(57)*	2·732 (3)	2·41 (4)	0·84 (4)	135 (3)
O(22)—H(22)···N(4ⁱ)	2·858 (3)	2·04 (4)	0·85 (4)	160 (3)
O(24A)—H(24A)···N(34ⁱⁱ)	2·792 (3)	1·93 (4)	0·87 (4)	169 (3)
O(52)—H(52)···O(57ⁱⁱⁱ)	2·870 (3)	2·13 (4)	0·80 (4)	154 (3)
O(54)—H(54)···O(50ⁱᵛ)	2·893 (3)	2·20 (4)	0·84 (4)	140 (3)
O(54A)—H(54A)···O(24Aᵛ)	2·768 (3)	1·85 (4)	0·95 (4)	162 (3)

(i) $1-x, -\frac{1}{2}+y, 1-z$; (ii) $1-x, -\frac{1}{2}+y, -z$; (iii) $-x, \frac{1}{2}+y, 1-z$; (iv) $-x, -\frac{1}{2}+y, 1-z$; (v) $1-x, \frac{1}{2}+y, 1-z$.

Jaconine hydrochloride ethanol solvate (IV)

X—H···Y	X···Y	H···Y	X—H	X—H···Y
O(22)—H(22)···O(20)*	2·694 (7)	2·45 (7)	0·72 (7)	136 (6)
O(24)—H(24)···O(27)*	2·691 (7)	2·45 (8)	0·68 (8)	138 (6)
N(4)—H(4)···Cl(1)	2·991 (6)	1·96	1·13	150
O(22)—H(22)···Cl(1ⁱ)	3·201 (5)	2·51 (7)	0·72 (7)	162 (6)
O(24)—H(24)···Cl(1ⁱⁱ)	3·165 (6)	2·50 (8)	0·68 (8)	165 (6)
O(Et)—H···O(22)	2·911 (11)			

(i) $1+x, y, z$; (ii) $\frac{1}{2}-x, 1-y, \frac{1}{2}+z$.
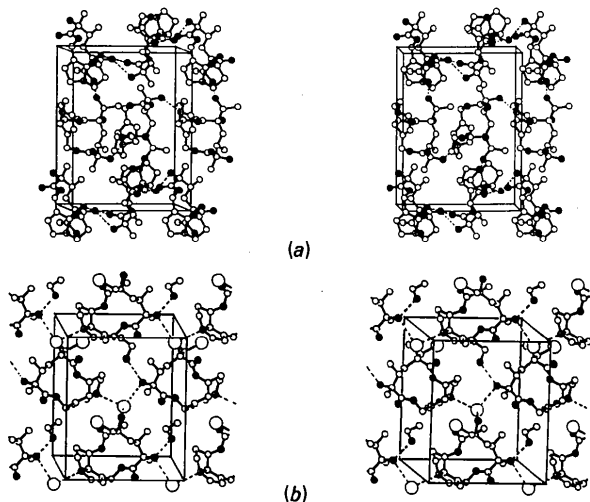
* Intramolecular interaction.

(a)

(b)

Fig. 2. (a) Crystal packing of jacoline. Direction of projection c; the b axis is horizontal. (b) Crystal packing of jaconine hydrochloride ethanol solvate. Direction of projection b; the a axis is horizontal. Half the unit-cell contents only are shown for clarity.

atoms C(7), H(7), O(17), C(16), O(27), C(15) would be coplanar and H(7) cis to O(27). Atoms C(7), O(17), C(16), O(27), C(15) are coplanar within ±0·056 (5) (IIa), ±0·012 (5) (IIb) and ±0·07 (1) Å (IV) [torsion angles C(7)—O(17)—C(16)—C(15) 174·0 (2) (IIa), −178·9 (2) (IIb) and 171·1 (5)° (IV)], but the angles between the planes defined by atoms H(7), C(7), O(17) and O(17), C(16), O(27), C(15) are 46 (1) (IIa), 56 (1) (IIb) and 43 (2)° (IV) compared with 68 (1)° in senecionine. The hydroxyl at C(15) lies nearly in the plane of the ester group [torsion angle O(24)—C(15)—C(16)—O(17) −178·7 (2) (IIa), −179·2 (2) (IIb) and

−177·8 (5)° (IV)] and cis to the carbonyl oxygen, O(27), with which it forms an intramolecular hydrogen bond.

There is extensive intra- and intermolecular hydrogen bonding in both structures (see Table 2d). In (II) the molecules are linked into a three-dimensional network (Fig. 2a) by interactions involving the three hydroxyl substituents of each independent molecule. The interactions which involve the oxygens [O(22) and O(52)] of the hydroxyl substituents at C(12) and C(42) respectively are bifurcated, each hydroxyl forming an intra- and intermolecular interaction. Similar asymmetric bifurcated interactions are also formed by the hydroxyl substituent at C(45). Three unique intermolecular hydrogen bonds in (IV) with the chloride ion form bridges between three adjacent jacoline cations. These interactions, and one involving the ethanol, link the unit-cell contents into layers parallel to the ac plane (Fig. 2b). Each hydroxyl participates in the interactions, with both O(22) and O(24) forming asymmetric bifurcated intra- and intermolecular H bonds. The protonated nitrogen, N(4), on the pyrrolizidine nucleus forms the strongest interaction with the chloride ion, the N(4)···Cl distance being 2·991 (6) Å. Other intermolecular contacts in the structures are normal.

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Structure of 6-Methyl-4-phenyl-8-phenylmethylene-3,4,5,6,7,8-hexahydro-2(1H)-quinazolinethione

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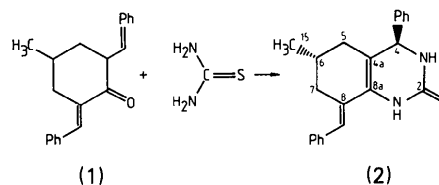
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Abstract. $C_{22}H_{22}N_2S$, $M_r = 346.50$, monoclinic, $P2_1/c$, $a = 15.919$ (1), $b = 6.320$ (1), $c = 19.039$ (2) Å, $\beta = 105.00$ (1)°, $V = 1850.2$ (4) Å^3, $Z = 4$, $D_x = 1.24$ Mg m^{-3}, $\lambda(Cu\ K\bar{\alpha}) = 1.54184$ Å, $\mu = 0.154$ mm^{-1}, $F(000) = 736$, $T = 296$ (1) K, $R = 0.047$ for 3348 observed reflections. Only X-ray analysis could reveal the stereochemistry of the title compound furnished by the reaction of 2,6-dibenzylidene-4-methylcyclohexanone with thiourea. It has been shown to be the diastereomer in which the 4-phenyl moiety is bound axially while the 6-methyl group assumes an equatorial position.

Introduction. Earlier we have studied the reactions of 2,6-diarylidenecyclohexanones with thiourea in basic media (Lóránd, Szabó & Neszmélyi, 1977). Now, these investigations have been extended over the cyclohexane-ring-substituted 2,6-diarylidenecyclohexanones. The reaction of 2,6-dibenzylidene-4-methylcyclohexanone (1) with thiourea yielded 6-methyl-4-phenyl-8-phenylmethylene-3,4,5,6,7,8-hexahydro-2(1H)-quinazolinethione (2). According to ¹H NMR spectra of (2) only one diastereomer is formed, which is depicted in the reaction scheme. However, on the basis

of the ¹H NMR studies we could not decide on the two possible isomers. Furthermore, we were also interested in the stereochemistry of 4-phenyl-8-phenylmethylene-3,4,5,6,7,8-hexahydro-2(1H)-quinazolinethione, studied earlier (Lóránd, Szabó & Neszmélyi, 1977). Therefore, an X-ray analysis of (2) (melted at 384–387 K) has been performed.

(1)   (2)

Experimental. Colourless crystals of which a sample of dimensions *ca* 0.17 × 0.34 × 0.56 mm was mounted on a CAD-4 diffractometer equipped with graphite monochromator. Cell constants were refined by least-squares fit for 25 centred reflections collected in the range $20 \leq \theta \leq 39°$. $\omega/2\theta$ scan in the range $0.017 \leq (\sin\theta)/\lambda \leq 0.626$ Å^{-1} with scan width $0.45° + 0.30°\tan\theta$. 3801 unique, non-zero and not systematically absent ($h0l\ l = 2n + 1$, and $0k0\ k = 2n + 1$ for space group $P2_1/c$) reflections were recorded with h: 0 to 19, k: 0 to 7 and l: −23 to 23, of which – after

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