(0·8 e Å^{-3}), giving a feature just intermediate between those in the difference Fourier maps of γ-Fe$_2$SiO$_4$ and γ-Ni$_2$SiO$_4$. This trend in the density distributions of $3d$ electrons is parallel to the degree of flattening of the coordination octahedra. Namely, the Fe^{2+} ion, which only gives a pair of residual densities on the threefold rotation axis, has the most flattened coordination octahedron among those around the three kinds of cations. The distances of the peaks from the Co^{2+} site are also about 0·46 Å.

Residual densities are observed on the Si—O bonds in both γ-Fe$_2$SiO$_4$ and γ-Co$_2$SiO$_4$. A common feature is that the positive regions are guitar-shaped with double maxima.

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The Crystal Structure and Absolute Configuration of Condelphine Hydroiodide

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Condelphine, a C$_{19}$ diterpene alkaloid isolated from *Delphinium denudatum*, has been investigated by an X-ray crystal structure determination of its hydroiodide derivative, C$_{25}$H$_{39}$NO$_6$.HI. The crystals are triclinic, $P1$, $a = 9·3404$ (9), $b = 17·442$ (2), $c = 9·0953$ (8) Å, $\alpha = 94·891$ (9), $\beta = 118·891$ (7), $\gamma = 86·594$ (9)°. The unit cell contains two independent molecules, related by approximate I-centering. The structure has been refined to $R = 0·100$, $R_w = 0·111$, based on 3828 observed reflections. The absolute configuration is established as 1S,4S,5R,7S,8S,9R,10R,11S,13R,14S,16S,17R, by examination of Friedel pairs of reflections. The alkaloid is a member of the aconitine family, and bears 1α-hydroxy, 8β-hydroxy, 14α-acetyl, 16β-methoxy and *N*-ethyl substituents. Intramolecular hydrogen bonding between the protonated N atom and the 1α-hydroxy group stabilizes ring *A* in a boat form. The two independent molecules have no significant contacts with each other. Because condelphine has been correlated with isotalatizidine and talatizidine, this work confirms the molecular structure and establishes the absolute configuration of the latter two alkaloids as well.

Introduction

The alkaloids of the C$_{19}$ diterpene family are based on a skeleton which is heavily substituted with oxygenated groups. The structures of these alkaloids have generally been elucidated on the basis of chemical correlations, supported by crystallographic and spectral studies. Condelphine (I) is a member of this family which has been isolated from both *Delphinium denudatum*

(I) R = COCH$_3$
(II) R = H
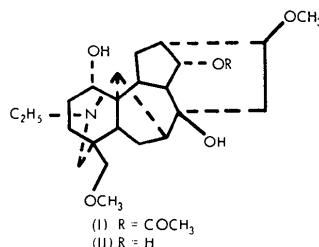
(Pelletier, Keith & Parthasarathy, 1966, 1967) and *D. confusum* (Rabinovich & Konovalova, 1942). It has been correlated with only two other alkaloids, isotalatizidine (II) and talatizidine (III), both isolated from *Aconitum talassicum* (Konovalova & Orekhov, 1940). None of this group has been related to any other C_{19} diterpene alkaloid. In order to establish the molecular structure and absolute configuration of these three alkaloids, we have investigated the crystal structure of condelphine as its hydroiodide derivative.

(III)
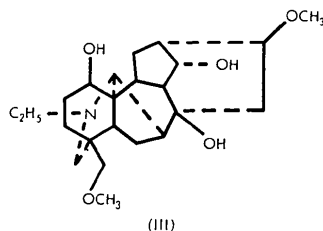
Experimental

Condelphine was isolated by ethanol extraction of the roots of *Delphinium denudatum* (Pelletier, Keith & Parthasarathy, 1966, 1967). Initial attempts to prepare the hydroiodide by treatment of a solution of the alkaloid in methanol with 47% hydroiodic acid yielded an amorphous solid which showed evidence of decomposition on recrystallization. Attempts to prepare a methiodide derivative by treatment of a solution of condelphine in 95% ethanol with methyl iodide failed at room temperature, but in methanol and at elevated temperatures (80 °C, 2 h in a sealed tube), a crystalline product was obtained. Purification by thin-layer chromatography on alumina, followed by recrystallization, first from isopropyl alcohol, and subsequently from ethanol/ethyl acetate, gave material which melted at 221–227 °C (corrected) (lit. 203–205 °C, dec., Rabinovich & Konovalova, 1942), and gave a positive halogen test with silver nitrate. NMR spectra did not show the presence of an *N*-methyl singlet, and the free base could be regenerated by chromatography in chloroform over alumina, indicating that the crystalline product was the hydroiodide, rather than the expected methiodide. This conclusion was confirmed by the results of this investigation, as well as the elemental analysis (calculated for the hydroiodide, $C_{25}H_{40}NO_6I$, C 51·99, H 6·98%; calculated for the methiodide, $C_{26}H_{42}NO_6I$, C 52·79, H 7·16%; found C 51·94, H 6·99%). The formation of a hydroiodide on treatment with methyl iodide has been previously observed (Pelletier, Iyer, Bhalla, Newton & Aneja, 1970).

Recrystallization of condelphine hydroiodide from either isopropyl alcohol/ethyl acetate or absolute ethanol/diethyl ether gave large, colorless, multifaceted prisms. Precession photographs established

that the crystals were triclinic; since condelphine is optically active {$[\alpha]_D^{30} = +21\cdot3°$, $c = 12\cdot4$ mg cm^{-3}, $CHCl_3$; lit. $+21\cdot3°$, concentration not given (Pelletier, Keith & Parthasarathy (1967)}, the space group was assumed to be $P1$. The density was measured by flotation in hexane/CCl_4, showing two independent molecules per unit cell.

Integrated intensites were measured for all reflections to a limit of $2\theta = 115°$ on an Enraf–Nonius CAD-3 diffractometer with Ni-filtered Cu $K\alpha$ radiation ($\lambda = 1\cdot5418$ Å). Reflections for which $h + k$ was odd were systematically weak, implying pseudo-*C*-centering of the two independent molecules. The solution and refinement of this set of data (see *Structure solution and refinement*) did not satisfactorily establish the absolute configuration of the molecule, and a second set of data was collected, from a new crystal.

Small differences in the corresponding values of β and γ for the two crystals were observed, considered to result from absorption, and hence ignored. This assumption was subsequently shown to be unjustified (see below). The new data were measured under essentially similar conditions, except that the diffractometer had, in the interim, been upgraded to a CAD-4, the maximum 2θ was 150°, and a graphite monochromator was used. Of 5377 reflections measured, 5362 (99·7%) were observed at a 3σ level of significance; because of the large number of observed data, all further calculations were limited to the 120° sphere (Cu $K\alpha$, sin $\theta/\lambda < 0\cdot5617$), consisting of 3828 reflections, all observed. The data were corrected for Lorentz and polarization effects, as well as crystal decomposition. Although the latter was severe (30–40%), the loss of intensity for the standard reflections was essentially linear, and similar for all three standard reflections, suggesting that the data were properly scaled. Pseudo-*I*-centering was implied by the intensity distribution.

The differences between the cell dimensions found for the two crystals led to the discovery that the two sets of data were referred to different unit cells (De Camp, 1976). Only the second set of data was referred to the reduced cell. Table 1 gives the crystal data for condelphine hydroiodide. The cell dimensions reported here are based on a least-squares refinement of precisely determined 2θ values for 29 reflections, and refer to the reduced cell. The relation between the two cells is such that the approximate *C*-centering found for the first crystal corresponds to approximate *I*-centering for the second.

Table 1. *Crystal data for condelphine hydroiodide*

Condelphine hydroiodide, $C_{25}H_{39}NO_6 . HI$
$M_r = 577\cdot513$, m.p. 221–227°C
Triclinic, $P1$, $a = 9\cdot3404$ (9), $b = 17\cdot442$ (2), $c = 9\cdot0953$ (8) Å
$\alpha = 94\cdot891$ (9), $\beta = 118\cdot891$ (7), $\gamma = 86\cdot594$ (9)°, $V = 1290\cdot3$ Å^3
$D_m = 1\cdot479$, $D_x = 1\cdot486$ g cm^{-3}, $Z = 2$, μ(Cu $K\alpha$) = 101 cm^{-1}

Structure solution and refinement

On the basis of a Patterson map, the coordinates of one iodide ion were determined to be ca $\frac{1}{2},\frac{1}{2},0$, with the origin being fixed by the other iodide. Successive structure factor calculations, followed by Fourier syntheses of the electron density map, revealed peaks corresponding to molecules of the anticipated geometry, but pseudosymmetry gave problems in distinguishing between a correctly positioned atom and its centrosymmetrically related image. Refinement with all non-hydrogen atoms located converged at $R = 0.130$. For the opposite enantiomorph, the residual was 0.133, giving insufficient certainty in establishing the enantiomorph by Hamilton's (1965) test.

The atomic positional parameters from the refinement of the first set of data were transformed to the reduced cell. Refinement, using the second set of data and varying all positional and thermal parameters, resulted in divergent oscillation, possibly due to high correlation between x and z for each atom. The procedure followed in the refinement was to fix all x parameters for two cycles, allowing z to vary, and then fix all z parameters for two more cycles, allowing x to vary. Only the iodide ions were assigned anisotropic thermal parameters. The refinement was thus based on 18.6 observations per variable parameter. Under these conditions, convergence was slow, but oscillation did not occur. The function minimized in the refinement was $\Sigma w\|F_o| - |F_c\|^2$, with weights assigned empirically

Table 2. *Atomic positional and thermal parameters for condelphine hydroiodide*

(a) Iodide ions $\{x, y,$ and z are multiplied by 10^4, and U_{ij} by 10^3; the anisotropic thermal parameter is of the form:
$$T = \exp[-2\pi^2(U_{11}h^2a^{*2} + \cdots + 2U_{12}hka^*b^* + \cdots)]\}.$$

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
I(1)	0†	10000†	10000†	62 (1)	84 (1)	63 (1)	23 (1)	43 (1)	27 (1)
I(2)	5027 (2)	4832 (1)	5231 (2)	36 (1)	71 (1)	44 (1)	−5 (1)	11 (1)	22 (1)

(b) Carbon, oxygen and nitrogen atoms (x,y,z and U are multiplied by 10^3)

Molecule 1 | | | | | Molecule 2

	x	y	z	U		x	y	z	U
C(101)	446 (2)	862 (1)	467 (2)	31 (3)	C(201)	1016 (2)	402 (1)	32 (2)	33 (3)
C(102)	562 (2)	911 (1)	455 (3)	52 (5)	C(202)	1092 (2)	466 (1)	3 (3)	53 (4)
C(103)	506 (2)	998 (1)	450 (2)	49 (4)	C(203)	973 (2)	539 (1)	−35 (2)	41 (4)
C(104)	455 (2)	1022 (1)	590 (2)	38 (4)	C(204)	922 (2)	558 (1)	100 (2)	45 (4)
C(105)	505 (2)	958 (1)	719 (2)	37 (4)	C(205)	1004 (2)	504 (1)	250 (2)	48 (4)
C(106)	430 (2)	975 (1)	839 (2)	49 (4)	C(206)	926 (2)	512 (1)	364 (2)	49 (4)
C(107)	266 (2)	932 (1)	753 (2)	42 (4)	C(207)	801 (2)	444 (1)	297 (2)	48 (4)
C(108)	293 (2)	861 (1)	862 (2)	36 (4)	C(208)	870 (2)	378 (1)	425 (2)	38 (4)
C(109)	442 (2)	817 (1)	880 (2)	44 (4)	C(209)	1042 (2)	361 (1)	467 (2)	46 (4)
C(110)	465 (2)	813 (1)	724 (2)	45 (4)	C(210)	1071 (2)	358 (1)	307 (2)	44 (4)
C(111)	416 (2)	884 (1)	617 (2)	41 (4)	C(211)	973 (2)	421 (1)	176 (2)	40 (4)
C(112)	365 (2)	739 (1)	614 (3)	54 (5)	C(212)	1031 (2)	275 (1)	227 (3)	55 (5)
C(113)	291 (3)	704 (1)	709 (3)	56 (5)	C(213)	986 (3)	235 (1)	345 (3)	58 (5)
C(114)	426 (2)	732 (1)	895 (2)	43 (4)	C(214)	1086 (3)	276 (1)	510 (3)	58 (5)
C(115)	129 (3)	808 (1)	776 (3)	54 (5)	C(215)	748 (2)	312 (1)	359 (2)	50 (4)
C(116)	132 (3)	738 (1)	678 (3)	57 (5)	C(216)	802 (2)	240 (1)	281 (3)	52 (5)
C(117)	236 (2)	905 (1)	579 (2)	34 (3)	C(217)	795 (2)	414 (1)	134 (2)	34 (3)
C(118)	542 (3)	1093 (1)	683 (3)	61 (5)	C(218)	957 (2)	639 (1)	166 (3)	55 (5)
C(119)	273 (2)	1037 (1)	510 (2)	51 (4)	C(219)	732 (2)	545 (1)	23 (2)	44 (4)
C(120)	581 (4)	1222 (2)	646 (4)	86 (7)	C(220)	899 (3)	767 (1)	77 (3)	77 (6)
C(121)	−130 (3)	692 (2)	628 (4)	81 (7)	C(221)	581 (6)	152 (3)	207 (6)	132 (13)
C(122)	−2 (2)	998 (1)	423 (2)	53 (5)	C(222)	507 (2)	463 (1)	−61 (2)	45 (4)
C(123)	−130 (2)	935 (1)	325 (3)	55 (5)	C(223)	440 (3)	381 (2)	−120 (3)	80 (7)
C(124)	482 (3)	693 (1)	1159 (3)	70 (6)	C(224)	1147 (2)	218 (1)	759 (2)	46 (4)
C(125)	419 (3)	665 (1)	1264 (3)	72 (6)	C(225)	1095 (3)	198 (1)	881 (3)	77 (6)
O(101)	288 (1)	860 (1)	312 (1)	40 (3)	O(201)	865 (1)	376 (1)	−121 (1)	41 (3)
O(108)	319 (2)	893 (1)	1024 (2)	56 (3)	O(208)	877 (2)	414 (1)	581 (2)	59 (3)
O(114)	374 (2)	708 (1)	1004 (2)	55 (3)	O(214)	1049 (2)	260 (1)	641 (2)	73 (4)
O(116)	46 (2)	682 (1)	697 (3)	85 (5)	O(216)	748 (2)	174 (1)	315 (2)	73 (4)
O(118)	497 (2)	1155 (1)	574 (2)	69 (4)	O(218)	880 (2)	687 (1)	37 (2)	65 (4)
O(124)	623 (3)	714 (1)	1211 (3)	114 (7)	O(224)	1264 (3)	191 (1)	760 (3)	111 (7)
N(1)	164 (2)	972 (1)	457 (2)	44 (3)	N(2)	683 (2)	464 (1)	−13 (2)	33 (3)

† Parameter fixed to define origin of unit cell.

by the function $w = 1/\{1 + [(F_o - 22)/8]^2\}$. For the last two cycles of refinement, all parameters (except for the iodide ion used to define the origin) were allowed to vary, lowering the over-determination to 14·1 observations per variable parameter. With the nearly converged structure, no oscillation occurred. In the final least-squares cycle, no parameter was shifted by more than 0·24 times its e.s.d., and the average shift/e.s.d. was 0·071. At convergence, the agreement residuals were $R = 0·100$, $R_w = 0·111$, based on 3828 observed reflections, $2\theta < 120°$. A final difference map showed eight maxima for which $\Delta(\rho) > 1$ e Å^{-3}, seven of which were sufficiently close to one of the iodide positions that they might represent thermal anisotropy unaccounted for by the model. No significant trend of ΔF as a function of $|F_o|$ could be found, except for a slightly greater likelihood that $|F_c| < |F_o|$ for $|F_o| < 12$, consistent with the possibility that some of the weaker structure amplitudes were actually statistically insignificant. Reflections for which $h + k + l$ was even had a lower residual: $h + k + l$ even, $R = 0·085$, $R_w = 0·097$; $h + k + l$ odd, $R = 0·124$, $R_w = 0·126$.

Because the questions of chemical structure and absolute configuration could be answered from the data at this stage of refinement, and because a slight increase in precision did not seem to us to justify the additional expenditure of time and computer funds, no attempts were made to improve the model by introduction of H atoms or further refinement with the full set of data.

Analytic approximations to the atomic scattering factors were used for C, N and O (Cromer & Mann, 1968). The atomic scattering factor for I was based on the Thomas–Fermi–Dirac statistical model (Table 3.3.1B, *International Tables for X-ray Crystallography*, 1968), corrected for anomalous dispersion effects ($\Delta f' = -1·1$, $\Delta f'' = 7·2$, Table 3.3.2B). The computer programs used in the structure solution and refinement were those of the X-RAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). The final atomic positional and thermal parameters are given in Table 2. A comparison of the observed and calculated structure factors based on these parameters may be found in Table 3.*

Determination of absolute configuration

A structure factor calculation for the opposite enantiomorph gave $R = 0·122$, $R_w = 0·144$ compared with $R = 0·100$, $R_w = 0·111$ above, indicating conclusively that the correct enantiomorph had been selected. How-

ever, because of the uneven distribution of intensity ($\langle|F_o|\rangle = 17·0$ for $h + k + l$ odd, 28·9 for $h + k + l$ even), we elected to examine Friedel pairs of reflections as well.

A third crystal was mounted and used for the subsequent measurements. After verifying the orientation of the unit cell, 121 Friedel pairs of reflections were measured, 17 having $h + k + l$ even and the remainder odd. The reflections ranged from 22 to 105° in 2θ, and included a wide range of intensities. No attempt was made to include all sensitive reflections, but each pair of $|F_c|$ values differed by at least 1 e. In each case, the observed and calculated values had the same relation to each other. Table 4* lists the observed and calculated ratios of the structure amplitudes for each of the Friedel pairs.

Results

The numbering scheme used for the molecule of condelphine hydroiodide is shown in Fig. 1. For atoms C(1) to C(19), this corresponds to the conventional numbering scheme for C_{19} diterpene alkaloids (Pelletier & Keith, 1970).† O atoms attached to the C_{19} skeleton are given the number of the C atom to which they are attached; further numbering of side chains is arbitrary. The two independent molecules are distinguished by the digit immediately following the atom type, *e.g.* C(101) is atom C(1) of molecule 1, and C(201) is the corre-

* See previous footnote.

† This numbering scheme differs slightly from that used by Pelletier, Keith & Parthasarathy (1966, 1967). Our C(14) and C(16) correspond to C(10) and C(15), respectively, from the earlier work; other differences in the numbering are not relevant to our structural conclusions.
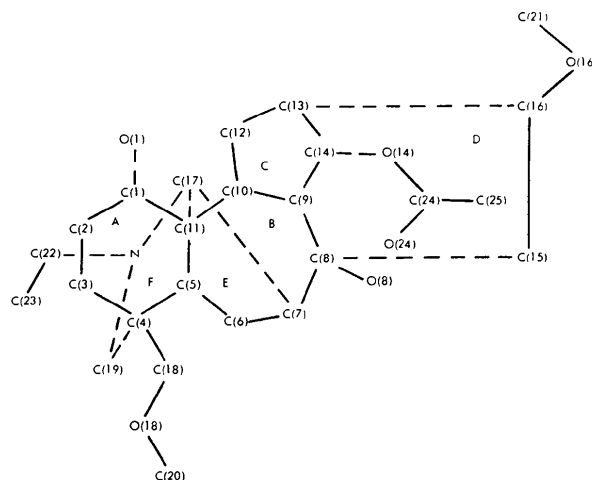

Fig. 1. Numbering scheme used for the molecule of condelphine hydroiodide.

sponding atom in molecule 2. Unless otherwise stated structural details apply to both molecules.

The molecular geometry of condelphine hydroiodide is given in Table 5.* The structure of the naturally occurring alkaloid is confirmed to be (I), as proposed by Pelletier, Keith & Parthasarathy (1966, 1967), with the substituents being 1α-hydroxy, 8β-hydroxy, 14α-acetyl, 16β-methoxy, and N-ethyl. The absolute configuration of the molecule is $1S,4S,5R,7S,8S,9R,10R,$ $11S,13R,14S,16S,17R$, consistent with that found for delphisine (Pelletier, Djarmati, Lajšić & De Camp, 1976) and chasmanine (Pelletier, De Camp & Djarmati, 1976).

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* Only parts (b) and (e) are printed here. The full version of Table 5 has been deposited (see footnote on p. 719).

Table 5. *Interatomic distances and angles in condelphine hydroiodide*

(b) Hydrogen-bonding distances (Å, e.s.d.'s in parentheses)

	Molecule 1	Molecule 2
N···O(1)	2·76 (2)	2·69 (2)
I···O(8)	3·35 (2)	3·43 (2)
O(8)···O(1)^i	2·88 (2)	2·90 (2)
I···O(1)^i	3·77 (1)	3·89 (1)
I···N^i	3·74 (2)	3·75 (1)

(i) $x, y, z + 1$.

(e) Non-bonding interatomic distances around the C(14) acetyl group (Å, e.s.d.'s in parentheses)

	Molecule 1	Molelcule 2
O(24)···O(18)^{ii}	3·45 (4)	3·34 (4)
O(24)···C(18)^{ii}	3·50 (4)	3·34 (4)
O(24)···C(19)^{ii}	3·40 (3)	3·62 (3)
O(24)···C(20)^{ii}	3·54 (5)	3·66 (5)
C(25)···I^{ii}	3·93 (3)	3·97 (3)
$(x,y,z)^{ii}$	$x + 1, y - 1, z$	$x, y, z + 1$

Ring A is stabilized in the boat form by an intramolecular hydrogen bond between O(1) and N. The N···O(1) distances in Table 5(b) may be compared with similar distances of 2·652 (3) Å, found in delphisine hydrochloride (Pelletier, Djarmati, Lajšić & De Camp, 1976), 2·694 (4) Å, found in chasmanine 14α-benzoate hydrochloride (De Camp & Pelletier, 1977), and 2·724 (8) Å, found in lappaconine hydrobromide (Birnbaum, 1970). The range of these values is unexpectedly small, since delphisine is an example of a hydroxyl O···H—N interaction, while the latter two are methoxyl O···H—N interactions, which would normally be expected to be weaker. H atoms were not located in the present work, and it cannot therefore be stated with certainty whether condelphine has an O—H···N or an N—H···O hydrogen bond.

The geometry of the remainder of the molecule is generally as expected for such a system of fused rings. As with the other aconite alkaloids which have been studied, ring C is in an envelope conformation, with C(14) at the flap. Ring D takes the form of a somewhat asymmetrical boat, with the C(15) end being flattened. An unexpected finding was that both carbonyl groups deviate slightly from planarity. While the value of χ^2 indicates statistically significant non-planarity only for the carbonyl C in molecule 1 ($6·94, p < 0·01$ for molecule 1; $2·89, p < 0·10$ for molecule 2), the fact that both carbonyl groups at C(24) show similar distortion suggests that it may be real.

The two independent molecules have nearly the same conformation, as shown in the stereo views in Fig. 2. There are significant differences, however, in the conformation of the acetyl group at C(14). The carbonyl C(24) is roughly *trans* to C(13) in molecule 1, and to C(9) in molecule 2. This is also apparent from the tor-
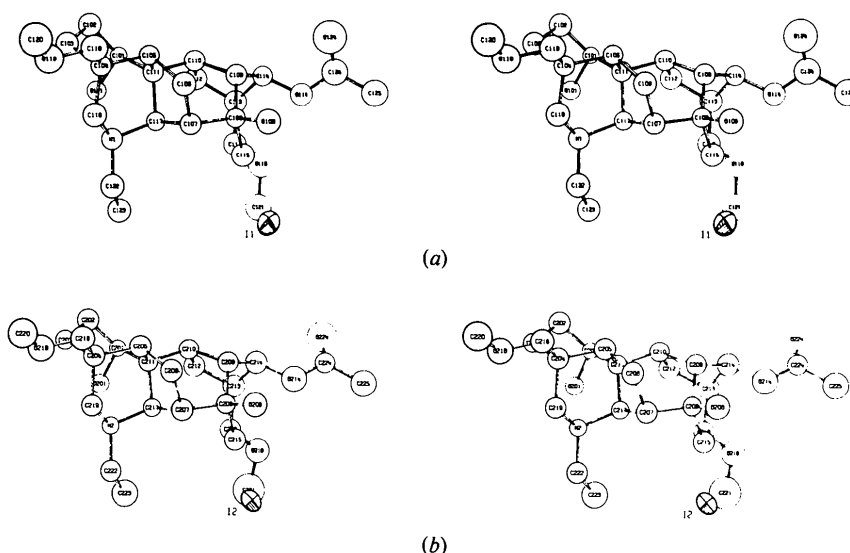

(a)

(b)

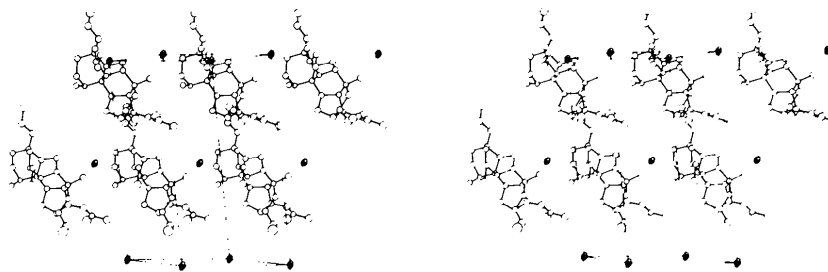Fig. 2. A stereoscopic view of condelphine hydroiodide: (a) molecule 1; (b) molecule 2.

Fig. 3. A stereoscopic view of the unit cell of condelphine hydroiodide. The view is taken along a*, with the origin of the unit cell at the lower left. The positive direction of a extends away from the viewer, b is upwards, and c along the horizontal axis to the right. The upper molecule is 1, and the lower 2.

sion angles listed in Table 5(d), as well as the non-bonding intermolecular contacts around O(24), listed in Table 5(e).

The existence of hydrogen bonds between O(1) and N and between O(8) and I is clearly consistent with the interatomic distances, even though H atoms were not located. The interatomic distances in Table 5(b) suggest, but do not confirm, additional weak or bifurcated hydrogen bonds. Three protons and three acceptors are available for hydrogen bonding, and hence the formation of three bonds might be anticipated. Neither the I··· O(1) nor O(8)··· O(1) is consistent with hydrogen bonding, however, leaving the disposition of the third H atom in question.

The manner in which the two independent molecules of condelphine hydroiodide are packed into the unit cell is shown in a stereoscopic drawing (Fig. 3). There are effectively two independent chains of molecules extending along c, since there are no close contacts between molecules 1 and 2. Except for the contacts involving the C(14) acetyl groups [listed in Table 5(e)], all interatomic distances between atoms of molecule 1 and molecule 2 are greater than 3·6 Å. The reason for this unusual packing is not apparent, and it seems that it would have been more energetically favorable for the molecules to pack with exact body-centered symmetry. Examination of the precession photographs showed no diffuse streaks, and therefore the only plausible alternate structure (i.e. molecules which are symmetrically identical, but disordered) cannot be supported.

Condelphine has been chemically correlated with iso-talatizidine (II) and talatizidine (III) (Pelletier, Keith & Parthasarathy, 1966, 1967; Kuzovkov & Platonova, 1961). In addition to our establishing with certainty the location and β-orientation of the C(16) methoxyl group in condelphine, the molecular structure and absolute configuration of the latter two alkaloids have now been confirmed. Isotalatizidine is the saponification product of condelphine, and talatizidine has been reported to be the C(1) epimer of isotalatizidine (Kuzovkov & Platonova, 1961). None of these alkaloids has previously been reported to have been correlated with any other aconitine- or lycoctonine-type alkaloid.

(IV)
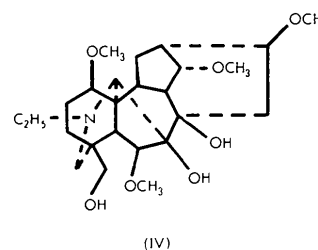
The distinction between the aconitine and lycoctonine groups of alkaloids is based on the chemical properties of the ditertiary α-glycol system found at C(7) and C(8) of lycoctonine (IV). Clearly, (I), (II), and (III) all lack this system, and hence should be placed in the aconitine family. (I), (II), and (III), together with lappaconine, belong to a relatively small group of C_{19} diterpene alkaloids which lack a C(6) substituent. Where both C(1) and C(6) are substituted, aconitine-type alkaloids have both groups in the α-orientation, and lycoctonine-type alkaloids are β (Keith & Pelletier, 1970). More importantly, no lycoctonine-type alkaloid is known which is unsubstituted at C(6). Talatizidine must, consequently, be considered an anomaly in that it is either the first example of an aconitine-type alkaloid with 1β-substitution, or the first example of a lycoctonine-type alkaloid in which there is no oxygenated group attached to C(6).

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The Crystal and Molecular Structure and Absolute Configuration of Chasmanine 14α-Benzoate Hydrochloride

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Chasmanine, a C_{19} diterpenoid alkaloid isolated from *Aconitum chasmanthum* Stapf, has been investigated by an X-ray crystal structure determination of the hydrochloride of its benzoate derivative. The crystals are orthorhombic, $P2_12_12_1$, $a = 11\cdot259$ (2), $b = 26\cdot093$ (3), $c = 10\cdot383$ (1) Å. The structure was solved by direct methods and refined by least squares to residuals $R = 0\cdot048$, $R_w = 0\cdot056$, based on 2493 observed reflections. By the R-ratio test, the absolute configuration is shown to be $1S,4S,5R,6R,7R,8R,9R,10R,11S,13R,14S,16S,17R$. Ring A is stabilized in the boat form by intramolecular hydrogen bonding. The 1-methoxy substituent is shown to be α-oriented, proving that the correlation of chasmanine with browniine by chemical methods was in error.

Introduction

Chasmanine (I) is a C_{19} diterpenoid alkaloid which was first isolated from the roots of *Aconitum chasmanthum* Stapf (Achmatowicz & Marion, 1964). Its molecular structure, demonstrating that it belongs to the aconitine group, was partially deduced by a combination of chemical and spectral methods (Achmatowicz, Tsuda, Marion, Okamoto, Natsume, Chang & Kajima, 1965). On the basis of a chemical correlation with browniine (II), a lycoctonine-type alkaloid, the C(1)-oxygenated substituent in chasmanine was assigned a β-orientation (Edwards, Fonzes & Marion, 1966). This work appeared to provide the first evidence of a chemical relation between the two previously distinct groups of alkaloids. A chemical correlation between chasmanine and neoline (III), another aconitine-type alkaloid, supported β-substitution at C(1) in the latter as well.

The recent isolation and X-ray crystal structure determination of delphisine (IV) (Pelletier, De Camp, Lajšić, Djarmati & Kapadi, 1974; Pelletier, Djarmati, Lajšić & De Camp, 1976), and its subsequent correlation with neoline (Pelletier, Djarmati & Lajšić, 1974) confirmed a 1α substituent in the latter, and stimulated a re-examination of the reported structure of chasmanine. We report here the determination of the crystal structure and absolute configuration of chasmanine 14α-benzoate (V) hydrochloride, which establishes the 1-methoxy group as α-directed. The correlation of chasmanine with neoline is thus con-