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

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Chasmanine, a C₁₉ 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, $P2_12_12_1$, $a = 11.259(2)$, $b = 26.093(3)$, $c = 10.383(1)$ Å. The structure was solved by direct methods and refined by least squares to residuals $R = 0.048$, $R_w = 0.056$, based on 2493 observed reflections. By the R -ratio test, the absolute configuration is shown to be 1*S*,4*S*,5*R*,6*R*,7*R*,8*R*,9*R*,10*R*,11*S*,13*R*,14*S*,16*S*,17*R*. 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.

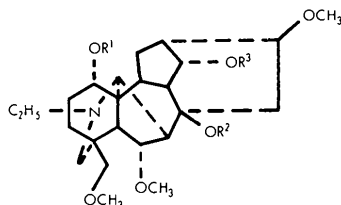
Introduction

Chasmanine (I) is a C₁₉ 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 lycocotnine-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

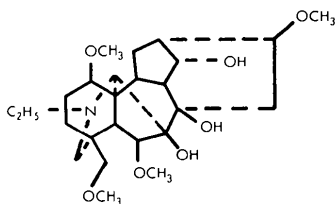
alkaloids. A chemical correlation between chasmanine and neoline (III), another aconitine-type alkaloid, supported β -substitution at C(1) in the latter as well.

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 1 α 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 14 α -benzoate (V) hydrochloride, which establishes the 1-methoxy group as α -directed. The correlation of chasmanine with neoline is thus con-

firmed as correct, leaving the reported correlation of chasmanine with browniine as a weak link connecting the aconitine- and lycoctonine-type alkaloids. On the basis of ^{13}C NMR studies (Pelletier, De Camp & Djarmati, 1976), greater certainty can be ascribed to the correlation of browniine with lycoctonine (Benn, Cameron & Edwards, 1963), and there appears to be no reason to question the correctness of structure II for browniine. Preliminary reports of portions of this work have appeared (De Camp & Pelletier, 1976; Pelletier, De Camp & Djarmati, 1976).



- (I) $\text{R}^1 = \text{CH}_3$, $\text{R}^2 = \text{R}^3 = \text{H}$
 (II) $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{H}$
 (IV) $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{R}^3 = \text{COCH}_3$
 (V) $\text{R}^1 = \text{CH}_3$, $\text{R}^2 = \text{H}$, $\text{R}^3 = \text{COC}_6\text{H}_5$
 (VI) $\text{R}^1 = \text{R}^2 = \text{CH}_3$, $\text{R}^3 = \text{H}$



(II)

Experimental

A sample of chasmanine (I) was provided through the kindness of Dr O. E. Edwards. Since we wished to determine its absolute configuration as well as its molecular structure, a derivative was sought which contained a heavy atom. The benzoyl derivative (V, for which a crystalline hydrochloride was known) was prepared according to the procedure of Achmatowicz *et al.* (1965) by Dr Z. Djarmati. The crystal data are summarized in Table 1. Integrated intensities for all reflections for which 2θ was less than 150° were

Table 1. *Crystal data*

Chasmanine 14 α -benzoate hydrochloride, $\text{C}_{32}\text{H}_{46}\text{NO}_7\text{Cl}$
 $M_r = 592.14$, m.p. $250\text{--}252^\circ\text{C}$
 Orthorhombic, $P2_12_12_1$; $a = 11.259(2)$, $b = 26.093(3)$,
 $c = 10.383(1)$ Å, $V = 3050.3$ Å 3 , $D_m = 1.279(5)$, $D_x = 1.289(1)$
 g cm^{-3} ($Z = 4$, flotation in toluene-chloroform)
 $F(000) = 1272$ e, $\mu = 14.08$ cm $^{-1}$ (Cu $K\alpha$, $\lambda = 1.5418$ Å)

measured with Cu $K\alpha$ radiation (graphite monochromator, $\lambda = 1.5418$ Å) on an Enraf-Nonius CAD-4 diffractometer. Less than 60% of the accessible reflections were observed at a 3σ level of significance. In an effort to increase the number of observed data, a second, somewhat larger, crystal was mounted and the data recollected. Although this second crystal was approximately 20% larger than the first, the percentage of observed data increased only slightly. The two sets of measurements were then placed on a common scale by reference to three standard reflections which had been monitored as a check on possible crystal decomposition, and reflections which exceeded the 2σ level of significance in either set of data were considered to be observed. Out of a total of 3542 reflections, 2493 (70.4%) constituted observed data. The data were corrected for Lorentz and polarization effects, but no absorption correction was applied.

Structure solution and refinement

The structure was solved by the direct method with *MULTAN* (Germain, Main & Woolson, 1971). Initial attempts gave no *apparent* solution, even with as many as four general reflections in the starting set of phases, thus producing 128 different sets of phases in tangent refinement. However, when the strongest phase indication from Σ_1 relations was accepted (040 , $\varphi = \pi$, $p = 0.977$), the solution proceeded in a straightforward manner. It is of interest to note that when the starting set of phases which ultimately led to the solution was extended by tangent refinement without the use of the Σ_1 relation, the figures of merit were so low as to suggest that the phase set did not contain the solution. The absolute figure of merit for the 'correct' set of phases, with three general reflections and one phase accepted from Σ_1 in the starting set of phases, was 0.9630, and the combined figure of merit (Arora, Bates, Grady, Germain & Declercq, 1975) was 2.7871; both were the highest values found in the 32 phase sets examined. *A posteriori*, this problem resulted from the fact that the first Σ_2 relation used in the convergence procedure indicated a phase of 2π for 040 ($p = 0.901$), while Σ_1 gave the correct phase of π .

An *E* map calculated from the 'correct' set of phases revealed 37 maxima, 36 of which formed a connected set. The C_{19} diterpenoid alkaloid ring system was evident in its entirety, and the remaining peaks corresponded to the substitution pattern proposed by Achmatowicz *et al.* (1965), with the exception of the C(1) substituent, which was clearly α -oriented. Refinement of this model with anisotropic temperature factors converged at $R = 0.087$, and 31 of the 46 H atoms were identified from successive difference maps. The remaining H atoms could not be found even though numerous weighting schemes were tried on the basis of

Table 2. Atomic positional ($\times 10^4$) and thermal ($\times 10^3$) parameters for chasmanine 14 α -benzoate hydrochloride

The e.s.d. of the parameter is in parentheses; the anisotropic thermal correction is of the form:

$$T = \exp[-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{12}hka^*b^* + \dots)].$$

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cl	3463 (1)	3904 (1)	-488 (1)	119 (1)	113 (1)	36 (1)	15 (1)	8 (1)	-12 (1)
C(1)	4682 (4)	4742 (1)	3042 (3)	50 (2)	55 (2)	31 (2)	-10 (2)	-4 (2)	9 (2)
C(2)	3662 (4)	5074 (1)	2644 (4)	62 (2)	52 (2)	45 (2)	0 (2)	-4 (2)	17 (2)
C(3)	2590 (3)	4762 (2)	2276 (4)	49 (2)	60 (2)	37 (2)	9 (2)	0 (2)	10 (2)
C(4)	2233 (3)	4353 (1)	3316 (3)	42 (2)	54 (2)	29 (2)	7 (2)	3 (1)	0 (2)
C(5)	3017 (3)	4398 (1)	4554 (3)	56 (2)	38 (2)	28 (2)	5 (2)	7 (2)	-3 (1)
C(6)	2914 (3)	3943 (1)	5498 (3)	47 (2)	53 (2)	29 (2)	-4 (2)	5 (2)	1 (2)
C(7)	3901 (3)	3565 (1)	5079 (3)	50 (2)	37 (2)	28 (1)	-8 (2)	4 (2)	0 (1)
C(8)	4904 (4)	3544 (1)	6097 (3)	54 (2)	40 (2)	30 (2)	-3 (2)	2 (2)	5 (1)
C(9)	5277 (4)	4098 (1)	6436 (3)	65 (2)	39 (2)	24 (1)	-4 (2)	0 (2)	2 (1)
C(10)	5266 (3)	4461 (1)	5245 (3)	50 (2)	42 (2)	31 (2)	-4 (2)	-9 (2)	3 (1)
C(11)	4343 (3)	4366 (1)	4149 (3)	46 (2)	38 (2)	30 (2)	-1 (2)	1 (1)	4 (1)
C(12)	6572 (4)	4425 (2)	4717 (4)	49 (2)	67 (3)	45 (2)	-16 (2)	-9 (2)	16 (2)
C(13)	7221 (3)	4039 (2)	5580 (4)	45 (2)	82 (3)	38 (2)	-9 (2)	-9 (2)	14 (2)
C(14)	6575 (4)	4135 (1)	6839 (3)	66 (3)	47 (2)	32 (2)	-8 (2)	-16 (2)	6 (2)
C(15)	5970 (4)	3217 (2)	5669 (4)	56 (2)	56 (2)	44 (2)	8 (2)	-4 (2)	-4 (2)
C(16)	7072 (4)	3485 (2)	5118 (4)	53 (2)	83 (3)	43 (2)	13 (2)	-4 (2)	-1 (2)
C(17)	4400 (3)	3792 (1)	3827 (3)	38 (2)	40 (2)	26 (1)	4 (2)	1 (1)	-2 (1)
C(18)	910 (4)	4438 (2)	3618 (4)	51 (2)	82 (3)	40 (2)	13 (2)	2 (2)	2 (2)
C(19)	2377 (3)	3812 (2)	2779 (3)	38 (2)	62 (2)	34 (2)	-2 (2)	-2 (2)	-5 (2)
C(20)	3745 (5)	3104 (2)	2248 (4)	85 (3)	55 (2)	50 (2)	7 (2)	-10 (2)	-23 (2)
C(21)	4970 (5)	2943 (2)	1894 (5)	86 (4)	100 (4)	80 (3)	39 (3)	-13 (3)	-43 (3)
C(1A2)	5803 (5)	4698 (2)	1059 (5)	64 (3)	125 (4)	53 (3)	-5 (3)	15 (2)	40 (3)
C(6A2)	1527 (5)	3444 (2)	6665 (5)	68 (3)	105 (4)	53 (2)	-26 (3)	9 (2)	27 (2)
C(14A2)	7895 (4)	3874 (2)	8474 (4)	83 (3)	53 (2)	51 (2)	-13 (3)	-21 (2)	9 (2)
C(14A3)	8238 (4)	3459 (1)	9376 (4)	81 (3)	48 (2)	41 (2)	7 (2)	-14 (2)	-1 (2)
C(14A4)	9348 (6)	3487 (2)	9948 (6)	106 (4)	66 (3)	77 (3)	3 (3)	-42 (3)	8 (3)
C(14A5)	9706 (7)	3103 (2)	10791 (6)	144 (6)	80 (4)	83 (4)	19 (4)	-60 (4)	4 (3)
C(14A6)	8966 (7)	2704 (2)	11049 (5)	145 (6)	66 (3)	58 (3)	36 (4)	-13 (4)	10 (2)
C(14A7)	7859 (6)	2664 (2)	10489 (5)	129 (5)	58 (3)	56 (3)	18 (3)	11 (3)	11 (2)
C(14A8)	7502 (5)	3049 (2)	9622 (4)	83 (3)	62 (3)	45 (2)	11 (2)	-1 (2)	7 (2)
C(16B2)	8792 (9)	3018 (3)	4658 (9)	177 (8)	159 (7)	133 (6)	117 (7)	-8 (6)	-13 (5)
C(182)	-945 (4)	4387 (2)	2603 (6)	49 (3)	107 (4)	94 (4)	14 (3)	3 (3)	21 (4)
O(1A1)	5131 (2)	4432 (1)	1996 (2)	54 (2)	75 (2)	30 (1)	-5 (1)	8 (1)	10 (1)
O(6A1)	1749 (2)	3721 (1)	5524 (2)	49 (2)	76 (2)	38 (1)	-9 (1)	7 (1)	13 (1)
O(8B1)	4441 (3)	3287 (1)	7204 (2)	83 (2)	44 (1)	32 (1)	-3 (1)	7 (1)	10 (1)
O(14A1)	6876 (3)	3781 (1)	7853 (2)	70 (2)	48 (1)	35 (1)	-4 (1)	-16 (1)	9 (1)
O(14A2)	8481 (4)	4250 (2)	8304 (4)	120 (3)	81 (2)	129 (3)	-45 (2)	-71 (3)	52 (2)
O(16B1)	8088 (3)	3189 (2)	5492 (4)	69 (2)	166 (4)	72 (2)	53 (3)	-5 (2)	-6 (3)
O(181)	282 (3)	4387 (1)	2433 (3)	42 (2)	123 (3)	52 (2)	8 (2)	2 (1)	5 (2)
N	3649 (3)	3664 (1)	2646 (2)	45 (2)	50 (2)	26 (1)	1 (1)	1 (1)	-6 (1)

	x	y	z	U_{iso}		x	y	z	U_{iso}
H(1B)	5375 (32)	4920 (13)	3362 (35)	42 (9)	H(202)	3391 (38)	2926 (15)	3022 (42)	62 (11)
H(2A)	3903 (40)	5289 (16)	1767 (43)	72 (13)	H(211)	5211 (63)	3232 (26)	1231 (70)	131 (23)
H(2B)	3519 (49)	5305 (19)	3405 (54)	98 (17)	H(212)	5645 (58)	2956 (25)	2489 (73)	131 (23)
H(3A)	2688 (38)	4604 (16)	1338 (44)	60 (12)	H(213)	4990 (60)	2531 (24)	1530 (70)	117 (22)
H(3B)	1847 (36)	4995 (15)	2184 (43)	61 (12)	H(1A21)	5323 (59)	5009 (24)	667 (65)	120 (21)
H(5B)	2837 (29)	4685 (12)	4883 (36)	33 (9)	H(1A22)	6570 (69)	4839 (28)	1301 (79)	148 (25)
H(6B)	3081 (31)	4038 (13)	6464 (35)	41 (10)	H(1A23)	6047 (59)	4519 (23)	252 (67)	128 (21)
H(7A)	3525 (34)	3200 (13)	5026 (39)	50 (10)	H(6A21)	1676 (66)	3621 (25)	7586 (74)	136 (25)
H(9B)	4829 (34)	4228 (15)	7155 (39)	50 (11)	H(6A22)	792 (35)	3398 (14)	6660 (38)	47 (10)
H(10B)	5111 (32)	4825 (13)	5506 (35)	44 (10)	H(6A23)	2101 (52)	3031 (22)	6659 (59)	100 (19)
H(12A)	6635 (36)	4319 (15)	3774 (40)	58 (12)	H(14A4)	9914 (65)	3724 (25)	9681 (76)	139 (26)
H(12B)	6893 (40)	4770 (17)	4766 (51)	78 (15)	H(14A5)	10500 (78)	3116 (29)	11237 (97)	166 (33)
H(13B)	8096 (35)	4104 (14)	5775 (40)	52 (11)	H(14A6)	9241 (56)	2467 (23)	11510 (65)	110 (19)
H(14B)	6740 (31)	4477 (12)	7218 (35)	39 (9)	H(14A7)	7090 (43)	2380 (18)	10613 (49)	79 (14)
H(15A)	5665 (36)	2918 (15)	5065 (45)	62 (12)	H(14A8)	6847 (36)	3005 (15)	9106 (40)	52 (11)
H(15B)	6233 (38)	3083 (15)	6444 (40)	54 (11)	H(16B21)	8317 (60)	2840 (23)	4061 (64)	151 (21)
H(16A)	7065 (45)	3486 (16)	4132 (50)	72 (14)	H(16B22)	9056 (60)	3325 (26)	4207 (67)	156 (22)
H(17A)	5185 (26)	3717 (10)	3635 (27)	16 (7)	H(16B23)	9489 (46)	2782 (17)	4868 (54)	101 (15)
H(181)	761 (47)	4843 (19)	4021 (55)	85 (16)	H(1821)	-1329 (50)	4667 (21)	2910 (61)	105 (19)
H(182)	598 (42)	4177 (18)	4246 (48)	81 (14)	H(1822)	-1460 (49)	4365 (19)	1495 (52)	98 (16)
H(191)	2048 (31)	3798 (13)	1951 (33)	35 (9)	H(1823)	-1332 (56)	4114 (23)	3318 (63)	121 (21)
H(192)	2035 (44)	3575 (16)	3320 (46)	65 (13)	H(8B1)	4282 (41)	3475 (16)	7776 (48)	72 (14)
H(201)	3293 (43)	3112 (17)	1404 (49)	69 (14)	H(N)	3978 (38)	3825 (16)	2029 (44)	65 (12)

the concept that the most information is contained in the residuals from a properly weighted refinement (Tukey, 1974, pp. 54–56). Coordinates for the missing H atoms were calculated with assumed ideal geometry and bond length of 1.05 Å. Further refinement, with a damping factor of 0.6 applied to all calculated shifts to reduce oscillation, converged at $R = 0.048$, $R_w = 0.056$ ($w = 1/\{1 + [(F_o - 14)/6]^2\}$).

All shifts in the final cycle were less than 1.1 e.s.d., except for three parameters for C(16B2) and the H atoms bonded to it. This terminal methyl group shows large thermal motion, and the shifts calculated for the four atoms of the group tended to diverge despite the application of the damping factor. The least-squares refinement minimized $\sum w(|F_o| - |F_c|)^2$. Unobserved reflections were excluded from the refinement, but at convergence only 133 of the 1049 unobserved data calculated greater than the 2σ threshold of observability. A final difference electron density map showed no maxima greater than 0.2 e \AA^{-3} . A weighting analysis showed no noticeable trend of $w\Delta F$ with either $|F_o|$ or $\sin\theta$. The final atomic positional and thermal parameters (following the numbering scheme shown in Fig. 1) are given in Table 2.*

A structure factor calculation was carried out on the opposite enantiomorph in order to establish the absolute configuration. The residuals were $R = 0.057$, $R_w = 0.070$, compared with the values of $R = 0.048$, $R_w = 0.056$, given above. By Hamilton's (1965) test, therefore, the parameters of Table 2 correspond to the correct enantiomorph with almost absolute certainty.

All calculations for the refinement of the structure

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32096 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

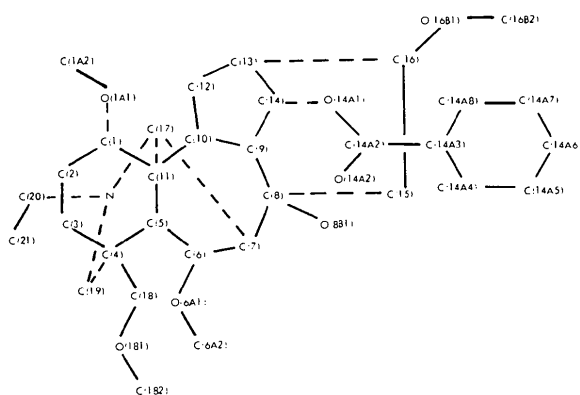
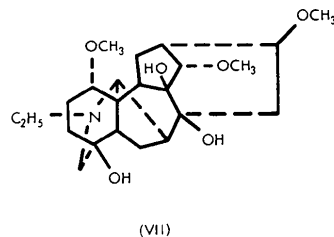


Fig. 1. Numbering scheme for the nonhydrogen atoms in chasmanine 14 α -benzoate. Hydrogen atoms are given the same number as the atom to which they are bonded, with A or B appended to indicate α or β orientation respectively; where a hydrogen atom is neither α nor β , an arbitrary number may be added.

were carried out on a CDC Cyber 70/74 computer with the programs of the X-RAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). The atomic scattering factors used for Cl, C, N and O were the analytical approximations of Cromer & Mann (1968), and those for H were taken from Stewart, Davidson & Simpson (1965). The scattering factors for Cl and O were corrected for the real and imaginary components of anomalous dispersion [Cl: $\Delta f' = 0.3$, $\Delta f'' = 0.7$ (*International Tables for X-ray Crystallography*, 1968); O: $\Delta f' = 0.0$, $\Delta f'' = 0.037$ (Engel, 1972)]. Because of the number of atomic parameters, the least-squares refinement was carried out by a large block-diagonal approximation, with each block containing all parameters for several atoms, the details of the blocking being determined by the number of parameters and the available core storage. In the final cycles of refinement, the model contained 87 atoms and used 816 parameters, 555 of which were varied, and the matrix was subdivided into nine blocks.

Discussion of the structure

Except for the orientation of the C(1) methoxy group, the molecular structure of chasmanine 14 α -benzoate hydrochloride corresponds exactly to that which would be expected on the basis of the structure proposed for chasmanine by Achmatowicz *et al.* (1965). The revision of the structures of chasmanine (I) and homochasmanine (VI) proposed by Pelletier, Djarmati & Lajšić (1974) on the basis of chemical and spectral data is confirmed by our results. In addition, since neoline (III) has now been correlated with two diterpenoid alkaloids, both of which are of known crystal structure and absolute configuration, the possibility that either its molecular structure or absolute configuration are in error must be regarded as remote.



As in the structures of delphisine (IV) hydrochloride (Pelletier, De Camp, Lajšić, Djarmati & Kapadi, 1974; Pelletier, Djarmati, Lajšić & De Camp, 1976) and lappaconine (VII) hydrobromide (Birnbbaum, 1969, 1970), ring A is stabilized in a boat form by an intramolecular N—H...O hydrogen bond in which the protonated N atom is the donor, and the O atom in the 1 α substituent is the acceptor. Furthermore, in chasmanine 14 α -benzoate hydrochloride, we find that the amino H atom is within a hydrogen-bonding radius of the Cl⁻ ion, thus suggesting that this is

Table 3. *Molecular geometry of chasmanine 14 α -benzoate hydrochloride*

The e.s.d.'s are given in parentheses. For all C—H bonds ($n = 44$): range = 0.84 to 1.29, mean = 1.01, $\sigma = 0.09$ Å.

(a) Interatomic distances (Å)

C(1)—C(2)	1.496 (6)	C(13)—C(14)	1.518 (5)
C(1)—C(11)	1.559 (5)	C(13)—C(16)	1.533 (6)
C(1)—O(1A1)	1.445 (4)	C(14)—O(14A1)	1.442 (4)
C(2)—C(3)	1.506 (6)	C(15)—C(16)	1.534 (6)
C(3)—C(4)	1.571 (5)	C(16)—O(16B1)	1.434 (6)
C(4)—C(5)	1.564 (5)	C(17)—N	1.526 (4)
C(4)—C(18)	1.539 (6)	C(18)—O(181)	1.425 (5)
C(4)—C(19)	1.525 (5)	C(19)—N	1.490 (5)
C(5)—C(6)	1.546 (5)	C(20)—N	1.522 (5)
C(5)—C(11)	1.553 (5)	C(20)—C(21)	1.488 (8)
C(6)—C(7)	1.549 (5)	C(142)—O(1A1)	1.414 (6)
C(6)—O(6A1)	1.433 (5)	C(6A2)—O(6A1)	1.411 (6)
C(7)—C(8)	1.547 (5)	C(14A2)—O(14A1)	1.338 (6)
C(7)—C(17)	1.535 (5)	C(14A2)—O(14A2)	1.195 (6)
C(8)—C(9)	1.546 (5)	C(14A2)—C(14A3)	1.483 (6)
C(8)—C(15)	1.539 (6)	C(14A3)—C(14A4)	1.386 (8)
C(8)—O(8B1)	1.429 (4)	C(14A3)—C(14A8)	1.377 (6)
C(9)—C(10)	1.557 (5)	C(14A4)—C(14A5)	1.390 (8)
C(9)—C(14)	1.523 (6)	C(14A5)—C(14A6)	1.360 (10)
C(10)—C(11)	1.561 (5)	C(14A6)—C(14A7)	1.379 (10)
C(10)—C(12)	1.573 (5)	C(14A7)—C(14A8)	1.407 (7)
C(11)—C(17)	1.537 (5)	C(16B2)—O(16B1)	1.256 (11)
C(12)—C(13)	1.534 (6)	C(182)—O(181)	1.393 (6)
O(8B1)—H(8B1)	0.79 (5)	N—H(N)	0.85 (4)

another example of heterologous bifurcated hydrogen bonding, in which two different atoms act as acceptors. The Cl⁻ ion also accepts a hydrogen bond from the 8 β -hydroxy group of the molecule translated by one unit cell along *c*. There are no other intermolecular contacts which are short enough to indicate hydrogen bonding. O(8B1) is closer than the sum of van der Waals radii to the *para* hydrogen [H(146)] of the benzoate group of another molecule [2.39 (6) Å, $(x,y,z)' = (x - \frac{1}{2}, -y + \frac{1}{2}, -z + 2)$], but this is a result of the packing of the molecules rather than evidence of hydrogen bonding.

Details of the molecular structure are essentially similar to delphisine hydrochloride, and are summarized in the interatomic distances and angles shown in Table 3. A stereoscopic pair of drawings of chasmanine 14 α -benzoate hydrochloride (omitting the H atoms, except for those involved in hydrogen bonding) is shown in Fig. 2, and a schematic illustration of the hydrogen-bonding environment of the Cl⁻ ion in Fig. 3.

The absolute configuration of the molecule is 1*S*,4*S*,5*R*,6*R*,7*R*,8*R*,9*R*,10*R*,11*S*,13*R*,14*S*,16*S*,17*R*.

Table 3 (cont.)

(b) Angles between bonded, nonhydrogen atoms (°)

C(2)—C(1)—C(11)	112.4 (3)	C(17)—C(11)—C(10)	106.6 (3)
O(1A1)—C(1)—C(11)	106.7 (3)	C(13)—C(12)—C(10)	106.3 (3)
C(2)—C(1)—O(1A1)	112.7 (3)	C(14)—C(13)—C(12)	99.5 (3)
C(3)—C(2)—C(1)	111.9 (3)	C(16)—C(13)—C(12)	112.6 (3)
C(4)—C(3)—C(2)	113.5 (3)	C(16)—C(13)—C(14)	111.9 (3)
C(5)—C(4)—C(3)	111.6 (3)	C(13)—C(14)—C(9)	102.3 (3)
C(18)—C(4)—C(3)	106.8 (3)	O(14A1)—C(14)—C(9)	112.7 (3)
C(19)—C(4)—C(3)	110.5 (3)	O(14A1)—C(14)—C(13)	114.2 (3)
C(18)—C(4)—C(5)	111.6 (3)	C(16)—C(15)—C(8)	119.1 (3)
C(19)—C(4)—C(5)	108.1 (3)	C(15)—C(16)—C(13)	113.7 (3)
C(19)—C(4)—C(18)	108.1 (3)	O(16B1)—C(16)—C(13)	109.5 (4)
C(6)—C(5)—C(4)	114.9 (3)	O(16B1)—C(16)—C(15)	107.5 (4)
C(11)—C(5)—C(4)	108.4 (3)	C(11)—C(17)—C(7)	100.2 (2)
C(6)—C(5)—C(11)	101.7 (3)	N—C(17)—C(7)	113.2 (3)
C(7)—C(6)—C(5)	104.9 (3)	N—C(17)—C(11)	111.3 (3)
O(6A1)—C(6)—C(5)	113.0 (3)	O(181)—C(18)—C(4)	106.9 (3)
C(7)—C(6)—O(6A1)	113.9 (3)	N—C(19)—C(4)	112.1 (3)
C(8)—C(7)—C(6)	110.7 (3)	N—C(20)—C(21)	113.8 (4)
C(17)—C(7)—C(6)	104.8 (3)	O(14A1)—C(14A2)—C(14A3)	113.3 (4)
C(8)—C(7)—C(17)	109.0 (3)	O(14A2)—C(14A2)—C(14A3)	123.2 (5)
C(9)—C(8)—C(7)	108.8 (3)	O(14A2)—C(14A2)—O(14A1)	123.5 (4)
C(15)—C(8)—C(7)	113.0 (3)	C(14A4)—C(14A3)—C(14A2)	117.8 (4)
O(8B1)—C(8)—C(7)	107.4 (3)	C(14A8)—C(14A3)—C(14A2)	121.9 (4)
C(15)—C(8)—C(9)	111.9 (3)	C(14A8)—C(14A3)—C(14A4)	120.3 (4)
O(8B1)—C(8)—C(9)	110.8 (3)	C(14A5)—C(14A4)—C(14A3)	119.5 (5)
O(8B1)—C(8)—C(15)	104.8 (3)	C(14A6)—C(14A5)—C(14A4)	119.9 (7)
C(10)—C(9)—C(8)	112.6 (3)	C(14A7)—C(14A6)—C(14A5)	121.9 (6)
C(14)—C(9)—C(8)	112.5 (3)	C(14A8)—C(14A7)—C(14A6)	118.3 (5)
C(14)—C(9)—C(10)	100.8 (3)	C(14A7)—C(14A8)—C(14A3)	120.1 (5)
C(11)—C(10)—C(9)	119.2 (3)	C(1A2)—O(1A1)—C(1)	115.5 (3)
C(12)—C(10)—C(9)	103.5 (3)	C(6A2)—O(6A1)—C(6)	112.6 (3)
C(12)—C(10)—C(11)	111.0 (3)	C(14A2)—O(14A1)—C(14)	115.9 (3)
C(5)—C(11)—C(1)	113.6 (3)	C(16B2)—O(16B1)—C(16)	120.5 (6)
C(10)—C(11)—C(1)	105.9 (3)	C(182)—O(181)—C(18)	112.4 (4)
C(17)—C(11)—C(1)	116.3 (3)	C(19)—N—C(17)	113.7 (3)
C(10)—C(11)—C(5)	115.7 (3)	C(20)—N—C(17)	112.8 (3)
C(17)—C(11)—C(5)	98.8 (3)	C(20)—N—C(19)	110.0 (3)

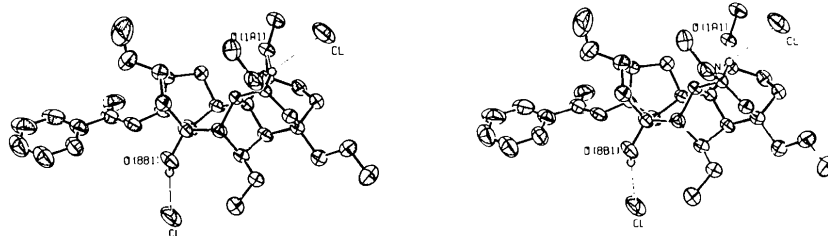


Fig. 2. A stereoscopic view of chasmanine 14 α -benzoate hydrochloride, taken approximately towards the α -face of the molecule. Hydrogen atoms are omitted for clarity, except for those involved in hydrogen bonding, which are drawn as small spheres.

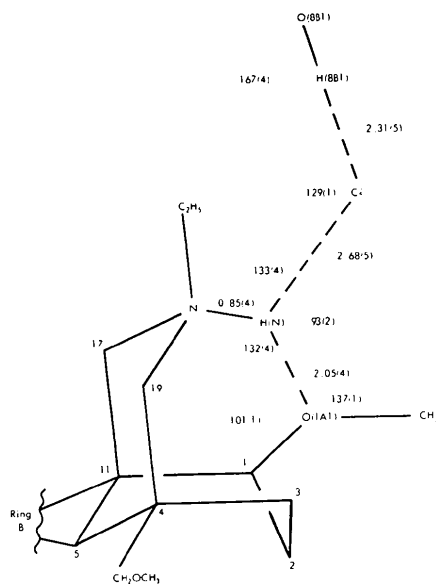


Fig. 3. A schematic representation of the hydrogen bonding around the chloride ion, showing ring A in the boat conformation.

This is identical to that found for delphisine hydrochloride, and is consistent with other determinations of absolute configuration for alkaloids of the aconitine group.

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