

## The Structure of Dehydromultiflorine Perchlorate

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**Abstract.**  $C_{15}H_{21}N_2O^+ \cdot ClO_4^-$ ,  $M_r = 344.8$ , orthorhombic,  $P2_12_12_1$ ,  $a = 12.876(9)$ ,  $b = 13.340(1)$ ,  $c = 9.207(1)$  Å,  $Z = 4$ ,  $D_c = 1.45$  Mg m $^{-3}$ ,  $V = 1581.5$  Å $^3$ ,  $\mu(Cu K\alpha) = 2.4$  mm $^{-1}$ . The structure, solved by Patterson and Fourier methods, was refined to  $R = 0.049$ . The conformation of ring C is the same as that found in the multiflorine cation (I) [Pyżalska, Gdaniec, Borowiak & Wolińska-Mocydlarz (1980). *Acta Cryst. B36*, 1602–1606]. The structure consists of infinite chains of cations linked by hydrogen bonds:  $N(16)^+ \cdots O$  2.678 (7) Å.

**Introduction.** This report is a continuation of the systematic investigations of the structures of sparteine derivatives (Kałuski, Skolik & Wiewiórowski, 1979). As mentioned in Pyżalska, Gdaniec, Borowiak & Wolińska-Mocydlarz (1980), the configurational-conformational changes of the C/D system of the alkaloids could be correlated with some specific alterations in ring A. In order to verify this hypothesis, an X-ray analysis of dehydromultiflorine (2,3,5,6-tetrahydro-4-oxosparteine) monoperchlorate (Fig. 1) containing the  $\gamma$ -pyridone system (ring A) has been carried out.

Crystals suitable for X-ray analysis were grown by slow evaporation from *n*-hexane solution. Precession photographs gave preliminary values for the unit-cell parameters. The systematic absences uniquely indicated the space group  $P2_12_12_1$ . The precise values of the unit-cell parameters were obtained by a least-squares fit of  $2\theta$ ,  $\omega$  and  $\chi$  settings for 15 diffractometer reflexions.

A crystal of approximate dimensions  $0.15 \times 0.15 \times 0.4$  mm was mounted on a Syntex  $P2_1$  diffractometer. The intensities of 1261 reflexions with  $2\theta$  less than  $116^\circ$  were collected by the  $\theta$ - $2\theta$  scan technique using Cu  $K\alpha$  radiation ( $\lambda = 1.54178$  Å) and a graphite monochromator. A variable scan rate in the range  $2$ – $29.30^\circ$  min $^{-1}$  was applied. The intensities of two monitor reflexions measured after every 30 reflexions showed no significant change during the data collection. 1026 reflexions with  $I \geq 1.96\sigma(I)$  were considered observed. The data were corrected for Lorentz and polarization factors; no absorption correction was applied.

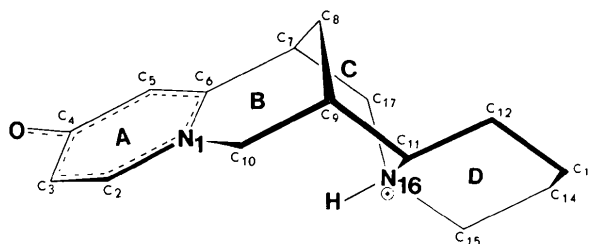


Fig. 1. The dehydromultiflorine cation (II).

The approximate position of the Cl atom was obtained from a Patterson map. A Fourier map based on the refined position of the heavy atom showed the positions of all non-hydrogen atoms, which were included in the subsequent cycles of full-matrix least-squares refinement. The coordinates of the H atoms were obtained from two successive difference-Fourier maps and were included in the structure factor calculations, but were not refined. H atoms were assigned  $B$  values of  $4.5$  Å $^2$ . The function minimized in the least-squares refinement was  $\sum w(F_o - F_c)^2$ . The reflexions were weighted as follows:  $w = (F_o/F_{low})^2$  if  $|F_o| < F_{low}$ ,  $w = 1$  if  $F_{low} \leq |F_o| \leq F_{high}$ ,  $w = (F_{high}/F_o)^2$  if  $|F_o| > F_{high}$ , with  $F_{low} = 7.3$  and  $F_{high} = 22$ . The final  $R$  and  $R_w$  values for all observed reflexions were 0.049 and 0.060 respectively. Final positional parameters are given in Table 1.\*

**Discussion.** Bond lengths and angles of the molecule are summarized in Tables 2 and 3. Torsion angles are in Table 4. The mean values of the  $C_{sp^3}-C_{sp^3}$  (1.524 Å) and  $N^+-C_{sp^3}$  (1.525 Å) bond lengths are in good agreement with those reported for other sparteine derivatives (Kałuski, Skolik & Wiewiórowski, 1979). The tetrahedral angles also have their expected values.

The C–C and C–N distances in ring A show a hybrid character, resonating between single and double

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35120 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final fractional atomic coordinates ( $\times 10^4$ ,  $\times 10^3$  for H atoms) and  $B_{eq}$  ( $\text{\AA}^2$ ) for non-hydrogen atoms

	$B_{iso}$ for all H atoms is $4.5 \text{\AA}^2$ .			$B_{eq}$
	$x$	$y$	$z$	
N(1)	652 (4)	4842 (4)	8857 (5)	2.6 (1)
C(2)	1253 (5)	4012 (5)	8979 (8)	3.3 (2)
C(3)	2036 (5)	3779 (5)	8037 (7)	3.4 (2)
C(4)	2252 (5)	4424 (5)	6850 (7)	3.3 (2)
O	2951 (4)	4242 (4)	5915 (7)	4.5 (1)
C(5)	1609 (5)	5290 (5)	6752 (7)	3.2 (2)
C(6)	840 (5)	5485 (5)	7727 (7)	2.9 (2)
C(7)	167 (5)	6421 (5)	7632 (7)	3.1 (2)
C(8)	-922 (5)	6188 (5)	8257 (8)	3.4 (2)
C(9)	-766 (5)	5961 (5)	9829 (8)	3.3 (2)
C(10)	-157 (5)	5003 (5)	9993 (8)	3.4 (2)
C(11)	-316 (5)	6855 (5)	10679 (8)	3.1 (2)
C(12)	-1064 (5)	7725 (5)	10768 (9)	3.9 (2)
C(13)	-592 (6)	8629 (6)	11591 (9)	4.9 (2)
C(14)	417 (6)	8966 (5)	10815 (11)	4.9 (2)
C(15)	1171 (6)	8094 (6)	10742 (10)	4.5 (2)
N(16)	723 (4)	7172 (4)	10007 (6)	3.0 (1)
C(17)	651 (5)	7318 (5)	8370 (8)	3.3 (2)
Cl	2198 (2)	1414 (1)	717 (2)	4.10 (5)
O(1)	2836 (7)	2217 (6)	538 (13)	12.7 (4)
O(2)	2426 (5)	957 (5)	2080 (8)	7.4 (2)
O(3)	1152 (5)	1745 (5)	672 (9)	7.8 (2)
O(4)	2337 (6)	700 (7)	-359 (9)	11.3 (3)
H(21)	110	355	979	
H(31)	244	310	830	
H(51)	174	571	597	
H(71)	13	645	655	
H(81)	-126	555	777	
H(82)	-138	691	783	
H(91)	-136	585	1037	
H(101)	14	496	87	
H(102)	-75	448	1006	
H(111)	-8	667	1174	
H(121)	-125	801	1004	
H(122)	-168	763	1149	
H(131)	-46	845	1289	
H(132)	-96	931	1169	
H(141)	87	945	1174	
H(142)	28	938	962	
H(151)	128	792	1163	
H(152)	169	802	995	
H(161)	124	659	1003	
H(171)	147	745	820	
H(172)	14	777	827	

Table 2. Intramolecular distances ( $\text{\AA}$ ) with their *e.s.d.*'s

N(1)—C(2)	1.356 (8)	C(17)—N(16)	1.522 (9)
C(2)—C(3)	1.365 (10)	N(16)—C(11)	1.535 (8)
C(3)—C(4)	1.419 (9)	C(11)—C(9)	1.539 (9)
C(4)—O	1.268 (9)	N(16)—C(15)	1.517 (9)
C(4)—C(5)	1.424 (9)	C(15)—C(14)	1.516 (10)
C(5)—C(6)	1.362 (9)	C(14)—C(13)	1.548 (11)
C(6)—C(7)	1.522 (9)	C(13)—C(12)	1.548 (11)
C(6)—N(1)	1.371 (8)	C(12)—C(11)	1.511 (9)
C(7)—C(8)	1.547 (9)	Cl—O(1)	1.360 (9)
C(8)—C(9)	1.493 (10)	Cl—O(2)	1.425 (7)
C(9)—C(10)	1.506 (9)	Cl—O(3)	1.418 (6)
C(10)—N(1)	1.491 (8)	Cl—O(4)	1.386 (9)
C(7)—C(17)	1.512 (10)		

Table 3. Bond angles ( $^\circ$ ) with their corresponding *e.s.d.*'s

N(1)—C(2)—C(3)	123.7 (6)	N(1)—C(10)—C(9)	114.6 (5)
C(2)—C(3)—C(4)	119.8 (6)	C(9)—C(11)—N(16)	109.7 (5)
C(3)—C(4)—C(5)	115.2 (6)	C(9)—C(11)—C(12)	112.6 (6)
C(5)—C(4)—O	121.7 (6)	C(12)—C(11)—N(16)	111.4 (5)
C(3)—C(4)—O	123.1 (6)	C(11)—C(12)—C(13)	112.0 (6)
C(4)—C(5)—C(6)	122.5 (6)	C(12)—C(13)—C(14)	109.2 (6)
C(5)—C(6)—N(1)	120.6 (6)	C(13)—C(14)—C(15)	109.6 (7)
C(5)—C(6)—C(7)	122.3 (6)	C(14)—C(15)—N(16)	113.5 (6)
C(7)—C(6)—N(1)	117.2 (5)	C(15)—N(16)—C(17)	111.1 (5)
C(6)—N(1)—C(2)	118.3 (5)	C(15)—N(16)—C(11)	112.0 (5)
C(6)—N(1)—C(10)	124.4 (5)	C(11)—N(16)—C(17)	112.4 (5)
C(2)—N(1)—C(10)	117.3 (5)	C(7)—C(17)—N(16)	111.7 (5)
C(6)—C(7)—C(8)	109.3 (5)	O(1)—Cl—O(2)	108.6 (5)
C(8)—C(7)—C(17)	111.4 (5)	O(1)—Cl—O(3)	109.0 (5)
C(6)—C(7)—C(17)	112.9 (5)	O(2)—Cl—O(3)	110.8 (4)
C(7)—C(8)—C(9)	106.2 (5)	O(1)—Cl—O(4)	112.1 (6)
C(8)—C(9)—C(10)	109.8 (6)	O(2)—Cl—O(4)	108.0 (5)
C(8)—C(9)—C(11)	112.7 (6)	O(3)—Cl—O(4)	108.4 (5)
C(10)—C(9)—C(11)	114.2 (6)		

Table 4. Torsion angles ( $^\circ$ )

Ring A	
N(1)—C(2)—C(3)—C(4)	-0.1 (9)
C(2)—C(3)—C(4)—C(5)	0.2 (8)
C(3)—C(4)—C(5)—C(6)	-0.1 (8)
C(4)—C(5)—C(6)—N(1)	-0.2 (9)
C(5)—C(6)—N(1)—C(2)	0.3 (8)
C(6)—N(1)—C(2)—C(3)	-0.2 (8)
Ring B	
N(1)—C(6)—C(7)—C(8)	-31.1 (7)
C(6)—C(7)—C(8)—C(9)	64.4 (7)
C(7)—C(8)—C(9)—C(10)	-66.6 (7)
C(8)—C(9)—C(10)—N(1)	35.4 (7)
C(9)—C(10)—N(1)—C(6)	-1.0 (8)
C(10)—N(1)—C(6)—C(7)	-0.5 (7)
Ring C	
C(9)—C(11)—N(16)—C(17)	50.4 (7)
C(11)—N(16)—C(17)—C(7)	-51.3 (7)
N(16)—C(17)—C(7)—C(8)	56.8 (6)
C(17)—C(7)—C(8)—C(9)	-61.0 (7)
C(7)—C(8)—C(9)—C(11)	62.1 (7)
C(8)—C(9)—C(11)—N(16)	-58.0 (6)
Ring D	
N(16)—C(11)—C(12)—C(13)	-54.8 (7)
C(11)—C(12)—C(13)—C(14)	58.3 (8)
C(12)—C(13)—C(14)—C(15)	-57.5 (9)
C(13)—C(14)—C(15)—N(16)	56.2 (8)
C(14)—C(15)—N(16)—C(11)	-52.8 (7)
C(15)—N(16)—C(11)—C(12)	51.0 (7)

bonds. The C(4)—O bond is significantly longer than the expected exocyclic C=O distance, indicating strong conjugation. The delocalization over all atoms in ring A can be supported by the calculation of the aromaticity index HOMA (Krygowski & Kruszewski, 1978) based on the bond lengths. HOMA for the present  $\gamma$ -pyridone system (Wolińska-Mocydla & Wiewiórowski, 1977) is 0.917 (for benzene HOMA = 1), showing a very high degree of delocalization of the  $p$ - $\pi$  electrons.

The configuration/conformation of the dehydromultiflorine skeleton, as determined by the present study, is shown schematically in Fig. 1. Ring *A* is planar as required by its conjugated bond system. Its planar conformation and the presence of the rigid C(7)–C(8)–C(9) bridge constrains ring *B* to adopt the sofa conformation with C(7), C(10) and C(9) lying almost in the *A*-ring plane. The *A*-ring conformation also forces the *A/B* ring junction to be planar.

The adoption of the sofa conformation by ring *B* increases the N(1)⋯N(16) distance to 3.285 (7) Å.

Details concerning the deviations of the atoms from selected least-squares planes, and asymmetry parameters (Duax & Norton, 1975) describing the conformations of the rings are given in Tables 5 and 6.

The geometry of the remaining part of the cation is nearly the same as in the multiflorine cation (I) (Pyżalska *et al.*, 1980). Ring *C* is observed as a slightly distorted chair. The mode of distortion is identical to that for (I) and involves loss of the rotation symmetry,  $\Delta C_2^{7,17} = 10.8^\circ$ , with retention of the orthogonal mirror plane,  $\Delta C_5^8 = 1.1^\circ$ , showing the flattening at N(16). The asymmetry parameters for ring *D* define it as an ideal chair. The *C/D* ring junction has the *cis* configuration.

Conformational data for sparteine perchlorate (Borowiak, Bokii & Struchkov, 1973), multiflorine perchlorate hemihydrate (I) (Pyżalska *et al.*, 1980)

Table 5. Weighted mean planes

Plane (1): ring <i>A</i> [N(1),C(2),C(3),C(4),C(5),C(6),O]
$-0.6516x - 0.5080y - 0.5634z + 8.4284 = 0, \chi^2 = 12.41$
Plane (2): [N(1),C(2),C(3),C(4),C(5),C(6),O,C(7),C(9),C(10)]
$-0.6572x - 0.5030y - 0.5614z + 8.3999 = 0, \chi^2 = 61.26$

Atom	Deviation (Å) from plane (1)	Deviation (Å) from plane (2)
N(1)	0.007 (5)	0.022 (5)
C(2)	0.001 (7)	0.006 (7)
C(3)	-0.009 (7)	-0.013 (7)
C(4)	-0.012 (7)	-0.014 (7)
C(5)	-0.008 (7)	-0.000 (7)
C(6)	-0.001 (6)	0.015 (6)
O	0.011 (5)	-0.000 (5)
C(7)		0.006 (6)
C(9)		-0.032 (7)
C(10)		0.011 (7)

Table 6. Asymmetry parameters ( $^\circ$ )

Ring <i>B</i>	Ring <i>D</i>	Ring <i>C</i>
$\Delta C_5^1 = 2.9$	$\Delta C_2^{13} = 1.4$	$\Delta C_5^8 = 1.1$
$\Delta C_2^{1,6} = 30.6$	$\Delta C_2^{11,16} = 2.1$	$\Delta C_2^{8,9} = 5.0$
$\Delta C_2^{6,7} = 65.3$	$\Delta C_2^{11,12} = 6.1$	$\Delta C_2^{7,17} = 10.8$

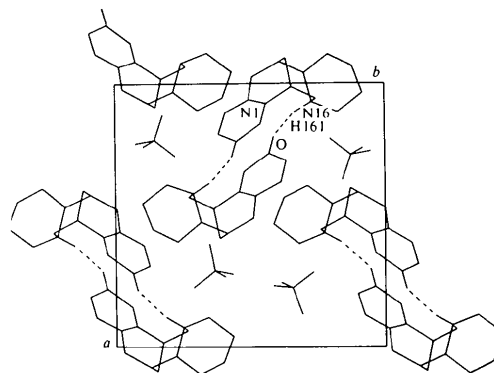


Fig. 2. Projection of the structure on to the (001) plane.

and dehydromultiflorine perchlorate (II) provide details of the molecular changes dependent upon structural modifications in ring *A*. They allow one to observe that even profound structural changes in the *A/B* alkaloid fragment are not transmitted to the *C/D* part.

A view of the packing along the *c* axis is presented in Fig. 2. The crystal structure consists of infinite hydrogen-bonded chains of cations located along the *c* screw axes (coil formation). Each cation of the chain is linked to two others, forming the following hydrogen bonds: N(16)<sup>+</sup>–H(161)⋯O<sup>i</sup> and O⋯H(161<sup>ii</sup>)–N(16<sup>ii</sup>)<sup>+</sup>, where the symmetry codes denote (i)  $\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$ , (ii)  $\frac{1}{2} - x, \frac{1}{2} - y, -\frac{1}{2} + z$ . The geometry of this H bond is characterized by N(16)<sup>+</sup>⋯O and H(161)⋯O distances of 2.678 (7) and 1.72 Å, respectively, and by the N(16)<sup>+</sup>–H(161)–O angle of 153.2°.

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