

simultaneously. We have also measured the positions of the *K*-absorption edges of cobalt, manganese and chromium in several compounds in which the valencies are well established. Table 2 shows our measurements of the *K*-absorption edges in the pure metals, in certain compounds and in the spinel. In this Table, the wavelengths of the *K*-absorption edges of the metals as given by Cauchois & Hulubei (1947) are also included for comparison.

It is well known that the position of the *K* absorption limit in a compound depends upon the valence state of the absorbing ion (Kunzl, 1932). From the magnitudes of the shifts for the cations in this spinel, it is seen that the manganese ion is divalent while the remaining ions are trivalent.

The structural properties, such as crystal symmetry, lattice constant and *u* parameter also give some indication about the ion configuration. The cubic symmetry shows that the spinel does not contain any distortive ion (Orgel & Dunitz, 1957) such as Mn^{+3} or Cr^{+2} . The calculated value of the lattice parameter $a = 8.30 \text{ \AA}$, determined by Mikheev's (1955) method for this configuration, taking the values of the ionic radii as given by Sanderson (1966), agrees very well with the observed lattice constant $a = 8.34 \pm 0.02 \text{ \AA}$. Thus from our X-ray crystallographic and spectroscopic studies it can be concluded that this spinel has the structure $Mn^{2+}[Co^{3+}Cr^{3+}O_4]^{-}$.

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References

- CAUCHOIS, Y. & HULUBEI, H. (1947). *Tables de Constantes et Données Numériques*. Paris: Hermann.
- HENRY, N. F. M., LIPSON, H. & WOOSTER, W. A. (1961). *The Interpretation of X-ray Diffraction Photographs*. London: Macmillan.
- KSHIRSAGAR, S. T. & BISWAS, A. B. (1967). *J. Phys. Chem. Solids*, **28**, 1493.
- KULKARNI, D. K. & MANDE, C. (1970). *J. Phys. D: Appl. Phys. Ser. 2*, **3**, 434.
- KUNZL, V. (1932). *Coll. Trav. Chem. Tchecos.* **4**, No. 5, p. 213.
- MANDE, C. & CHETAL, A. R. (1965). *Röntgenspektren und Chemische Bindung*. Leipzig: Physikalisch-Chemisches Institut der Karl-Marx-Universität.
- MANDE, C., KULKARNI, D. K. & CHETAL, A. R. (1969). *J. Phys. D: Appl. Phys., Ser. 2*, **2**, 635.
- MIKHEEV, V. I. (1955). *Dokl. Akad. Nauk SSSR*, **101**, 343.
- ORDEL, L. E. & DUNITZ, J. D. (1957). *J. Phys. Chem. Solids*, **3**, 318.
- SANDERSON, R. T. (1966). *Inorganic Chemistry*. New York: Reinhold.
- UMANSKIY, YA. S. (1961). *Dictionary of X-ray Structure Analysis of Polycrystals*, Moscow: Government Publishers of Physico-Mathematical Literature.

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The Crystal and Molecular Structure of Denudatine*

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The alkaloid denudatine, $C_{22}H_{33}NO_2$, crystallizes in space group $P2_1$ with two molecules per unit cell of dimensions: $a = 14.229 (12)$, $b = 7.296 (10)$, $c = 9.552(7) \text{ \AA}$ and $\beta = 107.64 (4)$, measured at $20^\circ C$. The observed and calculated densities are 1.194 and 1.207 g.cm^{-3} respectively. The intensity measurements were made by the moving-crystal moving-counter technique. The structure was solved by the symbolic addition procedure for non-centrosymmetric crystals. Anisotropic least-squares refinement was concluded with a final *R* value of 0.036 for 2084 observed reflexions. None of the bond distances or angles differ significantly from the expected values, except for one long carbon-carbon bond of 1.576 \AA . The molecules of denudatine are held, through hydrogen bonds, in chains parallel to the *b* axis.

Introduction

Denudatine is an alkaloid which was first isolated by Singh, Singh & Malik (1961) from *Delphinium denudatum*. They found that it had the molecular formula

$C_{21}H_{33}NO_2$, and assigned to it structure (I) (Fig. 1). Recently Götz & Wiesner (1969) repeated the isolation of denudatine and established its molecular formula as $C_{22}H_{33}NO_2$. Investigating its structure by chemical methods they concluded that it could be either (II) or (III), where C(20) could be connected to C(14) or C(7). At this stage it was decided to determine the structure of denudatine by X-ray diffraction. This investigation, first reported in a preliminary communication (Brisse, 1969), revealed that denudatine has structure (IV).

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This structure was solved with no other chemical evidence but the molecular formula.

Experimental

Well developed crystals of denudatine were obtained by slow evaporation of an ethanol solution. The crystals have the shape of elongated prisms whose longest dimension is parallel to the extinction direction. The crystals are monoclinic, space group $P2_1$, since the only systematic absences are for $0k0$ reflexions with k odd. The cell dimensions were determined at $20 \pm 1^\circ\text{C}$ by 2θ measurements of axial reflexions on the Picker diffractometer using $\lambda = 1.54056 \text{ \AA}$ as the wavelength for the $\text{Cu K}\alpha_1$ radiation (Bearden, 1964).

Crystal data

$\text{C}_{22}\text{H}_{33}\text{NO}_2$, F.W. 343.52;
 $a = 14.229(12)$, $b = 7.296(10)$, $c = 9.552(7) \text{ \AA}$;
 $\beta = 107.64(4)^\circ$;
 $V = 945.01 \text{ \AA}^3$; $D_m = 1.194 \text{ g.cm}^{-3}$ (by flotation),
 $D_x = 1.207 \text{ g.cm}^{-3}$;
 space group $P2_1$; $Z = 2$;
 $\mu = 5.59 \text{ cm}^{-1}$ for $\text{Cu K}\alpha$; $F(000) = 310$.

Three-dimensional intensity data were collected with an automatic Picker diffractometer for reflexions with 2θ values $\leq 130^\circ$ and then on the General Electric XRD5 manual diffractometer for $130 < 2\theta \leq 165^\circ$. The measurements were made using a 2° take off angle with $\theta - 2\theta$ scan of width varying between 2° for $0 < 2\theta \leq 40^\circ$ to 4° for $130 < 2\theta \leq 165^\circ$. Backgrounds of 20 seconds were measured at both scan limits. All the intensities were corrected for background and placed on a common scale. A total of 2084 independent reflexions were observed out of 2247 accessible reflexions within the Cu sphere. The unobserved reflexions were given an intensity equal to $\frac{2}{3}$ of the minimum observable intensity. Lorentz and polarization corrections were made but since the crystal is of small dimensions, ($0.12 \times 0.12 \times 0.25 \text{ mm}$), no absorption correction was applied. The X-ray scattering factors were obtained from Cromer & Waber (1965) for C, N, O and from Stewart, Davidson & Simpson (1965) for H.

Structure determination

A set of normalized structure factors $|E|$ was obtained after isotropic temperature factor correction. The statistical averages of the normalized structure factors shown in Table 1 indicate a non-centrosymmetrical distribution in agreement with the space group determination.

Table 1. *Statistical averages of the normalized structure factors*

	Theoretical (Hanic, 1966)	
	Observed Non-centrosymmetric	Centrosymmetric
$\langle E \rangle$	0.873	0.886
$\langle E ^2 - 1 \rangle$	0.790	0.736
$\langle E ^2 \rangle$	1.005	1.000

The phases were determined by the symbolic addition procedure described by Karle & Karle (1963, 1966b). The phases of three linearly independent reflexions with large $|E|$ values, shown in Table 2, were assigned in order to specify the origin. To facilitate the extension of the phase determining formula $\varphi_h \simeq \langle \varphi_k + \varphi_{h-k} \rangle_k$ (Karle & Karle, 1966a), a symbol was given to the phase of reflexion 153. From these four starting phases it was possible to derive fourteen new phases independent of the chosen symbol. These phases, listed in Table 2, were all multiples of $\pi/4$. The introduction of these initially phased reflexions in the tangent formula (Karle & Hauptman, 1956) was sufficient to assign phases to the 245 reflexions with $|E| \geq 1.50$. The E map calculated with the 245 phases, all of them still multiples of $\pi/4$, was confused by the existence of a pseudo mirror plane perpendicular to the y direction.* However, eleven atomic positions were selected which were within bonding distance from each other and were tetrahedrally coordinated. The set of structure factors calculated with the coordinates of the eleven carbon atoms and an overall temperature factor of 3.3 \AA^2 gave an R value of 0.55. Applying the technique developed by Karle (1967) the phases of 71 reflexions with $|E| \geq 1.80$ and for which $|F_c| \geq 0.33|F_o|$, were used as initial phases for a second round with the tangent formula. From the newly refined phases, no longer multiples of $\pi/4$, a second E map was calculated. All of the 25 peaks of relative height greater than 1.8 belonged to the structure. There was no spurious peak of this height and no pseudo-mirror plane.

Table 2. *Initial phases used in the tangent formula and their variations as the structure determination proceeds (expressed in terms of π)*

h	k	l	1	2	3	4	5
2	8	0	1.00	1.06	0.01	0.61	0.50
0	1	1	0.25	0.00	0.08	0.00	0.03
1	0	1	0.00	0.00	0.00	0.00	0.00
7	0	2*	0.00	0.00	0.00	0.00	0.00
9	8	2	1.00	0.98	0.94	0.91	0.82
9	3	3	0.75	0.74	0.79	0.73	0.73
9	7	3	1.75	1.71	1.46	1.44	1.39
10	6	3	0.50	0.00	0.25	0.09	0.11
13	3	3	1.75	1.81	1.97	1.91	1.97
10	1	4*	0.25	0.25	0.25	0.62	0.61
10	3	4	1.75	1.79	1.87	1.80	1.85
9	1	5	1.25	1.20	1.17	1.61	1.22
1	2	7	1.50	1.31	1.19	1.15	1.16
2	1	7	1.25	1.20	1.07	1.04	1.02
3	0	7*	0.00	0.00	0.00	0.00	0.00
8	5	10	0.25	0.94	0.10	0.01	0.02
9	4	10	1.00	1.00	1.19	1.13	1.13

* Origin defining reflexions.

- 1 Initial set of 17 phases, multiples of $\pi/4$, unchanged by the tangent formula refinement.
- 2 Phases derived from an eleven atom partial structure.
- 3 The same after tangent formula refinement.
- 4 Phases before anisotropic temperature refinement.
- 5 Phases at the end of the refinement.

* This was to be expected, since, as pointed out by the referee, no phase had been chosen to specify the enantiomorph.

Table 3. Observed and calculated structure amplitudes (x 10)

Unobserved reflexions are indicated by an X.

Table with multiple columns for Miller indices (h, k, l) and corresponding amplitudes. The table is organized into several groups, with unobserved reflexions marked with an 'X'.

Refinement

Using the coordinates of the 25 non-hydrogen atoms found in the *E* map and an overall temperature factor of 3.31 \AA^2 a structure factor calculation gave an *R* value of 0.33. The refinement of the coordinates was carried out using the block-diagonal least-squares programs of Ahmed, Hall, Pippy & Huber (1966) for the IBM/360 system. The weighting function adopted was $1/w = 1 + [(|F_o| - P_2)/P_1]^2$ and the coefficients P_1 and P_2 were determined, as $15e$ and $9e$ respectively, so that $(\sum w\Delta^2)/n$ remained constant with $|F_o|$.

The oxygen and nitrogen atoms were identified from the behaviour of their temperature factors. After 5 cycles of refinement with independent isotropic temperature factors the agreement index was brought down to 0.16. With new weighting coefficients $P_1 = 16e$ and $P_2 = 7e$ and 4 cycles of anisotropic refinement the *R* value reduced to 0.086. Thirty-one of the thirty-three hydrogen atoms were located from a difference Fourier synthesis calculated at this stage. The two missing hydrogen atoms belonged to the C(22) methyl group and their coordinates were calculated assuming a C-H distance of 1.01 \AA and tetrahedral angles. The

hydrogen atoms were given the isotropic temperature factors of the C atoms to which they are attached. Another 7 cycles of anisotropic refinement for the C, N and O atoms and isotropic for the H atoms gave a final *R* value of 0.036. The average shift to the coordinates was less than 0.5σ .

Observed and calculated structure amplitudes are given in Table 3. The atomic coordinates, the vibrational parameters and their standard deviations are listed in Table 4. The vibrational parameters are the coefficients of the expression $T = \exp -2\pi^2 (U_{11}a^*2h^2 + 2U_{23}b^*c^*kl \dots)$. The coordinates and the isotropic temperature factors for the hydrogen atoms are given in Table 5.

Table 5. *Coordinates, isotropic temperature factors and their estimated standard deviations for the hydrogen atoms*

All coordinates $\times 10^3$. The hydrogen atoms are referred to the C or O atom to which they are attached.

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i>
O(1)	458 (2)	393 (5)	918 (3)	5.4 (7)
O(2)	469 (2)	1087 (5)	856 (3)	4.7 (7)
C(1)	278 (2)	362 (4)	937 (3)	3.6 (5)

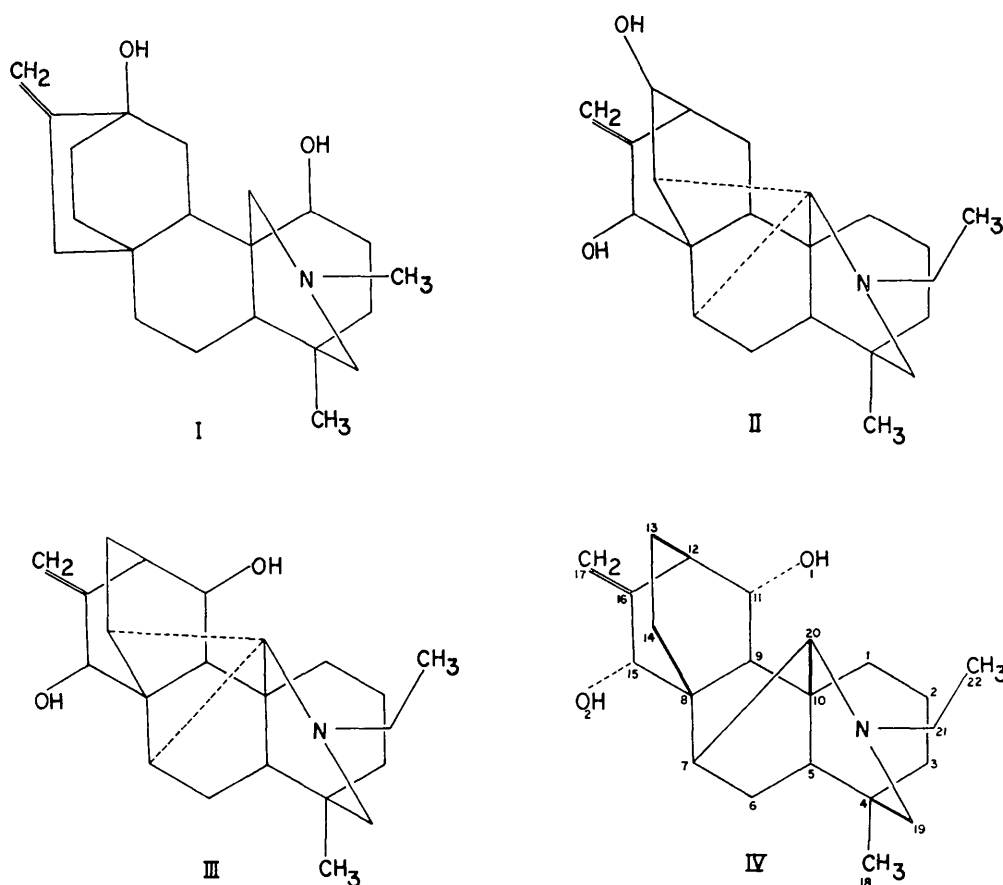


Fig. 1. Proposed and actual structure of denudatine. (I) Model of Singh, Singh & Malik (1961). (II) and (III) Structures proposed by Götz & Wiesner (1969). The broken lines represent possible bonds, not established. (IV) Actual structure and numbering of the atoms of denudatine.

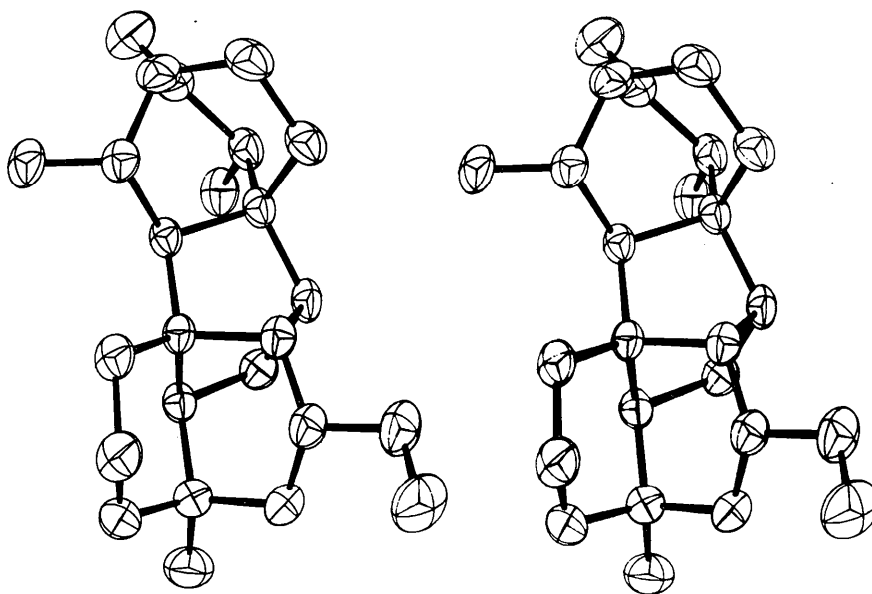


Fig. 2. Stereoscopic pair of drawings showing the structure of denudatine.

Table 5 (cont.)

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i>
C(1)	205 (2)	363 (4)	765 (3)	4.1 (6)
C(2)	69 (2)	443 (4)	830 (3)	4.3 (6)
C(2)	119 (2)	303 (4)	943 (3)	4.3 (6)
C(3)	81 (2)	559 (4)	1075 (3)	3.9 (6)
C(3)	196 (2)	525 (5)	1123 (3)	5.5 (7)
C(5)	314 (2)	722 (3)	1044 (2)	2.1 (4)
C(6)	229 (2)	1035 (3)	914 (2)	2.6 (5)
C(6)	342 (2)	990 (4)	934 (2)	2.6 (5)
C(7)	223 (2)	1014 (3)	662 (2)	1.9 (4)
C(9)	400 (2)	675 (3)	886 (2)	1.8 (4)
C(11)	334 (2)	402 (4)	661 (2)	2.9 (5)
C(12)	503 (2)	464 (4)	627 (3)	3.8 (6)
C(13)	350 (2)	522 (4)	444 (3)	3.5 (5)
C(13)	422 (2)	667 (4)	436 (3)	4.0 (6)
C(14)	241 (2)	711 (4)	485 (2)	2.9 (5)
C(14)	308 (2)	876 (4)	474 (2)	3.0 (5)
C(15)	444 (2)	987 (4)	648 (2)	2.3 (4)
C(17)	644 (2)	644 (5)	765 (3)	5.2 (7)
C(17)	635 (2)	851 (5)	822 (3)	5.2 (7)
C(18)	221 (2)	822 (4)	1214 (3)	5.1 (7)
C(18)	106 (2)	872 (4)	1157 (3)	4.2 (6)
C(18)	179 (2)	1008 (5)	1113 (3)	5.2 (7)
C(19)	73 (2)	961 (4)	875 (3)	2.9 (5)
C(19)	10 (2)	787 (4)	881 (2)	3.0 (5)
C(20)	162 (2)	679 (3)	614 (2)	2.1 (4)
C(21)	23 (2)	823 (4)	509 (3)	4.0 (6)
C(21)	21 (2)	978 (6)	616 (2)	6.3 (8)
C(22)	-108 (3)	661 (7)	602 (4)	9.5 (12)
C(22)	-118 (3)	846 (7)	693 (4)	8.7 (11)
C(22)	-146 (3)	861 (7)	499 (4)	9.6 (11)

Discussion of the structure

The molecular structure of denudatine is represented by Fig. 1 structure IV, and by the pair of stereoscopic drawings in Fig. 2.* This result is in agreement with one of the structures, shown in Fig. 1 structure III,

* The stereoscopic pair of drawings was made with the ORTEP program written by Dr C. K. Johnson.

proposed by Götz & Wiesner (1969) when C(20) is bonded to C(7).

Although this structure is similar to that of the hetisine alkaloids (Przybylska, 1963), a significant dif-

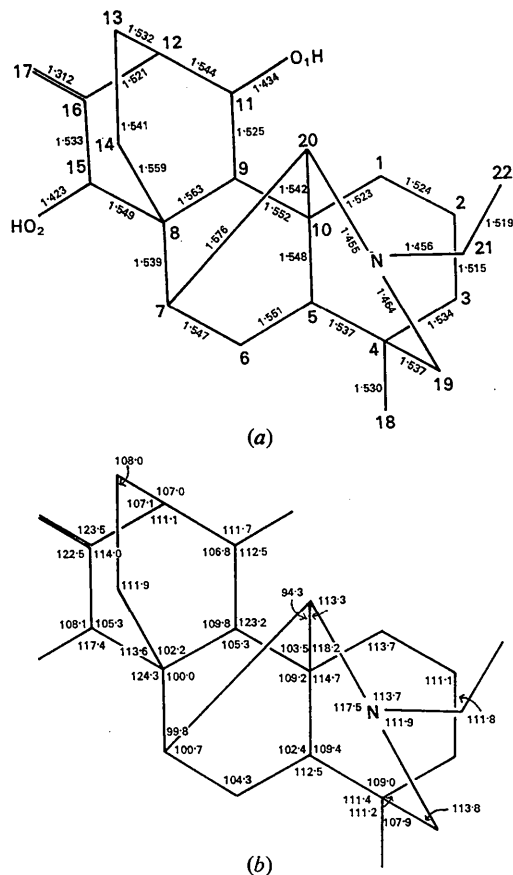


Fig. 3. (a) Bond distances, (b) bond angles.

ference lies in the fact that instead of having a C(20)–C(14) bond, in denudatine the bond is between C(20) and C(7).

Wiesner & Valenta (1958) predicted such a skeleton as one of the possible intermediates in the biogenetic transformation of the atisine skeleton into the skeleton of the aconitine type of alkaloids, and denudatine is the first representative of a new type of skeleton for diterpene alkaloids.

The two hydroxyl groups are attached in equatorial positions to C(11) and C(15). The C(18) methyl group is also in the equatorial position. C(19) and C(20) are bridged through a nitrogen atom to which a C₂H₅ group is attached in the equatorial position.

Bond distances and angles

The interatomic distances and angles between non-hydrogen atoms are summarized in Fig. 3 (a) and (b) respectively. The distances calculated from the final refined coordinates, by the expression of Ahmed & Cruickshank (1953), are not corrected for thermal motion. The estimated standard deviations have been doubled to allow for the block-diagonal approxima-

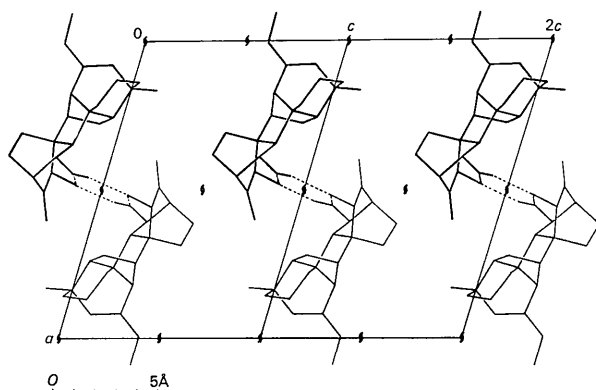


Fig. 4. Molecular packing as seen along the *b* axis. The broken lines indicate hydrogen bonds.

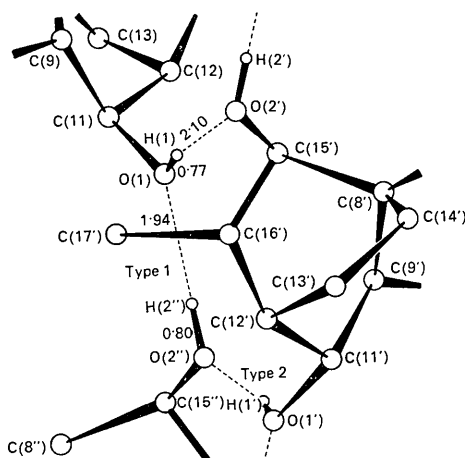


Fig. 5. The two types of hydrogen bonds in denudatine.

tion; they are of the order of 0.008 Å for the distances and about 0.4° for the angles. The average distances in denudatine are compared below with the values given by Sutton (1965).

Bond type	Number	Average distance	Sutton's values
C _{sp} ³ –C _{sp} ³	22	1.540 Å	1.537 Å
C _{sp} ³ –C _{sp} ²	2	1.527	1.506
C _{sp} ² –C _{sp} ²	1	1.312	1.335
C _{sp} ³ –N _{sp} ³	3	1.458	1.472
C _{sp} ³ –OH	2	1.428	1.426

Although the average C_{sp}³–C_{sp}³ distance is quite close to the expected value of 1.537 Å, the C(7)–C(20) bond distance is significantly longer at 1.576 Å. Such long bonds are not uncommon and some examples have been listed in a paper by Birnbaum & Ferguson (1969).

The distances and angles for bonds involving hydrogen atoms have also been calculated. All distances are reasonable, but because they are less reliable only the average and the extreme distances for any bond type are shown below.

Bond type	Number	Average distance	Extreme distances
C _{sp} ³ –H	29	1.00 Å	0.92–1.09 Å
C _{sp} ² –H	2	0.94	0.90–0.98
O–H	2	0.79	0.77–0.80

The estimated standard deviations are in the range 0.02 to 0.03 Å except for C–H bonds in =CH₂ and CH₃ groups where the e.s.d.'s are close to 0.05 Å.

For clarity the values of the following angles were not included in Fig. 3(b).

C(3)–C(4)–C(18) = 108.8, C(5)–C(4)–C(19) = 108.7,
C(6)–C(7)–C(8) = 110.9, C(7)–C(8)–C(14) = 110.2,
C(9)–C(8)–C(15) = 106.9, C(1)–C(10)–C(9) = 114.5
C(5)–C(10)–C(20) = 97.7, C(13)–C(12)–C(16) = 107.0
and C(7)–C(20)–N(1) = 121.1°.

Although the average bond angle is 109.6°, in keeping with the theoretical angle for tetrahedral coordination, the individual angles vary in the range 94.3 to 124.3°. The average angle for the six-membered rings is 108.8°, and it is 100.2° for the five-membered rings in agreement with the value of 99.8° calculated by Sim (1965), although one of the angles, C(7)–C(20)–C(10), is 94.4°. A similar low angle value in bicycloheptane has been reported by Sim. He ascribed this situation to probable eclipsed interactions of the C–H groupings at positions C(5), C(6) and C(9). The distances* H(51)–H(62) and H(51)–H(91) are 2.31 and 2.23 Å respectively.

The average of the bond angles around the nitrogen atom, 114.4°, is halfway between *sp*³ and *sp*² bond angles.

The largest deviation from the mean plane passing through C(12), C(15), C(16), C(17), H(171) and H(172)

* The number of a hydrogen atom is that of the carbon to which it is attached followed by 1, 2 or 3 according to the number of hydrogen atoms on this carbon.

is 0.02 Å and all the angles but C(12)–C(16)–C(15) have values close to the theoretical angle of 120° between sp^2 bonds. This and the distance of 1.312 Å confirm the existence of a double bond between C(16) and C(17).

Packing of the molecules

The molecular packing projected on (001) is shown in Fig. 4. The intermolecular contacts shorter than 4.00 Å, between pairs of non-hydrogen atoms, are listed in Table 6. None of the carbon–carbon or carbon–oxygen intermolecular contacts is shorter than 3.50 Å, but there are two short oxygen–oxygen contacts at about 2.80 Å. These oxygen atoms are involved in hydrogen bonds for convenience designated as type 1 and type 2. These are shown in Fig. 5.

Table 6. Intermolecular contacts shorter than 4.00 Å

From atom	To atom	Position*	Distance
O(1)	O(2)	1, -b	2.748
	O(2)	2, +c	2.866
	C(6)	1, -b	3.983
	C(15)	1, -b	3.536
	C(15)	2, +c	3.975
O(2)	C(9)	2, +c	3.627
	C(11)	2, +c	3.767
	C(11)	1, +b	3.912
C(1)	C(6)	1, -b	3.621
	C(17)	2, +c	3.920
C(3)	C(19)	2, +c	3.826
C(6)	C(17)	2, +b+c	3.794
C(13)	C(17)	2	3.857

* First symbol: Equivalent position 1 (x, y, z)
 2 ($1-x, \frac{1}{2}+y, 1-z$)
 Second symbol: Cell translations.

The molecules in similar positions in the cell are strung together in a direction parallel to the b axis through hydrogen bonds of type 1. Two adjacent strings of molecules are cross linked through hydrogen bonds of type 2 to form a single chain. The molecules of denudatine can thus be imagined as being placed

alternately on the sides of a chain as pinnately compound leaves are arranged on a stem.

I wish to thank Dr K. Wiesner for suggesting this investigation and for providing the crystals of denudatine, and Dr M. Przybylska for her encouragement and comments in reviewing the manuscript of this paper. I am also grateful to Dr C. P. Huber for her help with the computations and to Dr F. R. Ahmed and Mrs M. E. Pippy for the use of their set of programs for the IBM/360 system.

References

- AHMED, F. R. & CRUICKSHANK, D. W. J. (1953). *Acta Cryst.* **6**, 385.
 AHMED, F. R., HALL, S. R., PIPPY, M. E. & HUBER, C. P. (1966). NRC Crystallographic Programs for the IBM/360 System. *World List of Crystallographic Computer Programs*. 2nd ed. Appendix, p. 52.
 BEARDEN, J. A. (1964). *X-ray Wavelengths*. U.S. Atomic Energy Commission, Division of Technical Information Extension, Oak Ridge, Tennessee.
 BIRNBAUM, K. & FERGUSON, G. (1969). *Acta Cryst.* **B25**, 720.
 BRISSE, F. (1969). *Tetrahedron Letters*, **50**, 4369.
 CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **B24**, 337.
 GÖTZ, M. & WIESNER, K. (1969). *Tetrahedron Letters*, **50**, 4369.
 HANIC, F. (1966). *Acta Cryst.* **21**, 332.
 KARLE, I. L. & KARLE, J. (1963). *Acta Cryst.* **17**, 835.
 KARLE, I. L. & KARLE, J. (1966a). *Acta Cryst.* **21**, 860.
 KARLE, J. (1967). *Acta Cryst.* **B24**, 182.
 KARLE, J. & HAUPTMAN, H. (1956). *Acta Cryst.* **9**, 635.
 KARLE, J. & KARLE, I. L. (1966b). *Acta Cryst.* **21**, 849.
 PRZYBYLSKA, M. (1963). *Acta Cryst.* **16**, 871.
 SIM, G. A. (1965). *J. Chem. Soc.* p. 5974.
 SINGH, N., SINGH, A. & MALIK, M. S. (1961). *Chemistry and Industry*, p. 1909.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, N. T. (1965). *J. Chem. Phys.* **42**, 3175.
 SUTTON, L. E. (1965). *Tables of Interatomic Distances and Configuration in Molecules and Ions*. Supplement 1956-1959. London: The Chemical Society.
 WIESNER, K. & VALENTA, Z. (1958). *Progress in the Chemistry of Natural Products*, XVI. Wien: Springer-Verlag.