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The Crystal and Molecular Structure of Platycodigenin Bromolactone

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The crystal structure of the bromolactone of platycodigenin, $C_{30}H_{47}O_7Br$, has been determined in order to elucidate the molecular structure and the absolute configuration of platycodigenin, $C_{30}H_{48}O_7$, one of the sapogenins of *Platycodon grandiflorum* A. DC. The bromolactone of platycodigenin was prepared by the action of Br_2–NaOAc in acetic acid; it crystallized in a structure with space group $P2_1$ and unit-cell dimensions $a=16.81$, $b=7.49$, $c=13.52$ Å, $\beta=103.3°$; $Z=2$. The crystal structure was solved by the heavy-atom method and refined by the method of least squares. The final R value for 2205 observed reflexions was 0.09. The molecular structure of platycodigenin was determined by the present study to be $2\beta,3\beta,16\alpha,23,24$-pentahydroxyolean-12-en-28-oic acid, which is the first example of the naturally occurring triterpenes having geminal hydroxymethyl groups at C(4) of the A ring.

Introduction

Platycodigenin (Fig. 1, II), $C_{30}H_{48}O_7$, (Tsujimoto, 1940) is one of the sapogenins isolated from the roots of *Platycodon grandiflorum* A. DC. Later Kubota & Kitatani (1968) and Akiyama, Tanaka & Shibata (1968) isolated this sapogenin together with polygalacic acid (II) from the same plant. The structure of the latter compound was proposed by Rondest & Polonsky (1963). However, the configuration of the C(16) hydroxy group has recently been revised to α. Structural studies of platycodigenin by chemical and spectral methods have been carried out for several years past. Comparative studies on the corresponding derivatives of platycodigenin and polygalacic acid suggest that platycodigenin can be represented by one of the three possible structures; $2\beta,3\beta,16\alpha,23,24$-; $2\beta,3\beta,16\alpha,23,25$- and $2\beta,3\beta,16\alpha,24,25$-pentahydroxyolean-12-en-28-oic acids (Akiyama, Tanaka & Shibata, 1968).

In order to determine the chemical structure and the stereochemistry of platycodigenin, we carried out an X-ray study of the bromolactone of this substance (III) which showed the molecular structure of platycodigenin, including its absolute configuration, to be (II). A preliminary short note on this work has already been published (Akiyama, Iitaka & Tanaka, 1968).

Experimental

As in the case of the known olean-12-en-28-oic acid type triterpenes, platycodigenin yielded bromolactone (III) by the action of Br_2–NaAc in acetic acid. Crystallization of (III) was tried from various solvents in order to obtain a crystal of a suitable size for X-ray analysis; crystals grown from a mixed solvent of ethyl acetate and benzene were found to be of an appropriate size. They were colourless needles elongated along the b axis. During the refinement of the crystal structure it was found that the crystal contains one equivalent mole of benzene as a solvent of crystallization. The density was measured by the flotation method in a mixture of benzene and carbon tetrachloride. The cell

dimensions and space group were determined from precession photographs with Cu $K\alpha$ radiation.

Crystal data

Bromolactone of platycodigenin benzene solvate,
$C_{30}H_{47}O_7Br \cdot C_6H_6$, m.p. 203–206°, M.W. 677·3

Monoclinic

$a = 16·81 \pm 0·06$, $b = 7·49 \pm 0·02$, $c = 13·52 \pm 0·03$ Å
$\beta = 103·3° \pm 0·2°$.

$U = 1655·5$ Å³;

$D_x = 1·359$ g.cm⁻³, $D_m = 1·364$ g.cm⁻³, $Z = 2$.

$F(000) = 720$.

$\mu(\text{Cu } K\alpha) = 24·4$ cm⁻¹.

Absent reflexions: $0k0$ when k is odd,

Space group: $P2_1$.

The three-dimensional diffraction data were recorded on multiple-film equi-inclination Weissenberg photographs with Cu $K\alpha$ radiation. Layers zero through fifth about the b axis and zero through third about the a axis were photographed. The intensities of several thousands of reflexions were estimated by visual comparison with a standard scale. The reflexions which were too weak to be measured were not included in the present structure determination. The X-ray specimens used for the measurement were small enough to neglect the absorption correction. All the intensity data were corrected for Lorentz and polarization factors but not for

the absorption factor. The structure factors were put on a single scale by correlating those on various layers. A total of 2205 independent structure factors were finally derived. A Wilson plot was made to estimate an approximate scale factor and an overall temperature factor ($B = 2·63$ Å²).

Determination of the structure

The structure was solved by the heavy-atom method. A sharpened Patterson synthesis was computed with the structure factor values corresponding to atoms at rest. From the Harker peak at $(u, \tfrac{1}{2}, w)$ the coordinates of the bromine atom were found to be $x = 0·125$, $y = 0$ (arbitrarily chosen), $z = 0·303$. The structure factors calculated for 2205 reflexions based on the contributions of the bromine atom gave an R value of 0·38.

Fig. 1. Chemical formulae of (I) polygalacic acid, (II) platycodigenin, (III) bromolactone of platycodigenin.

Table 1. *Final atomic fractional coordinates and thermal parameters*

To represent the correct absolute configuration these coordinates should refer to the left-handed coordinate system. The temperature factors are expressed as

$$\exp\{-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{23}kl + 2\beta_{13}hl)\}.$$

A three-dimensional electron-density distribution map, calculated by use of the bromine phase angles and observed amplitudes, showed pseudo-mirror planes on (010) at $y=0$, $\frac{1}{2}$ etc. On this map several peaks were found which were consistent with the well-known skeletal structure of triterpenes. The whole structure

Table 2. *Observed and calculated structure factors*

Table 2 (cont.)

was revealed at the third Fourier synthesis and the R value at this stage was 0·20. The oxygen atoms were identified on this electron density map with the help of chemical and structural considerations.

Refinement of the structure

Refinement of the structural parameters was carried out by the block-matrix least-squares method to an

Table 2 (cont.)

R value of 0·16 in which allowance was made for the anisotropic thermal vibrations of the bromine atom.

The following atomic scattering factors were used for the present structure determination: for bromine, those of Thomas & Umeda (1957); for oxygen and carbon, those of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955).

The absolute configuration of the molecule was determined at this stage by calculating the structure factors for the Friedel's pairs of reflexions, corrected for dispersion.

At the end of the refinement the block-matrix least-squares calculations were carried out with the program *HBLS* of Okaya & Ashida (1967). Six cycles of calculations, on a HITAC-5020E computer, with anisotropic thermal parameters for all atoms gave the R value of 0·09 for 2205 reflexions. The weighting system adopted was:

$$\sqrt{w} = F_o/24 \quad \text{when} \quad F_o \leq 24$$
$$\sqrt{w} = 24/F_o \quad \text{when} \quad F_o > 24 .$$

The final atomic parameters and their standard deviations are given in Table 1. The observed and calculated structure factors are listed in Table 2. A final three-dimensional Fourier synthesis was then calculated; a composite projection of the electron density map is shown in Fig. 2.

Absolute configuration

The X-ray study of the absolute configuration was performed by the anomalous dispersion method (Bijvoet, Peerdeman & van Bommel, 1951). The dispersion corrections to the bromine scattering factor for Cu $K\alpha$ radiation given by Dauben & Templeton (1955) were used. The structure factors for the Friedel's pairs of reflexions were calculated and compared with the observed values by assuming that the atomic parameters are referred to a right-handed set of axes. Seven pairs of reflexions showed remarkable intensity differences in the *l*th layer Weissenberg photographs. The results are shown in Table 3. A comparison between observed and calculated intensities indicated that the assumed configuration was actually the antipode of the true structure. The absolute configuration of platycodigenin itself is established as that shown in Fig. 1(II). All Figures presented in this paper are drawn with the correct absolute configuration.

Table 3. *Comparison of the observed and calculated intensity differences used in the establishment of the absolute configuration*

h k l	$F_c{}^2(hkl)/F_c{}^2(h\bar{k}l)$	$I_o(hkl)/I_o(h\bar{k}l)$
0 1 7	1·254	<1
2 1 5	1·345	<1
2 1 6	1·356	<1
2 1 8	1·219	<1
3 1 0	0·759	>1
$\bar{3}$ 1 1	0·872	?
3 1 3	0·876	?
3 1 5	0·736	>1
3 1 6	0·747	>1

Discussion of the structure

The molecular structure

The molecular structure of the bromolactone of platycodigenin as determined by the present analysis is shown in Fig. 1 (III). The structure of platycodigenin is therefore deduced as shown in Fig. 1 (II). As was supposed by chemical studies, it consists of five six-membered rings forming a well known pentacyclic oleanane-type triterpene. The junctions of the A/B, B/C and C/D rings are in the *trans* form and that between the D and E ring is in the *cis* form.

The bond lengths and angles in the molecule, calculated from the coordinates given in Table 1 are

(a)

(b)

Fig.2. (a) Composite drawing of the final electron density map viewed along the b axis. Contour lines for light atoms are drawn at intervals of 1 e.Å⁻³ starting at 1 e.Å⁻³ and those for bromine are drawn at 2·5 e.Å⁻³ and 25 e.Å⁻³. (b) Molecular structure in the correct absolute configuration.

shown in Figs. 3 and 4. The mean standard deviations of bond lengths and angles calculated for each type of bond are listed in Table 4.

Table 4. *Mean standard deviations of bond lengths and angles*

$\sigma(C-C)$	0·023 Å	$\sigma(C-C-C)$	1·3°
$\sigma(C-O)$	0·018	Benzene molecule	
$\sigma(C-Br)$	0·014	$\sigma(C\text{---}C)$	0·053 Å
$\sigma(C=O)$	0·019	$\sigma(C\text{---}C\text{---}C)$	3·2°

The mean values of the thirty-four C–C single-bond lengths 1·56 Å, that of the seven C–O single bond lengths, 1·46 Å, and that of the six aromatic C–C bonds, 1·36 Å, are in good agreement with the usual values, although some of the bond lengths are too long or too short, in particular the C(2)–C(3) and C(8)–C(14) bonds are found to be 1·46 and 1·67 Å, respectively.

As was discussed by Hall & Maslen (1965), two factors, the degree of substitution at carbon atoms in the bonds and the presence of long range steric strain in the molecule, seem to be responsible for these deviations. In agreement with their results, the long C–C single bonds are seen to be associated with those involving the fully substituted carbon atoms. In the present structure, the atoms C(4), C(8), C(10), C(13), C(14), C(17) and C(20) are the fully substituted carbon atoms and the longest C–C bond, C(8)–C(14) is the one which links two such atoms.

The conformation of the steroid nucleus has been analysed in terms of the least-squares planes and interplanar angles (Cooper, Gopalakrishna & Norton, 1968). In the case of the present structure, the planarity of each ring can be seen in Table 5. It is clear that each of the five rings takes a chair conformation, but the distortion in the A, B, C, and D rings is remarkable. These distortions seem to be caused mainly by the interactions between the bulky axial groups which push each other away in order to release the repulsive forces. As a result of these distortions the 'bowing' of the basic plane is observed. In each of the ring systems involving A, B and C rings and that involving the C and D rings, the basic plane is bent in the opposite direction to the axial groups. The direction of bowing is opposite in these two basic planes since the axial groups in each ring system protrude from the rings in opposite directions. In addition to the repulsive forces between the axial groups the formation of the five-membered lactone ring is also responsible for the bowing of the latter ring system. In a six-membered ring, the non-bonded distances between 1,3-diaxial methyl groups would have been 2·52 Å if the ring took a regular chair form. These distances are here increased to, for example, 3·27 Å [between C(24) and C(25)] as shown in Table 6. Similar distances between the two axial methyl groups are observed, for instance, in labdanolic acid derivatives (3·31 Å) (Bjåmer, Ferguson & Melville, 1968).
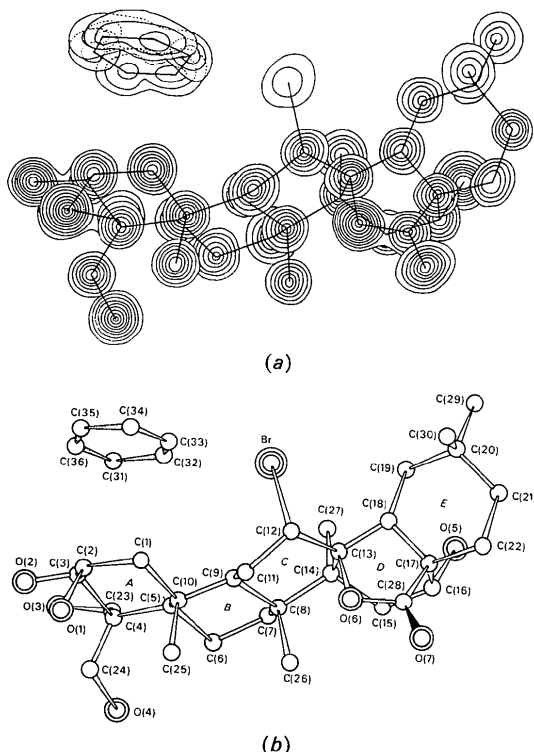
Table 5. *Least-squares planes*

(a) Equations of planes

Equations of the planes are of the form $lX + mY + nZ = p$, where X, Y, Z and p are in Å relative to the orthogonal axes with $X\|a^*$, $Y\|b$ and $Z\|c$.

Plane	Atoms	l	m	n	p
A	C(1), C(2), C(3), C(4), C(5), C(10)	−0·874	0·417	0·249	−3·902
B	C(5), C(6), C(7), C(8), C(9), C(10)	−0·902	0·428	−0·053	−4·440
C	C(8), C(9), C(11), C(12), C(13), C(14)	−0·828	0·488	−0·275	−4·762
D	C(13), C(14), C(15), C(16), C(17), C(18)	−0·776	0·621	0·111	−2·253
E	C(17), C(18), C(19), C(20), C(21), C(22)	0·130	0·977	0·171	1·718

(b) Interplanar angles

Planes	
A/B	163°
B/C	166
C/D	156
D/E	122

(c) Deviations (Å) from the least-squares planes

A ring		B ring		C ring		D ring		E ring	
C(1)	0·179	C(5)	0·280	C(8)	−0·252	C(13)	−0·274	C(17)	0·249
C(2)	−0·200	C(6)	−0·259	C(9)	0·358	C(14)	0·169	C(18)	−0·291
C(3)	0·227	C(7)	0·221	C(11)	−0·322	C(15)	−0·112	C(19)	0·299
C(4)	−0·233	C(8)	−0·213	C(12)	0·212	C(16)	0·174	C(20)	−0·277
C(5)	0·247	C(9)	0·221	C(13)	−0·144	C(17)	−0·260	C(21)	0·255
C(10)	−0·220	C(10)	−0·249	C(14)	0·149	C(18)	0·303	C(22)	−0·235
C(23)	0·570	C(25)	−1·811	C(26)	−1·808	C(27)	1·666	C(28)	−0·482
C(24)	−1·733	C(26)	−1·757	C(27)	1·623	C(28)	−1·653	C(29)	0·481
C(25)	−1·773							C(30)	−1·794

The distortion of the *A* ring is obviously a result of the interaction between the methyl group, C(25), methylene group, C(24) and the hydroxyl group, O(1),
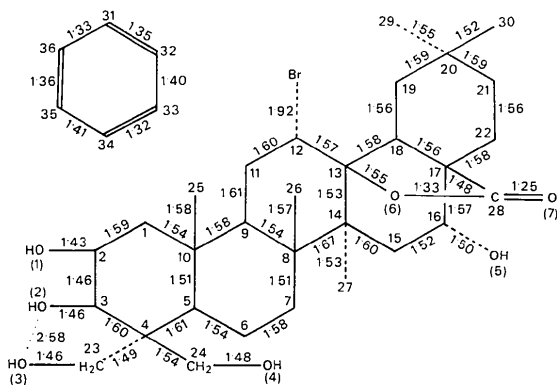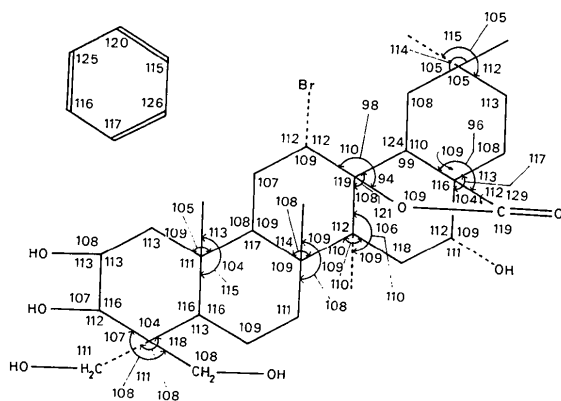

Fig.3. Bond lengths (Å).

Fig.4. Bond angles (°).

Table 6. *Some non-bonded distances between* 1,3-*diaxial groups and the distances between the ring carbon atoms to which the diaxial groups are attached*

Between axial groups		Between ring carbon atoms	
C(24)–C(25)	3·27 Å	C(4)—C(10)	2·65 Å
C(25)–C(26)	3·16	C(8)—C(10)	2·66
C(24)–O(1)	3·05	C(2)—C(4)	2·60
C(25)–O(1)	3·07	C(2)—C(10)	2·61
C(26)–O(1)	2·98	C(8)—C(13)	2·66
C(27)–Br	3·46	C(12)—C(14)	2·67
C(19)–Br	3·55	C(12)—C(18)	2·57
C(27)–O(5)	3·32	C(14)—C(16)	2·68
C(19)–O(5)	3·03	C(16)—C(18)	2·66
C(19)–C(27)	3·27	C(14)—C(18)	2·71

which are attached to the atoms C(10), C(4) and C(2) respectively. The degree of interaction may be estimated by comparing the interatomic distances shown in Table 6. As a result of the steric repulsion of these groups, ring *A* is flattened giving rise to the large angles C(2)–C(3)–C(4), C(4)–C(5)–C(10) and C(5)–C(4)–C(24) of 116, 116 and 118° respectively. A tensile strain between these groups and the distortion from the ideal tetrahedral configuration could be responsible for the lengthening of the bonds C(3)–C(4) and C(4)–C(5) and the shortening of the bond C(2)–C(3).

The distortion of ring *B* may be due to the interaction between the two methyl groups, C(25) and C(26), which would result in the large angles C(10)–C(5)–C(6), C(8)–C(9)–C(10), C(5)–C(10)–C(25) and C(9)–C(8)–C(26).

The distortion of ring *C* is probably caused by the interaction between Br···C(27) and that between C(26)···O(6), which together with the degree of substitution at C(8) and C(14), appear to be responsible

for the lengthening of the bonds involved in ring C. The degree and direction of the steric strain resulting from the repulsions among the overcrowded axial substituents in ring C are difficult to assess but consideration of a Dreiding model of the structure indicates that the strain could account for the long C(9)–C(11) and C(11)–C(12) bonds of about 1·60 Å. This kind of strain and the presence of the five-membered lactone ring would result in the increase in the bond angle C(12)–C(13)–C(14).
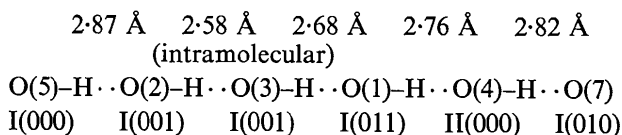
Ring D takes a distorted chair conformation. The distortion is probably caused by the 1,3-diaxial interaction between the hydroxyl group, O(5), the methyl group, C(27) and the methylene group, C(19), and also by the presence of the five-membered lactone ring. As a consequence of this intramolecular overcrowding almost all the *endo*- and *exo*- bond angles of ring D are significantly distorted from the usual tetrahedral angle. The conformation of ring E, on the other hand, is almost of the normal chair form.

The present X-ray analysis revealed the presence of an intramolecular hydrogen bond of 2·58 Å between O(2) and O(3). However, the poor solubility of this substance in suitable solvents makes difficult the observation of the infrared spectrum, which might be useful in discussing the intramolecular hydrogen bonding in solution.

The crystal structure

Figs. 5 and 6 show the projection of the crystal structure along the b and c axes. In these Figures hydrogen bonds are shown by bold broken lines and short intermolecular distances less than 4 Å are shown by dotted lines. The positions of the molecules are: I at x, y, z and II at $1-x, \frac{1}{2}+y, 1-z$, with x, y and z coordinates given in Table 1. The subscript attached to the molecular number indicates a translation along the three edges of the unit cell.

A distinct feature of the crystal structure is the presence of a hydrogen-bond system which connects the molecules in double layers. As shown in Fig. 6, this hydrogen bond system consists of a series of hydrogen bonds such that:

$$2·87 \text{ Å} \quad 2·58 \text{ Å} \quad 2·68 \text{ Å} \quad 2·76 \text{ Å} \quad 2·82 \text{ Å}$$
$$\text{(intramolecular)}$$
$$O(5)–H\cdots O(2)–H\cdots O(3)–H\cdots O(1)–H\cdots O(4)–H\cdots O(7)$$
$$I(000) \quad I(001) \quad I(001) \quad I(011) \quad II(000) \quad I(010)$$

The molecules are bound together through these hydrogen bonds to form a double layer of the following type:

$$\cdots I \cdots I(001) \cdots I(002) \cdots$$
$$\vdots \qquad \vdots \qquad \vdots$$
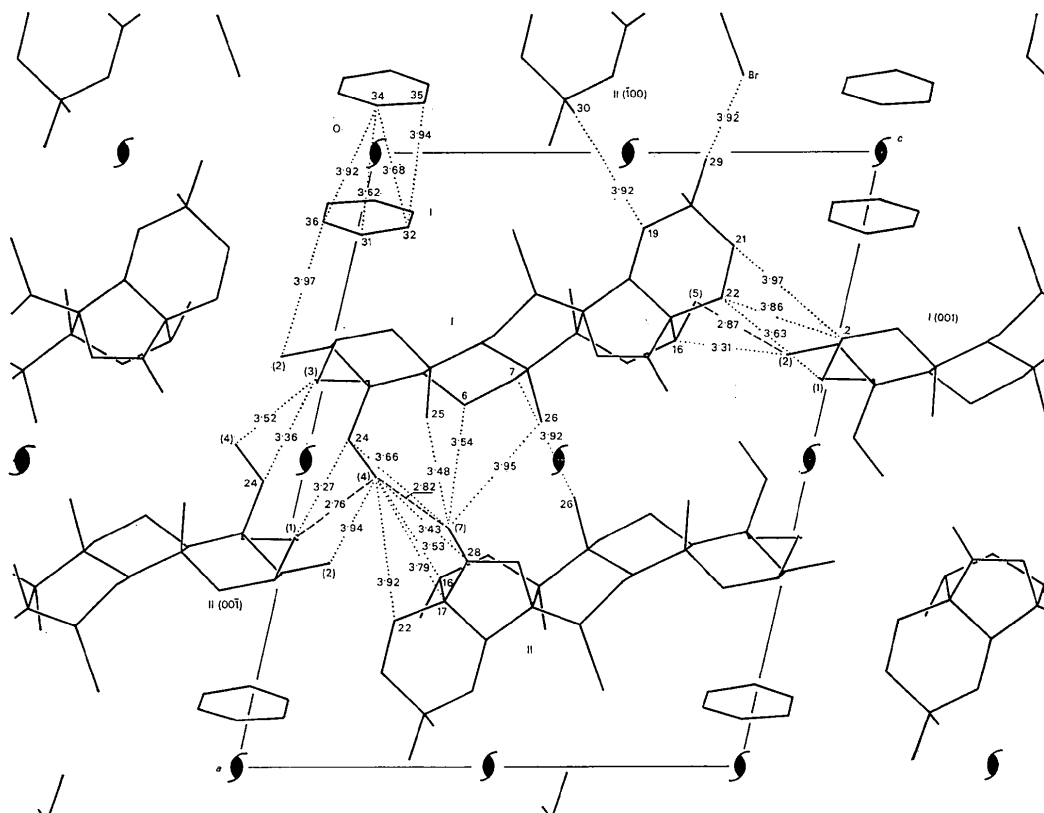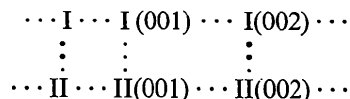$$\cdots II \cdots II(001) \cdots II(002) \cdots$$

Fig. 5. The crystal structure projected along the b axis. To represent the correct absolute configuration the positive direction of the b axis should be upward towards the observer. Intermolecular short distances less than 4·0 Å are shown by dotted lines and hydrogen bonds are shown by broken lines.

Apart from the hydrogen bonds, many close van der Waals contacts are found among the molecules within the double layer. The packing of the double layers, on the other hand, is surprisingly loose. The molecules of the neighbouring double layers are separated by a large distance. Only the shortest contacts between the double layers occur for $Br\cdots C(29)$ (3·92 Å) and $C(30)\cdots C(19)$ (3·92 Å), and large columnar holes are left between the double layers. The holes are filled by the molecules of benzene which plays a role as solvent of crystallization.

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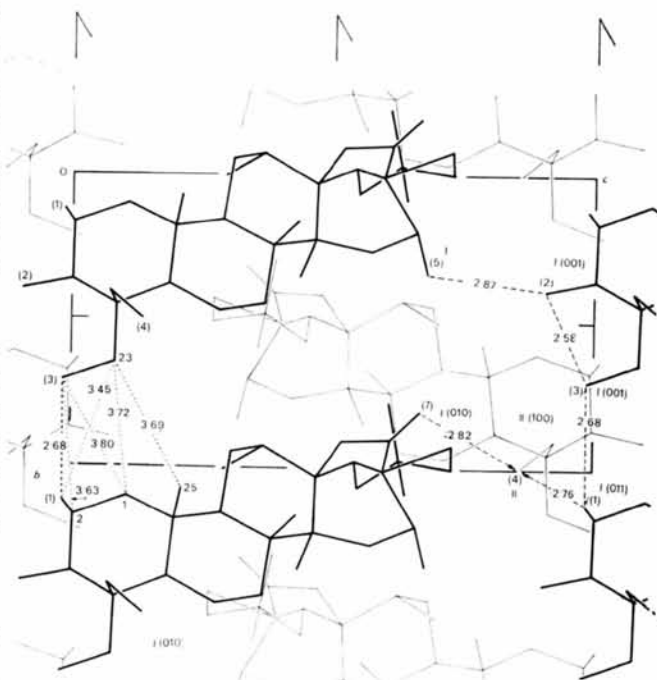

Fig.6. The crystal structure projected along the a axis. To represent the correct absolute configuration the positive direction of the a axis should be downwards away from the observer. Benzene molecules are omitted for the sake of simplicity. Hydrogen bonds are shown by broken lines.

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The Crystal and Molecular Structure of Verticinone Methyl Bromide*

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The structure of verticinone methyl bromide, $C_{27}H_{43}O_3N\cdot CH_3Br$, was solved by the heavy-atom method. Anisotropic least-squares refinement proceeded to a final R value of 0·091 for 2450 observed reflexions. The crystals are monoclinic, space group $P2_1$, with two molecules in a unit cell of dimensions: $a=12\cdot548$, $b=12\cdot046$, $c=9\cdot161$ Å, $\beta=92\cdot07°$. The structure found for verticinone methyl bromide differs from that proposed by Itô for verticinone in that two six-membered rings are *cis*-fused and not *trans*. A configurational inversion at the nitrogen atom probably takes place on formation of the methyl bromide derivative.

Introduction

Verticine is the main alkaloid of *Fritillaria verticillata*

var. *Thumbergii*. As a result of chemical degradation studies Itô, Kato, Shibata & Nozoe (1961, 1963) proposed the structure shown in Fig. 1(*a*). The stereochemistry at positions C(8), C(9), C(12), C(14), C(16) and C(17) was not unequivocally established but was derived by analogy with the steroid series and from biogenetic considerations.