phases colloïdales des amphiphiles, mais conditionne également leur pouvoir d'incorporer de l'hydrocarbure: plus les chaînes sont désordonnées et plus le savon est susceptible d'incorporer d'hydrocarbure. C'est effectivement ce que l'on observe en comparant les phases 'subwaxy' et 'waxy' du savon pur: la phase 'subwaxy', où les chaînes bien que 'liquides' sont nettement plus ordonnées que dans la phase 'waxy' (cf. III), incorpore moins de 5% de tétradécane, cependant que la phase 'waxy' en incorpore presque 50%.

Nous tenons à remercier M. V. Luzzati pour l'intérêt avec lequel il a suivi notre travail et pour ses conseils qui nous ont été d'une aide inestimable à tout moment.

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The Structure of (+)-Des-(oxymethylene)-Lycoctonine Hydriodide Monohydrate

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Crystals of (+)-des-(oxymethylene)-lycoctonine hydriodide monohydrate,

$$C_{18}H_{20}N\,.\,C_2H_5(OH)_2(OCH_3)_4\,.\,HI\,.\,H_2O\ ,$$

are monoclinic, space group $P2_1$ with

$$a=12\cdot79,\ b=9\cdot44,\ c=11\cdot00\ \text{Å};\ \beta=97^\circ\ 45';\ Z=2\ .$$

The x and z coordinates of the iodine atom were derived from a Patterson projection on (010). The structure was solved from a three-dimensional Fourier synthesis based on phases of the iodine-atom contributions, which represented the superposition of the optically active molecule and its centrosymmetrical related image. The determination of the molecular structure has been carried out solely on the expanded empirical formula given above. The coordinates were refined by two-dimensional methods, and one set of three-dimensional structure factors was calculated using all the atomic coordinates except those of hydrogen atoms. The absolute configuration of the dextro-rotatory compound has been determined.

Introduction

The polyoxygenated *Aconitum* and *Delphinium* alkaloids have long resisted attempts by organic chemists to define their skeletons. The chemical work was complicated by the occurrence of rearrangements and abnormal reactions, so that this field appeared to be one in which determination of structure by X-rays could be of great value to the chemist.

The alkaloid, lycoctonine, is of special interest as its derivatives were found in species of both these genera. The chemical investigations of lycoctonine by Edwards & Marion (1952, 1954*a*, 1954*b*) led to the determination of the functional groups and their environment. Numerous transformations were also described by these authors, but since it was difficult on the basis of the chemical evidence alone to arrive at an unambiguous structural proposal, they suggested a detailed X-ray study.

The crystals of lycoctonine hydriodide were found to be unstable, but those of des-(oxymethylene)-lycoctonine hydriodide monohydrate, $C_{24}H_{39}O_6N.HI.H_2O$, were satisfactory. This compound could be prepared from lycoctonine under conditions which were unlikely to lead to rearrangement and it could safely be assumed that it has the original lycoctonine skeleton. A short note giving a photograph of the molecular model of des-(oxymethylene)-lycoctonine was published in 1956 (Przybylska & Marion, 1956). Since then, great progress has been made in the chemistry of lycoctonine and related compounds (Edwards, Marion & Stewart, 1956; Edwards, Marion & Palmer, 1957; Edwards, Los & Marion, 1959) and it has been proved by chemical methods that the same carbon–nitrogen skeleton exists in delpheline (Cookson & Trevett, 1956; Edwards, Marion & Palmer, 1958; Carmack *et al.*, 1958), delphinine (Wiesner, Bickelhaupt *et al.*, 1959) and aconitine (Wiesner, Götz *et al.*, 1959). It appears that it is also probably present in delcosine (Anet & Marion, 1958; Skaric & Marion, 1958). The presence of the same skeleton in demethanolaconinone has also been confirmed by X-ray analysis (Przybylska, 1961).

Two extensive reviews, one concerning the *Delphinium* alkaloids (Marion, 1957), and another the *Aconite–Garrya* alkaloids (Wiesner & Valenta, 1958), survey the development of the chemistry of lycoctonine and some of the above compounds.

Experimental

The authenticated crystals of des-(oxymethylene)-lycoctonine hydriodide monohydrate were kindly provided by Dr O. E. Edwards (1952). They were colourless, m.p. = 173–4 °C., (dec.) when immersed at 140°. The anhydrous compound was found by Dr Edwards to be dextrorotatory.

$$[\alpha]_D^{28} = +6 \pm 2° \text{ (}c\text{, 1·0 in absolute ethanol).}$$

The monohydrate crystallises from a mixture of methanol and acetone in monoclinic prisms, elongated along the *b* axis, with prominently developed pinacoids (100) and (001) and small orthodomes (101). There are two molecules per unit cell, and since the only reflections absent are 0*k*0 when *k* is odd, the space group is $P2_1(C_2^2)$.

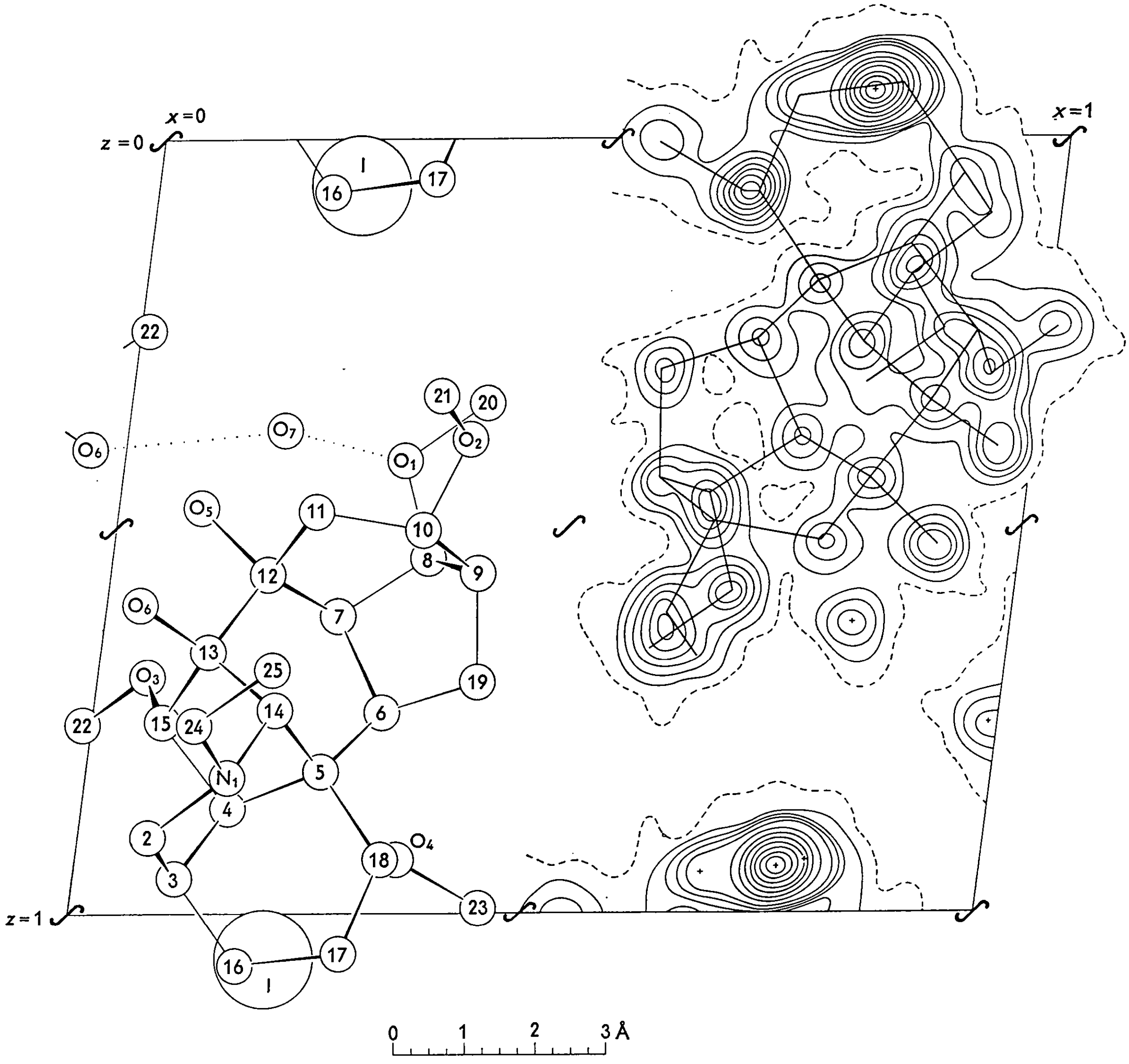

Fig. 1. A projection of the structure of (+)-des-(oxymethylene)-lycoctonine hydriodide monohydrate along the *b* axis. Light atom contours are drawn at intervals of 2 e.Å^{-2}, starting with a broken line at 2 e.Å^{-2}. The iodine atom contours above 10 e.Å^{-2} are at 10 e.Å^{-2}.

The unit-cell dimensions measured from precession photographs are:

$$a=12\cdot79\pm0\cdot03,\ b=9\cdot44\pm0\cdot02,\ c=11\cdot00\pm0\cdot03\ \text{Å};\quad \beta=97^\circ\,45'\pm20'.$$

The calculated density is 1·477 g.cm.$^{-3}$; that measured by flotation using carbon tetrachloride and toluene at 24 °C. was 1·476 g.cm.$^{-3}$. The number of electrons per unit cell, $F(000)$, is 604. The absorption coefficient $\mu=109$ cm.$^{-1}$ (Cu $K\alpha$).

Three-dimensional data were collected from equi-inclination Weissenberg films of $h0l\ldots h7l$, $0kl$ and $hk0$ reflections. The intensities were measured by visual comparison with a graded scale of standard reflections. The total number of reflections observed was 2162; the number theoretically possible with copper radiation is 3190. The crystal used for all levels normal to the b^* axis was roughly of square cross section of mean side 0·15 mm. and absorption corrections were not applied. The intensities were corrected for Lorentz and polarization factors and were put on an approximately absolute scale by the method of Wilson (1942).

Determination of the structure

The Patterson projection on (010) gave the fractional coordinates of the iodine atom. They were found to be: $x=0\cdot225$ and $z=0\cdot064$. The $hk0$ Patterson synthesis confirmed the above value of the x coordinate and the presence of a screw axis, as it showed a marked concentration of peaks along the line $V=0\cdot5$. The y coordinate of the iodine atom was taken as 0·250 and a three-dimensional Fourier synthesis was then computed on FERUT, using the heavy-atom technique. All structure factors of doubtful phases were omitted. The resulting electron-density sections perpendicular to the b axis showed real atoms at 1. x, y, z; 2. $\bar{x}, \frac{1}{2}+y, \bar{z}$; and their mirror-image peaks at 3. $x, \frac{1}{2}-y, z$; 4. $\bar{x}, \bar{y}, \bar{z}$. These are the equivalent positions of the centrosymmetric space group $P2_1/m$ and the atoms 1, 3 and 2, 4 are related by planes of symmetry at $y=\frac{1}{4}$ and $y=\frac{3}{4}$ respectively.

The interpretation of this three-dimensional synthesis, carried out with the help of the (010) Fourier projection, gave the complete skeleton of the molecule. It is shown in Fig. 1, which gives the projection of the structure along the b axis.

The structure was solved only on the basis of the empirical formula $C_{18}H_{20}N.C_2H_5(OH)_2(OCH_3)_4.HI.H_2O$ and no other chemical assumptions were made.

The first F_o-F_c synthesis of the $h0l$ zone was computed, having used for structure-factor calculations the carbon scattering factor for all the light atoms of the molecule. This synthesis indicated clearly which of the light atoms should be taken as oxygen atoms. The ethyl group was thus distinguished from the methoxyl groups and since it has been chemically proved (Edwards & Marion, 1954*b*) to be attached to the nitrogen atom, the latter was indirectly located.

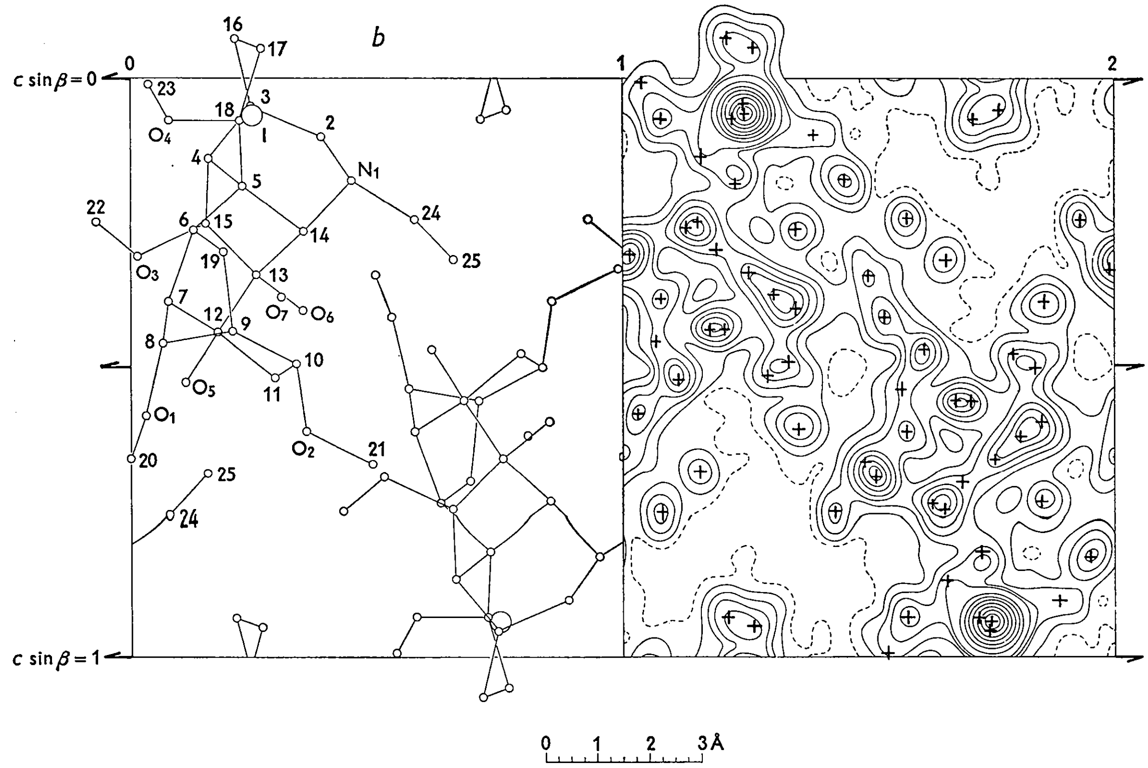

Fig. 2. The structure viewed up the a axis. Contour interval is 2 e.Å^{-2} and for the iodine atom 10 e.Å^{-2}, starting at 10 e.Å^{-2}. The first broken line is at 2 e.Å^{-2}.

The atomic coordinates were then refined by two cycles using simultaneously *h0l*, *0kl* and *hk0* zones. At this stage the *hkl* structure factors were also calculated, and the overall reliability index was found to be 0·24 (omitting the unobserved reflections). The temperature factor for all atoms was taken as 4·5 Å^2. McWeeny's *f*-curves (1951) were employed for the light atoms and that of Thomas & Umeda (1957) was used for the iodine atom.

Two more cycles of refinement using F_o-F_c projections brought the final values of R (including unobserved reflections) to: $R(h0l)=0{\cdot}20$, $R(hk0)=0{\cdot}16$, $R(0kl)=0{\cdot}11$. The contributions made by hydrogen atoms were not taken into account in structure-factor calculations.

Table 1. *Fractional atomic coordinates*

Atom	*x*	*y*	*z*
N_1	0·842	0·452	0·175
C_2	0·921	0·390	0·099
C_3	0·886	0·246	0·045
C_4	0·838	0·160	0·136
C_5	0·740	0·230	0·184
C_6	0·681	0·130	0·260
C_7	0·742	0·077	0·384
C_8	0·651	0·067	0·457
C_9	0·594	0·209	0·439
C_{10}	0·660	0·337	0·495
C_{11}	0·780	0·294	0·518
C_{12}	0·825	0·178	0·438
C_{13}	0·881	0·257	0·339
C_{14}	0·798	0·353	0·263
C_{15}	0·922	0·154	0·249
C_{16}	0·806	0·214	−0·069
C_{17}	0·695	0·266	−0·053
C_{18}	0·662	0·224	0·069
C_{19}	0·580	0·190	0·299
C_{20}	0·607	0·000	0·657
C_{21}	0·659	0·492	0·667
C_{22}	1·009	−0·068	0·245
C_{23}	0·547	0·039	0·006
C_{24}	0·886	0·579	0·244
C_{25}	0·807	0·657	0·316
O_1	0·690	0·032	0·584
O_2	0·621	0·358	0·611
O_3	0·944	0·016	0·306
O_4	0·645	0·080	0·069
O_5	0·907	0·114	0·525
O_6	0·962	0·352	0·400
O_7	0·826	0·807	0·623
I	0·223	0·250	0·061

The electron density derived from (*0kl*) spectra is given in Fig. 2, and the atomic coordinates are listed in Table 1.

Discussion

Reliability of the structure

Since no three-dimensional Fourier synthesis was carried out after the structure had been solved, it may seem that a substantial proof of the correctness of the solution is missing. There are, however, several important features connected with this work which leave no doubt about the reliability of the proposed structure.

(*a*) No difficulty was experienced in interpreting the heavy-atom three-dimensional Fourier synthesis. Only two spurious peaks of lower height than the atoms were observed. They were included in the consideration of structural possibilities, but when a large-size model was made of all the acceptable atoms, it was possible to eliminate them at a comparatively early stage of interpretation. Also the peak electron densities in that synthesis were re-examined after the oxygen and nitrogen atoms were distinguished from carbon atoms by the use of F_o-F_c projections and they were found to agree well with the locations chosen for these heavier atoms.

(*b*) The two-dimensional difference maps did not show any appreciable peaks except those due to the anisotropic thermal motion of the iodine atom. None of the negative peaks on the maps for (*h0l*) and (*hk0*) zones exceeded 1·5 e.Å^{-2} and on the projection along the *a* axis 0·7 e.Å^{-2}. Most of the positive peaks could be accounted for by hydrogen atoms which were not included in structure-factor calculations.

(*c*) The agreement between individual observed and calculated structure factors obtained with the final set of coordinates for the three zones was found to be satisfactory. The same applies to the complete set of *hkl* structure factors calculated with atomic coordinates which were quite close to the finally accepted values.

(*d*) The same carbon–nitrogen skeleton was found independently in demethanolaconinone hydriodide trihydrate (Przybylska, 1961).

(*e*) The plausibility of the molecular structure has been fully demonstrated by the chemical work that followed the publication of the note by Przybylska & Marion (1956).

Absolute configuration

The absolute configuration determination of (+)-des-(oxymethylene)-lycoctonine hydriodide monohydrate was carried out (Przybylska & Marion, 1959) and it was deduced that the skeleton shown in Fig. 1 represents the structure of this compound. By turning this molecule upside down, a formula given in Fig. 3 can be obtained, which emphasizes its diterpenoid character.

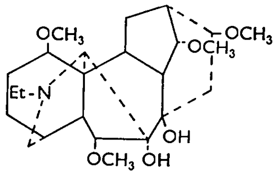

Fig. 3. The diterpenoid representation of (+)-des-(oxymethylene)-lycoctonine.

Description of the molecule

The intramolecular bond lengths and bond angles are shown in Fig. 4. The C–C bonds vary from 1·48 to 1·58 Å with an average of 1·54 Å and the C–O bonds vary from 1·38 to 1·46 with an average of 1·43 Å. Using Cruickshank's formulae (1949, 1950) for centric and acentric zones and $\Delta F = F_o - F_c$, the r.m.s. value of $\sigma(x)$ was found to be about 0·06 Å. This corresponds to a probable error of 0·06 Å in bond length and therefore none of the variations in length within the above two groups of bonds should be taken as significant. The bond lengths are, however, adequately accurate to differentiate between the C–C and C–O bonds and the results obtained confirm well the position of all the oxygen atoms identified by means of electron-density maps.

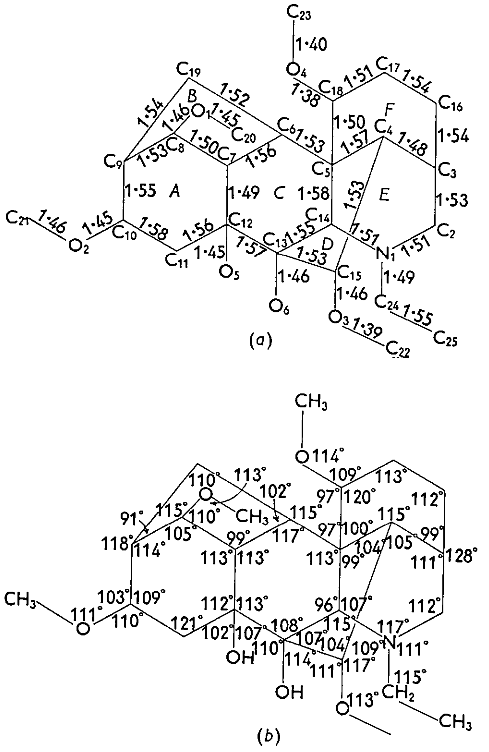

Fig. 4. (*a*) Intramolecular bond lengths, (*b*) angles.

The six-membered ring *A* is boat-shaped but considerably flattened at one end, as the atom C_{11} lies close to the plane of C_7, C_9, C_{10} and C_{12} atoms. By the least-squares method the equation best fitting these four atoms was found and then the distances of C_8 and C_{11} from that plane were calculated. They were found to be +0·78 and +0·35 Å respectively. This distortion, which leads to a considerable increase in the angle $C_{10}C_{11}C_{12}$ from the tetrahedral value is no doubt due to the position of the hydroxyl and methoxyl groups attached to the C_8, C_{10} and C_{12} atoms of that ring. The distances O_1–O_5, O_1–O_2 and O_2–O_5 were found to be 3·04, 3·23 and 4·53 Å respectively. If the ring *A* were of a 'chair' form, then all these distances would be about 2·5 Å, i.e. appreciably smaller than the sum of the van der Waals radii of two oxygen atoms (2·8 Å). In an unflattened 'boat' form, on the other hand, the atoms O_1 and C_{11} would come too close to each other.

The rings *C*, *E* and *F* are in 'chair' form. The distance C_3–C_5 was found to be 2·57 Å, whereas the distances C_5–C_{13} and C_7–C_9 are somewhat shorter, 2·32 and 2·41 Å respectively. This result was expected as the C_3–C_4 and C_4–C_5 bonds are shared by two six-membered rings, whereas C_{14} and C_8 form bridges between six- and five-membered rings. The five-membered rings, *B* and *D* are puckered at C_8 and C_{14}.

The distance between the atoms O_5 and O_6 was found to be 2·77 Å, and that between C_{25} and C_{14}, 2·93 Å.

Intermolecular distances

Of all carbon–carbon intermolecular distances eight are below 4·0 Å, ranging from 3·65 to 3·91 Å. The closest carbon–oxygen contact is between C_{24} and O_5, which was found to be 3·43 Å. All other C · · · O approaches are above 3·80 Å. All O · · · O distances are above 3·0 Å and are in accordance with normal packing considerations except the distances of the oxygen atom of the molecule of water of crystallization to O_1 of one molecule and O_6 of another, which are shown in Fig. 1. They were found to be 2·74 and 2·79 Å respectively. The examination of $(F_o - F_c)$ synthesis for the $h0l$ zone reveals peaks of 0·6 e.Å^{-2} and 0·9 e.Å^{-2} at distances which indicate the presence of O_7–H · · · O_1 and O_6–H · · · O_7 hydrogen bonds. The angles C_{20}–O_1–O_7, C_8–O_1–O_7, O_1–O_7–O_6 and O_7–O_6–C_{13} were calculated and they vary from 104° to 120°.

The closest iodine ion to the nitrogen atom lies at a distance of 3·84 Å. All contacts of the iodine atom with carbon atoms are greater than 4·15 Å, which is the sum of the radii of I^- and CH_2 group, except with C_{24} and C_{21} of neighboring molecules, which were found to be 3·81 and 3·99 Å respectively. The I^-–O_7 distance is 3·65 Å, whereas all other I to O approach distances are above 3·9 Å.

I wish to express my indebtedness to Dr Léo Marion for enabling me to carry out this investigation and for his support and helpful discussions, and to Dr O. E. Edwards for his unfailing encouragement and for the authenticated crystalline material. I wish to thank Dr W. H. Barnes for his continued interest in this work, and Dr F. R. Ahmed for computational assistance. An acknowledgment is made to Mr C. N. Hellyer for computing some of the structure factors and to Mrs I. R. Hilchey for her help in computing some of the Fourier syntheses.

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The Structure of (+)-Demethanolaconinone Hydriodide Trihydrate

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(*Received* 7 *April* 1960)

The space group of (+)-demethanolaconinone hydriodide trihydrate,

$$C_{19}H_{17}N.C_2H_5(OH)_4.O.(OCH_3)_3.HI.3\,H_2O$$

is $P2_12_12_1$, the unit-cell dimensions are

$$a=14\cdot69,\ b=22\cdot08,\ c=8\cdot33\ \text{Å};\ Z=4\ .$$

The coordinates of the iodine atom were found by means of two-dimensional Patterson syntheses and ϱ_0 maps were obtained for the three projections using the heavy-atom technique. The structure was solved only on the basis of the above empirical formula from a three-dimensional Patterson synthesis interpreted by vector convergence method. The coordinates were refined by two-dimensional methods and one three-dimensional differential synthesis. The carbon–nitrogen skeleton was found to be the same as in the case of des-(oxymethylene)-lycoctonine. The absolute configuration of the (+)-isomer has been determined.

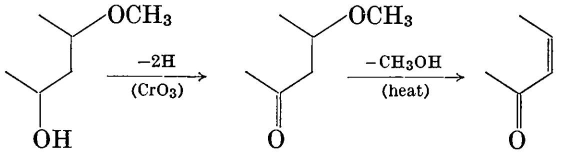
Introduction

Aconitine is the most readily accessible and important alkaloid of the Aconitum class. The chemical studies on aconitine reported before 1900 have been fully reviewed by Schulze (1906), and those covering the first half of the 20th century by Stern (1954).

When this investigation was undertaken the ring structure of aconitine was unknown. Although Schneider (1956) suggested that aconitine possesses the same carbon–nitrogen skeleton as that derived for lycoctonine from an X-ray analysis of des-(oxymethylene) lycoctonine hydriodide (Przybylska & Marion, 1956), no chemical evidence of this postulate was forthcoming until 1959. It was certain, however, that it contains three hydroxyls, four methoxyl groups, an acetate, a benzoate and an ethyl group attached to the nitrogen atom.

The examination of crystals and determination of space groups of aconitine hydriodide, aconine hydriodide, benzoylaconine hydriodide and demethanolaconinone hydriodide showed that the last compound is the most suitable for a detailed analysis.

Aconitine is oxidised by chromic acid to the ketone aconitinone, which very readily loses one methoxyl group which is eliminated as methanol and gives rise to aconitoline.



Aconitine Aconitinone Aconitoline