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Preliminary examination of the crystal structures of colchiceine and its copper salt.

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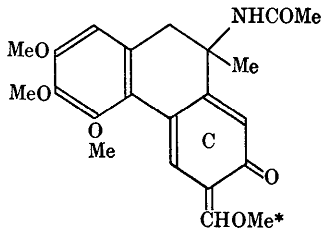
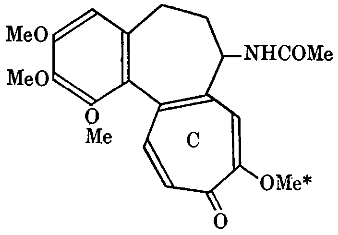
The structure of the alkaloid colchiceine is of considerable interest, and a great deal of attention has been given to the determination of its constitution by organic chemical methods (Loudon, 1948).

The structure assigned by Windaus (I) in 1924 has now been discarded in favour of (II) or a closely related structure.



(I)



(II)

For structure analytical work by X-ray methods, the most hopeful line of approach is by the study of colchiceine, in which the starred methyl group in (I) and (II) has been replaced by a hydrogen atom, the remainder of the structure being assumed to remain unchanged. Colchiceine is acidic in properties, and forms salts with a number of metals, the most favourable for X-ray work being that with copper.

The crystal data for colchiceine and its copper salt were determined by rotation and moving-film photographs about the principal axes, and are as follows:

Colchiceine

Pale yellow needles, triclinic $P1$ or $P\bar{1}$.

$a = 8{\cdot}23 \pm 0{\cdot}01,\quad b = 8{\cdot}36 \pm 0{\cdot}01,\quad c = 16{\cdot}93 \pm 0{\cdot}04$ A.

$\alpha = 90^\circ\, 52',\quad \beta = 93^\circ\, 52',\quad \gamma = 118^\circ\, 48'$.

These values confirm those obtained earlier by Abrahams (1948).

Volume of unit cell = 1014 A.^{3}. $D = 1{\cdot}24$ g.cm.$^{-3}$.
Molecular weight $C_{21}H_{23}O_6N = 385{\cdot}2$.
Number of molecules per cell = 2.

Copper colchiceine

Almost opaque bluish green octahedra, tetragonal $P4_12_1$

$a = 13{\cdot}85 \pm 0{\cdot}05,\quad c = 52{\cdot}23 \pm 0{\cdot}15$ A.

Volume of unit cell = 10193 A.^{3}. $D = 1{\cdot}32$ g.cm.$^{-3}$.
Molecular weight $(C_{21}H_{22}O_6N)_2 . Cu . 6H_2O = 949{\cdot}4$.
Number of colchiceine molecules per cell = 16.
Asymmetric unit is $Cu . 2(C_{21}H_{22}O_6N) . 6H_2O$.

Weissenberg series were taken of the $h0l$ zone, 175 planes being recorded. A Patterson synthesis was carried out on these intensities, and although the percentage of the metal in the compound is small (7 % by weight) it proved possible to determine the positions of the copper atoms in the structure (Fig. 1).

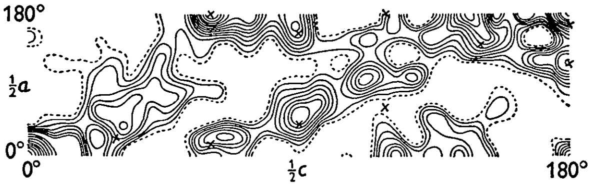


Fig. 1. Patterson projection of ($h0l$) zone of copper colchiceine. The calculated vector positions are marked with crosses.

A Fourier synthesis of the $h0l$ terms was now carried out, using phases calculated on the basis of the copper atom alone. The resulting projection, which gives the x, y and z co-ordinates, enabled the positions of the copper atoms to be located more accurately, and also showed some detail of the surrounding molecular structure. Four peaks surrounding the copper atom were coplanar with it, with bond lengths as in Fig. 2. These peaks were assumed to be due to oxygen atoms, and the structure factors were recalculated.

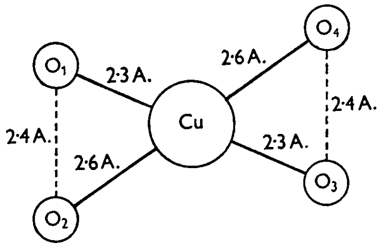
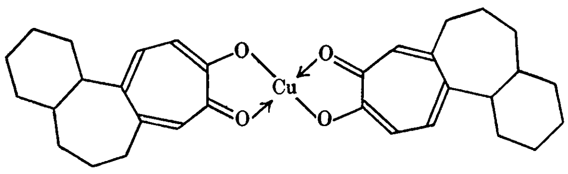


Fig. 2. Copper–oxygen distances.

The final projection is shown in Fig. 3, in which some of the organic ring structure appears. There are other peaks above and below the plane of the oxygen atoms, at about 2·9 A. from the central copper atom and forming a distorted octahedral arrangement somewhat similar to that observed in other copper compounds (Beevers & Lipson, 1934; Wells, 1947, 1949). It seems probable that the planar oxygen atoms are the salt-forming groups attached to the organic molecules, which adds some weight to the structure (II) for colchiceine, in which two molecules of the asymmetric unit could be expected to chelate with the copper atom, additional stabilisation being conferred on the aromatic seven-membered rings:



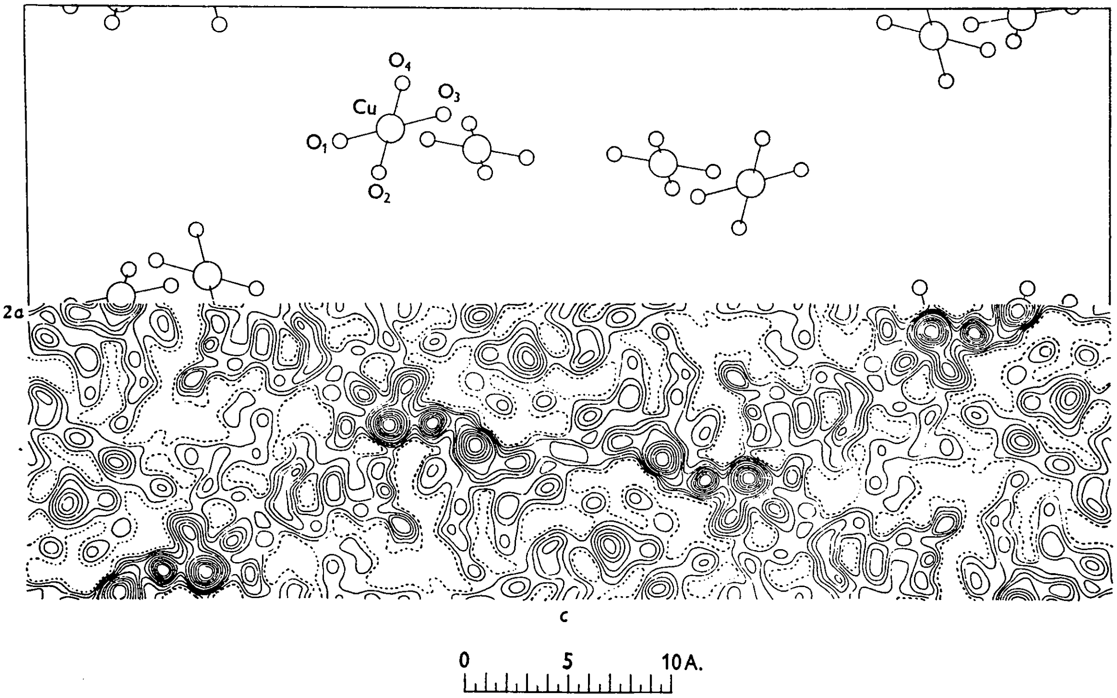


Fig. 3. Projection on (010) showing two unit cells. Contours are drawn at intervals of approximately 1 e.A.$^{-2}$, except at the copper atoms, where every second line is omitted. The lowest contour drawn is the three-electron line, shown dotted.

The peaks above and below the plane of the oxygen may be due to two molecules of the water of crystallization, the remaining four water molecules being presumably at general positions in the lattice.

Further work is in progress on this structure by the methods of trial and error.

I would like to express my thanks to Prof. J. W. Cook, F.R.S., and Dr J. D. Loudon for the crystals employed and for helpful discussion of the organic data, and to Prof. J. M. Robertson, F.R.S., for his advice and help with the crystallographic aspects of the problem.

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Étude par diffraction électronique de la transformation ordre–désordre de l'alliage $AuCu_3$.

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Dans l'application des méthodes de diffraction à l'étude de la structure des alliages métalliques, l'utilisation des cristaux uniques donne des renseignements plus détaillés sur la constitution de l'espace réciproque que celle des poudres cristallines. Pour étudier par diffraction électronique les alliages examinés jusqu'ici sous forme microcristalline (Eisenhut & Kaupp, 1931; Germer, Haworth & Lander, 1942; Boettcher, 1942) nous avons cherché à obtenir des monocristaux assez minces pour donner des diagrammes électroniques par transmission. Nous y sommes parvenus par vaporisation des alliages dans le vide et ensuite condensation de la vapeur sur une face clivée de sel gemme chauffé.

Parmi les nombreux problèmes qui pourront être étudiés grâce à cette technique, nous avons d'abord entrepris l'examen de la transformation ordre–désordre dans l'alliage $AuCu_3$. Par vaporisation d'un alliage de cette composition et sa condensation sur la face (100) de NaCl chauffée à 380–400° C. on obtient des monocristaux d'une épaisseur de quelques centaines d'angstroms. La mesure de leur distance réticulaire ($3{,}73_2$ A.) montre que le monocristal a conservé la composition de l'alliage de départ. Le traitement thermique de tels cristaux donne les résultats suivants. Le diagramme d'un monocristal $AuCu_3$, chauffé au-dessus de 500° C. pendant une demi-heure et trempé, montre en dehors des interférences ordinaires (*hkl* de même parité) des taches faibles et diffuses, centrées sur les nœuds de surstructure du réseau $AuCu_3$ ordonné. Un revenu d'une heure entre 100 et 200° C. augmente légèrement l'intensité de ces taches de surstructure. Au-dessus de 200° C., elles prennent une forme spéciale: des croix pour les taches d'indice *hk*0 avec *h* et *k* impairs, des taches allongées quand *h* ou *k* est pair. La Fig. 1 (*a*) montre la direction de l'allongement