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The unit-cell dimensions and space group of rauwolscane.

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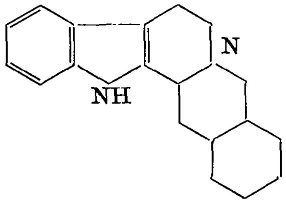
Rauwolscine (Chatterjee, 1953) $C_{21}H_{26}O_3N_2$, m.p. 232° C., is the only alkaloid of *Rauwolfia Canescence* Linn of the Bengal variety. It has been isolated from an alcoholic percolate of the air-dried leaves. Rauwolscine crystallizes from alcohol in thick colourless plates. On applying the Huang-Minlon variant of the Wolff-Kishner reduction, Rauwolscine yields a hydrocarbon rauwolscane, $C_{19}H_{24}N_2$, m.p. 156–157° C.:



This was purified through its hydrochloride. The substance crystallizes from methanol in stout white rods. After several recrystallizations from the same solvent, chromatic purification, and drying over P_2O_5 at 85° C. at a pressure of 0·01 mm. Hg, the pure substance was obtained.

Single crystals suitable for X-ray investigation were prepared by slow evaporation of a solution in acetone at a low temperature. Rauwolscane was found to crystallize in transparent quadrangular plates with one molecule of acetone of crystallization. The reflexion spots recorded in all photographs taken with transparent single crystals begin to disappear, and diffraction lines as in powder photographs are observed, as soon as the crystal loses its acetone of crystallization and transforms into an opaque mass. It may thus be inferred that the acetone of crystallization forms an integral part of the crystalline structure of the substance. Consequently the crystal selected for X-ray investigation was covered with a thin coating of collodion.

Morphological and goniometric studies, carried out by reflection goniometer, showed the crystal to be orthorhombic (Ray, 1955). The crystals were elongated parallel to [100] and were bounded by faces of the forms {100}, {010}, {001} (large), {101} and {011}. The axial ratios calculated from the goniometric measurements were found to agree fairly well with those derived from the X-ray measurements.

Optical properties

Studies under a polarizing microscope, using monochromatic light, showed that rauwolscane is an optically negative orthorhombic crystal. The *a*, *b* and *c* crystallographic directions were found to coincide with the *X*, *Y* and *Z* optical directions respectively:

$$\alpha = 1\cdot490,\quad \beta = 1\cdot616,\quad \gamma = 1\cdot650\,.$$

The optic axial angle, measured on the Federov universal stage, is $V_Z = 64°$; and hence $2V_X = 52°$.

Unit-cell dimensions and space group

Oscillation, rotation, and normal and equi-inclination Weissenberg photographs were taken, using copper radiation filtered through a nickel foil of proper thickness. The cell dimensions were found to be

$$a = 7\cdot1,\quad b = 12\cdot2,\quad c = 23\cdot4\ \text{Å}\,.$$

A higher degree of accuracy is not claimed, since no allowance was made for film shrinkage.

The measured density of the sample was 1·13 g.cm.$^{-3}$ and the calculated density, corresponding to four molecules in the unit-cell, was 1·14 g.cm.$^{-3}$.

The reflexions appearing on the *a*-, *b*- and *c*-axis zero-layer Weissenberg photographs and also on the first and second layer photographs on the *a*-axis taken by the equi-inclination method show the following systematic absences:

hkl, 0*kl*, *h*0*l*, *hk*0: none;
*h*00, 0*k*0, 00*l*: when *h*, *k* and *l*, respectively, are odd.

These conditions indicate the space group $P2_12_12_1$, and packing considerations were found to agree with the assumed space group.

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Systematic absences corresponding to false symmetry.

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The presence in a crystal of screw axes or glide planes is accompanied by certain systematic absences in the X-ray reflections. It is recognized that special arrangements of atoms can cause weak reflections which may be mistaken for systematic absences, especially in the cases of screw axes where the number of relevant reflections observed may be quite small.

There exists, furthermore, a kind of special arrangement, of which an unlimited number of examples can be constructed, in which the absences will be indeed systematic but without the corresponding symmetry. Consider the atoms divided into two or more sets. The members of the first set have positions related, for example, by a set of glide planes. The members of the second set have positions related by a set of glide planes parallel with but not coincident with the first set. Similar statements apply to the other atomic sets, if any. None of these 'glide planes' is a property of the total assembly, because none operates properly on all the atoms. The structure factor of the crystal is, however, zero for reflections corresponding to absences for such a glide plane, and thus the intensity data would suggest the presence of the glide plane. This follows from the fact that for appropriate *hkl* each set has zero structure factor, and the total structure factor is a vector sum of the set structure factors. For the absences to be perfect, of course, the electron density of each set must correspond to the 'glide planes', as it will if the atoms are spherical.

Similar examples can be constructed in obvious ways for screw axes, for combinations of screw axes and glide planes, or for combinations of non-primitive translations with screw axes and glide planes. Any extinction rule common to the 'symmetries' of the sets will be obeyed by the total assembly.

Consider four pairs of atoms in space group $P2_1$, in positions x, y, z; $\bar{x}, \frac{1}{2}+y, \bar{z}$ with x, y, z, respectively:

$$\begin{array}{l} m, n, p \\ m, t-n, \frac{1}{2}+p \\ q, r, s \\ q, u-r, \frac{1}{2}+s\,. \end{array}$$

The first two pairs considered alone have symmetry $P2_1/c$ with a center of symmetry at $(0, \frac{1}{4}+\frac{1}{2}t, \frac{1}{4})$. Similarly the last two pairs have a center at $(0, \frac{1}{4}+\frac{1}{2}u, \frac{1}{4})$. But, if t and u are unequal (mod 1), the complete assembly has no center of symmetry though the absences correspond to $P2_1/c$.

This kind of arrangement is rare or perhaps even nonexistent in Nature. But it is not unreasonable that it could occur in substitution or defect structures with large unit cells which are based on simple substructures. Such statements as 'The systematic absences prove that the space group is $P2_1/c$', of which I have been guilty as have others, are to be deplored. It does not seem to be unreasonable to say that the space group is determined only when a structure is found which is in satisfactory agreement with the data. We should remember that *probable space group* means just that.

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Sur quelques composés du type M_2O_3-Cu_2O.

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La structure du composé Fe_2O_3–Cu_2O est connue depuis longtemps (Soller & Thomson, 1935): rhomboèdrique, groupe d'espace $R\bar{3}m$–D_{3d}^5, Cu en (0, 0, 0), Fe en $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, 2 O en $\pm(\frac{1}{9}, \frac{1}{9}, \frac{1}{9})$. Confirmation en a été donnée par Pabst (1946*a*, *b*). Nous-mêmes avons précisé (Delorme & Bertaut, 1953) par un calcul d'énergie électrostatique que la formule la plus probable était $Fe^{+++}Cu^{+}O_2^{--}$.

D'autres composés isomorphes ont déjà été signalés: Co_2O_3–Cu_2O (Bertaut & Delorme, 1954) et Cr_2O_3–Cu_2O (Stroupe, 1949); pour ce dernier l'auteur ne donne pas le groupe d'espace.

Nous avons pu en obtenir un nouveau: Al_2O_3–Cu_2O par décomposition et chauffage à 1200° C. à l'air d'un mélange de nitrates d'aluminium et de cuivre.

Le Tableau 1 rassemble les divers résultats.

Pour Cr_2O_3–Cu_2O à la suite d'une étude paramagnétique effectuée avec R. Benoît nous avons obtenu une droite correcte de Curie–Weiss d'où l'on déduit la constante de Curie moléculaire $C_m = 1{,}74$, un moment effectif de $3{,}74\mu_B$ et une température de Curie paramagnétique de $-178°$ K. Ce résultat confirme l'hypothèse de la formule $Cr_2^{+++}Cu_2^{+}O_4^{--}$, attribuant le moment théorique de $3{,}87\mu_B$ à l'ion Cr^{+++}.

Je remercie M. Bertaut, maître de recherches, pour ses conseils au cours de cette étude.

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Tableau 1

Composé	Paramètres: Notation hexagonale	Paramètres: Notation rhomboèdrique	Distance M–O (Å)	Rayon ionique M^{+++} (Å)	Distance Cu–O (Å)
Fe_2O_3–Cu_2O	$a = 3{,}03$, $c = 17{,}09$ Å	$a = 5{,}96$ Å, $\alpha = 29° 26'$	1,99	0,67	1,90
Co_2O_3–Cu_2O	$a = 2{,}85$, $c = 17{,}16$ Å	$a = 5{,}95$ Å, $\alpha = 27° 42'$	1,90	0,58	1,90
Cr_2O_3–Cu_2O	$a = 2{,}97$, $c = 17{,}07$ Å	$a = 5{,}94$ Å, $\alpha = 29°$	1,96	0,64	1,90
Al_2O_3–Cu_2O	$a = 2{,}86$, $c = 16{,}94$ Å	$a = 5{,}88$ Å, $\alpha = 28° 8'$	1,90	0,58	1,88