X-Ray Structure and Absolute Configuration of (—)-Pseudocopsinine

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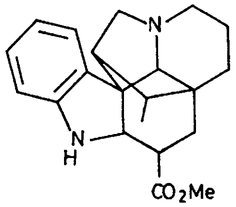
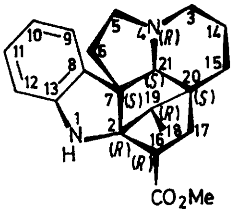
Summary The structure and molecular configuration of the alkaloid pseudocopsinine has been established unequivocally by an *X*-ray diffraction study of its hydrobromide; this is the first determination of absolute stereochemistry in this group of indole alkaloids.

THE alkaloid (—)-pseudocopsinine was first isolated from *Vinca erecta* Rgl. et Schmalh.[1] To establish its structure and absolute configuration we have undertaken a complete *X*-ray study of its hydrobromide $C_{21}H_{26}N_2O_2$, HBr, H_2O.



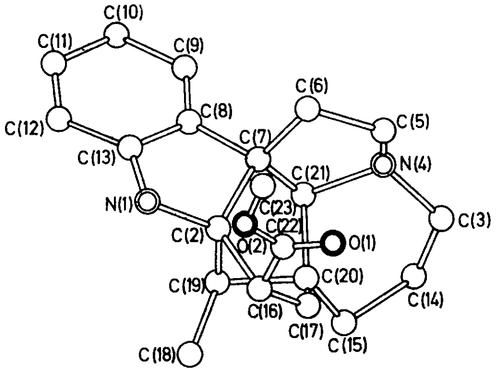
(I)



(II)

Crystal data. Orthorhombic, space group $P2_12_12_1$, $a = 9{\cdot}777(6)$, $b = 16{\cdot}056(8)$, $c = 12{\cdot}714(6)$ Å, $V = 1996$ Å^3, $M = 437{\cdot}4$, $D_m = 1{\cdot}46$, $D_c = 1{\cdot}46$ g cm^{-3} for $Z = 4$. Intensities of 3160 independent reflections with $|F|^2 \geqslant 3\sigma(|F|^2)$ were measured by an automatic Hilger-Watts diffractometer (Cu-K_α radiation, graphite monochromator, ω-scan, ordinate analysis, no absorption correction). The structure was solved by the heavy-atom technique and refined by the anisotropic least-squares procedure to $R = 0{\cdot}058$. The absolute configuration was determined by 24 Friedel pairs[2] using the programme in ref 3.

The present study has shown that pseudocopsinine has the structure (II) which differs from (I) proposed earlier.[1] The skeleton formula (II) was established by the ^{13}C n.m.r. study of vindolinine.[4] The absolute configuration is 2*R*, 4*R*, 7*S*, 16*R*, 19*R*, 20*S*, 21*S*.



The configuration of molecular fragments determined by torsional angles is as follows: benzene ring A planar, pyrrolidine rings B and F envelope, 5-membered ring ,C (2,7,21,20,19) a half-chair, 5-membered ring D (2,16,17,20,19) an envelope, cyclohexane ring E (2,16,17,20,21,7) a boat, pyrrolidine ring F an envelope, piperidine ring G a twist-boat. Fusion of cycles: B/C-*trans*, C/F-*cis*, C/G-*trans*, F/G-*cis*. The bond lengths and angles have usual values.

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