Crystal Structure of two Quasi-Racemates of (−)-Podopetaline and (−)-Ormosanine isolated from *Podopetalum ormondii*; the Absolute Configuration of (−)-Ormosanine

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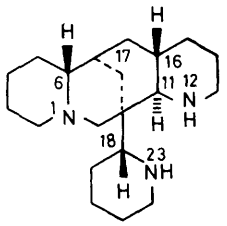
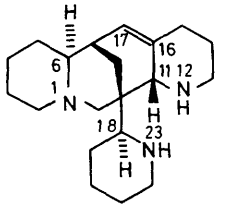
Summary A constant m.p. alkaloid fraction obtained from *Podopetalum ormondii* has been shown by *X*-ray analysis to contain two polymorphs, one monoclinic, the other triclinic, both being quasi-racemates of (−)-podopetaline and (−)-ormosanine.

THE ormosia alkaloids[1] form a group of bases related to the $C_{20}H_{35}N_3$ alkaloid ormosanine (**1**). *X*-Ray analysis[2] of a derivative of (±)-ormosanine provided the key to the structures of alkaloids of this series, many of which are simply diastereoisomers of ormosanine, and most of their complexity arises from stereochemical features. Both racemic and optically active forms of some alkaloids have been found and a particular plant may produce some racemic alkaloids and some that are optically active;[3] there are therefore obvious points of interest concerning their biosynthesis.



(1)



(2)

The structure and absolute configuration of (−)-podopetaline (**2**), isolated from *P. ormondii*, has also been determined by *X*-ray analysis of the hydrobromide.[4] Podopetaline, $C_{20}H_{33}N_3$, exhibits one of the few structural variations found in these alkaloids, a 16,17 double bond. Podopetaline is formally 16,17-dehydro-ormosanine and a member of the second set of diastereoisomers. We have isolated another diastereoisomer, 6-epipodopetaline, from the same extract, and reported on its structure.[5] This extract afforded another fraction, m.p. 160—161 °C (constant after repeated crystallizations), which was recognised by g.l.c.–m.s. analysis to contain both $C_{20}H_{35}N_3$ and $C_{20}H_{33}N_3$ components. Separation of these was effected through the derivatives they form with formaldehyde; these were identified as the derivatives of (−)-ormosanine [*i.e.* (−)-jamine][6] and (−)-podopetaline.

The material with m.p. 160—161 °C, recrystallized from acetone, was of considerable crystallographic interest and was obtained largely as triplets, two outer triclinic (*t*) crystals flanking a monoclinic (*m*) crystal. Initial attempts to separate all three were not successful although a *t*+*m* twin was cleaved and *X*-ray data were collected from it. However, many of the *t* and *m* reflections overlap and the structure of neither component could be solved. At a second attempt, an *m* crystal, virtually uncontaminated with *t*, was obtained. The data did not yield to direct methods alone but the structure was eventually solved.†

Crystal data: monoclinic, space group $P2_1$, $a = 10{\cdot}418$, $b = 19{\cdot}634$, $c = 18{\cdot}685$ Å, $\beta = 104{\cdot}51°$, D_c (four molecules each of $C_{20}H_{35}N_3$ and of $C_{20}H_{33}N_3$) = 1·14 g cm^{-3}. Out of 6128 reflections measured by automatic diffractometry using Cu-K_α radiation 4319 with $I > 2\sigma(I)$ were considered significant. After structure solution, refinement with

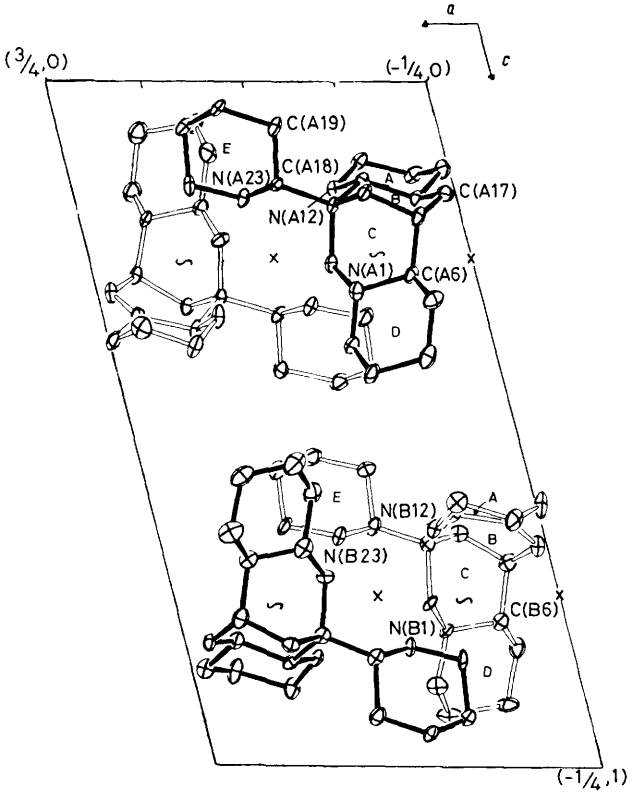


FIGURE. Crystal structure in *y*-projection. The choice of origin is non-standard for $P2_1$. Only the four non-equivalent molecules are shown because of overlapping in this projection. Dark molecules: (−)-ormosanine; light: (−)-podopetaline. There are eight pseudo-centres of one type per cell (four pairs with $(x,z) = (\pm\frac{1}{4}, \pm\frac{1}{4})$ overlapping in projection) indicated by ×. A further eight (not shown) relate each of the molecules in the Figure to screw-related versions of the others.

† Full details will be published elsewhere.

hydrogen atoms in fixed positions ($B = 6$ Å^2) gave a conventional R factor of 0 085 ‡

Four crystallographically independent molecules are shown in y-projection in the Figure Despite being of opposite chirality, there is a marked similarity in the stereochemistry of the (−)-podopetaline and (−)-ormosanine molecules The effect of the double bond in the former is to give ring B a sofa rather than a chair conformation The presence of crystal pseudo-centres of symmetry should be noted

From the known absolute configuration of (−)-podopetaline (**2**) the absolute configuration of (−)-ormosanine can be given as (**1**)

Solution of the m structure permitted proper allowance to be made for overlapping reflections from the $t+m$ twin and led to solution of the t form This also has four molecules of each of the two alkaloids per cell packed differently

We thus have the case of a single plant producing two closely related alkaloids with opposite configurations The co-existence of two enzymatic pathways of opposite chirality seems unlikely, perhaps racemic ormosanine is formed first and the dextrorotatory component is stereospecifically oxidised to (−)-podopetaline

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‡ The atomic co ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd , Cambridge CB2 1EW Any request should be accompanied by the full literature citation for this communication

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