

### THE ABSOLUTE CONFIGURATION OF DIOSCORINE

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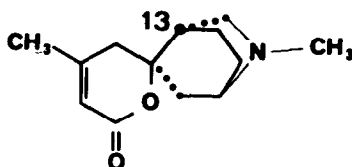
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The structure, I, has been established for dioscorine by chemical means (1) and by X-ray structure analysis (2). The structure analysis has shown that the five atoms of the lactone grouping, C-CO-O-C, are coplanar (3) and that the carbon-carbon double bond of the lactone ring lies at an angle to this plane. The  $\alpha\beta$  - unsaturated lactone system is, thus, a dissymmetric chromophore.

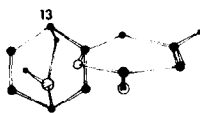


I

Possible absolute configurations for the molecule form two enantiomeric pairs, in which the tertiary carbon atom, numbered 13 in I, is either pseudo-axial or pseudo-equatorial to the lactone ring. The helical sense of the  $\alpha\beta$  - unsaturated lactone chromophore is directly related to this feature of the molecule, as shown in II - V. It has been established (4-6) for such ene-lactones that the sign of the CD associated with the lowest energy absorption band depends on helical sense, as designated for II - V.



In the CD spectrum of dioscorine, 0.001M in water, positive dichroism was detectable from 270m $\mu$ , with  $\Delta\epsilon_{\text{max}} = +1.6 \pm 0.2$  at 225-230m $\mu$ . Dioscorine hydrochloride, 0.0001M in water had  $\Delta\epsilon_{\text{max}} = +2.5 \pm 0.5$  at 225-230m $\mu$ . The predominant conformers of dioscorine and its hydrochloride in the solutions studied must therefore, be either III or IV. C-13 is pseudo-equatorial and pseudo-axial, respectively, in III and IV. The structure analysis (2) has shown that C-13 is pseudo-equatorial in the crystal. If we assume that this conformation persists as the predominant one in dioscorine and its hydrochloride in aqueous solution, then IV is eliminated and the absolute configuration of dioscorine is VI.



VI

## References

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