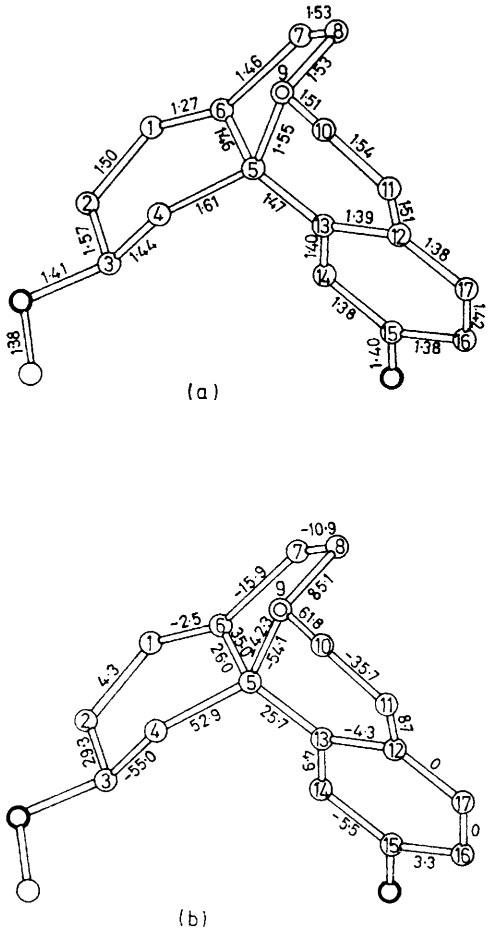
X-Ray Crystallographic Determination of the Structure and Absolute Configuration of the Alkaloids Cocculine and Cocculidine

By Radzhab Razakov and Sabir Yu. Yunusov
(*Institute of Phytochemistry, Uzbek Academy of Sciences, Tashkent, USSR*)

and Said-Murat Nasyrov, Anatol N. Chekhlov, Valentine G. Andrianov*, and Yuri T. Struchkov
(*Institute of Organo-Element Compounds, USSR Academy of Sciences, Moscow*)

Summary The structure and molecular configuration of the alkaloids cocculine and cocculidine has been established unequivocally by spectral and *X*-ray crystallographic data.



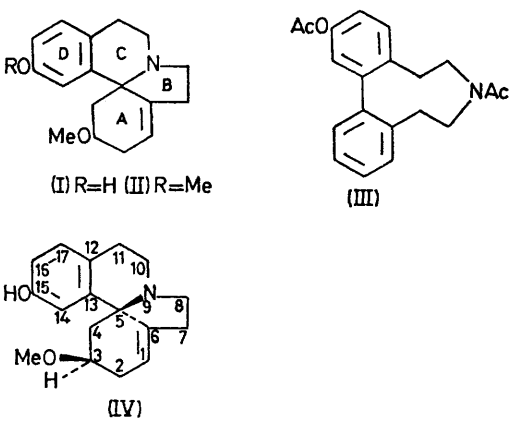
FIGURE

(a) Bond lengths. (b) Torsion angles.

COCCULINE and cocculidine, first isolated[1] from *Cocculus laurifolius* D.C., were assigned[2] structures (I) and **(II)**, respectively, by us, but others[3] gave them different structures. We now provide information confirming structures (I) and (II) and establishing their stereochemical configuration.

The spiro-structure of (I), and also of (II), was shown by the formation of the *NO*-diacetyl derivative (III) with Ac$_2$O. The spectral data for (III) are in agreement with the structure assigned. The ^{1}H n.m.r. spectra of (I) and (II) show that they are related to the *cis*-series of $\Delta^{1(6)}$-erythrina alkaloids.[4]

Compounds (I) and (II) give smooth positive o.r.d. curves with a small Cotton effect at 285 and 295 nm. The same pattern of o.r.d.-curves was found[5] for model erythrina alkaloids with the 3*R*,5*S*- configuration.[6]



(I) R=H (II) R=Me

(III)

(IV)

SCHEME

We undertook also a complete *X*-ray study of the hydro, bromide of (I) C$_{17}$H$_{21}$NO$_2$,HBr, triclinic, a = 8·839(9)-b = 7·400(8), c = 7·115(8) Å, α = 80·98(5), β = 109·44(6), γ = 112·23(6)°, D_m = 1·45 g cm^{-3} for Z = 1, space group *P*1, Hilger-Watts diffractometer, Mo-K_α, *ca.* 1400 non-zero independent reflections. The structure was solved by the heavy-atom technique and refined by the isotropic least-squares procedure. At the present stage of refinement R = 0·15. The absolute 3*R*,5*S*-configuration (IV) was established by the Bijvoet method[7] on the basis of 120 Friedel pairs and is in full accord with o.r.d. data. The molecular geometry found is shown in the Figure. The conformation of molecular fragments determined by torsional angles is as follows: ring A an envelope ^4E, B a half-chair $^9T_5$, C a half-chair $^{10}H_9$, D a planar benzene ring.

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