Tetrahedron Letters No. 15, pp. 1219-1220, 1970. Pergamon Press. Printed in Great Britain.

LOROQUIN, A NEW NECINE ISOLATED FROM URECHITES KARWINSKY MUELLER

(1-HYDROXY-METHYLENE-7-KETO-DIHYDROPYRROLIZINE)

J. Borges del Castillo [+] and A.G. España de Aguirre
Departamento de Química, Universidad de El Salvador

J.L. Bretón, A.G. González and J. Trujillo
Departamento de Química Orgánica, Universidad de La Laguna.
Instituto de Investigaciones Químicas de Tenerife. C.S.I.C.
Canary Islands, Spain.

(Received in UK 17 February 1970; accepted for publication 26 February 1970)

The flowers of Urechites karwinsky Mueller (Apocynaceae) (1,2,3), popularly called loroco, are widely used as condiments in Salvadorian food; the roots, however, have toxic properties and are employed in the country for killing small animals. The tests for alkaloids were positive for the roots only.

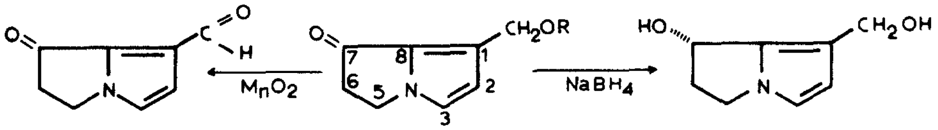
The ethanolic extract, obtained by maceration of the roots at room temperature, was acidified with 1N HCl to pH 2, filtrated and alkalified with 1N NH_4OH. Extraction with EtOAc yielded a syrup which was chromatographed on neutral alumina (activity II-III). We thus obtained three alkaloids, two of them in very small quantity. The third and most abundant one, not yet found in nature, which we propose to name loroquin (Ia), $C_8H_9NO_2$, m.p. 77-78° (cyclohexane), M^+ 151, λ_{max}^{EtOH} 289 nm (ε 2500), is quite stable in solid state. It possesses a free hydroxyl group as shown by the IR band at 3400 cm^{-1} (KBr) and by the formation of a monoacetate (Ib), m.p. 67-69° (i-propyl ether). The absorption at 1650 cm^{-1} indicates the presence of a conjugated keto group and the bands at 3100, 1560, 1490, 1460 and 820 cm^{-1} that of an aromatic skeleton, probably of pyrrole type.

Its NMR spectrum has the characteristic low field doublets at τ 3·06 and 3·66 (J = 3 Hz) of an α,β-disubstituted pyrrole. Two clean triplets at τ 5·70 (2H) and 6·95 (2H) (J = 6 Hz) are assigned to $\rangle N-(CH_2)_2-C{\lessgtr}^{O}$. A doublet at τ 5·26 (2H) coupled with a triplet at τ 6·30 (1H, J = 6 Hz) provides further

---

[+] Present address: Facultad de Ciencias, Universidad Autónoma, Casa de Campo, Madrid.

evidence for the primary nature of the hydroxyl group. By exchange with D_2O the signal at τ 6·30 disappears and the doublet collapses to a singlet at the same position.



III Ia, R=H Ib, R=Ac II

By reduction with $NaBH_4$ in water loroquin affords the diol II,whose chromatographic data and NMR spectrum are identical with those of 1-hydroxy-methylene-7α-hydroxy-dihydropyrrolizine prepared by Culvenor et al. (4). Oxidation of Ia with MnO_2 (5) gives the aldehyde III, m.p. 95-97°, IR (KBr) 1710, 1670, 1555, 1500 cm^{-1}, NMR τ-0·5 ($-C^{\nearrow O}_{\searrow H}$), also identical with the aldehyde obtained by the above cited authors (4).

The analyses of the compounds mentioned were satisfactory. M.ps were determined on a Kofler block and are uncorrected. The NMR spectra were recorded on a PE mod. R-10 (60 MHz) in $CDCl_3$ with TMS as internal standard.

The authors are indebted to Dres. C.C.J. Culvenor and J.A. Edgar, CSIRO, Melbourne, for a sample of 1-hydroxy-methylene-7α-hydroxy-dihydropyrrolizine and for valuable advice. They also wish to thank Prof. Dr. Fabio Castillo Figueroa, ex-rector of the University of El Salvador, for financial help.

REFERENCES

(1) S. Calderón & C. Stanley, Lista preliminar de las plantas del Salvador, Ediciones de la Universidad del Salvador, 2nd ed., 1941, p. 225.

(2) F.D. Godman & O. Salvin, eds., Biologia Centrali Americana, or Contributions to the Knowledgement of the Fauna and Flora of Mexico and Central America, London, vol. I-II, p. 1879-1915.

(3) A preliminary communication on the isolation of loroquin was presented at the VII Central American Congress of Pharmacy and Biochemistry, San Salvador (El Salvador), in November 1967.

(4) C.C.J. Culvenor, J.A. Edgar, L.W. Smith & H.J. Tweeddale, Tetrahedron Letters, 3599 (1969).

(5) J. Attenburrow, A.F.B. Camerón, J.H. Chapman, R.M. Evans, B.A. Hems, A.B.H. Jansen & T. Walker, J. Chem. Soc. 1952, 1094.