Tetrahedron Letters No. 56, pp. 4975-4978, 1969. Pergamon Press. Printed in Great Britain.

STUDIES ON THE GENUS PIPER - IX.STRUCTURE OF TRICHOSTACHINE, AN ALKALOID FROM PIPER TRICHOSTACHYON*

Jagdev Singh, K. L. Dhar and C. K. Atal
Regional Research Laboratory,
Jammu-Tawi (India).

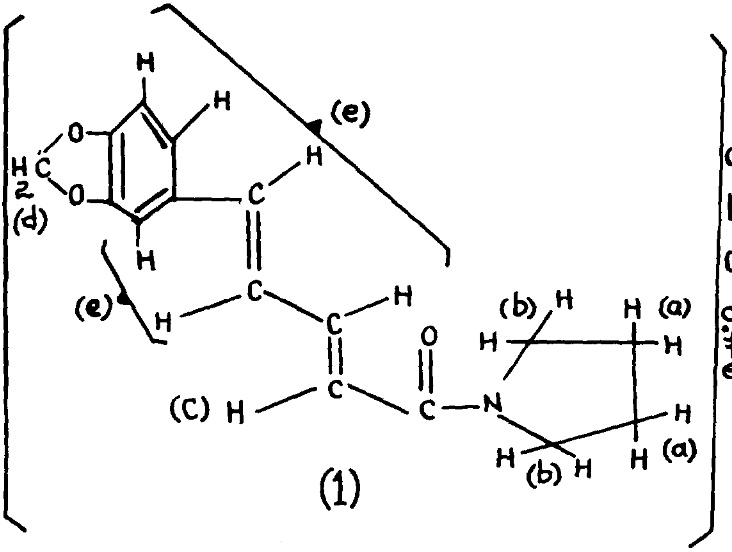
(Received in UK 25 October 1969; accepted for publication 11 November 1969)

Recently the presence of a new alkaloid peepuloidin[I], a pyrrolidine amide of 2, 3-dimethoxy, 4, 5-methylene-dioxy cinnamic acid has been reported from P. peepuloides. In the present investigation we wish to report the isolation and structure elucidation of a new alkaloid trichostachine.

Petroleum ether extract of the air dried coarsely powdered leaves on concentration deposited a crystalline material which on recrystallisation with ethyl acetate/petroleum ether gave white crystalline needles, m. p. 142-43°. More of trichostachine was obtained (total yield; 0. 029%) on elution of the concentrated mother liquor with chloroform over neutral alumina. It responded to the test for unsaturation and the Labat test for methylenedioxyaryl group.

Trichostachine analysed for $C_{16}H_{17}NO_3$, M^+, 271, UV, λ_{max}^{MeOH}, 345, 307, 268 mμ exhibits a chromophoric system similar to piperine. The I. R. spectrum exhibits the principal peaks at 1592 cm^{-1} & 1635 cm^{-1} (extended α - β - unsaturated amide), 1255 cm^{-1} 1035 cm^{-1} & 925 cm^{-1} (Methylenedioxy aryl) and 1610 cm^{-1} (trans configuration of olefinic double bond).

The NMR spectrum ($CDCl_3$) was consistent with structure 1 and the positions of all the protons are according to the expectations.



(1)

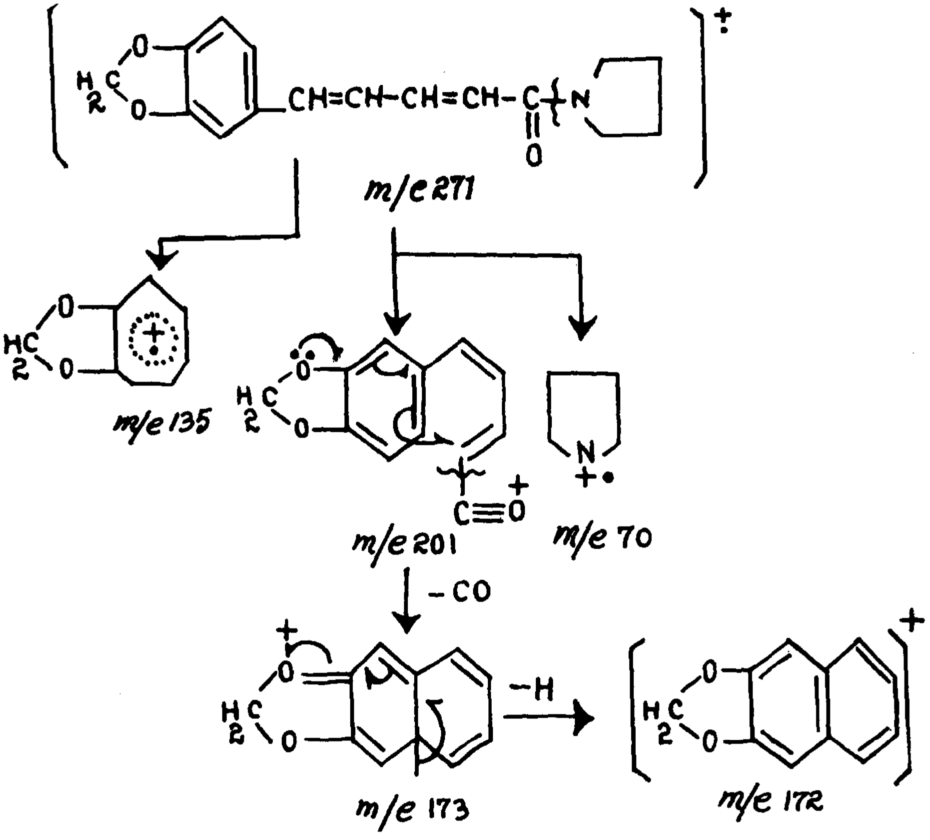
a—δ 1·65-2·2,(4H,m)
b—δ 3·55,(4H,t)
c—δ 6·25,(1H,d) J=14 Hz
d—δ 5·96,(2H,S)‡
e—δ 6·65-7·65,(6H)

Hydrolysis of the alkaloid with 10% alcoholic KOH afforded a base and an acid which were identified as pyrrolidine and piperic acid respectively.

---

‡ Same as for piperine, Varian Spectra Catalogue of High Resolution NMR (Varian Associates, 1962).

The molecular ion peak of trichostachine was obtained at m/e 271 and the other characteristic peaks at m/e 243, 201, 173, 172, 135, 115 and 70. The fragments obtained fit very well[2] in accordance with the proposed structure.



Fragment at m/e 135 may be assigned[3] to piperonylidene or piperonyl group.

The other evidence in support of our formulation was substantiated by the synthesis of this compound. Piperic acid prepared from piperine, on treatment with thionyl chloride in dry benzene gave piperoyl chloride. Pyrrolidine was taken in dry benzene and added to piperoyl chloride. This on refluxing and chromatography of the product over neutral alumina afforded 1-piperoyl pyrrolidine identical to the natural product in TLC and mixed m.p.

Acknowledgements

The authors are thankful to Dr. T.R. Govindachari, Director, Ciba Research Centre, Bombay for providing the micro-analysis and IR spectra and to Dr. B.D. Tilak, Director, National Chemical Laboratory, Poona for mass spectra.

REFERENCES

* For part VIII see Jagdev Singh & C.K. Atal, Indian J. Pharm., in press.

1. C.K. Atal, P.N. Moza & A. Pelter, Tetrahedron Letters, 1397-1400 (1968).
2. A.C. Chatterjee & C.P. Dutta, Tetrahedron, 23, 1776 (1967).
3. B. Willhalm, A.F. Thomas and F. Gautschi, Tetrahedron, 20, 1185, (1964).