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STUDIES ON THE GENUS PIPER - PART XII. STRUCTURE OF TRICHONINE, A NEW N-PYRROLIDINYL EICOSA-TRANS-2 TRANS-4 DIENAMIDE*

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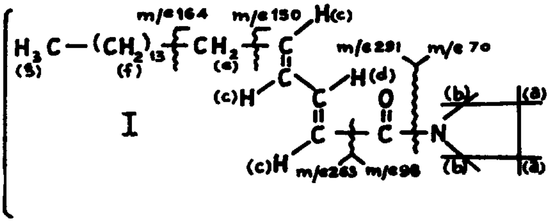
In an earlier communication we reported the structure of a new alkaloid trichostachine[1] isolated from *P. trichostachyon* leaves. This time we wish to report the structure of another new and novel compound N-Pyrrolidinyl eicosa-trans-2-trans-4 dienamide designated now as trichonine (I). This is the first report of a pyrrolidine amide of an aliphatic acid from plant source.

The petroleum ether extract of the leaves of *P. trichostachyon* on chromatography over neutral alumina afforded trichonine (I) in benzene eluates. Trichonine crystallised from petroleum ether into a white crystalline material, m.p. 65-67°. The compound analysed for $C_{24}H_{43}NO$; M^{+}, 361 ; UV, λ_{max}^{MeOH} 261 nm indicated a conjugated dienone system[2].

The IR (KBr) of the compound indicated it to be a tertiary amide. The absence of the cis-peak between 950-965 cm^{-1} and the appearance of a single peak at 1005 cm^{-1} shows the trans-configuration[2,3] of the double bond conjugated with C=O (1625 cm^{-1}). The peaks at 1656 and 1595 cm^{-1} further indicate the unsaturated character of the compound.

The NMR spectrum ($CDCl_3$, 60 Mc) was consistent with structure (I) and the positions of all the protons are according to expectations. The mass fragmentation pattern as explained below is also in agreement with the proposed structure (I).



I

a – δ 1·88–2·01 (4H,m)
b – δ 3·52 (4H,t)
c – δ 5·82–6·25 (3H,m)
d – δ 7·05–7·52 (1H,m)
e – δ 2·05–3·32 (2H,m)
f – δ 1·24 (26H,s)
g – δ 0·86 (3H,t)

Trichonine on hydrogenation with 10% Pd/C and purification by column chromatography gave a white crystalline compound $C_{29}H_{47}NO$ from petroleum ether, m.p. 38-40°, M^+, 365. Its IR and mass spectrum showed its straight chain nature. The NMR ($CDCl_3$) showed a triplet at δ 0.88 ($-CH_3$), a broad singlet at δ1.24 $(-CH_2-)_{13}$ a multiplet at δ 1.75-2.35 (H_2C), a triplet at δ 3.55 ($N\!<\!\begin{matrix}CH_2-\\CH_2-\end{matrix}$) and a multiplet at δ 1.68-2.08.

Hydrolysis of the hydrogenated product with concentrated HCl in ethanol (heating at 100° for 80 hours) in a sealed tube afforded eicosanoic acid m.p. 75-77° and pyrrolidine as HCl. Eicosanoic acid was identified by m.p. and mixed m.p. of its amide m.p. 107-9° and by conversion to its methyl ester, m.p.45-7°; M^+326. Pyrrolidine was identified by mixed TLC with an authentic sample and by m.p. and mixed m.p. of its picrate m.p. 110-12°.

Alkaline hydrolysis of the hydrogenated product with 10% alcoholic KOH also afforded eicosanoic acid and pyrrolidine identified as above.

The other evidence in support of our structure (I) was supported by the synthesis of the hydrogenated product. Eicosanoic acid on treatment with thionyl chloride gave the corresponding acid chloride. Pyrrolidine was taken in dry benzene and added to the acid chloride. The product was refluxed and benzene removed in vacuo to give a thick semisolid. This on crystallisation from petroleum ether afforded 1-eicosanoyl pyrrolidine identical to the hydrogenated product in TLC, mixed m.p. IR and NMR spectra.

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* For Part XI see Jagdev Singh, K.L. Dhar and C.K. Atal, Indian Journal Pharmacy, communicated.

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