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STRUCTURE OF A NEW PYRROLIDINE ALKALOID FROM *PIPER TRICHOSTACHYON**

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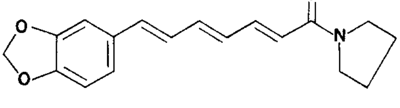
Key Word Index—*Piper trichostachyon*; Piperaceae; 1-piperettyl pyrrolidine (pyrrolidine amide of 7-(3,4-methylene dioxyphenyl)-hepta-2,4,6-trienoic acid).

The presence of the alkaloid trichostachine (1-piperyl pyrrolidine) was previously reported[1] by us from the leaves of *Piper trichostachyon*. This time we report the structure of a new alkaloid (**1**) which is a higher homologue of trichostachine,[1] from the stems of *P. trichostachyon*.

The petrol extract of the stems of *P. trichostachyon* on chromatography over neutral alumina gave yellow crystalline needles of (**1**), m.p. 147–149°. The compound analysed for $C_{18}H_{19}NO_3$ (Found: C, 72·03; H, 6·6; N, 4·72. Calc. for $C_{18}H_{19}NO_3$: C, 72·72; H, 6·73; N, 4·61%. λ_{max}^{MeOH} 360 nm indicate of a chromophoric system similar to piperttine.[2] The compound also indicated the presence of methylene dioxyphenyl group and the unsaturated nature by applying the usual chemical tests. IR(KBr) of the compound further indicated the presence of tertiary amide (1637 cm^{-1}) with trans configuration of the olefinic double bonds (1615, 1000 cm^{-1}) and methylene dioxyphenyl group (1255, 935 cm^{-1}).

A computerized NMR(60 MHz, $CDCl_3$), spectrum showed a four proton multiplet between δ 1·7 and 2·1 ($-CH_2-CH_2-$), a four proton triplet at δ 3·55 ($-CH_2-N-CH_2-$), a two proton singlet at δ 5·98 ($-O-CH_2-O-$), a one proton doublet at δ 6·18 (*J*14Hz, HC–C=O–) and eight proton bond multiplet between δ 6·55 and 7·62 (three aromatic and five aliphatic protons).



(1)

In the MS, the molecular ion peak (M^+) for the compound was obtained at *m/e* 297. The mass fragmentation pattern (Scheme 1) is an extension of the scheme proposed by Loder *et al.*[3] The structure of (**1**) was further confirmed by its alkaline hydrolysis which

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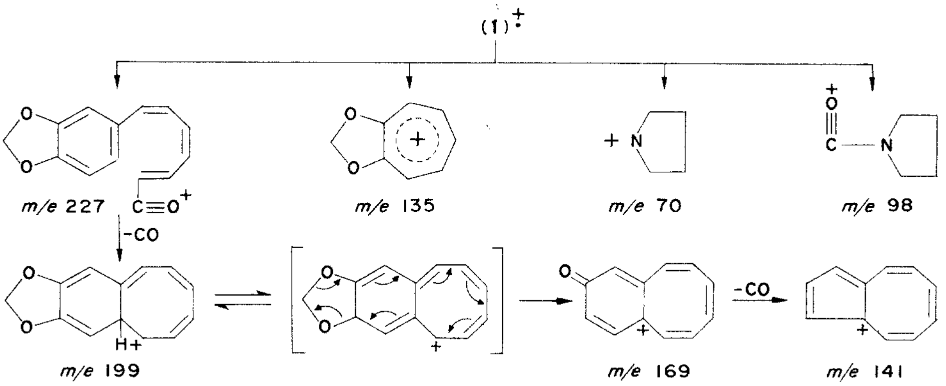
* Part XIII in the series "Studies on the Genus *Piper*". For Part XII see SINGH, J., DHAR, K. L. and ATAL, C. K. (1971) *Tetrahedron Letters* 2119.

[1] SINGH, J., DHAR, K. L. and ATAL, C. K. (1969) *Tetrahedron Letters* **56**, 4975–78.

[2] SPRING, F. S. and STARK, J. J. (1950) *J. Chem. Soc.* 1177–80.

[3] LODER, J. W., MOORHOUSE, A. and RUSSEL, G. B. (1969) *Australian J. Chem.* **22**, 1531–38.

yielded piperettic acid, m.p. 221–223°, λ_{max}^{MeOH} 360 nm and the base pyrrolidine. Further chemical evidence on its structure could not be obtained due to paucity of the compound.



SCHEME 1. MASS FRAGMENTATION PATTERN OF 1-PIPERETTYL PYRROLIDINE.

EXPERIMENTAL

Extraction and isolation procedure. The air dried coarsely powdered stems (1250 g) *P. trichostachyon* were extracted (Soxhlet) with petrol. (60–80°) for 70 hr. The residue (20 g) after the removal of the solvent was extracted with C_6H_6 to yield a yellow semisolid (0·55 g). This semisolid was chromatographed over a column of neutral alumina. Elution with a mixture of EtOAc and petrol. (60–80°) yielded 1, (105 mg), which was crystallized from EtOAc–petrol. mixture, m.p. 147–149°; R_f 0·42 (EtOAc–C_6H_6, 1:1).

Hydrolysis. The compound in 10% alcoholic KOH (1·25 ml/10 mg) was heated under reflux for 50 hr. The crystalline K salt was collected by filtration, dissolved in H_2O (10 μml^3) and acidified with dil.HCl. The yellow ppt. was extracted with $CHCl_3$. After removal of the solvent the residue crystallized from alcohol into yellow crystals of piperattic acid, m.p. 221–223°, λ_{max}^{MeOH} 360 nm (lit.[2] m.p. 224°, λ_{max}^{MeOH} 360 nm).

The alcoholic filtrate was treated with dil. HCl and evaporated to dryness. This agreed on mixed and co-TLC with an authenic sample of pyrrolidine, R_f 0·65 (phenol–H_2O; 8·3).

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STEROIDAL ESTROGENS OF *PRUNUS ARMENIACA* SEEDS

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Key Word Index—*Prunus armeniaca*; Rosaceae; apricot seeds; sterols; estrogenic substances; estrone; α-estradiol.

Estrone has been recently identified in several plants including seeds of *Elaeis guineensis*,[1] Phoenix dactylifera,[2,3] *Punica granatum*,[4] and apple.[5] It has also been

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[1] BUTENANDT, A. and JACOBI, H. (1933) *Z. Physiol. Chem.* **218,** 104.

[2] BENNETT, R. D., KO, S.-T. and HEFTMANN, E. (1966) *Phytochemistry* **5,** 231.

[3] HEFTMANN, E., KO, S.-T. and BENNETT, R. D. (1965) *Naturwissenschaften* **52,** 451.

[4] HEFTMANN, E., KO, S.-T. and BENNETT, R. D. (1966) *Phytochemistry* **5,** 1337.

[5] GAWIENOWSKI, A. M. and GIBBS, C. C. (1969) *Phytochemistry* **8,** 685.