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

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Key Word Index—*Piper trichostachyon*; Piperaceae; tricholein (pyrrolidine amide of 9-(3,4-methylene dioxy phenyl)-Δ^8 nonenoic acid).

The presence of the alkaloid 1-piperettyl pyrrolidine was reported [1] earlier by us. In the present report the isolation and structural elucidation of a new alkaloid tricholein (**1**), a pyrrolidine amide of 9-(3,4-methylene dioxy phenyl)-Δ^8-nonenoic acid is described.

The petrol extract of the stems of *Piper trichostachyon* on chromatography over neutral Al_2O_3 after the removal of 1-piperettyl pyrrolidine [1] gave a slightly impure brownish-yellow waxy substance (**1**). The compound analysed for $C_{20}H_{27}NO_3$ (M^+ 329). The UV spectrum λ_{Max}^{MeOH} 269 nm (ϵ = 14860) indicated a chromophoric system similar to piperolein-B [2]. That **1** also had a methylene dioxy phenyl group and was unsaturated was shown by the usual chemical tests. IR (Nujol) of the compound further indicated the presence of a tertiary amide (1655 cm^{-1}), a phenyl nucleus (1608 cm^{-1}, 1500 cm^{-1}), a *trans* configuration of the olefinic double bond (969 cm^{-1}) and a methylene dioxy phenyl group (1255 cm^{-1}, 1030 cm^{-1}, 925 cm^{-1}).

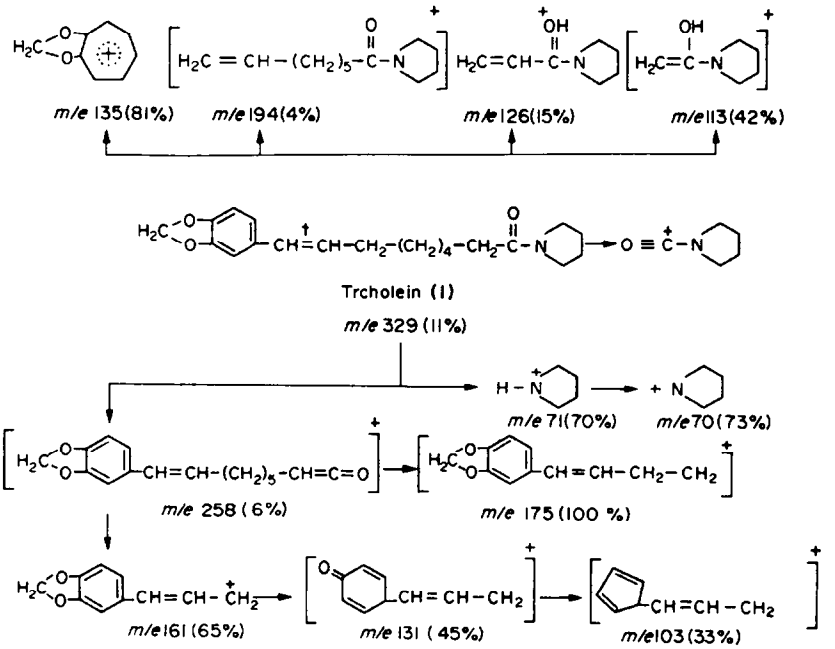
The PMR (60 MHz, $CDCl_3$) showed an 8 proton singlet at δ 1.23, a 4 proton multiplet between δ 1.65–2.00, a 4 proton multiplet between δ 2.10–2.85 ($-CH_2-\overset{O}{\overset{\|}{C}}-$ and $=C-CH_2-$), a 4 proton triplet at δ 3.55 ($-CH_2-N-CH_2-$), a 2 proton singlet at δ 5.90 ($-O-CH_2-O-$), a multiplet between δ 5.6–6.2 due to $-HC=\underline{CH}-CH_2$ olefinic proton and a doublet at δ 6.37 (J = 15 Hz) due to the other olefinic proton, and a three proton multiplet between δ 6.55–7.00 (three aromatic protons).

In the MS, an M^+ was observed at *m/e* 329. The fragmentation pattern (Scheme 1) for tricholein (**1**) is explained in a manner similar to that of piperolein-B [2] and is in agreement with structure (**1**).

The structure of the alkaloid was further confirmed by acid hydrolysis which yielded a waxy acid identified as 9-(3,4-methylene dioxy phenyl)-Δ^8-nonenoic acid by its UV and PMR spectra and the base identified by mixed and co-TLC with an authentic sample of pyrrolidine.

Hydrogenation of the alkaloid using Pt black yielded a yellowish waxy dihydro product. The absence of the 969 cm^{-1} *trans* olefinic peak in the IR (neat) and the PMR spectra agreed with a hydrogenated product. The M^+ at *m/e* 331 could not be obtained for the hydro-

* Structure presented at the 27th Indian Pharmaceutical Congress, Patna, India.



genated derivative. However, the presence of M^+-70 (5%), M^+-98 (4%), M^+-112 (4%) and M^+-135 (5%) peaks supported the presence of one double bond in the structure (**1**).

Oxidation of the alkaloid with $KMnO_4$ in Me_2CO gave two acid spots on TLC, one of which was indentified as piperonylic acid by comparison with an authentic sample of piperonylic acid obtained by the oxidation of piperine.

EXPERIMENTAL

Extraction and isolation. Air-dried coarsely powdered stems (1.25 kg) of *P. trichostachyon* were extracted (Soxhlet) with petrol (60–80°) for 70 hr. Residue (20 g) after the removal of the solvent was dissolved in C_6H_6 and chromatographed on a column of neutral Al_2O_3. Late C_6H_6 and early $CHCl_3$ eluates after the removal of the solvent yielded a waxy crystalline material. This on rechromatography over neutral Al_2O_3 and elution with petrol–EtOAc yielded 1-piperettyl pyrrolidine [1] and the compound (**1**) as a brownish waxy substance (0.535 g), repurified by PLC over Si gel, R_f 0.52 (EtOAc–C_6H_6, 1:1).

Hydrolysis. Compound (**1**) (150 mg) in 10% alcoholic HCl (10 ml) was heated at 100° in a sealed ampoule for about 70 hr. The solvent was removed *in vacuo* and residue dissolved in H_2O and filtered to give insoluble residue (A) and filtrate (B). Residue (A) was dissolved in alcoholic KOH (5%, 10 ml) and acidified with dil HCl to give a ppt. which was extracted with $CHCl_3$. After removal of solvent the acid was obtained as a brownish waxy substance (72 mg); R_f 0.82 (*n*-BuOH–HOAc–H_2O, 4:1:1). It analysed for $C_{16}H_{20}O_4$ (M^+ 276). λ_{max}^{MeOH} 214 nm (ϵ = 23 500), 269 nm (ϵ = 12 400) and 286 nm (ϵ = 7200); PMR (60 MHz, $CDCl_3$): δ 1.24 (*s*, 8H, $(-CH_2-)_4$, δ 1.56–2.10 (*m*, 4H, $=C-CH_2-$ and $-CH_2-\overset{O}{\overset{\|}{C}}-$), δ 5.9 (*s*, 2H, $-O-CH_2-O-$), δ 6.0–6.22 (*m*, 2H olefinic) and δ 6.58–6.82 (*m*, 3H, Aromatic H).

Hydrogenation. Compound (**1**) (70 mg) in EtOAc (20 ml) was hydrogenated using Pt black (20 mg) at ordinary temp and pres. After completion of the reaction the catalyst was removed by filtration and the filtrate distilled *in vacuo* to give a yellowish waxy residue (50 mg) which could not be crystallized, R_f 0.45 (C_6H_6–EtOAc, 4:1; IR (neat): 1635 cm^{-1} (>N–C=O), 1500 cm^{-1}, 1490 cm^{-1} (Aromatic), 2950 cm^{-1}, 1030 cm^{-1} and 930 cm^{-1} ($-O-CH_2-O-$); PMR (60 MHz, $CDCl_3$): δ 1.26 (*s*, 12H, $(-CH_2-)_6$, δ 1.78 (*m*- 4H, $-CH_2-CH_2-$), δ 2.18–3.3 (*m*, 4H, CH_2-Ar and $-\overset{O}{\overset{\|}{C}}-CH_2-$) δ 3.55 (*t*, 4H, $-CH_2-N-CH_2-$) δ 5.85 (*s*, 2H, $-O-CH_2-O-$) and δ 6.59–7.25 (*m*, 3H, Aromatic H); MS described in the text.

Oxidation. Compound (**1**) (200 mg) was dissolved in Me_2CO (10 ml), oxidised with $KMnO_4$, and processed by usual methods. Residue was dissolved in H_2O, acidified with dil HCl and extracted with $CHCl_3$. $CHCl_3$ extract after removal of solvent gave a crystalline material on recrystallization from EtOH, mp 228–29° identified as piperonylic acid by mmp and co-TLC with an authentic sample of piperonylic acid. The aq fraction on evaporation gave a solid, R_f 0.05 (EtOH (96%)–H_2O–NH_4OH (25%), 5:6:8 which could not be crystallized and identified.

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REFERENCES

1. Singh, J., Potdar, M. A., Atal, C. K. and Dhar, K. L. (1974) *Phytochemistry* **13**, 677.
2. Grewe, R., Freist, W., Newmann, H. and Kersten, S. (1970) *Chem. Ber.* **103**, 3752.

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ALCALOIDES DE *ACACIA SIMPLICIFOLIA**

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Dans le cadre d'études systématiques entreprises sur les plantes à alcaloides de Nouvelle-Calédonie, deux espèces du genre *Acacia*: *A. spirorbis* Labill. [1] et *A. simplicifolia* Druce ont été étudiées. *Acacia simplicifolia* Druce (série des Phyllodinées) est une espèce sabulicole croissant en bord de plage sur calcaire; c'est un arbre de 6–12 m, à phyllodes entières, ovales, très élargies. Les fleurs, jaunes, sont groupées en capitules globuleux. Les fruits sont des gousses non arquées, à étranglements. Le matériel végétal étudié§ (plante en fruits) a été récolté en mai 1974 au Mont Dore (Nouvelle-Calédonie).

Trois alcaloides ont été identifiés dans l'extrait obtenu à partir des écorces de tronc: la N_b-méthyltryptamine **1**, la N_bN_b-diméthyltryptamine **2** et la méthyl-2 tétrahydro-1,2,3,4 β-carboline **3**; si les deux premiers ont déjà

* Partie 38 dans la série "Plantes de Nouvelle-Calédonie". Pour partie 37, voir B. C. Das *et al.*, Alcaloides de *Alstonia vieillardii*, (à paraître).

§ Un échantillon botanique a été déposé au Muséum National d'Histoire Naturelle de Paris sous le numéro Sévenet 660.