

TWO HEXAHYDROPROAPORPHINE ALKALOIDS, LAUFORMINE AND
N-METHYLLAUFORMINE FROM PHOEBE FORMOSANA[§]

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Abstract - Lauformine and N-methylauformine isolated from the
barks of Phoebe formosana Hay. (Lauraceae), were assigned
structures (4) and (5), respectively.

Previously we have reported the isolation of two alkaloids with mp 222-224°C and mp 239-240°C along with ushinsunine and liriodenine from the non-phenolic basic extract of the barks of Phoebe formosana.¹ Further purifications of both alkaloids with mp 222-224°C and mp 239-240°C by silica gel column chromatography (solvent: CHCl₃) and recrystallisation (Me₂CO) were carried out until to give mp 235-237°C and 255-256°C, respectively. We wish to describe the structural elucidation of both alkaloids, named lauformine and N-methylauformine.

Lauformine (4) is colorless needles, mp 235-237°C, $[\alpha]_D^{23} +62^\circ$ (c=1.0, MeOH), C₁₇H₂₁NO₃ (M⁺, m/z 287), ir [$\nu_{\max}$ (KBr): 3200 cm⁻¹ (OH), 1040 and 925 cm⁻¹ (OCH₂O)], uv [$\lambda_{\max}$ (EtOH) nm (log ϵ): 240sh (3.32), 290 (3.36)]. The ¹Hnmr spectrum (in CDCl₃) showed signals assignable to a methylenedioxy protons at δ 5.85 (2H, s), aromatic proton at δ 6.50 (1H, s), and alcoholic hydroxy proton at δ 4.05 (1H, br. s). The molecular formula, optical rotation, uv absorption curve, ¹Hnmr and mass spectra are all similar with those of (+)-litsericine (2)². However, the melting point of lauformine is higher than its of (+)-litsericine and the ir spectra (KBr) of 2 and 4 found not to be superimposable each other. These facts suggested that both lauformine and litsericine have same plane structure (1).

Treatment of 4 with formalin and NaBH₄ afforded N-methylauformine, which was also isolated from the same plant, and two samples were shown to be identical by the tlc, mp, $[\alpha]_D$, and ir (KBr) comparisons.

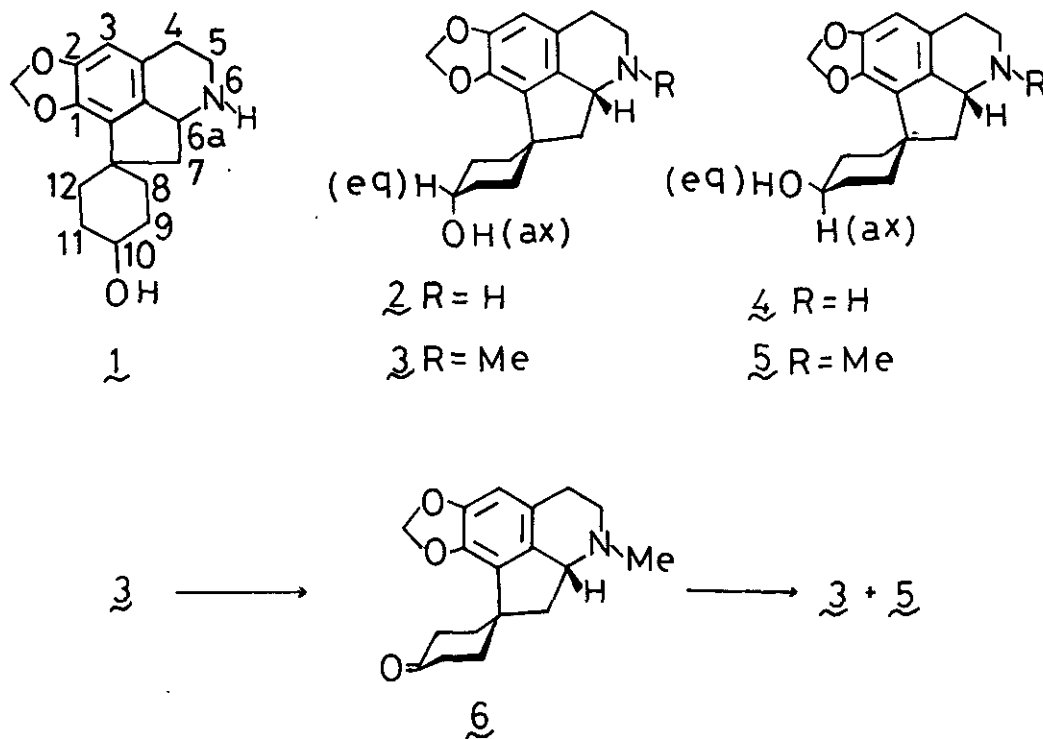
The natural N-methylauformine (5) is colorless needles with mp 255-256°C, $[\alpha]_D^{23} +68^\circ$ (c=0.1, MeOH), C₁₈H₂₃NO₃ (M⁺, m/z 301), ir [$\nu_{\max}$ (KBr): 3125 cm⁻¹ (OH), 1035 and 940 cm⁻¹ (OCH₂O)] and uv [$\lambda_{\max}$ (EtOH) nm (log ϵ): 240sh (3.18), 292 (3.23)]. In

the $^1\text{Hnmr}$ spectrum (in CDCl_3) the signals of methylenedioxy group, aromatic proton, N-methyl group and alcoholic hydroxy group appear at δ 5.95 (2H, s), 6.60 (1H, s), 2.44 (3H, s) and 3.84 (1H, br. s), respectively.

Oxidation of 3 with Jones reagent gave a keto compound as colorless needles, mp 146-148°C, $[\alpha]_D^{23} +100^\circ$ (c=1.0, EtOH), $\nu_{\text{max}}(\text{KBr})$: 1710 cm^{-1} (C=O), and $^1\text{Hnmr}$ (CDCl_3): δ 2.50 (3H, s, N- CH_3), 6.10 (2H, s, OCH_2O) and 6.78 (1H, s, C-3). These data agree with those of N-methyllytsericinone (6) obtained by Oppenauer oxidation of 3.²

Reduction of 6 with NaBH_4 ² afforded N-methyllytsericine (3) and its C-10 stereoisomer, mp 256-258°C and $[\alpha]_D^{23} +58^\circ$, which was shown to be identical with N-methyllytsericine by mixed mp, tlc and ir (KBr) spectral comparisons.

From above facts, lytsericine and N-methyllytsericine were assigned structures (4) and (5), respectively.



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REFERENCES

§ This forms part XXV of "Studies on the Alkaloids of Formosan Lauraceous Plants" by Sheng-Teh Lu; Part XXIV: S. T. Lu, T. L. Su and C. Y. Duh, J. Taiwan Pharm. Assoc., 1979, 31, 23.

1 S. T. Lu and T. L. Su, J. Chinese Chem. Soc., 1973, 20, 87.

2 T. Nakasato and S. Asada, Yakugaku Zasshi, 1966, 86, 1205.

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