HETEROCYCLES, Vol 22, No 5, 1984

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

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Abstract - Lauformine and N-methyllauformine 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: $CHCl_3$) and recrystallisation (Me_2CO) were carrid 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-methyllauformine.

Lauformine (4) is colorless needles, mp 235-237°C, $[\alpha]_D^{23}$+62° (c=1.0, MeOH), $C_{17}H_{21}NO_3$ (M^+, m/z 287), ir [ν_{max}(KBr): 3200 cm^{-1} (OH), 1040 and 925 cm^{-1} (OCH_2O)], uv [λ_{max}(EtOH) nm (log ε): 240sh (3.32), 290 (3.36)]. The ^{1}Hnmr spectrum (in $CDCl_3$) 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, ^{1}Hnmr 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).

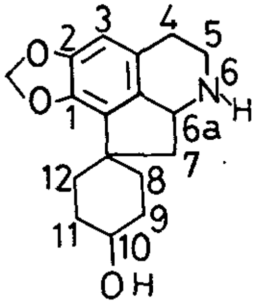
Treatment of 4 with formalin and $NaBH_4$ afforded N-methyllauformine, which was also isolated from the same plant, and two samples were shown to be identical by the tlc, mp, $[\alpha]_D$, and ir (KBr) comparisons.

The natural N-methyllauformine (5) is colorless needles with mp 255-256°C, $[\alpha]_D^{23}$ +68° (c=0.1, MeOH), $C_{18}H_{23}NO_3$ (M^+, m/z 301), ir [ν_{max}(KBr): 3125 cm^{-1} (OH), 1035 and 940 cm^{-1} (OCH_2O)] and uv [λ_{max}(EtOH) nm (log ε): 240sh (3.18), 292 (3.23)]. In the ^{1}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° (c=1.0, EtOH), ν_{max}(KBr): 1710 cm^{-1} (C=O), and ^{1}Hnmr ($CDCl_3$): δ 2.50 (3H, s, $N\text{-}CH_3$), 6.10 (2H, s, OCH_2O) and 6.78 (1H, s, C-3). These data agree with those of N-methyllitsericinone (6) obtained by Oppenauer oxidation of 3.[2]

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

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



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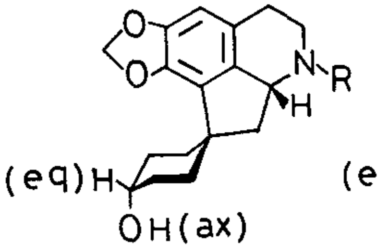

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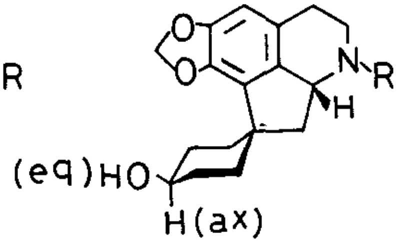
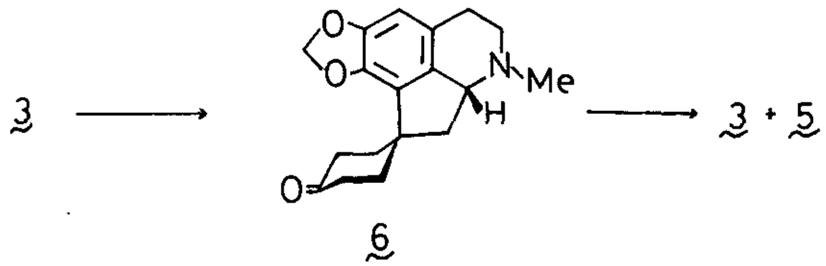
3 R = Me



4 R = H

5 R = Me



ACKNOWLEDGEMENT We are grateful to Prof. H. Ishii and Dr. T. Ishikawa, Chiba University, for the ^{1}Hnmr and ms measurements and the elemental analysis. We are also thank Miss S. P. Leou, Kaohsiung Medical College, for experiment of this study.

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Received, 6th January, 1984