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MASS SPECTRA OF HEXAHYDROPROAPORPHINE TYPE ALKALOIDS[§]

Sheng-Teh Lu[*] and Ian-Lih Tsai
School of Pharmacy, Kaohsiung Medical College, 100 Shih-Chuan
1st Road, San-Min District, Kaohsiung, Taiwan

Abstract - Mass spectra of litsericine (1), N-methyllitsericine (2), lauformine (3) and N-methyllauformine (4) belonging to the hexahydroproaporphine group were measured, and the main fragmentation pathways for these alkaloids were presumed from the examination of their mass shifts.

In the previous papers,[1,2] we have reported the natural occurrence of litsericine (1) and N-methyllitsericine (2) in *Neolitsea aurata* and *N. buisanensis*[1] (Lauraceae), and lauformine (3) and N-methyllauformine (4) in *Phoebe formosana*[2] (Lauraceae). In this paper, we wish to describe the studies on the mass spectra[3] of these hexahydroproaporphine alkaloids.

These four alkaloids (1 - 4) essentially show the same spectrometric pattern. Litsericine (1) and lauformine (3) commonly show intensive fragment peaks at m/z 286 (base peak), 258 (58), 242 (6), 240 (10), 228 (16), and 189 (48%) (Figure 1), but N-methyllitsericine (2) and N-methyllauformine (4) show those at m/z 300 (base peak), 258 (63), 242 (15), 240 (14), 228 (21), and 203 (88%) (Figure 2). The molecular ion peak of each alkaloid was observed at m/z 287 (48) in the former two and at m/z 301 (48) in the latter two. In the region lower than m/z 258, all of these four alkaloids (1 - 4) exhibit the same spectrum except for the peaks at m/z 189 on litsericine (1) and lauformine (3) and at m/z 203 on N-methyllitsericine (2) and N-methyllauformine (4). These spectral data suggest that these four alkaloids (1 - 4) belong to a group of hexahydroproaporphine alkaloids and the latter two (2 and 4) should be N-methyl derivatives of the former two, respectively. The fragmentation of these alkaloids (1 - 4) may be explained by formation of two species of molecular ions. Loss of an electron from their nitrogen atoms in the molecules gave the molecular ions 5 and 6, while a loss of an electron from oxygen atom located at their cyclohexanol rings produced the ions 10 and 11.

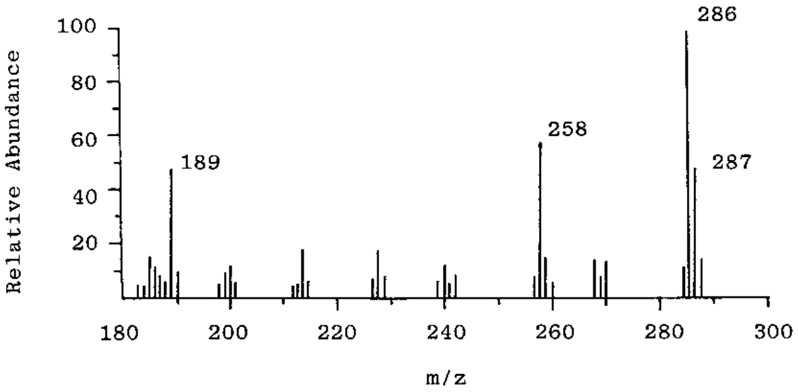


Figure 1. Mass spectrum of litsericine (1) or lauformine (3).

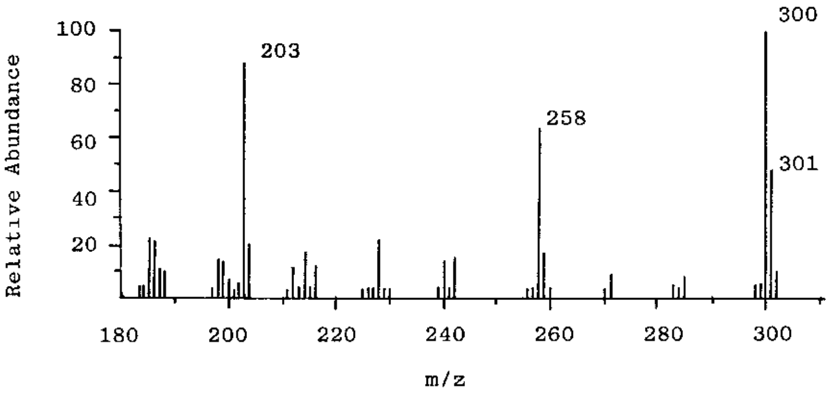
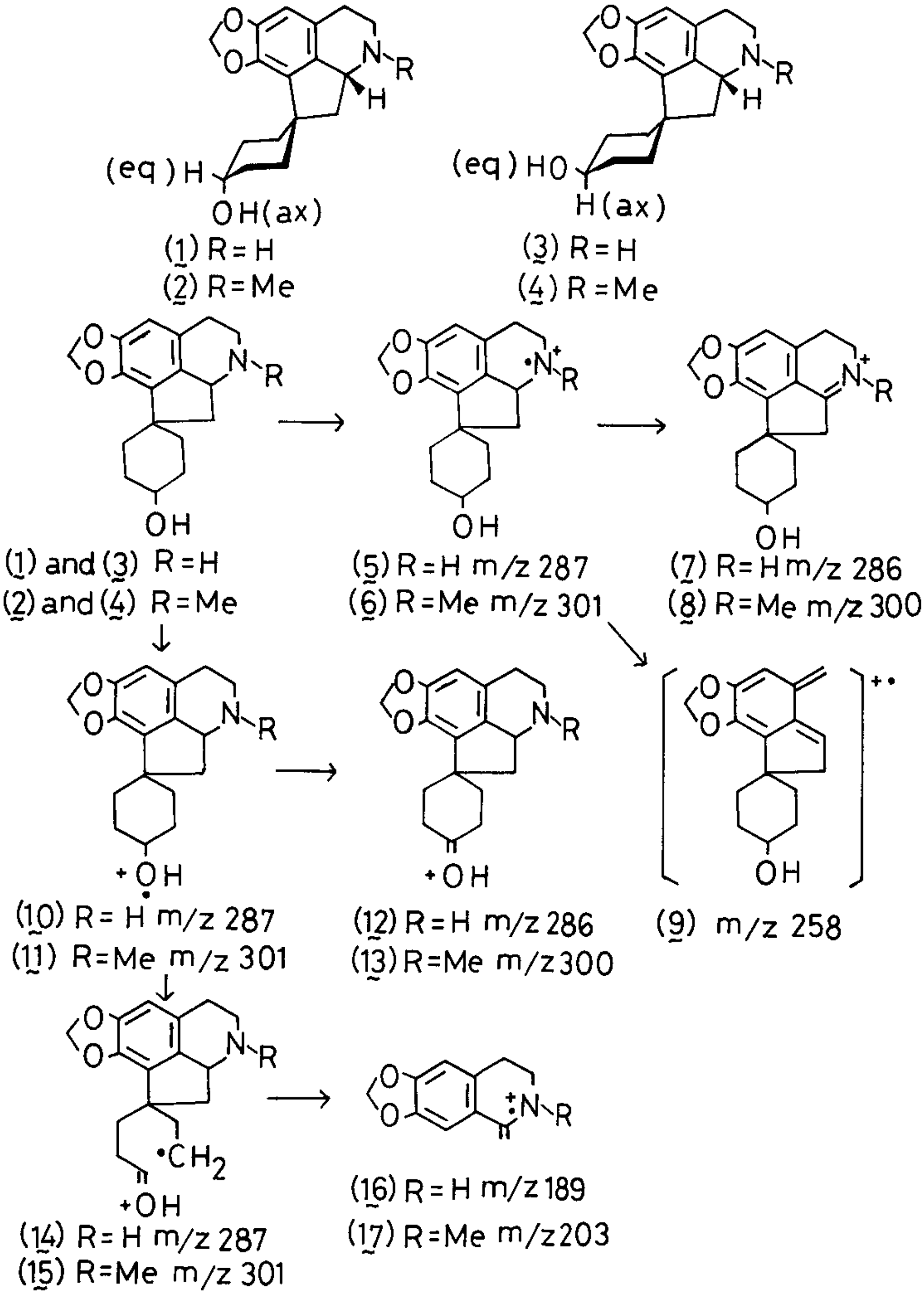


Figure 2. Mass spectrum of N-methyllitsericine (2) or N-methyllauformine (4).

The presence of the (M$^+$-1) ion [m/z 286 in litsericine (1) and lauformine (3) and m/z 300 in N-methyllitsericine (2) and N-methyllauformine (4)] as a base peak in each spectrum was ascribable to a loss each of one proton from the C_1-position of the molecular ions 5 and 6 and C_{10}-position of the molecular ions 10 and 11. Moreover, the common appearance of the peak at m/z 258 indicates that the retro Diels-Alder reaction of the molecular ions 5 and 6 took place at the tetrahydroisoquinoline skeleton to give the fragment ion (9). On the other hand, fragmentation of the molecular ions 10 and 11 seem to result in α-β-bond cleavage of their cyclohexanol ring, because the similar fragmentation of cyclohexanols has already been studied extensively[4]. The formation of the principal fragment ions


(eq) H
OH(ax)
(1) R = H
(2) R = Me
(eq) HO
H(ax)
(3) R = H
(4) R = Me
(1) and (3) R = H
(2) and (4) R = Me
(5) R = H m/z 287
(6) R = Me m/z 301
(7) R = H m/z 286
(8) R = Me m/z 300
(9) m/z 258
(10) R = H m/z 287
(11) R = Me m/z 301
(12) R = H m/z 286
(13) R = Me m/z 300
(14) R = H m/z 287
(15) R = Me m/z 301
(16) R = H m/z 189
(17) R = Me m/z 203

Scheme 1

of litsericine (1) and lauformine (3) at m/z 189 (Figure 1) and those of their N-methyl derivatives (2 and 4) at m/z 203 (Figure 2) was explainable by the degradation of their O-ionized molecular ions (10 and 11) into the fragment ion (16 and 17) by elimination of a methyl radical, an ethylene molecule and a $CH_2=CH-CH=O^+H$ ion [or two ethylene molecules and a $CH_2=CHOH^+$ ion (a $\cdot CH_2-CH=O^+H$ radical)].

These deductions supported our assignment that these alkaloids (1 - 4) belong to the hexahydroproaporphine group.

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§ This forms Part XXVI of "Studies on the Alkaloids of Formosan Lauraceous Plants", by Sheng-Teh Lu; Part XXV: S. -T. Lu and I.-L. Tsai, Heterocycles, 1984, in press.

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3 HITACHI Double Focus Mass Spectrometer MODEL RMU-6E was used. Measured Conditions: Total emission, 80uA; Target current, 74uA; Chamber voltage, 70 eV; Malt., 1.5 kV; I. Slit, 200u; C. Slit, 150u; Direct Inlet Sys. S. Heater Temp. 125-130°C.

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