HIMALAYAMINE AND LIMOGINE: ALKALOIDS OF A NEW SKELETAL TYPE

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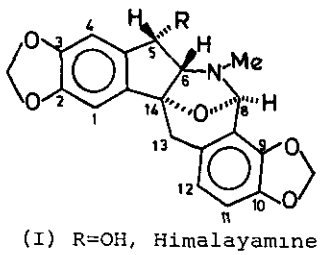
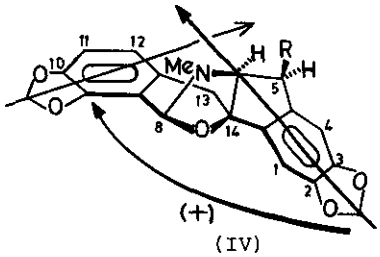
The basic fraction of Meconopsis villosa Hook. f. (Papaveraceae), collected on the Himalayas (altitude~3200 m) in view of Mt. Kanchenjunga, furnished a novel alkaloid himalayamine (I), $C_{20}H_{17}O_6N$, mp 218°, $[\alpha]_D^{25}$ +137° (MeOH): UV indicated an unusual type isoquinoline; it formed a monoacetyl derivative (II). ^{1}H NMR analysis and a nuclear Overhauser enhancement difference study (NOEDS)[1] led to the structure (I) having a new indenobenzazepine type skeleton with an oxide bridge linking C_8 to C_{14}. The structure (I) was consistent with its mass spectrum.

Corydalis claviculata (L.) DC (Fumariaceae), collected near Limoges, France also afforded a new alkaloid limogine (III), $C_{20}H_{17}O_5N$, $[\alpha]_D^{25}$ +113° (MeOH) exhibiting an almost identical UV and a similar ^{1}H NMR spectra. Upfield shifts of H-4,H-5 and H-6 demonstrate that 5-OH in (I) is α-oriented. An NOEDS of limogine, resolution enhancement through Gaussian multiplication (GM), ^{13}C NMR shifts using the recently developed gated spin echo (GASPE) technique[2] fully supported structure (III).

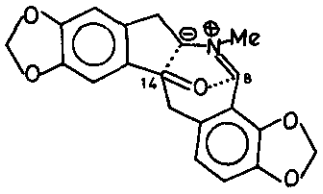
The positive Cotton effect (due to Davydov splitting) near 200 nm (A⟶B) of the CD spectra of both alkaloids dictates that the two chromophores interact as depicted in expression (IV) (positive chirality)[3] having the same absolute configuration as (I) and (III). It is noteworthy that intramolecular 1,3-dipolar cycloaddition of the ylid (V) of protopine, a major alkaloid of C. claviculata, would formally biosynthesise limogine.



(I) R=OH, Himalayamine
(II) R=OAc, O-Acetylhimalayamine
(III) R=H, Limogine



(IV)



(V)

[1] L. D. Hall and J. K. M. Sanders, J. Amer. Chem. Soc., 102, 5703 (1980).
[2] D. J. Cookson and B. E. Smith, Org. Magn. Reson., 16, 111 (1981).
[3] N. Harada, K. Nakanishi and S. Tatsuoka, J. Amer. Chem. Soc. 91, 5896 (1969).