

HIMALAYAMINE AND LIMOGINE: ALKALOIDS OF A NEW SKELETAL TYPE

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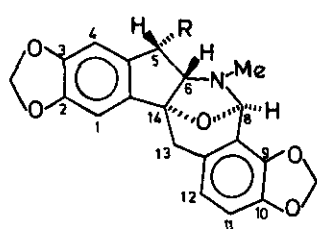
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The basic fraction of *Meconopsis villosa* Hook. f. (Papaveraceae), collected on the Himalayas (altitude ~3200 m) in view of Mt. Kanchenjunga, furnished a novel alkaloid himalayamine (I), $C_{20}H_{17}O_6N$, mp 218° , $[\alpha]_D^{25} +137^\circ$ (MeOH): UV indicated an unusual type isoquinoline; it formed a monoacetyl derivative (II). 1H 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), $C_{20}H_{17}O_5N$, $[\alpha]_D^{25} +113^\circ$ (MeOH) exhibiting an almost identical UV and a similar 1H 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) technique² fully supported structure (III).

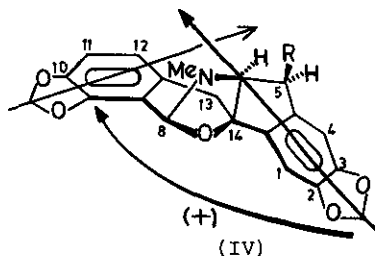
The positive Cotton effect (due to Davydov splitting) near 200 nm (A \rightarrow B) of the CD spectra of both alkaloids dictates that the two chromophores interact as depicted in expression (IV) (positive chirality)³ having the same absolute configuration as (I) and (III). It is noteworthy that intramolecular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



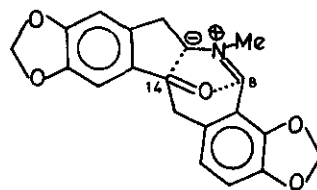
(I) R=OH, Himalayamine

(II) R=OAc, O-Acetylhimalayamine

(III) R=H, Limogine



(IV)



(V)

¹L. D. Hall and J. K. M. Sanders, *J. Amer. Chem. Soc.*, **102**, 5703 (1980).

²D. J. Cookson and B. E. Smith, *Org. Magn. Reson.*, **16**, 111 (1981).

³N. Harada, K. Nakanishi and S. Tatsuoka, *J. Amer. Chem. Soc.* **91**, 5896 (1969).