A NEW β -CARBOLINE ALKALOID FROM VESTIA LYCIOIDES

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Vestia lycioides Willd. was collected in Concepción, Chile and identified by Prof. R. Rodríguez, Instituto Central de Biología, Universidad de Concepción. Ground defatted leaves were exhaustively extracted with MeOH. After removal of solvent, the residue was dissolved in 5% HCl and extracted with CHCl₃. Repeated preparative TLC of the chloroform fraction led to the isolation of a new compound as yellow needles (CHCl₃-MeOH) mp 234-236°. We propose the novel structure 1,1-acetyl-3-carbomethoxy-β-carboline for this alkaloid on the basis of the following spectroscopic and synthetic evidence. Elemental analysis C, 67.42; H, 4.54; N, 10.52. Calcd for

 $C_{15}H_{12}N_2O_3$: C, 67.15; H, 4.51; N, 10.44. UV λ_{max}^{EiOH} (ϵ) 270 sh (29.400), 286 (45.900), 374 (7.180) nm. The IR spectrum (KBr discs) exhibited a sharp peak at 3397 cm⁻¹ (indolic N-H) and carbonyl absorptions at 1715 and 1665 cm⁻¹, ascribed to the methyl ester and conjugated carbonyl functions, respectively.

These assignments are in agreement with the NMR spectrum of 1 (90 MHz, CDCl₃, TMS) which exhibited signals at : δ 10.5 (1H, bs, N-H); δ 4.02 (3H, s, —OMe); δ 2.92 (3H, s, —COMe); δ 9.05 (1H, C-4); δ 8.15 (1H, d, J=8 Hz, C-5); δ 7.10–7.80 (3H, m, aromatics). The

high resolution electron impact MS exhibited an M^+ ion at m/e 268.0842 (100%, $C_{15}H_{12}N_2O_3$). The remainder of the spectrum exhibited the combined fragmentation pattern expected for an aromatic methyl ester, together with features common in other β -carboline alkaloids [1]: m/e 236 [25%, M^+ -MeOH]; m/e 210 [27%, M^+ -(CO + H_2 CO)]; m/e 209 [18%, $C_{13}H_9N_2O$, M^+ -(CO₂Me)]; m/e 208 [38%, $C_{13}H_8N_2O$, M^+ -(MeOH + CO)]; m/e 194 [35%, $C_{12}H_6N_2O$, M^+ -(CO₂Me + Me)]; m/e 166 [15%, $C_{11}H_6N_2$, M^+ -(CO₂Me + Me + CO)].

This structural assignment was confirmed by synthesis. Pyruvaldehyde and (\pm) -tryptophan were condensed following a procedure reported for the synthesis of tetrahydro- β -carbolines [1, 2]. Fischer esterification of the acid formed and sublimation of the crude methyl ester product gave, albeit in very low yield*, a pale yellow crystalline product, mp 230–234°, identical in all respects (TLC, IR, UV and NMR) with the natural product.

Alkaloids with a β -carboline skeleton are found among several families, notably the Rubiaceae, Elaeagnaceae and Malpighiaceae. However, this is the first report of the occurrence of a β -carboline alkaloid in the Solanaceae.

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^{*}The low yield observed arises probably from the extensive self-condensation of pyruvaldehyde in the reaction medium. Also, the quinone formed by this dimerization might be the oxydazing agent promoting the 'spontaneous' aromatization of the piperidine ring in the intermediate product.