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ALKALOIDS FROM *RAUWOLFIA PSYCHOTRIOIDES*

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Key Word Index—*Rauwolfia psychotrioides*; Apocynaceae; alkaloids; harman; ethyl harman; rauvoxinine; triterpenes.

Rauwolfia psychotrioides H. B. & K. (Apocynaceae) is a perennial tree found in the northern part of South America, where it grows in a temperate climate.

The alkaloidal fraction of the leaves,* extracted with EtOH and isolated with 10% HOAc, showed the presence of many compounds by TLC, some of which were separated by preparative TLC. Compounds A and B showed UV spectra characteristic of non-oxygenated indole alkaloids [1] $\lambda_{\max}$(EtOH) 347, 334, 287 (sh), 239 (sh), 234 and 212 nm. The IR spectra of these alkaloids showed bands for the N-H function ($\nu_{\max}$(KBr) 3125 cm^{-1}) and for the aromatic system ($\nu_{\max}$(KBr) 3060, 1625, 1560 and 1500 cm^{-1}). The mass spectral fragmentation for both alkaloids was relatively simple, A showing its molecular ion at m/e 182 and B at m/e 210. A was identified as harman based on the UV spectrum and the mass spectral fragmentation [2] showing the following ions: 182 (100, M^+), 181 (12, $M^+ - H$), 167 (12, $M^+ - Me$), 154 (18, $M^+ - H - HCN$), 127 (11, $M^+ - H - 2\,HCN$). B was identified as ethyl harman because of the typical fragmentation pattern showing the following ions: 210 (24, M^+), 195 (18, $M^+ - Me$), 182 (100, $M^+ - C_2H_4$), 181 (24, $M^+ - C_2H_5$), 154 (18, $M^+ - C_2H_5 - HCN$), 127 (11, $M^+ - C_2H_5 - 2\,HCN$). Another eluate from the TLC showed the same characteristics as harman, but its mass spectrum showed an additional small fragment at m/e 196, which seems to be due to some methyl harman impurity. The UV spectrum of alkaloid C showed absorptions at 216 and 280 nm, characteristic for the oxindole moiety [3] and was identified as rauvoxinine based mainly on its mass spectrum [4] which showed ions at m/e 428 (68, M^+), 413 (7, $M^+ - Me$), 411 (6, $M^+ - OH$), 397 (6, $M^+ - OMe$), 223 (67), 219 (25), 208 (26). The ion at 223 belonging to the alicyclic moiety of the molecule and by further loss of C-9 Me gives the fragment at m/e 208; one typical oxindole fragment occurs at m/e 219, which retains the triptamine bridge; the indole fragment occurring at m/e 206, 190 and 204.

From the neutral fraction, after column chromatography using silica gel and eluting with petrol, C_6H_6 and $CHCl_3$, lupeol, sitosterol and stigmasterol were isolated and identified according to their physical properties, spectroscopic evidence and comparison with authentic compounds.

It is noteworthy that while the *Rauwolfia* genus and the Apocynaceae family are very rich in indole complex alkaloids [5], it seems that harmine-type alkaloids, found in several families, i.e. Styraceae, Rubiaceae, Eleagnaceae, Malpighiaceae, Passifloraceae, Leguminosae, Loganiaceae and Polygonaceae, do not occur widely in this genus and family, *Rauwolfia psychotrioides* being one of the few species of this genus containing harmine-type alkaloids.

EXPERIMENTAL

Isolation of bases. The air-dried leaves (1.15 kg) were extracted by refluxing with 95% EtOH, HOAc was added and extracted with C_6H_6. The acid soln was basified with 10% NH_4OH precipitating a gummy material which was extracted with $CHCl_3$ after decanting. The alkaline soln was extracted with $CHCl_3$ and the chloroformic solns were combined, dried over Na_2SO_4 and evapd leaving 10.2 g of solid which were chromatographed over Si gel (1:25) and eluted with EtOH–HOAc–C_6H_6 (20:3:80; 20:3.6:80; 20:8:80) and EtOH. Partially separated alkaloids were obtained after alkalinizing with NH_4OH and were purified by preparative TLC using Si gel and eluting with a mixture of $CHCl_3$–MeOH (3.8:0.2). The separated bands were scraped off and extracted with Et_2O–MeOH (9:1) to recover the pure alkaloids. *Compound A.* Band VII (R_f 0.55) crystallizing as brownish crystals with mp 236–7° (Me_2CO)

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* Source: San Juan de Marcarapana, South of Cumaná (voucher specimen No. Cumana 0070 deposited in the University).

showed a fluorescent blue spot under UV light; IR ν_{max}^{KBr} cm^{-1}: 3125, 1625, 1560 and 1500; UV λ_{max}^{EtOH} nm: 212, 234, 239 (sh), 255 (sh), 282 (sh), 287, 344 and 347: MS *m/e* (% base peak): 182 (100, M^+), 181 (12, $M^+ - H$), 167 (12, $M^+ - Me$), 154 (18, $M^+ - H - HCN$), 127 (11, $M^+ - H - 2HCN$). (Found: C, 78.82; H, 5.27; N, 15.03. $C_{12}H_{10}N_2$ requires: C, 79.12; H, 5.49; N, 15.03). *Compound B*. Band IX (R_f 0.58) crystallizing as brownish crystals with mp 215–17° (Me_2CO) showed a fluorescent blue spot under UV light. IR ν_{max}^{KBr} cm^{-1}: 3125, 1625, 1560 and 1500; UV λ_{max}^{EtOH}: 212, 235, 251 (sh), 283 (sh), 288, 325 and 348 nm; MS m/*e* (% base peak): 210 (24, M^+), 195 (18, $M^+ - Me$), 182 (100, $M^+ - C_2H_4$), 181 (24, $M^+ - C_2H_5$), 154 (18, $M^+ - C_2H_5 - HCN$), 127 (11, $M^+ - C_2H_5 - 2HCN$). (Found: C, 79.82; H, 6.25; N, 13.02. $C_{14}H_{14}N_2$ requires: C, 80.00; H, 6.66; N, 13.25). *Compound C*. Band XI (R_f 0.48) crystallizing as brownish crystals with mp 202–204° (Me_2CO) showed a fluorescent pink spot under UV light. UV λ_{max}^{EtOH} nm: 216 and 280; MS *m/e* (% base peak): 428 (68, M^+), 413 (7, $M^+ - Me$), 411 (6, $M^+ - OH$), 397 (6, $M^+ - OMe$), 223 (67), 219 (25), 208 (26), 206 (20), 205 (11), 204 (16), 190 (14) and 69 (26). (Found: C, 64.07; H, 6.43; N, 6.39. $C_{23}H_{28}N_2$ requires: C, 64.48; H, 6.54; N, 6.54). Column chromatography of the neutral fraction on Si gel and eluting with $CHCl_3$ yielded a white solid, mp 202–204° (MeOH–$CHCl_3$), giving a violet colour with Liebermann–Burchard reagent; mp and mmp 202–204°. IR ν_{max}^{KBr} cm^{-1}: 3300, 3055 and 880; MS *m/e* (% base peak): 426 (38, M^+), 411 (10, $M^+ - Me$), 408 (4, $M^+ - H_2O$), 393 (3, $M^+ - H_2O - Me$), 220 (14), 218 (100), 207 (36), 203 (39) and 189 (38). Co-comparison of mmp and IR and the preparation of both lupenyl acetate, mp 215° (MeOH) and lupenone, mp 170 (Et_2O), confirmed the identification of this compound as lupeol. β-Sitosterol and stigmasterol were eluted as a mixture, mp 138–140° ($CHCl_3$–MeOH), giving a green colour with Liebermann–Burchard reagent. IR ν_{max}^{KBr} cm^{-1}: 3400–3300, 1640. 1380, 1375 and 835; MS *m/e* at 414 and 412.

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