SPECIALIA

N_a-demethyl-purpeline and N_a-demethyl-dihydropurpeline, new alkaloids from *Rauwolfia cumminsii* Stapf

M. M. Iwu and W. E. Court

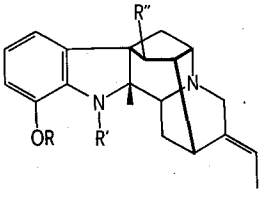
Postgraduate School of Studies in Pharmacy, University of Bradford, Richmond Road, Bradford (West Yorkshire BD7 1DP, England), 18 April 1977

Summary. N_a-demethyl-purpeline and N_a-demethyl-dihydropurpeline, new indole alkaloids, were isolated from the stem bark of Rauwolfia cumminsii Stapf. Dihydroindole alkaloids have not previously been reported as occurring in this species.

Previous work concerning the alkaloids of Rauwolfia cumminsii Stapf showed the presence of the 18-hydroxy-yohimbine esters reserpine[1] and rescinnamine and the anhydronium base serpentine in the roots and traces of reserpine and rescinnamine in the stem[2]. Most of the Rauwolfia species so far investigated yield dihydroindole (indoline) bases of the ajmaline type and we have reinvestigated Ghanaian R. cumminsii roots and stems specifically to locate such alkaloids. None were detected in the roots but 2 new alkaloids were isolated from the stems. The first compound (**I**) occurred as yellow crystals, $[\alpha]_D = 0$ and yielded UV spectral maxima (MeOH) at 229, 254 and 290 nm (log ε 4.50, 3.92 and 3.45) and gave a violet colour when sprayed with 5% ferric chloride and 35% perchloric acid reagent on silica gel layers. This suggested a methoxy substituted dihydroindole alkaloid. IR measurements using KBr discs revealed bands at 2950 s, 1735 s, 1595 s, 1470 m, 1230 m, 820 m, 760 m, 740 m cm^{-1} agreeing with an indoline structure with a keto group attached to a 5-membered ring as in purpeline (**II**). The 60 MH_Z-NMR spectrum in $(CD_3)_2$ SO showed τ 1.68 (1H, s, indole NH proton), 3.30–3.45 (3H, aromatic protons, monosubstituted aromatic ring), 6.20 (3H, s, OCH_3 protons), 6.30 (1H, d, C-2H proton), 7.5 (2H, s) and 8.4 (1H, m). The mass spectrum produced peaks at m/e 322 (100%) (M^+, accurate mass 322.1682, calculated for $C_{20}H_{22}N_2O_2$), 293 (45%), 211 (10%), 199(30%), 198 (20%), 174 (10%), 173 (20%), 160 (60%), 108 (24%), 98 (20%). From this data is was concluded that the structure (**I**) of the compound resembled purpeline (**II**) and showed decrease of the molecular ion peak by 14 mass units. As the fragment ions embodying the indole part of the molecule demonstrated similar decreases and there was no shift of the UV spectral peaks in strong alkali, it was probable that the compound was N_a-demethyl-purpeline. The presence of MS peaks at m/e 199 and 198, corresponding to m/e 213 and 212 respectively in purpeline, and the absence of a peak at m/e 166 confirmed the β-orientation of the C-2 hydrogen[3]. From biogenetic considerations and the co-occurrence of mitoridine (19, 20-didehydro-12-hydroxy-ajmalan-17-one) (**IV**) it was concluded that the compound must be N_a-demethylpurpeline (norpurpeline or 1-demethyl-19, 20-didehydro-12-methoxy-ajmalan-17-one).

The second compound (**III**), a yellow amorphous powder, was found to be a dihydro derivative of N_a-demethyl-purpeline (M^+ 324.1186, calculated for $C_{20}H_{24}N_2O_2$). Reduction of N_a-demethylpurpeline with sodium borohydride in the cold yielded the dihydro derivative. Such reduction could only yield a C-17α hydroxyl group[4] and the compound was therefore the N_a-demethyl derivative of reflexine[5] (1-demethyl-19, 20-didehydro-12-methoxy-ajmalan-17-ol). The identity of mitoridine (**IV**) was confirmed by comparison with published data (m.p., $[\alpha]_D$, UV, IR, MS)[4].

The present communication is the 1st report of the isolation of dihydroindole alkaloids in R. cumminsii. The occurence of the N_a-demethyl alkaloids of the ajmaline series, e.g. norajmaline[6], norseredamine[7] and norpurpeline, may prove to be necessary in the production of the large group of ajmaline-derived alkaloids now known to occur in plants of the genus Rauwolfia.



I R = CH_3, R′ = H, R″ = O
II R = CH_3, R′ = CH_3, R″ = O
III R = CH_3, R′ = H, R″ = α-OH
IV R = H, R′ = CH_3, R″ = O

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