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NEW QUINAZOLINOCARBOLINE ALKALOIDS FROM EUXYLOPHORA PARAËNSIS HUB.

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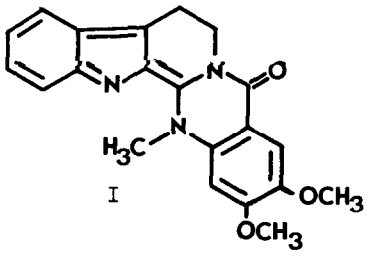
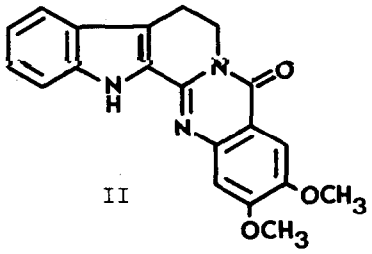
Euxylophora paraënsis Hub. (Rutaceae) is a Brazilian plant called "Pão Amarello" (1). Alumina chromatography of the methanolic extract of the bark of this plant has allowed the separation of three new, optically inactive, alkaloids : euxylophorine(I), $C_{21}H_{19}N_3O_3$ (*) (yield 0.3%), orange-red needles from anhydrous benzene, m.p. 227-30° ; euxylophoricine A (II), $C_{20}H_{17}N_3O_3$ (0.03%), colourless needles from chloroform-methanol, m.p. 295-8° ; euxylophoricine B (III), $C_{20}H_{15}N_3O_3$ (0.01%), yellow prisms from chloroform-methanol, m.p. 310-12°.

Euxylophorine(I) had the following spectroscopic characteristics : $\nu_{max.}^{nujol}$ 1670, 1656, 1618, 1603, 1545 cm^{-1}; $\lambda_{max.}^{CH_3CN}$ 253, 402 mμ (log ε 4.44 , 4.60). Its n.m.r. spectrum (60 Mc , C_5D_5N) showed two symmetrical triplets, each of two protons, centered at 3.30 and 4.75 δ ($\geqslant C-CH_2-CH_2-N \leqslant$), two singlets at 3.90 and 3.96 δ (2 $-OCH_3$) a singlet at 5.23 δ ($\geqslant N-CH_3$) and a complex multiplet between 7.2 and 8.2 δ corresponding to six aromatic protons. Treatment of I with refluxyng amyl alcoholic potash afforded 1-tetrahydronorharmanone(IV)(2) and 6-methylaminoveratric acid(V) (m.p. 167-8°, $\nu_{max.}^{nujol}$ 3400, 2700-2500, 1656 cm^{-1}, the n.m.r. spectrum included two singlets at 7.40 and 6.12 δ corresponding to two aromatic protons). An authentic sample of V was prepared by treatment of methyl 6-aminoveratrate(VI)(3) with dimethyl sulphate in $CHCl_3$ followed by alkaline hydrolysis.

On the basis of these results, structure I was assigned to euxylophorine. Conclusive proof of this was obtained by the synthesis of I which was achieved via the condensation of IV with VII(m.p. 82° from ligroin) with $POCl_3$ in refluxing

(*) Molecular weights were determined by M.S. ; all compounds mentioned in this paper gave satisfactory elemental analysis.


I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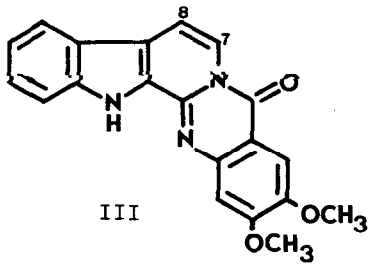
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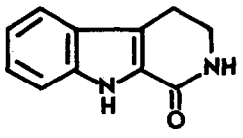
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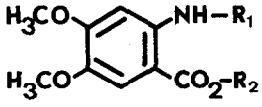

V : $R_1=CH_3$, $R_2=H$
VI : $R_1=H$, $R_2=CH_3$
VII : $R_1=CH_3$, $R_2=CH_3$
VIII: $R_1=H$, $R_2=H$

toluene.

The second alkaloid, euxylophoricine A (II), showed $\nu_{max.}^{nujol}$ 3300-3200,1650, 1615,1590 cm^{-1} ; $\lambda_{max.}^{MeOH}$ 255,337,253,360 mμ (log ε 4.50,4.49,4.54,4.43). Accor- to its n.m.r. spectrum ($CDCl_3$), euxylophoricine A (II) contained the system $\geqslant C-CH_2-CH_2-N\leqslant$ (two symmetrical triplets at 3.10 and 4.60 δ), two $-OCH_3$ groups (two singlets at 3.85 and 3.80 δ), a proton on nitrogen and six aromatic protons (multiplet between 7.2 and 7.9 δ). Hydrolysis of II with amyl alcoholic potash gave IV and 6-aminoveratric acid(VIII)(3), identified by comparison with authentic samples. The structure II for euxylophoricine A was confirmed by synthesis(IV+VI) accomplished following the procedure as described for the synthesis of I.

The third alkaloid, euxylophoricine B (III), exhibited $\nu_{max.}^{nujol}$ 3350,1656,1634, 1600,1575 cm^{-1} ; $\lambda_{max.}^{EtOH}$ 256,294,304,330,353,372,392 mμ (log ε 4.54,4.40,4.53, 4.37,4.27,4.45,4.51). Evidence for the presence of a double bond at C_7-C_8 in III resulted from its n.m.r. spectrum (CF_3COOH) which lacked signals for the $\geqslant C-CH_2-CH_2-N\leqslant$ system present in II and showed an AM pattern at 8.20 and 9.13 δ (J=7 cps). The formation of euxylophoricine B on Se dehydrogenation of II at 290° confirmed the proposed structure III.

These alkaloids represent the first examples of quinazolinocarboline alkaloids with substituents on the aromatic ring which arises biogenetically from an anthranilic acid unit (4).

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