We are intensively pursuing further studies of the photochemical behavior of aromatic nitriles and related compounds.

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Thomas S. Cantrell
Chemistry Department, American University
Washington, D. C. 20016
Received May 4, 1972

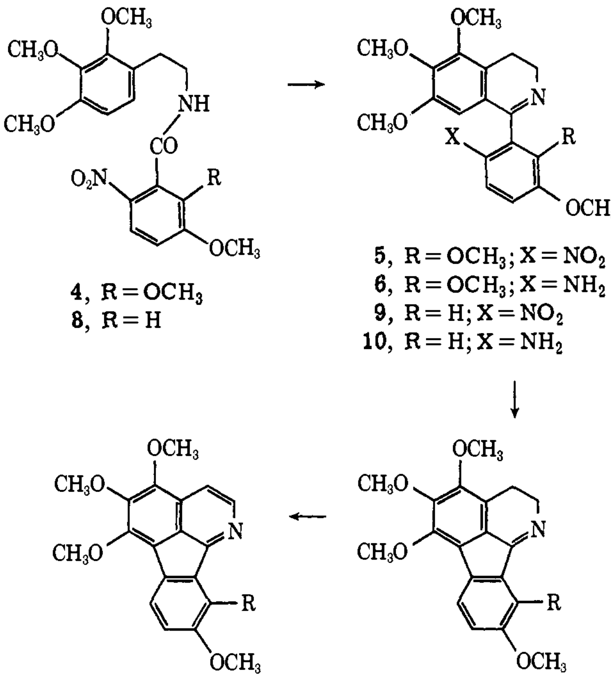
Azafluoranthene Alkaloids. A New Structural Type

Sir:

We wish to report the isolation, characterization, and structural confirmation of the first representatives of a new class of natural products, the azafluoranthene alkaloids.[1]

Two nonphenolic yellow bases imeluteine (**1**, $C_{20}H_{19}NO_5$, mp 146–147°) and rufescine (**2**, $C_{19}H_{17}NO_4$, mp 88–90°) were isolated (ptlc) from the stem alkaloid fractions of the Amazonian vines *Abuta imene* and *Abuta rufescens* (Menispermaceae).[2,3] Neither **1** nor **2** shows hydroxyl or carbonyl absorption in the infrared. Their uv–visible spectra are quite similar and are indicative of a highly conjugated system. For **1**, $\lambda_{\max}^{\mathrm{EtOH}}$ 233 nm (log ϵ 4.48), 253 (4.49), 288 (4.43), 317 (3.75), 365 (sh) (3.72), 380 (3.85), 400 (sh) (3.72); for **2**, 247 (4.52), 285 (sh) (4.31), 295 (4.34), 304 (4.29), 315 (sh) (3.84), 356 (3.65), 373 (3.78), 400 (sh) (3.32). The 100-MHz nmr spectrum ($CDCl_3$) of imeluteine shows only five aromatic methoxyls (δ 3.94, 4.02, 4.08, 4.10, and 4.17) and two aromatic AB quartets (δ 6.91, 7.60, J = 8 Hz; δ 7.57, 8.65, J = 6 Hz), consistent with structure **1**. The corresponding nmr spectrum ($CDCl_3$) of rufescine shows four aromatic methoxyls (δ 3.94, 4.05, 4.11, and 4.13), an aromatic AB quartet (δ 7.63 and 8.59, J = 6 Hz), and an aromatic ABC system (δ 7.82, 7.68, and 6.96; J_{AC} = 8 Hz, J_{BC} = 2 Hz), consistent with structure **2**.

The structures of imeluteine and rufescine were established by the following unambiguous syntheses. Reaction of β-(2,3,4-trimethoxyphenyl)ethylamine (**3**)[4] with the acid chloride of 2,3-dimethoxy-6-nitrobenzoic acid[5] gave the corresponding amorphous amide **4**, which was converted by phosphorus oxychloride in acetonitrile into the dihydroisoquinoline **5**, mp 168–170° (55% from amine **3**). Reduction of **5** with hydrazine and 10% palladium/charcoal in ethanol gave amine **6**, isolated as the crystalline hydrochloride, mp 199–200° dec (81%). Diazotization of **6** in 60% sulfuric acid, followed by treatment with activated copper, gave dihydroimeluteine (**7**), mp 105–106° (67%). Dehydrogenation of **7** by 10% palladium/charcoal in refluxing p-cymene afforded imeluteine (**1**) (48%), identical (ir, mixture melting point) with the natural base. Rufescine (**2**) was similarly synthesized from **3** and 3-methoxy-6-nitrobenzoic acid[6] by an analogous route, by way of the corresponding intermediates **8**, **9**, **10**, and **11**.



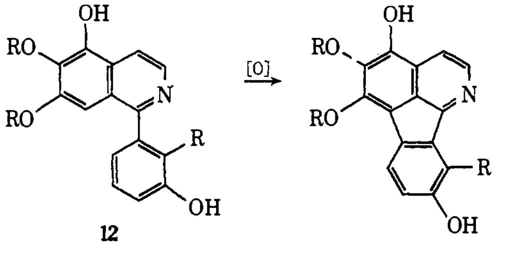
4, R = OCH_3
8, R = H

5, R = OCH_3; X = NO_2
6, R = OCH_3; X = NH_2
9, R = H; X = NO_2
10, R = H; X = NH_2

1, R = OCH_3
2, R = H

7, R = OCH_3
11, R = H

The azafluoranthene alkaloids **1** and **2** probably arise biogenetically from phenolic 1-phenylisoquinoline precursors (**12**) by oxidative cyclization, followed by methylation. The recent report of the natural occurrence of 1-phenyl-1,2,3,4-tetrahydroisoquinoline alkaloids[7,8] lends some support to this hypothesis.



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M. P. Cava,* K. T. Buck
Department of Chemistry, University of Pennsylvania
Philadelphia, Pennsylvania 19104

A. I. daRocha
Instituto Nacional de Pesquisas da Amazonia
Manaus, Brazil
Received May 1, 1972

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[1] The systematic name for the ring system found in these alkaloids is indeno[1,2,3-*i*,*j*]isoquinoline.

[2] The isolation of the novel aporphine alkaloid imenine from *A. imene* has been reported earlier: M. D. Glick, R. E. Cook, M. P. Cava, M. Srinivasan, J. Kunitomo, and A. I. daRocha, *Chem. Commun.*, 1217 (1969).

[3] The empirical formulas of **1** and **2** were determined by mass spectrometry. Found for **1**: m/e 353.1235. Found for **2**: m/e 323.1135. Satisfactory elemental analyses were obtained for all other compounds reported except for the amorphous **4** and **8**.

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[6] I. M. Heilbron, F. N. Kitchen, E. B. Parkes, and G. D. Sutton, *ibid.*, **127**, 2167 (1925).

[7] K. Leander, B. Luning, and E. Ruusa, *Acta Chem. Scand.*, **23**, 244 (1969).

[8] A. Brossi and S. Teitel, *Helv. Chim. Acta*, **54**, 1564 (1971).