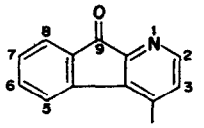
quency only slightly. Thus, since onychine must be represented by structure **1**, its biosynthesis seems to involve phenylalanine and mevalonate in an interesting pathway leading to the pyridine nucleus.



(**1**)

EXPERIMENTAL

Isolation of the constituents. The C_6H_6 ext. (70 g) of a trunk wood sample (12 kg) of *Onychopetalum amazonicum* R. Fries (voucher specimen INPA Herbarium 42234, conferred with 27847), was filtered through a Si gel column with $CHCl_3$. The solvent was evap. and the residue chromatographed on Si gel. Elution with C_6H_6–$CHCl_3$ (9:1) gave a mixture of sitosterol and stigmasterol (25 mg) and with C_6H_6–$CHCl_3$ (8:2 to 6:4) gave **1** (90 mg).

Onychine (**1**). Light yellow needles, mp 133–135° (C_6H_6–hexane 3:2), subl. 90° [Found: C, 80.26; H, 4.80; N, 7.30; M^+ 195.0678, $C_{13}H_9NO$ requires: C, 79.98; H, 4.65; N, 7.17%; M^+ 195.0684]. IR ν_{max}^{KCl} cm^{-1}: 1703, 1596, 1560, 1448, 1383, 920, 879, 831, 760, 681. UV λ_{max}^{EtOH} nm (log ϵ): 253 (4.62), 279 (3.85), 289 (3.88), 308 (3.30) (9-Fluorenone, λ_{max}^{MeOH} nm: 256, 282 inf, 292, 305 [2c]), $\lambda_{max}^{EtOH+HCl}$ nm (log ϵ): 252 (4.42), 292 inf. (4.00), 298 (4.04), 320 inf. (3.60), 331 inf (3.48). NMR (100 MHz, $CDCl_3$, τ): 1.61 (*d*, J = 5.5 Hz, mean $W_{1/2}$ = 1.1 Hz, H-2), 2.19 (apparent *dt*, J = 7.0, 1.5, 1.0 Hz, H-5 or H-8), 2.33 (apparent *dt*, J = 7.0, 1.5, 1.0 Hz, H-8 or H-5), 2.43 (*td*, J = 7.0, 7.0, 1.5 Hz, H-6), 2.60 (*td*, J = 7.0, 7.0, 1.5 Hz, H-7), 3.04 (*d*, J = 5.5 Hz, mean $W_{1/2}$ = 1.3 Hz, H-3), 7.39 (*s*, Me-4). MS *m/e* (rel. int.): 196 (15%, M^+ + 1), 195 (100, M^+), 167 (11), 166 (15), 140 (11), 139 (12).

Dihydroonychine. **1** (20 mg) in dry EtOH was hydrogenated over 10% Pd/C (10 mg). The soln. was filtered and evap. The residue, recryst. from C_6H_6–hexane, gave needles, mp 156–158°. [M^+ found: 197.0848. $C_{13}H_{11}NO$ requires: 197.0841]. IR ν_{max}^{KBr} cm^{-1}: 3160–3290, 1607, 1573, 1390, 1260, 1250, 1200, 1089, 1040, 1030, 760. UV λ_{max}^{EtOH} nm (log ϵ): 283 (3.92), 298 (3.90), 310 (4.04); $\lambda_{max}^{EtOH+HCl}$ nm (log ϵ): 296 (3.88), 326 (4.26). NMR (100 MHz, $CDCl_3$, τ): 1.97 (*d*, J = 5.5 Hz, mean $W_{1/2}$ = 1.0 Hz, H-2), 2.22–2.46 (*m*, H-5, H-7), 2.65 (*td*, J = 5.5, 5.5, 1.5, H-6), 2.64 (apparent *dt*, J = 5.5, 1.5, 1.0 Hz, H-8), 3.25 (*d*, J = 5.5 Hz, mean $W_{1/2}$ = 1.2 Hz, H-3), 4.43 (*s*, H-9), 6.8–7.2 (broad, disap. with D_2O, OH), 7.51 (*s*, Me-4). MS *m/e* (rel. int.): 198 (13%, M^+ + 1), 197 (100, M^+), 196 (62), 168 (13), 167 (15). Hydrogenolysis of dihydroonychine (7 mg) in EtOH with 7 mg Pd/C gave a mixture whose NMR spectrum included a singlet at τ 6.24. Acetylation (Ac_2O, C_5H_5N, room temp.) gave an *acetate*. IR ν_{max}^{KBr} cm^{-1}: 1735, 1600, 1565, 1230, 1020, 740. NMR (60 MHz, $CDCl_3$, τ): 1.52 (*d*, J = 5.5 Hz, H-2), 1.9–2.9 (*m*, H-5, H-6, H-7, H-8), 3.00 (*d*, J = 5.5 Hz, H-3 and *s*, H-9), 7.62 (*s*, Me-4), 7.81 (*s*, MeCO).

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OXOAPORPHINE ALKALOIDS FROM *FUSEA LONGIFOLIA* AND *SIPARUNA GUIANENSIS**

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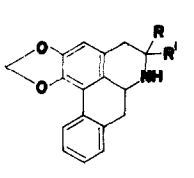
Key Word Index—*Fusea longifolia*; Annonaceae; *Siparuna guianensis*; Monimiaceae; liriodenine; cassamedine; fuseine; 1,2-methylenedioxy-5-oxoaporphine.

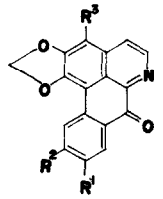
Plant. Fusea longifolia (Aubl.) Safford (Annonaceae), trivial name "envira", was collected in the vicinity of Manaus, Amazonas State, and identified by the botanist W. A. Rodrigues.

Trunk wood (7 kg) was extd. successively with C_6H_6 and EtOH. The EtOH ext. (157 g) was chromatographed on SiO_2, solvent of increasing polarity eluting in order aliphatic ketone (30 mg), mp 85–87°, sitosterol and stigmasterol (50 mg), fr. A and fr. B. Fr. A was extd. with aq HCl, the insol residue giving, after washings with MeOH, fuseine (**1a**, 18 mg). Fr. B was extd. with aq HCl,



(**1a**) R, R' = O

(**1b**) R = R' = H



(**2a**) R' = R² = H, R³ = H

(**2b**) R'–R² = OCH_2O, R³ = OMe

* Part 2 in the series "The Chemistry of Brazilian Annonaceae". For Part 1 see Ref. [1]. Part 1 in the proposed series "The Chemistry of Brazilian Monimiaceae". Sponsored by Ministério do Planejamento (FINEP) through Academia Brasileira de Ciências.

the aq soln giving, after neutralization, crude liriodenine (**2a**, 50 mg) [2]. MS indicated the presence of impurities corresponding in M^+ to a hydroxyliriodenine (15%) and a methoxyliriodenine (4%).

Plant. Siparuna guianensis Aubl. (Monimiaceae), trivial name "capitú", was collected in the vicinity of Manaus, Amazonas State, and identified by the botanist W. A. Rodrigues.

Trunk wood. The C_6H_6 ext. (10 g *ex* 2.4 kg) was chromatographed on SiO_2, solvent of increasing polarity eluting in order an oil, sitosterol and stigmasterol (60 mg), liriodenine (**2a**, 55 mg) [2] and cassamedine (**2b**, 80 mg) [3].

Identifications. The known compds. were identified by comparison of mp and spectral data with lit data [4].

Fuseine (**1a**), 180° subl, 280° dec. Formally, the replacement of 2 hydrogens in anonaine (**1b**, $C_{17}H_{15}NO_2$) [5] by oxygen leads to fuseine (M found: 279.0891; $C_{17}H_{13}NO_3$ requires: 279.0895). Indeed, fuseine contains a carbonyl group [ν_{max}^{KBr} (cm^{-1}): 3200, 1680], which is located at C-5 since the UV [λ_{max}^{EtOH} (nm): 235, 273, 317 ($\log \epsilon$ 4.48, 4.55, 3.91)] and the aromatic region of ^{1}HMR [τ(DMSO): 1.9–2.1 (*m*, H-11), 2.55–2.75 (*m*, H-8,9,10), 3.30 (*s*, H-3)] of the two compounds are very nearly identical. Again, as in the case of **1b**, the methylenedioxy group of **1a** forms an AB system [ν (DMSO): 3.81, 3.95, *J* 2Hz] and ring D contains 4 adjacent hydrogens [ν_{max}^{KBr} (cm^{-1}): 760]. Consistent with the formulation of fuseine as an amide is its insolubility in aq HCl (see above) and the elimination of the elements of HNCO through a retro Diels–Alder type reaction which, together with other fragmentation paths, is characteristic of aporphines [4,6] and accounts for all major MS peaks: M^+ (100%); M^+–H (76); M^+–HNCO (11), M^+–HNCO–H (10); M^+–CH_2O (20), M^+–CH_2O–H (12); M^+–CH_2O–CO (10), M^+–CH_2O–H–CO (23).

Comments. The amide group differentiates fuseine from all other, over 180, aporphine alkaloids [7]. 5-Oxoaporphines should arise by the oxidation of aporphines, a reaction which has precedent in the biogenesis of tetrahydroberberine derivatives [4], and may well function as intermediates in the biosynthesis of aristolochic acids.

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