(Me_2CO-d_6): δ 2.07(*m*, C-3 and impurities of solvent), 2.70(2H, *m*, C-4), *ca* 4.9(2H, *m*, C-2 and anomeric H of sugar), 6.02 and 6.23(2H, *d*, J=2Hz respectively, C-6 and 8), 6.84 and 7.26(4H, *d*, J=9Hz respectively, C-2',3',5' and 6'), 3.20–4.04(*ca* 5H, m, –O–CH of sugar), 4.24 and 4.55(3H, OH of sugar), 8.07 and 8.26(2H, *s* respectively, aromatic OH). MS *m/e*: 390(M^+), 258(M^+-sugar). Dimethyl ether **2**. CH_2N_2, mp 159°(MeOH-H_2O), IR ν_{max}^{KBr} cm^{-1}: 3370, 1620, 1595, 1500, 1142, 1052, 821; PMR($CDCl_3$). δ 3.61 and 3.76(6H, *s*, respectively, 2 × phenolic OMe). MS *m/e*: 418(M^+), 286(M^+-sugar). Penta-acetate **3**, C_5H_5N–Ac_2O, mp 183°(MeOH), IR ν_{max}^{KBr} cm^{-1}: 1768, 1750, 1615, 1602, 1495, 1375, 1220, 1197, 1130, 1076; PMR($CDCl_3$): δ *ca* 2.05(9H, 3 × MeCOO– of sugar moiety), 2.25 and 2.27(6H, 2 × phenolic CH_3COO–); MS *m/e*: 600(M^+), 342(M^+-sugar moiety) 300(342-CH_2CO). Dimethyl ether triacetate **4**, mp 183° (MeOH–H_2O), IR ν_{max}^{KBr} cm^{-1}: 1755, 1623, 1595, 1380, 1513, 1220, 1140, 1060; MS *m/e*: 544(M^+), 286(M^+-sugar moiety), 259. TMSiate **7** of **1**, HMDS-TMCS in C_5H_5N, PMR(CCl_4): δ 4.78(1H, *d*, J=7.5 Hz, anomeric H of sugar).

Hydrolysis of **1**. Enzymatic hydrolysis: **1**(140 mg) was suspended in H_2O(28 ml) and incubated at 30° for 4 days with emulsin (100 mg). The hydrolysate was extracted with Et_2O and extract evaporated and recrystallized with EtOH–H_2O to give **5**, mp 204°, Gibbs test, +. IR ν_{max}^{KBr} cm^{-1}: 3400, 1620, 1600, 1517, 1460, 1245, 1145, 1067, 827, 810.; MS *m/e*: 258(M^+), 139, 120; CD(in MeOH, *c* 0.001 g/ml): $(\theta)_{285}$O, $(\theta)_{269}$ − 732, $(\theta)_{250}$0, $(\theta)_{238}$ + 410. From aq layer, D-xylose was identified by PC(R_f 0.28). Hydrolysis using HCl: **1** was refluxed with 1% HCl in 90% MeOH in N_2 for 1 hr. **5** was isolated from Et_2O extract of the hydrolysate, and D-xylose in aqueous MeOH layer was identified by direct comparison of its osazone, mp 162°, with an authentic D-xylosazone.

Hydrolysis of **2**. **2** was refluxed with 1% HCl in 90% MeOH in N_2 for 2 hr. From the Et_2O extract, **6** was obtained. **6**, MS *m/e*: 286(M^+), mp 135° (*n*-hexane), undepressed on admixture with (2S)-7,4'-dimethoxy-5-hydroxyflavan prepared from naringenin, and IR spectra of both substances were identical. CD(in MeOH, *c* 0.001 g/ml): $(\theta)_{283}$O, $(\theta)_{271}$ −729, $(\theta)_{246}$O, $(\theta)_{240}$ +415.

Synthesis of (2*S*)-7,4'-*dimethoxy*-5-*hydroxyflavan*. By methylation using CH_2N_2, authentic naringenin ((2S)-5,7,4'-trihydroxyflavanone) afforded the dimethyl ether, mp 116°(MeOH), MS *m/e*: 300(M^+). This (60 mg) was dissolved in AcOH and was allowed to stand for 1 day with Zn Hg(5g) and conc HCl(5 ml). From Et_2O extract of reaction mixture, (2S)-7,4'-dimethoxy-5-hydroxyflavan was obtained. Its mp 134°(*n*-hexane), $C_{17}H_{18}O_4$ (Observed: *m/e* 286.12155, $C_{17}H_{18}O_4$ requires: 286.12051); IR ν_{max}^{KBr} cm^{-1}: 3365, 1620, 1605, 1515, 1246, 1140, 1080, 810.

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REFERENCES

1. Hopkins, C. Y. and Chisholm, M. J. (1966) *Chem. Ind.* 1533.
2. Cardillo, G., Merlini, L. and Nasini, G. (1971) *J. Chem. Soc.(C)*, 3967.
3. Kamerling, J. P., de Bie, M. J. A. and Vliegenthart, J. F. G. (1972) *Tetrahedron* **28**, 3037.
4. Arya, V. P., Erdtman, H., Krolikowska, M. and Norin, T. (1962) *Acta Chem. Scand.* **16**, 518.

Phytochemistry, 1976, Vol. 15, pp. 1186–1187. Pergamon Press. Printed in England.

ONYCHINE, AN ALKALOID FROM *ONYCHOPETALUM AMAZONICUM**

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Key Word Index—*Onychopetalum amazonicum*; Annonaceae; onychine; 1-aza-4-methylfluorenone; phenylalanine-mevalonate alkaloid.

The trunk wood of *Onychopetalum amazonicum* (Annonaceae), trivial name "envira cajú", from the vicinity of Manaus, Amazonas, contains besides sitosterol and stigmasterol an alkaloid designated onychine. The hydrogens of onychine, $C_{13}H_9NO$, were assigned to an *ortho*-disubstituted benzene ring, in view of the IR (760 cm^{-1} band) and NMR evidence, and a γ-methylpyridine unit. The NMR doublets (J = 5.5 Hz) due to the α-(τ 1.61) and β-(τ 3.04) protons appeared at the expected frequencies (τ 1.50 and 2.94 resp.) [1] and the Hβ-signal showed secondary splitting which could be cancelled by double irradiation at the methyl frequency. The ring systems must be bridged by a carbonyl (ν_{max} 1703 cm^{-1}), a consideration which, in view of the preceding evidence, pointed to 1-(or 4)-aza-4(or 1)-methylfluorenone as the structure for onychine.

Indeed, onychine and fluorenone (ν_{max} 1705 cm^{-1} [2a]) gave strikingly similar UV spectra (see Experimental). Also, reduction of onychine led to a mixture of enantiomeric secondary alcohols with two aromatic substituents, as evidenced by the frequency (τ 4.43) and shift upon acetylation (Δ −1.43 ppm) of the NMR singlet due to the oxymethine proton. Hydrogenolysis of the carbinol produced a methylene group which, precisely as the CH_2-group of fluorene [2b], gave rise to a singlet at τ 6.24.

The structural alternative in which the CO and methyl groups are *ortho*-related cannot represent onychine, reduction of the carbonyl affected the methyl NMR fre-

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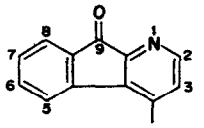
quency only slightly. Thus, since onychine must be represented by structure **1**, its biosynthesis seems to involve phenylalanine and mevalonate in an interesting pathway leading to the pyridine nucleus.



(**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).

REFERENCES

1. Jackman, L. M. and Sternhell, S. (1969) *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, 2nd ed., p. 211, Pergamon, Oxford.
2. *Sadtler Standard Spectra*: a. IR 7390, b. NMR 288, c. UV 2095, Sadtler Research Laboratories, Philadelphia.

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

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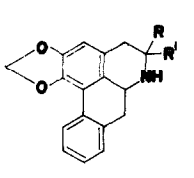
Key Word Index—*Fusea longifolia*; Annonaceae; *Siparuna guianensis*; Monimiaceae; liriodenine; cassamedine; fuseine; 1,2-methylenedioxy-5-oxoaporphine.

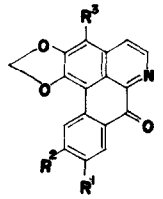
Plant. Fusea longifolia (Aubl.) Safford (Annonaceae), trivial name "envira", was collected in the vicinity of Manaus, Amazonas State, and identified by the botanist W. A. Rodrigues.

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.