which was crystallized from $CHCl_3$–C_6H_6, mp 195°. Yield 0.0015%. UV: λ_{max}^{EtOH} 236, 245, 266, 274, 306, 320 nm with log ε 4.6, 4.57, 4.64, 4.73, 3.88, 3.78. IR: ν_{max}^{Nujol} 3431 (—NH), 1690, (ester carbonyl) 1635, 1613, 1609 cm^{-1} (aromatic). (Found: C, 70.56; H, 5.12; N, 5.48%. Calculated for $C_{15}H_{13}NO_3$: C, 70.58; H, 5.13; N, 5.49%).

Hydrolysis of mukonine to mukoeic acid (**2**). Mukonine (8 mg) was dissolved in 10% alcoholic KOH (5 ml) and refluxed at 100° for 5 hr. After the completion of the reaction, the alcohol was removed keeping the soln vol, constant by addition of H_2O. The soln was then cooled, acidified with HCl and filtrated. The residue was washed with H_2O, dried and crystallized from C_6H_6, when a compound mp 242°, identical with mukoeic acid was obtained (mmp, TLC, UV, IR). Yield 7 mg.

4-Amino-3-hydroxy benzoic acid (**7**). 4-Nitro-3-hydroxybenzoic acid (2.5 g) dissolved in EtOH (100 ml) was catalytically hydrogenated at atm. pres. and room temp. using 10% Pd–C and Raney Nickel catalyst (1:1, 0.5 g) with constant stirring. After completion of the reaction it was freed from catalyst and the solvent removed by distillation. The residue was crystallized from C_6H_6, mp 215° (lit. 216°). Yield 2 g.

Cyclohexane 1,2-dione-1-(4′-carboxy-2′-hydroxy) phenylhydrazone (**9**). An aq. soln of NaOAc (5 g in 10 ml) was added to a soln of formyl cyclohexanone (3 g) in MeOH (35 ml). A diazotised soln of 4-amino-3-hydroxy benzoic acid (2 g) was added with mechanical agitation during 30 min, when crystals of compound (**9**) were obtained. This was further purified by crystallization from EtOH mp 178–179° (yield 2 g). UV: λ_{max}^{EtOH} 225, 270 nm with log ε 4.7, 4.6. IR: ν_{max}^{Nujol} 3480 (—NH), 3320 (—OH), 1700 ($>$C=O), 1610, 890 cm^{-1} (aromatic residue). (Found: C, 59.50, H, 5.30, N, 10.58%. Calculated for $C_{13}H_{14}N_2O$: C, 59.54, H, 5.38, N, 10.68%).

3-Carboxy-1-hydroxy-8-oxo-5,6,7,8-tetrahydrocarbazole (**10**). Compound (**9**) (2 g) was added to boiling HOAc (13 ml) and conc HCl (4 ml) for 3 min. The reaction mixture was poured in ice–H_2O and filtered. The product obtained was washed, dried and crystallized from C_6H_6 when (**10**) was obtained, mp 190–192° (yield 1.5 g). UV: λ_{max}^{EtOH} 232, 285 nm with log ε 4.42, 4.16. IR: ν_{max}^{Nujol} 3480 (—NH), 3200 (—OH), 1700, 1630 ($>$C=O), 1610, 870 cm^{-1} (aromatic residue). (Found: C, 63.58; H, 4.50; N, 5.68%; Calculated for $C_{13}H_{11}NO_4$: C, 63.67; H, 4.57; N, 5.71%)

1-Methoxy-3-carbomethoxy-5,6,7,8-tetrahydrocarbazole (**11**). Compound (**10**) (1.5 g) dissolved in freshly dist. ethylene glycol 25 ml) was heated with hydrazine hydrate (99–100%; 1 g) and KOH (0.9 g) at 190° for 1 hr and up to 200° under reflux for 3 hr. After the completion of the reaction the mixture was poured in ice-H_2O and extracted with Et_2O. On evapn of solvent an oily mass was obtained which was taken up in C_6H_6 and filtered through a Si gel column. The C_6H_6 soln on evapn furnished a semi solid product which could not be crystallized. A cold Et_2O soln of CH_2N_2 was added to a soln of the above tetrahydrocarbazole in MeOH (25 ml) kept at 0–5°. The mixture was then kept for 16 hr at 0°. After the decomposition of excess CH_2N_2 with HOAc and removal of solvent, a semisolid mass was obtained. This was taken up in Et_2O, washed with H_2O to free it from acid and then dried. After removal of Et_2O, (**11**) was obtained as colourless solid. On crystallization from C_6H_6–petrol (1:1), (**11**) was obtained, mp 172–173°. Yield 0.5 g. UV: λ_{max}^{EtOH} 240, 285, 300 nm with log ε 4.54, 4.12, 3.85; IR: ν_{max}^{Nujol} 3480 (—NH), 3220 (—OH), 1740 (—COOMe), 1200 cm^{-1} (aromatic ether). (Found: C, 69, H, 6.58; N, 5.35%; Calculated for $C_{15}H_{17}NO_3$; C, 69.48; H, 6.61; N, 5.40%).

1-Methoxy-3-carbomethoxy carbazole (**1**). The above compound (0.8 g) was dissolved in *p-cymene* (3 *ml*) and was intimately mixed with 10% palladized charcoal (50 mg) and the mixture heated in sealed tube at 200° for 5 hr. After the reaction, the solvent was separated from Pd/C by filtration and the solvent was evapd at 100°. An oily mass was obtained which on crystallization from C_6H_6–$CHCl_3$ yielded a compound mp 185–187°. This was identical in all respect with the natural and synthetic specimens stated above (mmp, TLC). Yield 0.5 g.

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ALKALOIDS OF *HAZUNTA MODESTA*

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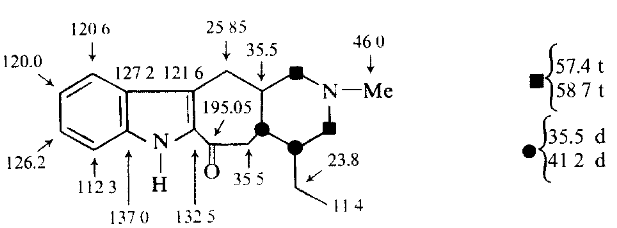
Key Word Index—*Hazunta modesta*; Apocynaceae; indole alkaloids; voacangine; coronaridine; 19-isoheyneanine; 16-decarbomethoxy-20-epiervatamine; 6-oxosilicine; tabernaelegantine A.

In a previous paper [1] we reported the isolation of 3 alkaloids, dregamine, tabernaemontanine and ibogamine from the roots of *Hazunta modesta* (Apocynaceae) collected in Madagascar. In this note we have described the characterization of a further 6 alkaloids we have found in this plant.

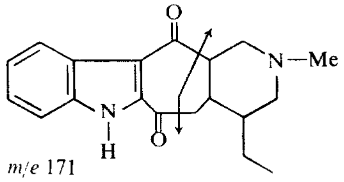
Alkaloid **1**, voacangine (mp, [α], UV, PMR and MS identical to those reported [2]). Alkaloid **2** coronaridine oily $[\alpha]_D^{20}$ −31.9 ($CHCl_3$ $c = 1$) UVλ_{max}^{MeOH} nm (log ε) 295 (3.88) 285 (3.98) 231 (4.28). ^{13}C-NMR identical with that reported [3]. Alkaloid **3** 19-isoheyneanine, recently isolated from *Peschiera affinis* [4a] and *Pandaca mocquerysii* [4b] that we have isolated as solvated with a molecule of solvent of crystallization, mp 155–158° (EtOAc) $[\alpha]_D^{20}$ −34.2 (MeOH, $c = 0.5$) mp 170–172° (cyclohexane) [4a]; acetate mp 215° (C_6H_6) $[\alpha]_D^{20}$

-7.1 ($CHCl_3$; $c = 1$), mp 215° [α] -12 [4b]. Its PMR and MS are identical with those reported. The ^{13}C-NMR spectrum is essentially identical with that published [3] apart from the differences at C-10, C-21 and C-14 that we have found at 119.3, 54.2 and 27.0 against 120.3, 54.7 and 26.0.

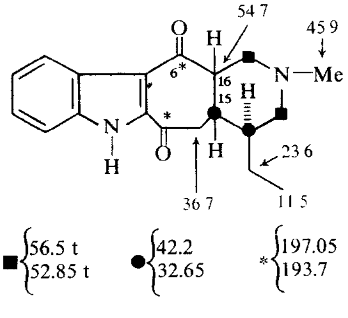
Alkaloid **4**, 16-decarbomethoxy-20-epiervatamine, mp 99–100° (MeOH) $[\alpha]_D^{20}$ -16 ($CHCl_3$, $c = 0.5$). A vobasinic structure, now revised [7, 10] to ervatamic had been ascribed to this substance isolated from *Rauwolfia discolor* [5] and *Hazunta siliciola* [6]. UV and MS spectra are identical to those reported [5]. PMR (C_5H_5N, 60 MHz) 7.83 (1H, *m*, indolic *NH*); 7.68 (1H, *t*), 7.6 (1H, *d*), 7.48 (1H, *d*), 7.35 (1H, *t*) aromatic; 2.22 (3H, *s*, $\underline{NCH_3}$); 0.7 (3H, *t*, $\underline{CH_3}$—CH_2—). Its ^{13}C-NMR spectrum in $CDCl_3$ is noteworthy as to the two low-field methylene triplets in α at N—Me, which may be regarded as characteristic of the ervatamic skeleton in comparison with the vobasinic [8].



Alkaloid **5**, mp 257–258° $[\alpha]_D^{20}$ -21 (C_5H_5N, $c = 0.16$) UV$\lambda_{max}^{CHCl_3/MeOH}$ nm (log ε) 335 (4.16) 257 (4.27) 227 (4.11); IR (KBr) cm^{-1} 3080, 2800, 1668, 1612 (the values at 1668 and 1612 cm^{-1} are in agreement with those of 1-amino-anthraquinone [9]), PMR (C_5H_5N, 60 MHz) 2.2 (3-H, *s*, $\underline{NCH_3}$). MS *m/e* 310 (100) (M^+) 293 (70) 171 (80) 124 (40). Of particular interest is the fragment at *m/e* 171 which may be ascribed to that shown below.



As the compound is extremely insoluble, its ^{13}C-NMR spectrum was recorded in C_5D_5N at 80°, thus masking the signals of the aromatic part. As to the remaining carbons, the following significant data may be given in comparison with **4**, apart from the differences due to interaction with the solvent:



The most significant changes are: $C(6)H_2$ disappearance and subsequent appearance of a second carbonyl and low-field displacement (54.75) of C(16)H according to its α-position at the carbonyl group. These data indicate for **5** the structure of the alkaloid 6-oxosilicine recently isolated from *Hazunta siliciola* [10].

Alkaloid **4** dimer, mp 223–224° (MeOH) $[\alpha]_D^{20}$ -33.6 ($CHCl_3$, $c = 1$) was identified as tabernaelegantine A [11]. Its ^{13}C-NMR proves identical with that reported whilst its PMR ($CDCl_3$, 270 MHz) shows some differences as compared with the reported data in the aromatic part. In particular, at 7.24 and 6.83 there are two doublets $J = 8.4$ Hz, which may be ascribed to the ibogainic part of the molecule whilst the vobasinic part gives rise to 4 signals, 7.62 (*d*), 7.11 (*t*), 7.04 (*t*), 6.98 (*d*) having 3 J_{prim} whose values range from 7 to 9 Hz; finally at 7.56 there are the two protons of the indolic NH as a broad singlet.

MS *m/e* 706 (100) (M^+) 524 (100) 393* (15) 367* (5) 353* (10) 337* (15) 196 (20) 182 (50) 136 (20) 124 (15) 122 (18). The spectrum corresponds to that reported and the asterisked fragments not reported in [11] are indicated because they seem to us to be indicative of the structure.

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