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N_a-FORMYLECHITAMIDINE, AN ALKALOID FROM *ALSTONIA BOONEI**

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Key Word Index—*Alstonia boonei*, Apocynaceae, alkaloids, N_a-formylechitamidine

Abstract—A known alkaloid, echitamidine, and a new alkaloid, N_a-formylechitamidine, have been isolated from the stem bark of *Alstonia boonei* The structure of this new alkaloid was assigned on the basis of chemical and spectroscopic data

INTRODUCTION

Alstonia boonei is a common plant in Nigeria. Since traditional healers use its stem bark in the treatment of malaria, a rampant disease in Nigeria, a thorough investigation of its alkaloidal and other constituents was initiated Much work has been done on various other species of *Alstonia* [1–11] However, little previous work has been reported on *A boonei*, although the hypotensive activity of echitamidine is well known and the compound has been previously identified in *A boonei* [12] Echitamidine also occurs in *A congensis* [13] and consequently *A boonei* is in the second group of the *Alstonia* species [14]

RESULTS AND DISCUSSION

The presence of a N_a-formyl indolinic structure in this new alkaloid was indicated from the ^{1}H NMR, UV and IR spectral data, as shown in the Experimental The deformyl derivative of this alkaloid was obtained by acidic hydrolysis and identified as echitamidine by comparison with an authentic sample The UV hypsochromic effect observed in this alkaloid in comparison with its deformyl derivative, echitamidine, is due to the partial double bond character of the N_a–CHO bond which does not allow resonance interaction of the lone pair of the nitrogen in the β-aniline acrylate chromophore The third alkaloid detected by TLC was present in insufficient quantities to allow further characterization

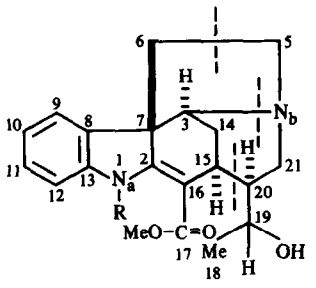
EXPERIMENTAL

Plant material The stem bark of *A boonei* De Wild was collected at Nsukka, Anambra State, Nigeria, the plant was identified by A Ozioko A voucher sample has been preserved at the Herbarium of the Department of Botany, University of Nigeria, Nsukka, under the cipher BH, UNN 261

Extraction and separation The stem bark was sun-dried, pulverized (2 5 kg) and extracted with petrol, 40–60° (2 5 l) in a Soxhlet (40 hr) and then eluted with 2% aq HOAc until a negative Dragendorff reaction was observed The pooled acidic solns were made alkaline to pH 8 with $NaHCO_3$ and then extracted × 3 with $CHCl_3$ (7 5 l) The pooled extracts were dried (Na_2SO_4) and evapd *in vacuo* to give a dark brown syrup (5 g) No quaternary alkaloids were detected in the aq phase TLC assays of the $CHCl_3$ extract indicated the presence of two major and one minor alkaloids The extract (5 g) was subjected to counter-current distribution (CCD) between $CHCl_3$ and Pi–citric acid buffer (mobile phase) at discontinuously decreasing pH [15] in a Craig Post apparatus (200 stages, 10 10 ml, upper and lower phase) The separation was monitored by TLC analysis on silica gel GF-254 (C_6H_6–EtOAc–Et_2NH, 5 4 1) At pH 4 8, alkaloid **2**, 218 mg, K_rK_b $3\,5 \times 10^{-10}$, and alkaloid **1**, 167 mg, K_rK_b $2\,3 \times 10^{-10}$, were eluted At pH 4 4, the minor alkaloid, 0 18 mg, K_rK_b 7×10^{-11}, was eluted The alkaloids were extracted with $CHCl_3$ from the aq soln after alkalinization with $NaHCO_3$

N_a-*Formylechitamidine* (**2**) Crystals from EtOAc and *n*-hexane, mp 171–173°, $[\alpha]_D^{25}$ – 163° (EtOH, *c* 0 8), UV λ_{max}^{EtOH} nm (log ε) 290 sh (3 4), 252 (3 95), 210 (4 24), IR $\nu_{max}^{CHCl_3}$ cm^{-1} 3480 (br), 1710, 1670, ^{1}H NMR (60 MHz, $CDCl_3$) δ1 20 (3H, *d*, *J* = 7 Hz, H_3-18), 3 70 (1H, partially overlapped, H-19), 3 80 (3H, *s*, COOMe), 7 10–7 24 (3H, *m*, H-9, H-10, H-11), 7 76 (1H, *br d*, *J* = 8 Hz, H-12), 8 78 (1H, *s*, CHO), MS *m/z* (rel int) 368 $[M]^+$ (48), 340 (27), 269 (100), 226 (14), 210 (11), 194 (30), 184 (43), 180 (47) (Found C, 67 80; H, 6 71, N, 7 40 $C_{21}H_{24}N_2O_4$ requires C, 68 46, H, 6 57, N, 7 60%)

Echitamidine (**1**) Crystals from EtOAc and *n*-hexane, mp 130–131°, $[\alpha]_D^{25}$ – 505° (EtOH, *c* 0 8), UV λ_{max}^{EtOH} nm (log ε) 334 (4 47), 300 (4 26), 237 (4 35)



		R
1	Echitamidine	H
2	N_a-Formylechitamidine	CHO

Dashed lines indicate mass fragmentation

*Part 2 in this series "Research on Nigerian Medicinal Plants" For Part 1 see Oguakwa, J U , *J Pharm Sci* (in press)

Deformylation of **2** 25 mg **2** was hydrolysed with 1 M HCl at 60° for 30 min The product was extracted with $CHCl_3$ after alkalinization with $NaHCO_3$, purified by CCD, and identified as echitamidine (12 mg) by direct comparison with an authentic sample

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