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16-EPIVENENATINE AND 16-EPIALSTOVENINE, NEW STEREOMERS FROM *ALSTONIA VENENATA*

A. CHATTERJEE, D. J. ROY and S. MUKHOPADHYAY†

Department of Pure Chemistry, University College of Science, 92, Acharya Prafulla Chandra Road, Calcutta 700009, India

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Key Word Index—*Alstonia venenata*; Apocynaceae; alkaloids; 16-epivenenatine; 16-epialstovenine; structural determination.

Abstract—16-Epivenenatine and 16-epialstovenine have been isolated from *Alstonia venenata*. The structures and stereochemistry of these two new bases have been determined from spectral analysis, chemical studies and correlation experiments with venenatine and alstovenine.

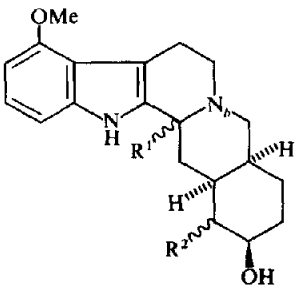
INTRODUCTION

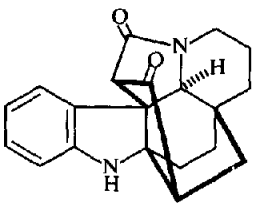
Two new compounds, 16-epivenenatine (**1**) and 16-epialstovenine (**2**), were obtained from the root bark of *Alstonia venenata* in addition to venenatine (**3**) [1–3], alstovenine (**4**) [2–4], venoxidine (**5**) [5] and 5,22-dioxokopsane (**6**) [6, 7]. The present communication is concerned with the structure and chemistry of these two new alkaloids.

RESULTS AND DISCUSSION

16-Epivenenatine (**1**), $C_{22}H_{28}N_2O_4$ (M^+ 384), mp 188–190° (acetone–methanol), $[\alpha]_D^{25}$ −52.68° (EtOH), yield 0.01%, exhibited UV absorption characteristic of a 4-methoxyindole system (**7**). The ^1H NMR spectrum showed the indole >NH at δ 8.99 (1 H, s, disappearing on deuteration), the aromatic OMe at 3.77 (3 H, *s*) and the carbomethoxyl at 3.74 (3 H, *s*). The spectrum further revealed the presence of an ABX pattern for the three aromatic protons which resonated at δ 7.01 (2 H, *m*) and 6.47 (1 H, *dd*, $J_o = 7$, and $J_m = 2$ Hz). This required that the aromatic OMe be placed either at C-9 or C-12. From the UV spectrum this group could be unambiguously placed at C-9. The two one-proton signals observed at δ 4.19 (1 H, *s*) were attributed to the equatorial C-17 proton [3, 8] and the other at 4.79 (1 H, *s*) to the C-3 equatorial proton. The C-17 OH appeared at δ 2.06 as a one-proton broad singlet which disappeared on deuteration. The reluctance of 16-epivenenatine to undergo oxidation with mercuric acetate to give the quaternary compound **8** supported the equatorial nature of the C-3 hydrogen.

Alkaline hydrolysis [9] of **1** with methanolic-KOH yielded venenatic acid (**9**), $C_{21}H_{26}N_2O_4$, mp 245° (dec.), which on subsequent methylation with diazomethane furnished the more stable isomer, venenatine (**3**), $C_{22}H_{28}N_2O_4$, mp 130°. This experiment conclusively proved that the C-16 carbomethoxy in 16-epivenenatine is





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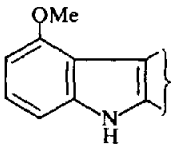

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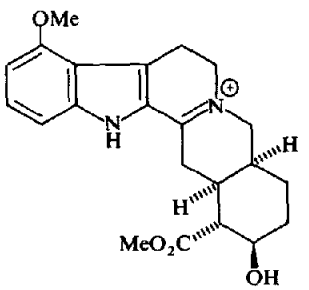
1	β-H	α-CO_2Me
2	α-H	α-CO_2Me
3	β-H	β-CO_2Me
4	α-H	β-CO_2Me
5	β-H	β-CO_2Me and $N_b \rightarrow O$
9	β-H	β-CO_2H



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† Present address: Department of Pharmacognosy and Pharmacology, University of Illinois at the Medical Center, P.O. Box 6998, Chicago, IL 60680, U.S.A.

α and axial, and the formation of venenatine, the β- and axial configuration of the OH group at C-17 in **1**.

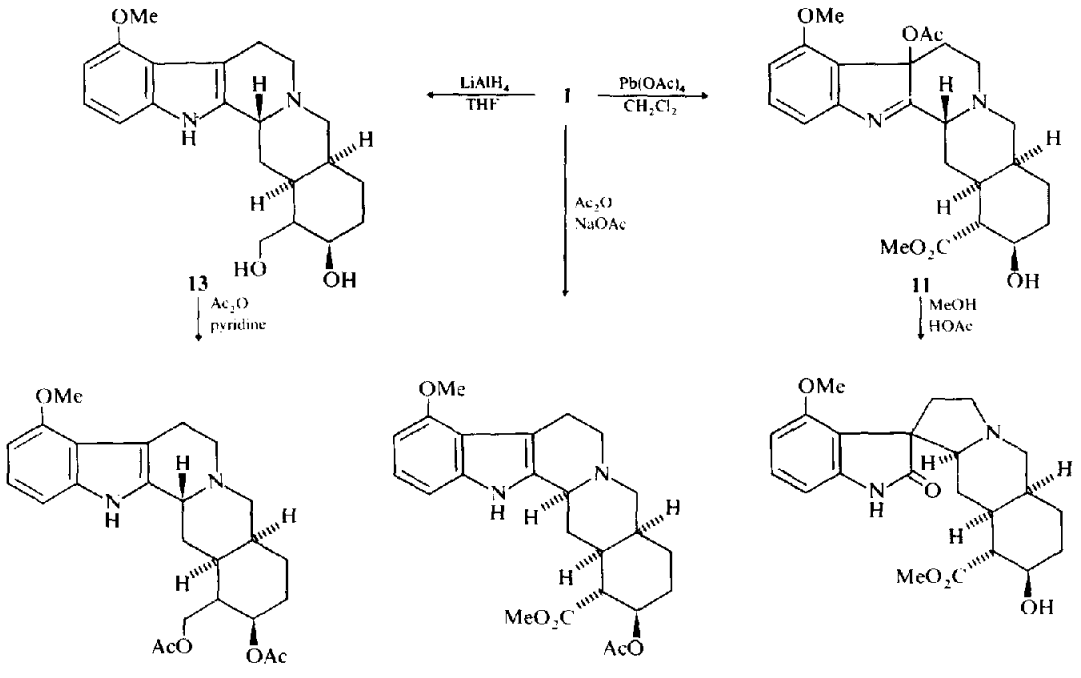
Acetylation of **1** with acetic anhydride and fused sodium acetate furnished a monoacetylated product **10**, $C_{24}H_{30}N_2O_5$, mp 130°, $[\alpha]_D^{25}$ +34.93° (EtOH). The UV absorption spectrum of this compound was comparable to that of 9-methoxyyohimbine alkaloids [4, 10]. The IR spectrum indicated the presence of an acetoxy carbonyl at 1740 cm^{-1}. This was further confirmed by the appearance of the singlet at δ 1.99 (3 H) in the ^{1}H NMR spectrum. The one-proton singlet at δ 5.35 was characteristic of the C-17-H. The OMe and carbomethoxyl protons resonated in the usual positions at δ 3.77 and 3.60 (3 H, *s* each) and the indolic proton (>NH) at δ 7.83 (1 H, *s*, disappearing on deuteration). The absence of the signal for the β and equatorial C-3 H in the region δ 4.30–4.50 for this yohimbinoid skeleton indicated that in the acetylated product **10** the configuration of this proton must be α and axial [11, 12]. It is interesting to note that 16-epivenenatine (1) undergoes isomerization at C-3 during acetylation.

16-Epivenenatine was converted to the corresponding oxindole (**12**) via 7-acetoxyindolenine (**11**), by the action of lead tetraacetate in methylene chloride, a reaction characteristic of D/E *cis* series of indole alkaloids [13]. The indolenine (**11**) on refluxing in methanol containing a few drops of acetic acid afforded the oxindole **12**, $C_{22}H_{28}N_2O_5$ (M^+ 400), mp 252°, $[\alpha]_D^{25}$ −29.20° (EtOH). The UV spectrum was characteristic of an oxindole chromophore. In ^{1}H NMR spectrum the indole (>NH) appeared at δ 8.08 (1 H, *s*, disappearing on deuteration), the OMe protons at 3.75 (3 H, *s*) and the carbomethoxyl protons at 3.51 (3 H, *s*). The C-17 OH appeared in the up-field region at δ 1.65 (1 H, *s*, disappearing on deuteration). The aromatic protons showed the ABX system at 7.09 (1 H, *m*, C-11 H) and 6.45 (2 H, *m*, C-10 H and C-12 H). The C-17 H appeared at δ 4.01 as a one-proton singlet.

Lithium aluminium hydride reduction of **1** afforded the diol **13**, $C_{21}H_{28}N_2O_3$ (M^+ 356), mp 165°, $[\alpha]_D^{25}$ −28.96° (EtOH), in which the carbomethoxy group was reduced to the corresponding alcohol. The ^{1}H NMR spectrum exhibited a broad singlet at δ 3.25 for the two protons of the two –OH groups which disappeared on deuteration. The acetylated product **14**, $C_{25}H_{32}N_2O_5$ (M^+ 440), mp 120–125°, $[\alpha]_D^{25}$ −17.12° (EtOH), of the diol **13** showed two broad bands (ν_{max}^{KBr} 1715–1735 cm^{-1}) for the two acetoxy carbonyls. The ^{1}H NMR spectrum showed two peaks at δ 1.96 and 1.84 (3 H, *s*, each) for the acetate Me groups. This clearly indicated that the carbomethoxyl group in alkaloid **1** was reduced to the corresponding alcohol which easily underwent acetylation to **14**.

The second new alkaloid **2**, $C_{22}H_{28}N_2O_4$ (M^+ 384), mp 227–230°, $[\alpha]_D^{25}$ +72.02° (EtOH), yield 0.001%, showed a close resemblance to 16-epivenenatine (**1**) in its chemical and spectral properties, the only difference being the nature of the C-3 H. In its ^{1}H NMR spectrum, **2** showed a one-proton signal at δ 4.11 (1 H, *s*) indicating the presence of the C-17 equatorial hydrogen [4, 8]. The absence of any proton signal in the region δ 4.3–4.5 indicated that the C-3 H was probably axial. The axial C-3 H signals appear at a higher field and are often obscured by other alicyclic proton signals [4, 11, 13].

The steric configuration of the C-3 H in **2** was established by mercuric acetate oxidation. Facile dehydrogenation of the base upon controlled oxidation and subsequent reduction of the intermediate Δ^3-dehydro base with zinc in acetic acid to give 16-epivenenatine (**1**) conclusively proved that the C-3 H in **2** is α and axial. Reduction of the intermediate Δ^3-dehydro base with sodium borohydride, however, regenerated **2** which therefore must be 16-epialstovenine which is thermodynamically the more stable isomer. Hence, alkaloids **1** and **2** must be C-3 epimers.



The structures proposed for **1** and **2** have received unambiguous support from ^{13}C NMR studies. The ^{13}C NMR of **3** and **4** were also studied and their probable assignments were made on the basis of the reported chemical shifts data for yohimbine alkaloids [14, 15]. A comparison of the carbon shifts of **1** with those of venenatine, and 16-epialstovenine with those of alstovenine (Table 1) permits the complete ring E shift allocation in 16-epivenenatine and 16-epialstovenine. That the configuration of the 16-substituents in 16-epivenanatine and 16-epialstovenine is α and axial is obvious from the shielding of C-18 and C-20 sterically perturbed γ-carbons induced by the bulky axial carbomethoxy group of the alkaloids.

EXPERIMENTAL

Mps are uncorr. UV spectra (λ_{max} in nm and log ε in parentheses) were recorded in 95% aldehyde-free EtOH; IR (ν_{max} in cm^{-1}) in KBr discs and Nujol null); specific rotations in EtOH; ^1H NMR (chemical shift in δ ppm) at 80 MHz and 270 MHz in $CDCl_3$, int. standard TMS. Column and TLC were carried out with neutral Al_2O_3 (BDH) and Si gel G (Merck). The analytical samples were dried *in vacuo* over P_2O_5 for 24 hr. Anhydrous Na_2SO_4 was used for drying solvents.

Isolation of constituents. Dried and finely powdered root bark (10 kg) of *A. venenata* R.Br. was defatted with petrol (60–80°) by extraction in a Soxhlet apparatus. The defatted portion was percolated with EtOH at room temp. The EtOH extract was concd and then mixed with 5% citric acid. The citrate-soluble part was filtered, basified with NH_4OH and then extracted with $CHCl_3$. The $CHCl_3$-soluble part was concd (200 gm) and chromatographed over neutral Al_2O_3.

Table 1. ^{13}C NMR data for 16-epivenenatine (**1**), venenatine (**3**), 16-epialstovenine (**2**) and alstovenine (**4**)

Carbon numbers	Chemical shifts in ppm ($CDCl_3$)				Multiplicity
	1	**3**	**2**	**4**	
C-2	127.48	130.62	134.03	132.45	*s*
C-3	53.99	53.82	60.49	59.74	*d*
C-5	49.88	50.77	52.76	52.97	*t*
C-6	18.06	18.74	24.26	23.12	*t*
C-7	105.86	107.10	106.29	107.80	*s*
C-8	117.05	117.56	117.15	*	*s*
C-9	154.14	155.06	154.16	154.33	*s*
C-10	99.50	104.29	99.34	99.64	*d*
C-11	122.46	121.49	121.34	121.80	*d*
C-12	104.99	105.66	105.13	104.12	*d*
C-13	137.84	137.07	137.88	137.25	*s*
C-14	22.41	22.77	32.89	31.35	*t*
C-15	31.29	32.02	36.32	36.50	*d*
C-16	49.49	51.86	51.46	55.10	*d*
C-17	66.84	67.14	67.03	66.84	*d*
C-18	30.11	31.61	32.80	34.12	*t*
C-19	30.81	30.96	23.36	23.55	*t*
C-20	37.80	39.74	34.88	40.40	*d*
C-21	51.59	50.68	61.43	61.13	*t*
O$\underline{C}H_3$	55.00	54.94	55.43	52.19	*q*
COO$\underline{C}H_3$	51.13	51.46	53.12	51.65	*q*
$\underline{C}$OOMe	174.16	174.67	173.25	175.36	*s*

* C-8 peak merged with noise.

Elution with C_6H_6–$CHCl_3$ (1:1) gave a crude, white solid which was crystallized from Me_2CO–MeOH (1:1) to afford 16-epivenenatine (**1**) (0.01%), $C_{22}H_{28}N_2O_4$; mp 188–190°; $[\alpha]_D^{25}$ −52.68° (EtOH); ν_{max}^{KBr} cm^{-1}: 3220–3260 (–OH and >NH); 2920, 2840 (C–H); 1735 (carbomethoxy C=O); 1620, 1590, 1570, 1510 (methoxylated aromatic nucleus); 1430, 1360, 1250 (Ar–O–C); 1140, 1000, 1070, 865, 770 and 710 (1,2,3-trisubstituted benzene). λ_{max}^{EtOH} nm: 225, 270–272, 293 (log ε: 4.53, 3.90, 3.83). ^1H NMR (270 MHz, $CDCl_3$): δ 8.99 (1 H, *s*, >NH, disappeared on deuteration), *ca* 7.01 (2 H, *m*, C-11 H and C-12 H), 6.47 (1 H, *dd*, J_o = 7 and J_m = 2 Hz, C-10 H), 4.79 (1 H, *br. s*, C-3 H), 4.19 (1 H, *br. s*, C-17 H), 2.06 (1 H, *s*, C-17 OH, disappeared on deuteration), 3.77 (3 H, *s*, –OMe), 3.74 (3 H, *s*, –COOMe), 3.27–1.25 (15 H, *m*, methylene and methine protons). MS *m/z* (rel. int.): 384 (M^+, 100), 383 (87), 367 (10), 325 (10), 214 (13), 200 (14), 199 (66), 186 (13) and 174 (13). Found: C, 68.4; H, 7.1; N, 7.2. $C_{22}H_{28}N_2O_4$ requires: C, 68.75; H, 7.29; N, 7.29%.

The solid obtained from the later fractions of the $CHCl_3$ eluate upon crystallization gave a 16-epialstovenine (**2**) (0.001%), $C_{22}H_{28}N_2O_4$; mp 227–230° (Me_2CO–MeOH, 1:1). $[\alpha]_D^{25}$ +72.02° (EtOH); ν_{max}^{KBr} cm^{-1}: 3340–3380 (–OH and >NH); 2940, 2900 (C–H); 1720 (carbomethoxyl C=O); 1610, 1590, 1560, 1500 (methoxylated aromatic nucleus); 1425, 1355, 1250 (Ar–O–C); 1200, 1145, 1100, 770 and 725 (1,2,3-trisubstituted benzene). λ_{max}^{EtOH} nm: 225–226, 271, 292 (log ε: 4.60, 3.95, 3.86). ^1H NMR (80 MHz, $CDCl_3$): δ 7.79 (1 H, s, >NH, disappeared on deuteration), *ca* 6.91 (2 H, *m*, C-11 H and C-12 H), 6.36 (1 H, *dd*, J_o = 7 and J_m = 2 Hz), 4.11 (1 H, *s*, C-17 H), 3.72 (3 H, *s*, –OMe), 3.71 (3 H, *s*, –COOMe), 2.68 (1 H, *s*, C-17 OH, disappeared on deuteration), 3.02–1.45 (16 H, *m*, methylene, methine and C-3 H). MS *m/z* (rel. int.): 384.205 (M^+, 98), 383 (100), 367 (20), 325 (21), 214 (38), 200 (53), 199 (60), 186 (47) and 174 (36). Found: C, 68.5; H, 7.0; N, 7.1. $C_{22}H_{28}N_2O_4$ requires: C, 68.75; H, 7.29%. The C_6H_6–$CHCl_3$ (1:3) eluate afforded venenatine (**3**), mp 130° and alstovenine (**4**), mp 169–170° and 5% methanolic $CHCl_3$ furnished venoxidine (**5**), mp 217–219°.

The basic portion of the conc. petrol extract was separated by usual procedures and chromatographed to afford 5,22-dioxokopsane (**6**), mp 307–308°, on $CHCl_3$ elution.

Action of methanolic KOH *on* **1**. 16-Epivenenatine (500 mg) in 2 N MeOH–KOH (100 ml) was refluxed for 3 hr. The solvent was evapd at room temp (20°) and the residual viscous jelly dissolved in 100 ml H_2O. The pH of the soln was adjusted to 6.5 by careful addition of HOAc. The white ppt. which separated out was separated, filtered, washed with H_2O and dried (yield: 250 mg, 52%), mp 245° (dec.). It was characterized as venenatic acid (**9**) from mmp, co-TLC and superimposable IR spectra with an authentic sample.

Action of CH_2N_2 *on* **9**. To a soln of venenatic acid (200 mg) in MeOH (5 ml) excess CH_2N_2–Et_2O was added at 0°. The soln was left overnight at room temp. and the solvent was then evaporated. The residual solid was dissolved in $CHCl_3$ and crystallized from MeOH as needles (yield: 40 mg, 20%), mp 130°. It was characterized as venenatine (**3**) from mmp, co-TLC and superimposable IR spectra with an authentic sample.

Acetylation of **1** *with* NaOAc/Ac_2O. 16-Epivenenatine (100 mg) in Ac_2O (5 ml) was refluxed with fused NaOAc (3 g) for 3 hr. The cooled reaction mixture was poured into H_2O (200 ml). NH_4OH was added carefully and the ppt. extracted with $CHCl_3$. Concn afforded a white crystalline solid **10** (yield: 50 mg, 45%), $C_{24}H_{30}N_2O_5$ (M^+ 426), mp 130° (petrol), $[\alpha]_D^{25}$ +34.93°

(EtOH). ν_{max}^{KBr} cm^{-1}: 3340–3380 (>NH); 2930 (C–H); 1740, 1710 (acetoxy C=O and ester C=O); 1630, 1570, 1510 (aromatic nucleus). λ_{max}^{EtOH} nm: 224, 254–257, 292 (log ε: 4.49, 3.95, 3.83). ^1H NMR (80 MHz, $CDCl_3$): δ 7.83 (1 H, *s*, >NH, disappearing on deuteration); *ca* 6.81 (2 H, *m*, C-11 H and C-12 H); 6.33 (1 H, *dd*, $J_o = 6.55$ and $J_m = 2$ Hz, C-10 H); 5.35 (1 H, *s*, C-17 H); 3.77 (3 H, *s*, –OMe); 3.60 (3 H, *s*, –COOMe); 1.99 (3 H, *s*, –OCOMe). Found: C, 67.1; H, 6.9; N, 6.3. $C_{24}H_{30}N_2O_5$ requires: C, 67.6; H, 7.04; N, 6.57%.

$Pb(OAc)_4$ *treatment of* **1**. To a soln of 16-epivenenatine (500 mg) in CH_2Cl_2 (20 ml), $Pb(OAc)_4$ (1.12 g) was added with continuous shaking. After 30 min the soln was poured into ice cold 10% aq. $KHCO_3$ soln (100 ml) and extracted with CH_2Cl_2. The extract was concd, the residual mass dissolved in C_6H_6–$CHCl_3$ mixture (1:1) to afford 7-acetoxy-7 H-16-epivenenatine (**11**) (yield: 300 mg, 52%) as white needles, $C_{24}H_{30}N_2O_6$ (M^+ 442), mp 205°, $[\alpha]_D^{25}$ −15.05° (EtOH). ν_{max}^{KBr} cm^{-1}: 3360–3520, *br* (–OH); 2940 (C–H); 1750 (acetoxy C=O) and 1710 (ester C=O). λ_{max}^{EtOH} nm: 219–220, 299–302 (log ε: 4.18, 3.58). ^1H NMR (80 MHz, $CDCl_3$): δ *ca* 7.19 (2 H, *m*, C-11 H and C-12 H), 6.65 (1 H, *dd*, $J_o = 6$ and $J_m = 2.1$ Hz, C-10 H), 4.01 (1 H, *s*, C-17 H), 3.74 (3 H, *s*, –OMe), 3.68 (3 H, *s*, COOMe), 2.01 (1 H, *s*, C-17 OH, disappearing on deuteration), 1.96 (3 H, *s*, OCOMe). Found: C, 65.0; H, 6.5; N, 6.1. $C_{24}H_{30}N_2O_6$ requires: C, 65.15; H, 6.79; N, 6.33%.

Conversion of 7-acetoxy-7 H-16-epivenenatine (**11**) *to the corresponding oxindole* **12**. 7-Acetoxy-7 H-16-epivenenatine (200 mg) in MeOH (8 ml) was treated with HOAc (5 drops) and H_2O (2 ml) and refluxed for 2.5 hr. The mixture was cooled and neutralized with satd $NaHCO_3$ soln and diluted with H_2O (50 ml). It was extracted with $CHCl_3$ and concd to yield 16-epivenenatine oxindole (**12**) (yield: 50 mg, 28%), as granules from C_6H_6–MeOH (1:1), $C_{22}H_{28}N_2O_5$ (M^+ 400), mp 252°, $[\alpha]_D^{25}$ −29.20° (EtOH). ν_{max}^{KBr} cm^{-1}: 3300 *br* (–OH and >NH); 2920 (C H); 1725 (ester C=O and lactam C=O); 1620, 1470 (aromatic nucleus). λ_{max}^{EtOH} nm: 220, 248, 291 (log ε: 3.45, 3.62, 4.44). ^1H NMR (80 MHz, $CDCl_3$): δ 8.0 (1 H, *s*, >NH, disappearing on deuteration), 7.09 (1 H, *m*, C-11 H), 6.45 (2 H, *m*, C-10 H and C-12 H), 4.01 (1 H, *s*, C-17 H); 3.75 (3 H, *s*, OMe), 3.51 (3 H, *s*, COOMe); 1.65 (1 H, *s*, C-17 OH, disappearing on deuteration). Found: C, 65.6; H, 6.9; N, 6.8. $C_{22}H_{28}N_2O_5$ requires: C, 66.0; H, 7.0; N, 7.0%.

$LiAlH_4$ *reduction of* **1**. A soln of 16-epivenenatine (400 mg) in dry THF (30 ml) was added dropwise to a slurry of $LiAlH_4$ (1 g) and THF (30 ml) at 0° under anhydrous condition with vigorous stirring. The mixture was stirred for 6 hr and cooled. Excess reagent was decomposed with cold, satd Na_2SO_4. The soln was filtered and the residue washed with hot $CHCl_3$. The combined filtrate was extracted with $CHCl_3$ and concd to yield the diol **13** (yield: 240 mg, 65%), $C_{21}H_{28}N_2O_3$ (M^+ 356.2093), mp 165° (petrol–$CHCl_3$, 1:1), $[\alpha]_D^{25}$ −29.96° (EtOH). ν_{max}^{KBr} cm $^{-1}$: 3300–3360 (–OH and >NH); 2940 (C–H); 1600, 1510, 1440 (aromatic nucleus). λ_{max}^{EtOH} nm: 225, 272, 293 (log ε: 4.52, 3.89, 3.81). ^1H NMR (80 MHz, $CDCl_3$): δ 9.10 (1 H, *s*, >NH, disappearing on deuteration), *ca* 6.82 (2 H, *m*, C-11 H and C-12 H), 6.33 (1 H, *dd*, $J_o = 6$ and $J_m = 2.1$ Hz, C-10 H), 4.34 (1 H, *br s*, C-3 H), 3.97 (1 H, *br s*, C-17 H), 3.78 (3 H, *s*, –OMe), 3.25 (2 H, *br s*, two OH, disappearing on deuteration). MS *m/z* (rel. int.): 356.2093 (M^+, 100), 355 (90), 339 (16), 214 (16), 200 (15), 199 (16), 186 (13), 174 (13). Found: C, 70.6; H, 7.6; N, 7.7. $C_{21}H_{28}N_2O_3$ requires: C, 70.78; H, 7.86; N, 7.86%.

Acetylation of **13**. The diol (100 mg) in pyridine (5 ml) was acetylated with Ac_2O (2 ml). The reaction mixture was poured into crushed ice and extracted with $CHCl_3$. The $CHCl_3$ extract was concd and excess pyridine removed to yield the diacetate **14** (yield: 70 mg, 66%), $C_{25}H_{32}N_2O_5$ (M^+ 440), mp 120–125° (petrol–C_6H_6, 1:1), $[\alpha]_D^{25}$ −17.12° (EtOH). ν_{max}^{KBr} cm^{-1}: 3360 (>NH); 2930 (C–H); 1715–1735 *br* (acetoxy C=O); 1590, 1505, 1435 (aromatic nucleus). λ_{max}^{EtOH} nm: 225, 270–271, 293 (log ε: 4.54, 3.94, 3.86). ^1H NMR (80 MHz, $CDCl_3$): δ 8.22 (1 H, *s*, >NH, disappearing on deuteration), *ca* 6.92 (2 H, *m*, C-12 H and C-12 H), 6.36 (1 H, *dd*, $J_o = 7$ and $J_m = 2$ Hz, C-10 H), 5.16 (1 H, *br s*, C-17 H), 4.37 (1 H, *br s*, C-3 H), 3.80 (3 H, *s*, OMe), 1.96 and 1.84 (3 H, *s*, each, two OCOMe). Found: C, 68.0; H, 7.1; N, 6.2. $C_{25}H_{32}N_2O_5$ requires: C, 68.18; H, 7.27; N, 6.36%.

$Hg(OAc)_2$ *oxidation of* **2** *and successive reduction with* Zn *in* HOAc *and* $NaBH_4$. 16-Epialstovenine (200 mg) in 10% aq. HOAc (5 ml) was treated with $Hg(OAc)_2$ (1 g) dissolved in 10% aq. HOAc (5 ml). The mixture was heated to 60–80° for 1 hr. A white ppt. of mercurous acetate separated. The soln was cooled and the ppt. removed by filtration. The yellow filtrate was satd with H_2S and conc HCl (5 ml) added. The soln was heated at 100° to coagulate the mercuric sulphide which was then filtered off. The bright yellow filtrate, free from Hg^{2+}, afforded the intermediate Δ^3-dehydro base as an oily mass.

A portion of the oily mass of the Δ^3-dehydro base was dissolved in 10% aq. HOAc (25 ml) and treated with Zn dust (500 mg). A further amount of HOAc (3 ml) and Zn dust (20 mg) was added. The soln was allowed to stand until the yellow colour had completely discharged. The soln was cooled, basified with NH_4OH, the liberated base taken up in $CHCl_3$ (100 ml) and concd to an oily mass which showed the presence of two components by TLC. They were separated by column chromatography. Elution with C_6H_6–$CHCl_3$ (1:1) gave a crystalline solid which was identified as 16-epivenenatine (**1**) (yield: 15 mg, 15%), mp 188–190° (Me_2CO–MeOH, 1:1) from superimposable IR spectra, mmp and co-TLC with an authentic sample. On elution with $CHCl_3$, the later fraction furnished a yellowish solid (yield: 50 mg, 50%), mp 227–230°, which was characterized as 16-epialstovenine (**2**) from mmp, co-TLC and superimposable IR spectra with an authentic sample.

The later portion of the intermediate Δ^3-dehydro base was dissolved in MeOH (5 ml) and $NaBH_4$ (2.5 gm) was added, in portions, at 0°. The reaction mixture was kept overnight at 20°. The solvent was removed at 20° and the residue diluted with H_2O (20 ml) to yield 16-epialstovenine (**2**) (yield: 50 mg, 50%), mp 227–230° (Me_2CO–MeOH, 1:1), characterized from mmp, co-TLC and superimposable IR spectra.

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