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Five New Iboga Alkaloids from *Tabernaemontana corymbosa*

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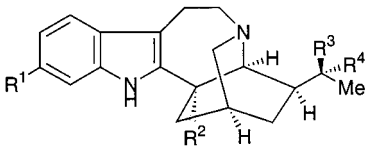
Five new indole alkaloids of the ibogan type (**1**−**5**), in addition to 12 other known iboga alkaloids, were obtained from the leaf and stem-bark extract of the Malayan species *Tabernaemontana corymbosa*, viz., 19(*S*)-hydroxyibogamine (**1**), 19-*epi*-isovoacristine (**2**), isovoacryptine (**3**), 3*R*/*S*-ethoxyheyneanine (**4**), and 3*R*/*S*-ethoxy-19-*epi*-heyneanine (**5**). The structures were determined using NMR and MS analysis and comparison with known related compounds.

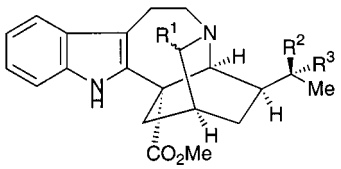
Plants belonging to the genus *Tabernaemontana* (Apocynaceae) are distributed over a wide area, occurring in tropical America, Africa, and Madagascar and extending to Asia, Oceanea, and Australia.[1] They are notable for producing a wide variety of indole alkaloids, including many with intriguing carbon skeletons as well as novel biological activity.[2−4] Several Malayan members of the genus have been previously investigated which have provided many new indole as well as bisindole derivatives.[4] A notable observation from the previous studies of the Malayan species is that although the iboga alkaloids exemplified by coronaridine abound in plants of the *Tabernaemontana* and many known iboga-type alkaloids such as coronaridine, voacristine, voacangine, and eglandine have been obtained from the plants investigated, only two new monomeric iboga alkaloids, viz., 3-oxo-19-*epi*-heyneanine and 3-hydroxy-3,4-secocoronaridine, have been previously reported, both of which were from *T. polyneura*.[4,5] We now wish to report the structures of five new iboga derivatives obtained from *T. corymbosa* Roxb. Ex Wall. Several new indole alkaloids possessing novel carbon skeletons have also been obtained from this plant.[6−9]



1 R^1 = H, R^2 = H, R^3 = OH, R^4 = H

2 R^1 = OMe, R^2 = CO_2Me, R^3 = H, R^4 = OH

3 R^1 = OMe, R^2 = CO_2Me, R^3, R^4 = O



4 R^1 = OEt, R^2 = OH, R^3 = H

5 R^1 = OEt, R^2 = H, R^3 = OH

3*R*/*S*-Ethoxycoronaridine R^1 = OEt, R^2 = H, R^3 = H

3-Methoxycoronaridine R^1 = OMe, R^2 = OH, R^3 = H

3-Hydroxycoronaridine R^1 = OH, R^2 = H, R^3 = H

Results and Discussion

A total of 17 iboga-type alkaloids, including five new derivatives (**1**−**5**), were obtained in the present study. The known iboga compounds include coronaridine, ibogamine, 3-oxocoronaridine, voacangine, isovoacangine, isovoacristine, heyneanine, 19-*epi*-heyneanine, 3-oxo-19-*epi*-heyneanine, coronaridine-7-hydroxyindolenine, 3-hydroxy-3,4-secocoronaridine, and 3*R*/*S*-ethoxycoronaridine. The five new compounds are 19(*S*)-hydroxyibogamine, 19-*epi*-isovoacristine, isovoacryptine, 3*R*/*S*-ethoxyheyneanine, and 3*R*/*S*-ethoxy-19-*epi*-heyneanine.

19(*S*)-Hydroxyibogamine (**1**) was obtained as a light yellowish oil, $[\alpha]_D$ −21° (*c* 0.16, $CHCl_3$). The UV spectrum (λ_{max} 226, 283, and 292 nm) was similar to that of ibogamine,[10] showing absorptions characteristic of an indole chromophore, while the IR spectrum showed an absorption band at 3355 cm^{-1} due to NH/OH functions. The mass spectrum showed a molecular ion at *m*/*z* 296, with a peak due to the loss of H_2O observed at *m*/*z* 278 (35%), indicating the presence of a hydroxy group. HRMS measurements established the molecular formula as $C_{19}H_{24}N_2O$. The ^{1}H NMR spectrum of **1** was generally similar to that of ibogamine, except for the presence of a hydroxyethyl group (δ 4.17, qd, *J* 6.5, 1.5 Hz, H-19; 1.12, d, *J* 6.5 Hz, CH_3-18) in place of an ethyl side chain at C-20. The presence of the hydroxyethyl side chain was further confirmed by the carbon resonances of C-19 (δ 71.5) and C-18 (δ 20.1) in the ^{13}C NMR spectrum. The configuration of C-19 is readily determined to be *S* from examination of the carbon shifts of C-15 (δ 23.0) and C-21 (δ 60.9), which correspond to that of heyneanine, exemplifying the 19(*S*) series in iboga alkaloids with a hydroxyethyl side chain (versus that of 19-*epi*-heyneanine, exemplifying the 19(*R*) series). The 19(*S*) compounds have the chemical shift of C-15 at ca. δ 23, which is shifted downfield by about 6.7 ppm compared to those in the 19(*R*) compounds, for which the C-21 resonances are shifted upfield by about 5 ppm to ca. δ 54.7, compared to the 19(*S*) epimers, which have the chemical shift of C-21 at ca. δ 60.[11,12]

19-*epi*-Isovoacristine (**2**) was obtained as a colorless oil, $[\alpha]_D$ −31° (*c* 0.05, $CHCl_3$). The UV spectrum showed absorption maxima at λ_{max} 226, 283, and 294 nm, while the IR spectrum indicated the presence of NH/OH (3533 cm^{-1}) and ester (1723 cm^{-1}) functions. The mass spectrum showed a molecular ion at *m*/*z* 384, and HRMS measurements established the molecular formula as $C_{22}H_{28}N_2O_4$, indicating that **2** is isomeric with isovoacristine.[13] The ^{1}H NMR spectrum of **2** was generally similar to that of

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Table 1. ^{1}H NMR Spectral Data for 3*R*/*S*-Ethoxycoronaridine and **1**−**3** (400 MHz, $CDCl_3$)[a]

H	3*R*-ethoxycoronaridine	3*S*-ethoxycoronaridine	**1**	**2**	**3**
3	4.10 d (1.9)	4.41 br s	3.00dt (9.5, 2)	2.83 dt (9, 2)	2.78 dt (9, 2)
			3.08 dt (9.5, 2)	3.01 m	2.95 m
5	3.20 ddd (13, 8, 6)	3.30 ddd (13, 8, 6)	3.20 ddd (15, 4, 1)	3.14 m	3.12 m
	3.53 dt (13, 5.5)	3.45 dt (13, 5.5)	3.34 dt (15, 4)	3.43 dt (12, 6)	3.35 m
6	3.09 m	3.09 m	2.75 ddd (15.5, 4, 1)	3.06 m	2.95 m
	3.09 m	3.09 m	3.31 dt (15.5, 4)	3.14 m	3.12 m
9	7.49 dd (7.5, 1)	7.49 dd (7.5, 1)	7.46 br dd (7.5, 1.3)	7.33 d (9)	7.34 d (9)
10	7.09 td (7.5, 1)	7.09 td (7.5, 1)	7.09 td (7.5, 1.3)	6.76 dd (9, 2)	6.76 dd (9, 2)
11	7.15 td (7.5, 1)	7.15 td (7.5, 1)	7.12 td (7.5, 1.3)		
12	7.25 dd (7.5, 1)	7.25 dd (7.5, 1)	7.25 ddd (7.5, 1.3, 0.7)	6.77 d (2)	6.77 d (2)
14	2.00 m	1.88 m	2.00 m	2.03 m	2.01 m
15	1.52 m	1.52 m	1.61 dddd (13, 11, 4, 2)	1.77 tdd (13, 4, 2)	1.58 br t (10)
	1.76 m	1.76 m	1.98 ddt (13, 8, 2.6)	1.85 ddt (13, 7.7, 2)	2.20 m
16			3.01 ddd (12, 3.5, 1.5)		
17	1.90 ddd (13.7, 3.8, 2)	1.98 ddd (13.7, 3.8, 2)	1.67 ddd (13, 6.5, 3.5)	1.96 ddd (13.5, 4, 2)	1.95 dt (13.5, 3)
	2.76 dd (13.7, 2.4)	2.72 dd (13.7, 2.4)	2.08 ddt (13, 12, 2.6)	2.56 dt (13.5, 2)	2.61 dt (13.5, 2)
18	0.90 t (7.4)	0.93 t (7.4)	1.12 d (6.5)	1.28 d (6)	2.24 s
19	1.52 m	1.52 m	4.17 qd (6.5, 1.5)	3.90 qd (6, 2)	
	1.76 m	1.76 m			
20	1.35 m	1.41 m	1.64 m	1.40 m	2.46 ddd (10, 6, 1.2)
21	3.81 d (0.7)	3.79 br s	3.13 t(1.5)	4.07 br s	4.24 d (1.2)
NH	7.94 br s	7.94 br s	7.79br s	7.71 br s	7.74 br s
OEt	1.16 t (7)	1.24 t (7)			
	3.35 q (7)	3.35 q (7)			
11-OMe				3.83 s	3.83 s
CO_2Me	3.68 s[b]	3.69 s[b]		3.73 s	3.79 s

[a] Assignments based on COSY and HMQC. [b] Assignments may be reversed.

isovoacristine, except for a significant change involving H-19, suggesting that **2** and isovoacristine are C-19 epimers. In compound **2**, the H-19 signals appeared as a quartet of doublets at δ 3.90 (J = 6, 2 Hz), while in isovoacristine, the H-19 signal was observed at δ 4.16 (J = 6, 1.5 Hz). The configuration of C-19 is readily confirmed to be *R* from the chemical shift analogy of C-15 and C-21 (δ 28.6 and 54.4, respectively) with those of 19-*epi*-heyneanine.[14]

Isovoacryptine (**3**) was obtained as a light yellowish oil, $[\alpha]_D$ +17° (*c* 0.85, $CHCl_3$). The UV spectrum showed absorption maxima at λ_{max} 225, 280, and 298 nm, characteristic of an indole chromophore, while the IR spectrum indicated the presence of NH (3382 cm^{-1}), ester (1725 cm^{-1}), and ketone (1711 cm^{-1}) functions. The EI-mass spectrum showed a molecular ion at *m*/*z* 382, and HRMS measurements established the molecular formula as $C_{22}H_{26}N_2O_4$. Other major fragments were observed at *m*/*z* 339 (M − $COCH_3$) and 323 (M − CO_2Me). The ^{13}C NMR spectrum showed a total of 22 separate carbon resonances, in agreement with the molecular formula. The ^{1}H NMR spectrum was generally similar to that of isovoacristine, except for the replacement of the hydroxyethyl side chain at C-20 by an acetyl group (δ 2.24). This is further confirmed by the observed carbon resonances at δ 27.7 and 208.1 in the ^{13}C NMR spectrum. Apart from these differences, the NMR spectral data of **3** were essentially similar to those of isovoacristine.[13] Compound **3** is therefore isovoacryptine (11-methoxy-10-demethoxyvoacryptine).

3*R*/*S*-Ethoxyheyneanine (**4**) was obtained as mixture of the 3*R*- and 3*S*-epimers, which was intractable to further resolution by chromatography. This was revealed by the ^{1}H NMR spectra which showed the presence of an approximately 1:1 mixture of the two epimers (Table 2). The UV spectrum was similar to that of heyneanine with absorption maxima observed at 225, 285, and 292 nm. The IR spectrum showed peaks due to NH (3378 cm^{-1}), OH (3274 cm^{-1}), and ester (1727 cm^{-1}) functions. The ^{1}H and ^{13}C NMR spectral data were consistent with that of an iboga compound and indicated the presence of a hydroxyethyl side chain at C-20. Since the epimeric compound 3*R*/*S*-ethoxy-19-*epi*-heyneanine (**5**) was also obtained, the C-19 configuration could be readily established from comparison of the carbon shifts of C-15 and C-20 (Table 3) of these two compounds (vide infra). The NMR spectral data also indicated the presence of an ethoxy substituent on C-3, from the observed H-3 (δ 4.09, d, J = 1.5 Hz, 3*R*; 4.45, br s, 3*S*) and the C-3 ethoxy group {δ 1.14, 3.38, OEt (*R*); 1.16, 3.28, OEt (*S*)} resonances. The presence of the 3*R* and 3*S* epimers was further confirmed by the distinct carbon resonances for C-3*R* at δ 93.5 and C-3*S* at δ 85.9.[15] The expected molecular ion (*m*/*z* 398, $C_{23}H_{30}N_2O_4$) was not detected in both the EI- and FAB-mass spectrum. The highest mass fragment observed in the EI-mass spectrum was at *m*/*z* 353 ($C_{21}H_{25}N_2O_3$, M − OEt, 30%), while the base peak was observed at *m*/*z* 352, which corresponds to loss of EtOH. When the mass spectrum was obtained using APIMS with methanol as solvent, the MH^+ peak was observed at *m*/*z* 385 ($C_{22}H_{28}N_2O_4$ + H), suggesting the formation of the methoxy-substituted derivative, 3-methoxyheyneanine. Since compound **4** is stable in methanol solution and could be recovered intact, formation of the methoxy carbinol amine ether must have occurred during the ionization process.

As in the case of the previous compound **4**, 3*R*/*S*-ethoxy-19-*epi*-heyneanine (**5**) was also obtained as an approximately 1:1 mixture of the 3*R* and 3*S* epimers. The UV and IR spectra were virtually identical with that of the previous compound **4** (see Experimental Section). In common with the previous compound **4**, the molecular ion was not detected in both the EI- and FAB-mass spectrum; instead the fragment ions due to loss of OEt and EtOH were detected at *m*/*z* 353 and 352, respectively, with the latter fragment obtained as the base peak. The ^{1}H NMR spectrum of **5** also showed the two sets of signals due to H-3 at δ 4.10 (br s, H-3*R*) and 4.46 (δ *J* 7 Hz, H-3*S*), as well as the two ethoxy groups {δ 1.22, 3.38, OEt (*R*); δ 1.15, 3.29, OEt (*S*)}, while the carbon resonances due to C-3*R* and C-3*S* can be readily distinguished at δ 93.4 and 85.7, respectively.[15]

Table 2. ^{1}H NMR Spectral Data for Compounds **4** and **5** (400 MHz, $CDCl_3$)[a]

H	**4*R***	**4*S***	**5*R***	**5*S***
3	4.09 d (1.5)	4.45 br s	4.10br s	4.46 d (7)
5	3.13 m	3.13 m	3.16 m	3.16 m
	3.53 m	3.53 m	3.50 m	3.50 m
6	3.13 m	3.13 m	3.16 m	3.16 m
	3.13 m	3.13 m	3.16 m	3.16 m
9	7.49 br d (7.5)	7.49 br d (7.5)	7.49 br d (7.5)	7.49 br d (7.5)
10	7.11 td (7.5, 1)	7.11 td (7.5, 1)	7.10 td (7.5, 1)	7.10 td (7.5, 1)
11	7.17 td (7.5, 1)	7.17 td (7.5, 1)	7.17 td (7.5, 1)	7.17 td (7.5, 1)
12	7.27 br d (7.5)	7.27 br d (7.5)	7.27 br d (7.5)	7.27 br d (7.5)
14	2.10 m	2.10 m	2.01 m	2.01 m
15	1.48 m	1.48 m	1.88 m	1.88 m
	2.06 m	2.06 m	2.01 m	2.01 m
17	2.06 m	2.06 m	2.17 dt (13, 3)	2.17 dt (13, 3)
	2.76 dt (13, 3)	2.76 dt (13, 3)	2.75 br d (13)	2.75 br d (13)
18	1.15 d (6.7)	1.15 d (6.7)	1.29 d (6.7)	1.23 d (6.7)
19	4.19 qd (6.7, 1.5)	4.13 qd (6.7, 1.5)	3.90 qd (6.7, 1.5)	3.92 qd (6.7, 1.5)
20	1.48 m	1.48 m	1.42 m	1.42 m
21	4.01 br s	4.01 br s	4.27 br s	4.27 br s
19-OH	5.06 br s	5.06 br s		
NH	7.92 br s[b]	7.93 br s[b]	7.89br s[d]	7.90 br s[d]
OEt	1.14 t (6.7)	1.16 t (6.7)	1.22 t (6.7)	1.15 t (6.7)
	3.38 q (6.7)	3.28 q (6.7)	3.38 q (6.7)	3.29 q (6.7)
CO_2Me	3.72 s[c]	3.70 s[c]	3.72 s[e]	3.71 s[e]

[a] Assignments based on COSY and HMQC. [b–e] Assignments may be reversed.

Table 3. ^{13}C NMR Spectral Data (δ) for 3*R*/*S*-Ethoxycoronaridine and **1**–**5** (100 MHz, $CDCl_3$)[a]

	3-ethoxycoronaridine								
C	(*R*)	(*S*)	**1**	**2**	**3**	**4*R***	**4*S***	**5*R***	**5*S***
2	136.5	136.0	140.7	134.3	134.7	135.7	135.7	135.7	135.7
3	93.9	86.0	49.3	50.5	50.7	93.5	85.9	93.4	85.7
5	52.2	51.2	52.9	51.9	53.2	51.7	50.9	51.5	50.6
6	21.8[b]	21.7[b]	20.2	21.6	21.8	21.5[b]	21.4[b]	21.9[b]	22.0[b]
7	110.0[c]	109.9[c]	108.4	109.6	110.4	109.8	109.8	109.7[c]	109.8[c]
8	128.2	128.2	129.5	122.9	123.0	128.0	128.0	128.1	128.1
9	118.2[d]	118.3[d]	118.0	119.1	119.1	118.2[c]	118.4[c]	118.3[d]	118.4[d]
10	119.1[e]	119.2[e]	119.2	109.3	109.2	119.4[d]	119.5[d]	119.4[e]	119.5[e]
11	121.8[f]	121.9[f]	121.3	156.8	156.6	122.1[e]	122.3[e]	122.1[f]	122.2[f]
12	110.4	110.4	110.2	94.3	94.3	110.5[f]	110.6[f]	110.5[g]	110.6[g]
13	135.5	135.5	134.8	136.2	136.0	135.6	135.6	135.6	135.6
14	30.8	34.4	25.9	27.0	26.8	30.8	34.2	30.9	34.4
15	25.0	24.7	23.0	28.6	24.7	17.3	16.6	22.2	22.7
16	54.4	54.1	40.2	53.8	54.0	53.7[g]	53.2[g]	53.8[h]	53.9[h]
17	35.4	35.4	34.3	36.6	37.0	35.7[h]	35.9[h]	35.6[i]	35.8[i]
18	11.6	11.6	20.1	22.2	27.7	21.0	20.5	21.6	21.7
19	26.5	26.8	71.5	70.8	208.1	71.2	71.4	70.2	70.3
20	37.9	37.7	42.2	40.1	50.9	39.9	39.5	40.3	41.0
21	55.8	56.1	60.9	54.4	56.2	57.9	58.5	52.4	53.4
11-OMe				55.7	55.7				
OEt	15.6	18.3				15.6	17.3	15.7	17.3
	61.4	58.2				62.3	61.6	62.1	61.6
CO_2Me	52.5[g]	52.6[g]		52.7	52.9	52.9[i]	53.0[i]	52.7[j]	52.8[j]
CO_2Me	175.0[h]	174.9[h]		175.0	174.9	174.4[j]	174.6[j]	174.5[k]	175.0[k]

[a] Assignments based on HMQC and HMBC. [b–k] Assignments may be reversed between an *R*/*S* pair.

In addition to the two previous compounds **4** and **5**, the known compound 3*R*/*S*-ethoxycoronaridine was also isolated.[16] Since high-field NMR spectral data are not available for 3*R*/*S*-ethoxycoronaridine, we have included the full NMR data for this compound in the present report. It has been suggested in the case of the 3-hydroxyiboga alkaloids, which were also intractable to resolution by TLC, that they are in equilibrium with each other, a process possibly catalyzed by the SiO_2 layer.[15,16] The possibility that in the present instance the three carbinol amine ethers 3*R*/*S*-ethoxycoronaridine, **4**, and **5** were formed from the parent 3-hydroxyiboga precursors (e.g., 3-hydroxycoronaridine)[17] via formation of iminium ion intermediates cannot be completely discounted, since ethanol and $CHCl_3$ stabilized with 1% EtOH were used during extraction and chromatography.[18,19]

Experimental Section

General Experimental Procedures. Optical rotations were determined on a JASCO DIP-370 digital polarimeter. IR spectra were recorded on a Perkin-Elmer 1600 Series FT-IR spectrophotometer. UV spectra were obtained on a Shimadzu UV-3101PC spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ using TMS as internal standard on a JEOL JNM-LA 400 spectrometer at 400 and 100 MHz, respectively. API-MS were obtained on a Perkin-Elmer API 100 instrument. EIMS, HREIMS, and FABMS were obtained on a JEOL JMS-AX505H mass spectrometer, courtesy of Dr. K. Komiyama of the Kitasato Institute, Japan.

Plant Material. Plant material was collected in Perak, Malaysia (May, 1996) and identified by Dr. A. J. M. Leeuwenberg, Laboratory of Plant Taxonomy and Plant Geography, Agricultural University, Waneningen, The Netherlands. Herbarium voucher specimens (GK 604) are deposited at the

Herbarium of the Department of Chemistry, University of Malaya, Malaysia, and at Waneningen.

Extraction and Isolation. Extraction of the ground leaf and stem-bark material was carried out in the usual manner by partitioning the concentrated EtOH extract with dilute acid, as has been described in detail elsewhere.[20,21] The alkaloids were isolated by initial column chromatography on silica gel using $CHCl_3$ with increasing proportions of MeOH followed by rechromatography of appropriate partially resolved fractions using centrifugal TLC. Solvent systems used for centrifugal TLC were MeOH/$CHCl_3$, Et_2O, Et_2O/cyclohexane (1:5), $CHCl_3/NH_3$, and 2% MeOH/$CHCl_3$. The yields (g kg^{-1}) of the alkaloids were as follows: coronaridine (0.292), ibogamine (0.011), 3-oxocoronaridine (0.008), voacangine (0.0058), isovoacangine (0.013), isovoacristine (0.032), heyneanine (0.151), 19-*epi*-heyneanine (0.075), 3-oxo-19-*epi*-heyneanine (0.0075), coronaridine-7-hydroxyindolenine (0.005), 3-hydroxy-3,4-seco-coronaridine (0.0033), 3*R*/*S*-ethoxy-coronaridine (0.021), **1** (0.0025), **2** (0.0008), **3** (0.054), **4** (0.016), and **5** (0.002).

19(*S*)-Hydroxyibogamine (1): light yellowish oil; $[\alpha]_D$ −21° (*c* 0.16, $CHCl_3$); UV (EtOH) λ_{max} (log ϵ) 226 (4.28), 283 (3.66), 292 (3.62) nm; IR (dry film) ν_{max} 3355 cm^{-1}; ^1H NMR and ^{13}C NMR data, see Tables 1 and 3; EIMS *m*/*z* 296 $[M]^+$ (100), 281 (67), 278 (35), 251 (26), 195 (22), 162 (35), 152 (45), 138 (25), 136 (15), 122 (13); HREIMS *m*/*z* 296.1898 (calcd for $C_{19}H_{24}N_2O$, 296.1889).

19-*epi*-Isovoacristine (2): colorless oil; $[\alpha]_D$ −31° (*c* 0.05, $CHCl_3$); UV (EtOH) λ_{max} (log ϵ) 226 (4.31), 283 (3.64), 294 (3.61) nm; IR (dry film) ν_{max} 3533, 1723 cm^{-1}; ^1H NMR and ^{13}C NMR data, see Tables 1 and 3; EIMS *m*/*z* 384 $[M]^+$ (100), 366 (20), 339 (5), 325 (6), 244 (8), 184 (18), 154 (15), 148 (5), 136 (35), 124 (20), 122 (13); HREIMS *m*/*z* 384.2045 (calcd for $C_{22}H_{28}N_2O_4$, 384.2049).

Isovoacryptine (3): light yellowish oil; $[\alpha]_D$ +17° (*c* 0.85, $CHCl_3$); UV (EtOH) λ_{max} (log ϵ) 225 (4.25), 280 (3.88), 298 (3.97) nm; IR (dry film) ν_{max} 3382, 1725, 1711 cm^{-1}; ^1H NMR and ^{13}C NMR data, see Tables 1 and 3; EIMS *m*/*z* 382 $[M]^+$ (100), 339 (12), 323 (10), 244 (25), 184 (7), 160 (10), 136 (10), 124 (12), 122 (9); HREIMS *m*/*z* 382.1890 (calcd for $C_{22}H_{26}N_2O_4$, 382.1893).

3*R*/*S*-Ethoxyheyneanine (4) (mixture 3*R*:3*S* ≈ 1:1): colorless oil; UV (EtOH) λ_{max} (log ϵ) 225 (3.94), 285 (3.33), 292 (3.26) nm; IR (dry film) ν_{max} 3378, 3274, 1727 cm^{-1}; ^1H NMR and ^{13}C NMR data, see Tables 2 and 3; EIMS *m*/*z* 353 $[M - OEt]^+$ (30), 352 $[M - EtOH]^+$ (100), 337 (10), 308 (18), 270 (30), 229 (32), 214 (52), 182 (12), 154 (20), 138 (22), 136 (4), 124 (5), 122 (5); HREIMS *m*/*z* 352.1823 $[M - EtOH]^+$ (calcd for $C_{21}H_{24}N_2O_3$, 352.1787); FABMS *m*/*z* 353 $[M - OEt]^+$; HRFABMS *m*/*z* 353.1865 (calcd for $C_{21}H_{25}N_2O_3$, 353.1865); APIMS *m*/*z* 385 ($C_{22}H_{28}N_2O_4$ + H).

3*R*/*S*-Ethoxy-19-*epi*-heyneanine (5) (mixture 3*R*:3*S* ≈ 1:1): colorless oil; UV (EtOH) λ_{max} (log ϵ) 225 (3.91), 285 (3.29), 292 (3.23) nm; IR (dry film) ν_{max} 3378, 1728 cm^{-1}; ^1H NMR and ^{13}C NMR data, see Tables 2 and 3; EIMS *m*/*z* 353 $[M - OEt]^+$ (45), 352 $[M - EtOH]^+$ (100), 337 (34), 308 (20), 270 (30), 229 (24), 214 (58), 182 (11), 154 (22), 138 (16), 136 (5), 124 (10), 122 (10); HREIMS *m*/*z* 352.1772 $[M - EtOH]^+$ (calcd for $C_{21}H_{24}N_2O_3$, 352.1787); FABMS *m*/*z* 353 $[M - OEt]^+$; HRFABMS *m*/*z* 353.1913 (calcd for $C_{21}H_{25}N_2O_3$, 353.1865); APIMS *m*/*z* 385 ($C_{22}H_{28}N_2O_4$ + H).

3*R*/*S*-Ethoxycoronaridine[16] (mixture 3*R*:3*S* ≈ 2:1): light yellowish oil; UV (EtOH) λ_{max} (log ϵ) 224 (4.41), 285 (3.81), 292 (3.76) nm; IR (dry film) ν_{max} 3375, 1728 cm^{-1}; ^1H NMR and ^{13}C NMR data, see Tables 1 and 3; EIMS *m*/*z* 337 $[M - OEt]^+$ (80), 336 $[M - EtOH]^+$ (100), 323 (25), 293 (20), 277 (20), 154 (48), 136 (40), 124 (35), 122 (30); FABMS *m*/*z* 337 $[M - OEt]^+$; APIMS *m*/*z* 369 ($C_{22}H_{28}N_2O_3$ + H).

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