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NEW ALKALOIDS FROM *CRYPTOLEPIS SANGUINOLENTA*

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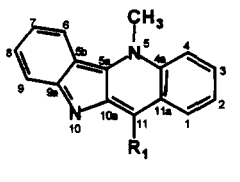
ABSTRACT.—An extract of *Cryptolepis sanguinolenta* yielded five alkaloids. Two of these were the known compounds cryptolepine [**1**] and quindoline [**2**]. Three of the compounds have not been reported previously and were named hydroxycryptolepine [**3**], cryptoheptine [**4**], and cryptoquindoline [**5**]. Compound **5** was shown to be an artifact.

Cryptolepis sanguinolenta (Lindl.) Schlechter (Asclepiadaceae) is a shrub indigenous to West Africa. In Guinea Bissau, a root decoction of this plant has been used by traditional healers for the treatment of various fevers, including hepatitis, and the leaves have been used for the treatment of malaria or powdered as a cicatrizant of wounds (1,2). In Ghana, the roots have been used in the clinical therapy of malaria and of urinary and upper respiratory tract infections for at least two decades (3).

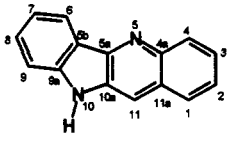
The major alkaloid in *C. sanguinolenta* roots, the indoloquinoline alkaloid cryptolepine [**1**], was isolated in 1931 (4), and has since been reported present in plant material from Ghana and Nigeria by others (5,6). The nmr assignments of its structure have been reported recently (7,8). The pharmacological activity of **1** has been extensively investigated and it shows hypotensive (9), antipyretic (10), anti-inflammatory (11), in vitro antibacterial (12–14), and antimalarial (15) effects.

Another indoloquinoline alkaloid, quindoline [**2**], was first synthesized from **1** by Gellért *et al.* (5). In 1978, Dwuma-Badu *et al.* reported the isolation of **2** from the roots of *C. sanguinolenta* (6). Recently, the isolation of a third alkaloid from this species, a unique spiro-nonacyclic alkaloid, cryptospirolepine, has been reported (16).

This report describes the isolation and structural elucidation of three new indole alkaloids, hydroxycryptolepine [**3**], cryptoheptine [**4**], and cryptoquindoline [**5**], and of



1 $R_1=CH_3$; $R_2=H$
3 $R_1=CH_3$; $R_2=OH$



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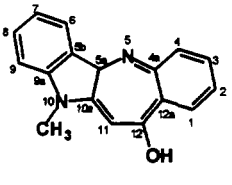

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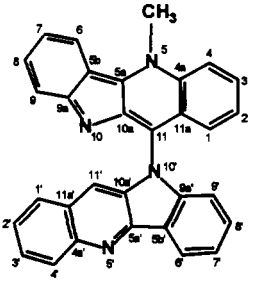

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the known alkaloids **1** and **2**, from the roots of *C. sanguinolenta* obtained in Guinea Bissau. The ^{1}H- and ^{13}C-nmr assignments for **2** are reported here for the first time. The new alkaloid cryptoheptine [**4**] has revealed antibacterial activity against Gram-negative and Gram-positive bacteria (17).

RESULTS AND DISCUSSION

A summary of ^{1}H- and ^{13}C-nmr assignments for compounds **1–4** is shown in Tables 1 and 2. The assignments were established on the basis of 2D homo- and hetero-correlation data. Compound **1** was identified as cryptolepine by comparison of its spectral characteristics with literature values (6–8) and by chromatographic comparison with a sample of authentic **1**. The chemical shifts in the ^{1}H-nmr spectrum were 0.1–0.4 ppm downfield compared to literature values (7,8). This may be explained if the molecule exists in an ionized state as suggested by Gellért *et al.* (5), which would give a more downfield shift to the protons. The ionized state could be due to the extraction process.

The mass spectrum of compound **2** showed a molecular ion at *m/z* 218, which is consistent with the molecular formula $C_{15}H_{10}N_2$, and the uv and ir spectral data were in agreement with literature values for quindoline (6). The ^{1}H- and ^{13}C-nmr chemical shifts for **2** are reported here for the first time. Our data from the nmr studies confirmed the structure proposed originally for quindoline [**2**].

Compound **3** showed a molecular ion at *m/z* 248, 16 mass units more than that of **1**, and accurate ms measurement gave *m/z* 248.2835 ($C_{16}H_{12}ON_2$, calcd for 248.2836). A broad band at 3460 cm^{-1} in the ir spectrum and a broad singlet ^{1}H-nmr signal at 10.17 ppm demonstrated the presence of a hydroxy group. The ^{1}H- and 2D COSY nmr spectra were very similar to those of compound **1**, indicating the existence of two aromatic four-spin systems. Also, in comparison with **1**, the absence of the aromatic singlet in the ^{1}H-nmr spectrum and the presence of an extra quaternary carbon signal in the decoupled ^{13}C-nmr spectrum were noted. The 2D-COSY spectrum allowed the subgrouping of the two four-spin systems. One system is comprised of the protons, in sequence, resonating at 8.19, 7.13, 7.42, and 7.50 ppm and the other of the protons at 7.72, 7.69, 7.31, and 8.47 ppm.

TABLE 1. ^{1}H-nmr Data of Compounds **1–4**.

Proton(s)	Compound			
	1[a]	**2**[b]	**3**[c]	**4**[b]
1	8.16, d (8.2) [7.92]	7.93, d (8.2)	8.47, d (8.1)	7.96, d (8.1)
2	7.59, dd (8.2,7.3) [7.46]	7.54, dd (8.2,6.7)	7.31, dd (8.1,6.6)	7.24, dd (8.1,6.6)
3	7.79, dd (8.9,7.3) [7.69]	7.67, dd (8.5,6.7)	7.69, dd (8.3,6.6)	7.45, dd (7.7,6.6)
4	8.06, d (8.9) [7.83]	8.34, d (8.5)	7.72, d (8.3)	7.92, d (7.7)
NCH_3-5	4.72, s [4.32]		4.39, s	
5a				3.81, s
6	8.13, d (8.5) [7.75]	8.55, d (7.8)	8.19, d (8.4)	8.95, d (8.0)
7	6.99, dd (8.5,6.6) [6.76]	7.34, dd (7.8,7.3)	7.13, dd (8.4,7.3)	7.65, dd (8.0,6.7)
8	7.53, dd (8.6,6.6) [7.37]	7.60, dd (8.1,7.3)	7.42, dd (8.3,7.3)	7.75, dd (8.5,6.7)
9	7.81, d (8.6) [7.65]	7.46, d (8.1)	7.50, d (8.3)	7.72, d (8.5)
NH-10		8.20, br s		
NCH_3-10				4.27, s
11	8.73, s	8.04, s		8.75, s
OH-11			10.17, br s	
OH-12				9.87, br s

[a]Run at 400 MHz in $CDCl_3$. Literature data (300 MHz, $CDCl_3$) of **1** (7) given in square brackets.
[b]Run at 600 MHz in $CDCl_3$.
[c]Run at 600 MHz in $CDCl_3$-CD_3OD (2:1).

TABLE 2. ^{13}C-Nmr Data of Compounds **1–4** (δ from TMS).

Carbon	Compound				
	1[a]		**2**[b]	**3**[c]	**4**[b]
1	130.01	[129.6]	127.17	125.03	118.81
2	123.60	[123.4]	125.33	121.32	120.57
3	128.76	[128.5]	126.62	130.49	126.52
4	114.87	[114.8]	129.16	114.04	117.93
4a	132.82	[132.5]	144.39	139.51	125.52
NCH_3-5	38.10	[37.8]		36.38	
5a	139.40	[138.9]	146.51	131.47	65.46
5b	113.60	[113.3]	122.10	115.53	120.48
6	123.67	[123.5]	122.21	122.14	125.19
7	117.27	[117.0]	120.39	119.22	125.53
8	130.87	[130.6]	129.87	127.36	129.42
9	120.30	[119.8]	110.95	112.01	115.91
9a	161.46	[161.0]	143.56	139.21	135.54
NCH_3-10					43.36
10a	145.52	[145.0]	132.42	123.19	136.92
11	126.87	[126.3]	113.19	167.01	135.51
11a	124.61	[124.3]	126.97	122.87	
12					152.12
12a					124.35

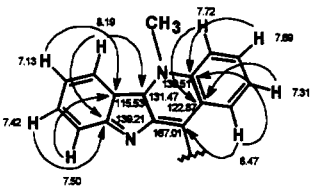
[a]Run at 400 MHz in $CDCl_3$. Literature data (300 MHz, $CDCl_3$) of **1** given in square brackets.
[b]Run at 600 MHz in $CDCl_3$.
[c]Run at 600 MHz in $CDCl_3$-CD_3OD (2:1).

The three-proton singlet resonating at 4.39 ppm could arise from either *O*-Me or a *N*-Me substituent. Because the molecular formula has only one oxygen atom and this is linked to a hydrogen atom forming an hydroxy group, as shown by the ir spectrum, the singlet in question could only be assigned to a *N*-Me group. Assuming that compound **3** has an indoloquinoline structure similar to the major alkaloid **1**, the methyl group could be linked to the nitrogen at position 5 or 10. The 2D-NOESY spectrum showed through-space connectivities between the *N*-Me and two doublets resonating at 8.19 and 7.72 ppm. This observation established the *N*-Me at position 5 rather than position 10 where the methyl group could only be correlated with one doublet corresponding to H-9. Consequently, the two one-proton doublets resonating at 8.19 and 7.72 ppm could be assigned either to H-4 or H-6. The proton at 7.72 ppm was correlated via long-range coupling to the aromatic CH resonating at 121.32 ppm and to one quaternary carbon resonating at 122.87 ppm. Long-range connectivities were observed from the proton resonating at 8.19 ppm to two quaternary carbons at 131.47 and 139.21 ppm and one aromatic CH at 127.36 ppm. Given this information, we could assign the signal at 7.72 ppm to H-4 and the signal at 8.19 ppm to H-6, because H-4 can only be three-bond correlated with one quaternary carbon at C-11a, while H-6 can be long-range correlated to two quaternary carbons at C-5a and C-9a. Combining the data from 2D-COSY and HMQC spectra we could now assign the ^{1}H- and ^{13}C-nmr chemical shifts to positions 1 to 4 and 6 to 9. Connectivities observed in the HMBC spectrum allowed the assignment of the quaternary carbons, as shown by the arrows in **6**. The remaining quaternary carbon resonating at 123.19 ppm could be only assigned to C-10a. Finally, the hydroxy group could only be linked to the quaternary carbon at C-11, resonating downfield at 167.01 ppm. Thus, compound **3** was named hydroxycryptolepine.

Compound **4** gave a molecular ion of *m/z* 262 and hrms gave *m/z* 262.3102 ($C_{17}H_{14}ON_2$, calcd 262.3104), 14 mass units more than that of **3**. The presence of OH

was shown by the peak at 3464 cm^{-1} in the ir spectrum and a broad singlet at 9.87 ppm in the ^{1}H-nmr spectrum. A three-proton singlet resonating at 4.27 ppm and an aliphatic one-proton singlet resonating at 3.81 ppm were also observed. For the same reasons indicated in the discussion on the structure of **3**, the three-proton singlet at 4.27 ppm corresponds to a *N*-Me group resonance. The ^{13}C-nmr spectrum showed that the molecule contained an extra aliphatic methine carbon resonating at 65.46 ppm when compared with the other indoloquinoline alkaloids. No signals were observed that might indicate that this is contained in a side-chain or ring substituent. The 2D-COSY spectrum showed evidence of two aromatic four-spin systems. The HMQC data allowed the establishment of the direct ^{1}H-^{13}C correlations in these two systems. One of the spin-systems comprised the ^{1}H-^{13}C pairs, in sequence, resonating at 7.96/118.81, 7.24/120.57, 7.45/126.52, and 7.92/117.93 ppm. The other spin-system comprised the ^{1}H-^{13}C pairs at 8.95/125.19, 7.65/125.53, 7.75/129.42, and 7.72/115.91 ppm. Analyzing the HMBC spectrum for the first four-spin system established, we observed that the proton resonating at 7.96 ppm was three-bond correlated with an aromatic CH resonating at 126.52 ppm and with two quaternary carbons resonating at 125.52 and 152.12 ppm. Long-range connectivities were also observed from the proton resonating at 7.92 ppm to the quaternary carbon resonating at 124.35 ppm and to the CH resonating at 120.57 ppm. These observations allowed the establishment of substructure **7** where long-range connectivities are shown by arrows.

The one-proton singlet at 8.75 ppm was long-range coupled with the quaternary carbon resonating at 124.35 ppm. Through-space connectivities from the *N*-Me substituent to the singlet at 8.75 ppm and to one of the peri protons of the second four-spin system, resonating at 7.72 ppm, were observed in the 2D-NOESY spectrum. The *N*-Me group was also three-bond correlated with the quaternary carbons resonating at 135.54 and 136.92 ppm. The other peri proton of this second four-spin system, resonating at 8.95 ppm, was long-range correlated with the quaternary carbon at 135.54 ppm. Given this information and the data arising from the 2D-COSY and HMQC spectra, substructure **8** could be established. The arrangement of atoms in **8** resembles a indolobenzazepine ring as denoted by the dashed lines. This resemblance seems reasonable as an indolobenzazepine substructure was proposed for the alkaloid cryptospirolepine, also isolated from the roots of *C. sanguinolenta* (16). The remaining quaternary carbon resonating at 120.48 ppm was assigned to C-5b based on long-range connectivities observed from this signal to the signals of H-7 and H-9. The HMBC spectrum also showed connectivities, represented by arrows in **9**, from the aliphatic



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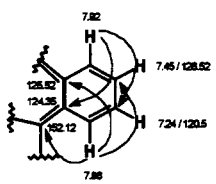

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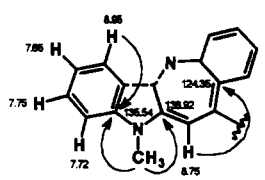

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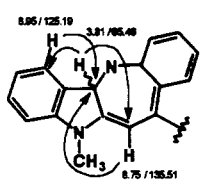

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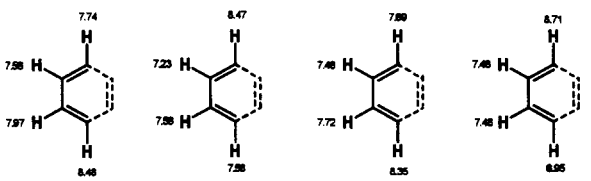
methine proton-carbon pair resonating at 3.81/65.46 ppm and the aromatic pairs resonating at 8.75/135.51 and 8.95/125.19 ppm. These observations allowed the establishment of the last bridge between the indole and benzazepine rings. The hydroxy group can only be linked to C-12 resonating downfield at 152.12 ppm. Alkaloid **4** was named cryptoheptine.

Compound **5** gave a $[M+H]^+$ ion at *m/z* 449 and two major fragments at *m/z* 217 (100%) and *m/z* 231 (91%). The accurate mass measurement established a molecular formula of $C_{31}H_{20}N_4$. This formula and the major fragments suggested that **5** was a congener of **1** and **2**. Although congested, the 2D-COSY spectrum established four aromatic four-spin systems which is consistent with the existence of two indoloquinoline rings. The chemical shifts and the interrelationships of protons in the four-spin systems are shown by substructures **10–13**. The ^{1}H-nmr spectrum also showed one aromatic singlet resonating at 7.62 ppm and one three-proton singlet resonating at 5.13 ppm. The chemical shift of the three-proton singlet strongly implied a *N*-Me substituent. The 2D-NOESY spectrum showed connectivities from the *N*-Me group to two doublets resonating at 8.47 and 8.48 ppm, which correspond to peri protons of spin systems **10** and **11**. Assuming that compound **5** is composed of two indoloquinoline nuclei, the *N*-Me substituent could be only in one of the quinoline rings. The one-proton singlet at 7.62 ppm showed through-space connectivities with the doublet of spin system **12** resonating at 7.69 ppm. Given these observations, it was deduced that spin systems **10** and **11** belonged to the corresponding cryptolepine [**1**] half of the molecule and that no proton was linked to C-11 which was free to be linked to the half of the molecule corresponding to quindoline [**2**]. If this is so, the aromatic protons resonating at 7.62 and 7.69 ppm are at positions H-11′ and H-1′, respectively, and the remaining spin system **13** is part of the indole ring of this quindoline-like half. The link between the two indoloquinoline nuclei was placed between C-11 of the cryptolepine-like half and the indole nitrogen of the quindoline-like half because it was observed that H-1′ and H-11′ were resonating more upfield than the corresponding protons in the molecule of quindoline [**2**]. This observation suggested that these protons suffer a diamagnetic effect due to the proximity of protons of the other half of the molecule. This argument is supported by the upfield chemical shifts observed for protons in the same situation in cryptospirolepine, the other bis alkaloid isolated from *C. sanguinolenta* (16). The structure of compound **5**, named cryptoquindoline, was thus established and its ^{1}H- and ^{13}C-nmr chemical shift data are presented in the Experimental.

Compound **5** was shown to be an artifact produced during the process of acid-base partition. Densitometry was used to examine the crude EtOH extract, the filtrate of crude extract resuspended in $CHCl_3$ (II), the $CHCl_3$ extract of the powdered roots alkalinized with NH_3 (III), and the alkaloid extract (IV) obtained as described in the Experimental. These four extracts and compound **5** were chromatographed by tlc and the *in situ* uv spectrum of the chromatograms performed for the same zone corresponding to the R_f of **5**. From the uv spectra obtained, it was concluded that **5** was formed due to the alkalinization with NH_3 in the acid-base partition process.



10 **11** **12** **13**

Hydroxycryptolepine [**3**], cryptoheptine [**4**], and cryptoquindoline [**5**] have not been reported previously.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Uv spectra were taken in MeOH, 0.01 N ethanolic KOH, and 0.01 N ethanolic HCl solvents on a Hitachi U-2000 spectrophotometer. Ir spectra were recorded in KBr on a Perkin-Elmer 1420. Eims, fabms, and hrms were obtained with an ionization voltage of 70 eV on a Kratos MS890. The ^{1}H- and ^{13}C-nmr spectra were taken in $CDCl_3$ ($CDCl_3$ and CD_3OD for **3** and **5**) with TMS as internal standard at 400 MHz (^{1}H) and 100 MHz (^{13}C) using a Bruker AMX-400 instrument or at 600 MHz (^{1}H) and 150 MHz (^{13}C) using a Bruker AMX-600 instrument. Chemical shifts are expressed as δ values (ppm) downfield from TMS. Assignments were made with the help of standard tables, 2D COSY, 2D NOESY, and hetero-correlation HMQC and HMBC spectra using standard programs from the library: $^nJ_{C\text{-}H}$=7 Hz was used for nmr experiments.

PLANT MATERIAL.—Roots of *Cryptolepis sanguinolenta* were purchased in Bandim market, Guinea Bissau, in February 1991. The samples were authenticated by Dr. Adélia Diniz from the Centro de Botânica, Instituto Investigação Científica Tropical, Lisbon (LISC) where voucher specimen No. 913 is deposited.

EXTRACTION AND ISOLATION.—Powdered roots (650 g) of *C. sanguinolenta* were extracted with EtOH at 50° to give 40 g of crude extract. The crude extract was dissolved in 6% HOAc and filtered; NH_3 was added to the filtrate until pH 10. It was then extracted with $CHCl_3$ and this was concentrated *in vacuo* to yield a purple alkaloid extract (8 g). Fractionation by vlc on an acid alumina column using a $CHCl_3$/MeOH gradient yielded five fractions (A–E). Purification of fraction B by prep. tlc on Si gel developed with $CHCl_3$-MeOH (95:5) yielded **2** (8.2 mg) and **3** (16.2 mg). Cc of fraction C on a neutral alumina column with EtOAc-MeOH (95:5) gave 5 fractions (I–V); fraction II was purified by prep. tlc on Si gel developed with $CHCl_3$-MeOH-35% NH_3 (89:10:1) and compound **5** (8.4 mg) was obtained. Cc of 50 mg of fraction D on a neutral alumina column with an EtOAc/MeOH gradient yielded a yellow compound (40 mg); it was suspended in 1% NaOH and this extracted with $CHCl_3$ to give a purple compound, **1** (36 mg). Fraction E was chromatographed on a neutral alumina column with EtOAc-MeOH (90:10) solution to give 3 fractions (1–3); fraction 2 was purified by prep. tlc on Si gel developed with $CHCl_3$-MeOH-35% NH_3 (90:10:1), yielding **4** (3.5 mg).

INVESTIGATION OF THE NATURAL OCCURRENCE OF **5** BY TLC-DENSITOMETRY.—Four extracts were examined: I, the crude EtOH extract; II, the filtrate of dried crude extract resuspended in $CHCl_3$; III, the $CHCl_3$ extract of the powdered roots alkalinized with NH_3; and IV, the alkaloid extract. Each extract (20 μg) and 2 μg of **5** were applied on a 20×20-cm Si gel plate (Merck Art. 5554) with a Camag Linomat IV applicator. Plates were developed with $CHCl_3$-MeOH-NH_3 (90:10:1) in a chamber pre-saturated for 15 min. The uv spectra were performed with a Camag Tlc Scanner III at y=10–13-cm plate position and between λ=210–390 nm with an increment of 10 nm.

Cryptolepine [**1**].—Obtained as dark purple crystals; spectral and chromatographic data agreed in all respects with an authentic sample and literature values for **1**; ^{1}H- and ^{13}C-nmr data, see Tables 1 and 2.

Quindoline [**2**].—Obtained as yellowish amorphous solid; agreed with literature values for uv and ir spectral data for **2** in all respects; ^{1}H- and ^{13}C-nmr data, see Tables 1 and 2; eims (70 eV) *m/z* $[M]^+$ 218 (36), 167 (10), 149 (19), 137 (12), 125 (18) 123 (17), 111 (30), 97 (44), 95 (34), 83 (46), 71 (62), 57 (100).

Hydroxycryptolepine [**3**].—Obtained as yellowish amorphous solid; uv (MeOH) λ max (log ε) 220 (3.82), 233 (3.86), 272 (4.05), 312 (3.64), 326 (3.58), 367 (3.17), 386 (3.42) 405 (3.52) nm; uv (0.01 N ethanolic KOH) λ max (log ε) 220 (3.90), 233 (3.94), 273 (4.11), 312 (3.72), 326 (3.66), 368 (3.25), 386 (3.49), 406 (3.59) nm; uv (0.01 N ethanolic HCl) λ max (log ε) 224 (3.93), 232 (3.82), 246 (3.76), 261 sh (3.84), 281 (4.03), 315 (3.37), 333 sh (3.53), 346 (3.80), 406 (3.20), 422 (3.16) nm; ir (KBr) ν max 3460 (OH), 2976, 1623, 1584, 1523, 1458, 1382, 1334, 1290, 1266, 1220, 1183, 1150, 1132, 1048, 910, 813, 743, 731, 702 cm^{-1}; ^{1}H- and ^{13}C-nmr data, see Tables 1 and 2; hrms *m/z* $[M]^+$ 248.2835 ($C_{16}H_{12}N_2O$, calcd 248.2836); fabms (thioglycerol) *m/z* $[M+H]^+$ 249 (100), $[M]^+$ 248 (22), $[M-Me]^+$ 233 (11), 181 (21), 179 (11), 171 (14), 149 (14), 147 (17), 133 (20).

Cryptoheptine [**4**].—Obtained as yellowish amorphous solid: uv (MeOH) λ max (log ε) 215 (sh, 4.14), 234 (4.28), 254 sh (4.03), 278 sh (4.27), 284 (4.31), 299 sh (3.95), 316 (3.60), 350 (3.77) nm; uv (0.01 N ethanolic KOH) λ max (log ε) 240 (4.18), 282 sh (4.27), 291 (4.47), 301 sh (3.91), 316 (3.94), 341 (3.65), 379 (3.76) nm; uv (0.01 N ethanolic HCl) λ max (log ε) 216 sh (4.05), 235 (4.29), 254 sh (4.07), 276 sh (4.28), 285 (4.32), 300 sh (3.97), 351 (3.83) nm; ir (KBr) ν max 3460 (OH), 2945, 1636, 1454, 1353, 1221, 1120, 749 cm^{-1}; ^{1}H- and ^{13}C-nmr data, see Tables 1 and 2; hrms *m/z* $[M]^+$ 262.3102 ($C_{17}H_{14}N_2O$, calcd

262.3104); eims (70 eV) *m/z* $[M-H]^+$ 261 (2), $[M-HCO]^+$ 233 (3), $[M-H-HCO]^+$ 232 (2), $[M-H-HCO-CH_3]^+$ 217 (4), 205 (8), 149 (5), 133 (9), 123 (11), 117 (14), 111 (19), 109 (24), 97 (100).

Cryptoquindoline [**5**].—Obtained as dark-green amorphous solid; uv (MeOH) λ max (log ε) 223 (4.24), 269 (4.29), 281 sh (4.06), 311 (3.41), 339 (3.65), 360 sh (3.65), 375 (3.89), 463 (3.16) nm; uv (0.01 N ethanolic KOH) λ max (log ε) 223 (4.10), 272 (4.14), 300 sh (3.97), 311 (4.09), 341 (3.56), 375 sh (3.53), 393 (3.81) nm; uv (0.01 N ethanolic HCl) λ max (log ε) 223 (4.51), 242 (4.21), 276 (4.58), 348 sh (4.06), 364 (4.31), 378 (4.23), 414 (3.53) nm; ir (KBr) ν max 2932, 1625, 1584, 1489, 1472, 1453, 1390, 1345, 1303, 1261, 1237, 1212, 1158, 1130, 1087, 1028, 860, 764, 735, 712 cm^{-1}; ^1H nmr ($CDCl_3$-CD_3OD, 1:1, 400 MHz) δ 8.71 (1H, d, *J*=6.8 Hz, H-6′), 8.48 (1H, d, *J*=9.0 Hz, H-4 or H-6), 8.47 (1H, d, *J*=8.5 Hz, H-6 or H-4), 8.35 (1H, d, *J*=8.7 Hz, H-4′), 7.97 (1H, dd, *J*=9.0 and 6.8 Hz, H-3 or H-7), 7.74 (1H, d, *J*=8.5 Hz, H-1 or H-9), 7.72 (1H, dd, *J*=8.7 and 6.7 Hz, H-3′), 7.69 (1H, d, *J*=7.5 Hz, H-1′), 7.62 (1H, s, H-11′), 7.56 (3H, m, H-2, H-8, H-9, or H-1), 7.48 (3H, m, H-2′, H-7′, H-8′), 7.23 (1H, dd, *J*=8.5 and 5.3 Hz, H-7 or H-3), 6.95 (1H, d, *J*=6.8 Hz, H-9′), 5.13 (3H, s, Me-N5); ^{13}C nmr ($CDCl_3$-CD_3OD, 1:1, 100 MHz) δ 160.43 (s), 146.40 (s), 145.66 (s), 144.50 (s), 142.70 (s), 141.43 (s), 134.88 (s), 134.24 (s), 132.83 (d), 130.50 (d), 129.92 (d), 129.09 (s), 128.28 (d), 127.79 (d), 127.75 (d), 127.16 (s), 125.96 (d), 125.48 (d), 125.15 (d), 124.39 (d), 122.57 (d), 122.38 (s), 122.32 (s), 121.97 (d), 119.62 (d), 119.08 (d), 116.67 (d), 114.94 (d), 114.87 (s), 111.37 (d), 39.33 (q, Me-N5); hrms *m/z* $[M]^+$ 448.5256 ($C_{31}H_{20}N_4$, calcd 448.5258); fabms (thioglycerol) *m/z* $[M+H]^+$ 449 (19), 239 (25), 237 (39), 234 (34), 231 (91), 217 (100), 216 (31), 215 (68), 214 (38), 197 (39), 181 (54).

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