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NEW HUMANTENINE-TYPE ALKALOIDS FROM *GELSEMIUM ELEGANS*

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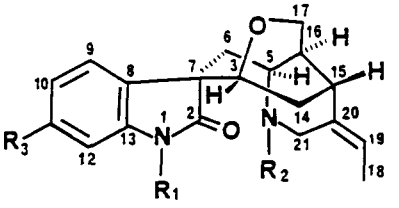
ABSTRACT.—The alkaloid extract of the whole plant of *Gelsemium elegans* has afforded four new alkaloids: *N*-desmethoxyrankinidine [**1**], 11-hydroxyrankinidine [**3**], 11-hydroxyhumantenine [**5**], and 11-methoxyhumantenine [**7**], as well as the known alkaloids rankinidine [**2**], humantenine [**4**] and humantenirine [**6**]. The structure of **5** was established through X-ray crystallographic analysis, and the structures of the other three new alkaloids were deduced by spectral analysis (^{1}H, ^{13}C, APT, 2D-COSY and 2D-HETCOR).

The genus *Gelsemium* in the family Loganiaceae is comprised of three species: *Gelsemium elegans* (Gardn. and Champ.) Benth., native to Southeastern Asia, and *Gelsemium sempervirens* (L.) Jaume St.-Hilaire and *Gelsemium rankinii* Small, native to the United States. All of the species are toxic. Chemical studies have afforded about 20 alkaloids in six different structure groups, i.e., gelsemine-type, gelsenicine-type, humantenine-type, sarpagine-type, sempervirine-type, and koumine-type (1,2).

G. elegans is a well-known Chinese medicinal plant (Kou-Wen or Hu-Man-Teng), used as an analgesic and antispasmodic and as a remedy for certain kinds of skin ulcers. Since 1930, this plant has been studied chemically yielding about 15 alkaloids, some of which have been pharmacologically evaluated (3–17). We have recently restudied this plant and obtained more than 40 alkaloids, and report here on the isolation and structure elucidation of four new humantenine-type alkaloids: *N*-desmethoxyrankinidine [**1**], 11-hydroxyrankinidine [**3**], 11-hydroxyhumantenine [**5**], and 11-methoxyhumantenine [**7**], as well as three known alkaloids: rankinidine [**2**], humantenine [**4**], and humantenirine [**6**]. Details of the structure elucidation of the remaining alkaloids will be published elsewhere.



1 $R_1=R_2=R_3=H$
2 $R_1=OMe$, $R_2=R_3=H$
3 $R_1=OMe$, $R_2=H$, $R_3=OH$
4 $R_1=OMe$, $R_2=Me$, $R_3=H$
5 $R_1=OMe$, $R_2=Me$, $R_3=OH$
6 $R_1=OMe$, $R_2=H$, $R_3=OMe$
7 $R_1=OMe$, $R_2=Me$, $R_3=OMe$

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RESULTS AND DISCUSSION

N-Desmethoxyrankinidine [**1**] displayed a molecular ion peak (eims) at *m/z* 310 ($C_{19}H_{22}N_2O_2$), 30 amu less than that of rankinidine [**2**], and a strong peak at *m/z* 164, characteristic of the fragment $C_{10}H_{14}NO$ produced by loss of the aromatic moiety of the molecule. Furthermore, **1** showed spectral characteristics (uv, ms, ^1H, ^{13}C and cd) nearly identical with those of rankinidine [**2**], except that **1** has no *N*-OMe group. Analysis of the ^1H and ^{13}C spectra (Tables 1 and 2) of **1** and **2** revealed that **1** contained an N-H group instead of the *N*-OMe; therefore, **1** should be *N*-desmethoxyrankinidine. Comparison of the nmr spectra of **1** with those of **2** and **6** led to the assignments of the ^1H and ^{13}C data shown in Tables 1 and 2, respectively.

The structure of compound **3** was assigned as 11-hydroxyrankinidine on the basis of spectral comparison with the parent compound rankinidine [**2**] and humantenirine [**6**]. Thus, in the ^1H-nmr spectrum of **3**, only three aromatic proton signals were observed at δ 7.14 (d, J = 8.1 Hz, H-9), 6.56 (d, J = 2.4 Hz, H-12), and 6.48 (dd, J = 8.1, 2.4 Hz, H-10), with the remaining resonances being very close to those of **2** and **6**. The presence of a phenolic function was supported by a marked bathochromic shift (13.5 nm) on the addition of strong base to its uv spectrum. The molecular ion (eims) at *m/z* 356 ($C_{20}H_{24}N_2O_4$), is 16 amu more than that of rankinidine [**2**], while both compounds displayed the same intense fragment ions at *m/z* 164 and 108, confining the hydroxy group to the aromatic ring. Because the aromatic proton spectral pattern is the same as that of humantenirine [**6**] in which the methoxy group at C-11 position was established through an nOe experiment, compound **3** has an 11-phenolic group and is 11-hydroxyrankinidine.

TABLE 1. ^1H-Nmr Spectral Data of Alkaloids **1–7**.[a]

Proton	Compound						
	1	**2**	**3**	**4**	**5**	**6**	**7**
H-3	3.60 (d, 8.4)	3.54 (d, 8.4)	3.53 (d, 6.0)	3.62 (d, 7.2)	3.59 (d, 7.2)	3.52 (d, 8.5)	3.56 (d, 7.2)
H-5	3.76 (m)	3.71 (m)	3.71 (m)	3.41 (m)	3.56 (m)	3.68 (m)	3.39 (m)
H-6α	2.23 (dd, 3.3, 16.5)	2.18 (dd, 3.3, 16.5)	1.93 (dd, 3.9, 16.5)	1.71 (dd, 8.4, 15.3)	1.78 (dd, 8.4, 15.9)	2.18 (dd, 4.2, 15.3)	1.62 (dd, 8.1, 15.3)
H-6β	2.35 (dd, 3.3, 16.5)	2.32 (dd, 3.3, 16.5)	2.31 (dd, 3.9, 16.5)	2.50 (dd, 8.4, 15.3)	2.44 (dd, 8.4, 15.9)	2.32 (dd, 4.2, 15.3)	2.49 (dd, 8.1, 15.3)
H-9	7.40 (d, 7.5)	7.42 (d, 7.2)	7.14 (d, 8.1)	7.40 (d, 7.8)	7.17 (d, 8.4)	7.31 (d, 8.7)	7.30 (d, 8.7)
H-10	7.08 (t, 7.5)	7.14 (t, 7.2)	6.48 (dd, 8.1, 2.4)	7.11 (t, 7.8)	6.52 (dd, 8.4, 1.5)	6.62 (dd, 8.7, 2.4)	6.62 (dd, 8.7, 2.4)
H-11	7.21 (t, 7.5)	7.30 (t, 7.2)	—	7.31 (t, 7.8)	—	—	—
H-12	6.85 (d, 7.5)	6.82 (d, 7.2)	6.56 (d, 2.4)	7.00 (d, 7.8)	6.57 (d, 1.5)	6.56 (d, 2.4)	6.60 (d, 2.1)
H-14α	2.48 (dd, 12.6, 8.4)	2.44 (dd, 12.6, 8.4)	2.39 (dd, 14.1, 7.5)	2.28 (m)	2.48 (m)	2.42 (dd, 12.6, 7.5)	2.25 (m)
H-14β	2.32 (dd, 12.6, 8.4)	2.33 (dd, 12.6, 8.4)	2.31 (dd, 14.1, 7.5)	2.28 (m)	2.48 (m)	2.31 (dd, 12.6, 7.5)	2.25 (m)
H-15	2.62 (m)	2.60 (m)	2.64 (m)	2.60 (m)	2.65 (m)	2.60 (m)	2.62 (m)
H-16	2.23 (m)	2.21 (m)	2.25 (m)	2.31 (m)	2.25 (m)	2.21 (m)	2.22 (m)
H-17α	4.34 (d, 10.8)	4.32 (d, 9.6)	4.29 (d, 10.8)	4.20 (d, 11.1)	4.16 (d, 10.8)	4.29 (d, 10.8)	4.17 (d, 11.1)
H-17β	4.05 (dd, 10.8, 4.5)	4.04 (dd, 9.6, 4.5)	3.99 (dd, 10.8, 4.2)	4.05 (dd, 11.1, 5.4)	4.08 (dd, 10.8, 5.4)	4.04 (dd, 10.8, 5.7)	4.05 (dd, 11.1, 5.1)
H-18	1.60 (d, 6.4)	1.60 (d, 6.6)	1.61 (d, 6.3)	1.65 (d, 6.9)	1.67 (d, 6.9)	1.59 (d, 6.6)	1.64 (d, 6.9)
H-19	5.28 (q, 6.6)	5.23 (q, 6.6)	5.32 (q, 6.3)	5.39 (q, 6.9)	5.48 (q, 6.9)	5.23 (q, 6.6)	5.37 (q, 6.9)
H-21α	3.34 (bd, 16.2)	3.31 (bd, 15.6)	3.29 (dd, 17.1, 1.2)	3.39 (m)	3.36 (m)	3.32 (d, 17.1)	3.36 (m)
H-21β	3.91 (d, 16.2)	3.86 (d, 15.6)	3.96 (d, 17.1)	3.39 (m)	3.36 (m)	3.88 (d, 17.1)	3.36 (m)
N_4Me	—	—	—	2.36 (s)	2.46 (s)	—	2.35 (s)
N_1OMe	—	3.99 (s)	4.04 (s)	3.98 (s)	3.97 (s)	3.98 (s)	3.98 (s)
ArOMe	—	—	—	—	—	3.83 (s)	3.83 (s)

[a]Recorded in $CDCl_3$. Chemical shift values are reported as δ values (ppm) from internal TMS at 300 MHz; signal multiplicity and coupling constants (Hz) are shown in parentheses.

TABLE 2. ^{13}C-Nmr Spectral Data of Compounds **1**–**7**.[a]

Carbon	Compound						
	1	**2**	**3**	**4**	**5**	**6**	**7**
2	184.67	174.31	174.97	174.29	174.73	174.49	174.80
3	73.84	74.04	74.51	72.07	72.20	73.96	72.09
5	58.56	57.16	56.65	61.43	61.49	56.31	61.39
6	34.19	34.33	33.61	28.28[b]	28.30	34.20	28.26
7	54.43	54.68	53.38	55.16	55.10	54.32	54.58
8	129.64	131.51	120.56	129.02	121.39	122.27	120.71
9	125.39	125.40	125.88	125.78	126.23	125.91	126.55
10	122.86	123.74	111.29	122.88	109.07	107.85	107.26
11	128.17	128.40	158.92	128.04	156.87	160.05	159.95
12	109.36	107.38	95.58	107.22	96.06	94.47	94.56
13	139.01	140.60	139.03	138.83	140.69	140.27	140.04
14	29.69	30.29	30.21	25.25	25.70	29.94	25.35
15	33.81	34.50	32.97	34.57	34.16	34.25	34.48
16	34.48	34.91	34.14	38.32	37.51	34.80	38.33
17	66.99	67.31	66.76	68.86	66.63	66.98	66.87
18	12.64	12.83	12.66	12.76	12.87	12.50	12.72
19	118.07	117.55	118.98	119.51	120.40	117.21	119.21
20	139.01	138.51	138.28	136.94	136.60	139.33	137.15
21	41.16	41.32	41.18	45.49	45.61	41.09	45.49
N_4Me	—	—	—	42.45	42.21	—	42.46
N_1OMe	—	63.60	63.75	63.30	63.31	63.31	63.28
ArOMe	—	—	—	—	—	54.50	55.41

[a]Recorded in $CDCl_3$. Chemical shift values are reported as δ values (ppm) at 75.6 MHz.
[b]Incorrectly reported as 38.01 in Yang and Chen (15).

The molecular ion (eims) of compound **5** at *m/z* 370 ($C_{21}H_{26}N_2O_4$) was 16 amu more than that of humantenine [**4**], while both compounds showed the same intense fragments at *m/z* 178 and 122. The ^{1}H-nmr spectrum of **5** was nearly identical with that of humantenine [**4**], except for the presence of an 11-hydroxy-substituted aromatic ring: δ 7.17 (d, J = 8.4 Hz, H-9), 6.57 (d, J = 1.5 Hz, H-12), and 6.52 (dd, J = 8.4, 1.5 Hz, H-10). Like 11-hydroxyrankinidine [**3**], a bathochromatic shift (14 nm) was observed on the addition of strong base to the uv solution, supporting the presence of a phenolic group. Therefore, compound **5** should be assigned as 11-hydroxyhumantenine, and this was confirmed by single-crystal X-ray analysis.

A computer-generated perspective drawing of 11-hydroxyhumantenine [**5**] is given in Figure 1. The absolute configuration shown was not experimentally determined by single-crystal X-ray diffraction analysis but was selected to agree with earlier work (1). The seven-membered ring C-3, C-5, C-6, C-7, C-14, C-15, and C-16 is in the boat conformation, as is the tetrahydropyran ring O-4, C-3, C-14, C-15, C-16, and

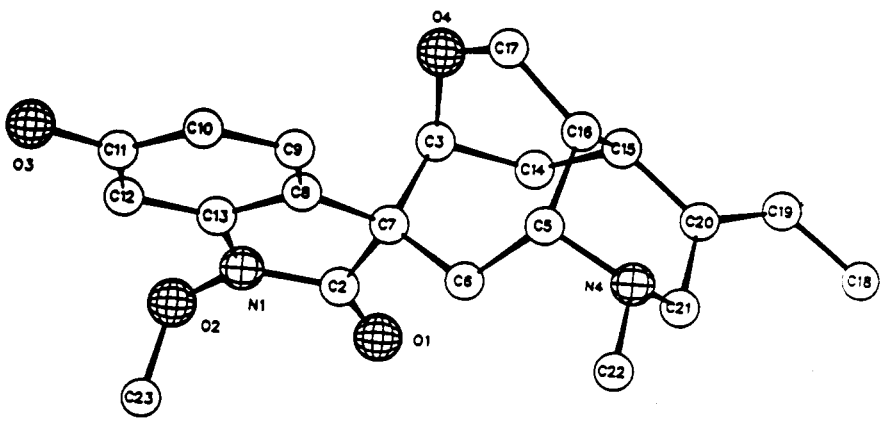

FIGURE 1. The molecular structure of compound **5**.

C-17. The nitrogen-containing ring N-4, C-5, C-16, C-15, C-20, and C-21 adopts a chair conformation.

Compound **7** showed a molecular ion peak at *m/z* 384 ($C_{22}H_{28}N_2O_4$), 30 amu more than that of humantenine [**4**] and 14 amu more than that of 11-hydroxyhumantenine [**5**], while the three compounds displayed the same intense fragments at *m/z* 178 and 122. The ^{1}H-nmr spectrum of **7** is nearly identical with that of **5**, except for the presence of an aromatic methoxy group at δ 3.83. For the structure determination of humantenirine [**6**], Yang and Chen (13) conducted *N*-methylation of humantenirine [**6**] to obtain **7** and reported some spectral data, but this is the first report of its natural occurrence. 2D-COSY, 2D-HETCOR, and APT spectra of this compound led to the assignments of the ^{1}H and ^{13}C data as shown in Tables 1 and 2, respectively.

Rankinidine [**2**] was first isolated from *G. rankinii* (18), and humantenine [**4**] and humantenirine [**6**] were isolated previously from this plant (13,15). There are no prior ^{13}C-nmr data for **2** and **6** available, and no 2D spectroscopic studies on **4**; these results are presented in Tables 1 and 2.

Compounds **3** and **5** are the first oxindole alkaloids known with an 11-hydroxy group, although some other oxindole alkaloids have an 11-methoxy group.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Melting points were determined using a Kofler hot-stage instrument and are uncorrected. Optical rotations were measured with a Perkin-Elmer 241 Polarimeter. The uv spectra were obtained on a Beckman DU-7 spectrometer, and ir spectra were measured on a Nicolet MX-1 FT-IR (KBr) interferometer. ^{1}H- and ^{13}C-nmr spectra were recorded in $CDCl_3$, using TMS as internal standard, employing a Varian XL-300 instrument. Low resolution mass spectra were obtained with a Varian MAT 112S instrument operating at 70 eV. Cd spectra were run in MeOH with a JASCO J-40A spectropolarimeter. X-ray data were collected on a Syntex $P2_1$ diffractometer using graphite monochromated CuKα radiation (1.54178 Å). All calculations were done on a Prime 9950 computer operated by the Cornell Chemistry Department. The major programs used were the SHELX85 system for solution, BDLS for refinement, and PLUTO for crystallographic illustrations.

PLANT MATERIAL.—Whole plants of *G. elegans* were collected in Guangxi Province, People's Republic of China in February 1987, and voucher specimens are deposited in the herbarium of the Shanghai Institute of Materia Medica, Chinese Academy of Sciences, Shanghai, People's Republic of China.

EXTRACTION AND FRACTIONATION.—The air-dried plant material (20 kg) was percolated with EtOH (200 liters) at room temperature, and the EtOH extract was concentrated in vacuo at 50° to afford a thick dark syrup, which was dissolved in 1% HCl solution. The residual solid was treated with 1% HCl until a Dragendorff's test was negative. After extraction with $CHCl_3$ three times, the acidic layer was basified with aqueous NH_4OH and extracted with $CHCl_3$ five times to give crude alkaloid extract A (112 g).

The $CHCl_3$ extract from the non-basified acidic layer was treated with 1% HCl, and the acidic solution was basified with NH_4OH and extracted with $CHCl_3$ to give alkaloid extract B (39 g). Alkaloid extract B (39 g) was chromatographed over Si gel (1200 g, 200–425 mesh, Column 1), using EtOAc gradually enriched with MeOH. The fractions were monitored by tlc on Si gel, using the system cyclohexane-EtOAc-diethylamine (6:4:1) and spraying with Dragendorff's reagent. Final separation and purification were on Si gel tlc (plate was pretreated with 0.5% NaOH solution), using the same solvent system for one or multiple developments to give compounds **4**, **7**, **2**, and **6**, in the order of elution. Alkaloid extract A (56 g) was chromatographed over Si gel (2 g, Column 2), using $CHCl_3$ gradually enriched with MeOH to yield successively compounds **5**, **3**, and **1**.

ISOLATION OF *N*-DESMETHOXYRANKINIDINE [**1**].—The residue (200 mg) of fraction 107 of Column 2 was subjected to preparative tlc using cyclohexane-EtOAc-diethylamine (6:4:1) as a solvent, and the third band at R_f 0.25 was eluted with Me_2CO to afford white needles of **1** (5 mg, 0.000025%), mp 258–260°; $[\alpha]^{22}D$ −169.2° (*c* = 0.052, MeOH); uv λ max (log ε) (MeOH) 207 (4.16), 252.5 (3.52) nm; ir ν max (KBr) 3252, 1702, 1697, 1694, 1682, 1196, 1113, 1104, 742 cm^{-1}; ^{1}H-nmr see Table 1; ^{13}C-nmr see Table 2; ms *m/z* (rel. int.) $[M]^+$ 310 (32), 295 (23), 164 (40), 108 (100); cd Δε nm (MeOH) +10.53 (230), −3.88 (258), −1.53 (285).

11-HYDROXYRANKINIDINE [**3**].—The residue (270 mg) of fractions 96–98 of Column 2 was sepa-

TABLE 3. Fractional coordinates and thermal parameters for Compound **5**.[a]

Atom	x	y	z	B
N-1	0.5502(8)	−0.1777(4)	0.5800(2)	8.7(2)[b]
C-2	0.5052(9)	−0.0717(5)	0.5703(3)	8.0(2)[b]
C-3	0.4356(11)	0.0177(5)	0.6697(3)	8.3(2)[b]
N-4	0.7271(6)	0.2920(4)	0.6109(2)	7.4(1)[b]
C-5	0.7197(9)	0.1869(5)	0.6445(3)	7.5(2)[b]
C-6	0.6799(9)	0.0941(5)	0.5978(3)	7.5(2)[b]
C-7	0.5949(9)	−0.0074(4)	0.6241(3)	7.9(2)[b]
C-8	0.7128(9)	−0.0928(5)	0.6509(3)	7.8(2)[b]
C-9	0.8514(9)	−0.0853(5)	0.6920(3)	7.8(2)[b]
C-10	0.9439(9)	−0.1779(5)	0.7079(3)	8.4(2)[b]
C-11	0.8954(9)	−0.2790(5)	0.6832(3)	8.1(2)[b]
C-12	0.7638(8)	−0.2869(5)	0.6401(3)	7.8(2)[b]
C-13	0.6771(9)	−0.1927(5)	0.6253(3)	7.4(2)[b]
C-14	0.3381(10)	0.1194(5)	0.6490(3)	8.1(2)[b]
C-15	0.4121(9)	0.2270(5)	0.6759(3)	8.0(2)[b]
C-16	0.5970(9)	0.2048(5)	0.7007(3)	7.9(2)[b]
C-17	0.5942(10)	0.1161(5)	0.7520(3)	8.3(2)[b]
C-18	0.2704(12)	0.4895(6)	0.5893(3)	10.1(3)[b]
C-19	0.2861(10)	0.3949(5)	0.6326(3)	9.0(2)[b]
C-20	0.4136(10)	0.3203(5)	0.6312(3)	8.2(2)[b]
C-21	0.5593(10)	0.3241(3)	0.5829(3)	8.5(2)[b]
C-22	0.8603(10)	0.2952(6)	0.5614(3)	9.3(2)[b]
C-23	0.5732(12)	−0.2794(7)	0.4867(4)	10.5(3)[b]
O-1	0.4085(7)	−0.0377(3)	0.5298(2)	8.9(1)[b]
O-2	0.4795(6)	−0.2637(3)	0.5453(2)	8.5(1)[b]
O-3	0.9873(6)	−0.3674(3)	0.7030(2)	9.5(2)[b]
O-4	0.4883(7)	0.0247(3)	0.7351(2)	8.6(1)[b]
O-5	0.7907(6)	−0.5374(3)	0.6912(2)	8.4(1)[b]
H-3	0.3530	−0.0460	0.6660	10.0
H-5	0.8332	0.1615	0.6632	9.1
H-6a	0.6091	0.1234	0.5611	9.1
H-6b	0.7887	0.0732	0.5742	9.1
H-9	0.8852	−0.0122	0.7106	9.4
H-10	1.0467	−0.1724	0.7374	10.1
H-12	0.7317	−0.3592	0.6200	9.4
H-14a	0.3352	0.1231	0.6008	9.7
H-14b	0.2124	0.1124	0.6616	9.7
H-15	0.3310	0.2504	0.7111	9.6
H-16	0.6459	0.2707	0.7235	9.5
H-17a	0.5519	0.1484	0.7936	9.9
H-17b	0.7160	0.0903	0.7606	9.9
H-18a	0.1632	0.5326	0.6005	12.1
H-18b	0.2618	0.4630	0.5437	12.1
H-18c	0.3756	0.5379	0.5939	12.1
H-19	0.1933	0.3854	0.6661	10.8
H-21a	0.5312	0.2742	0.5459	10.2
H-21b	0.5686	0.4003	0.5646	10.2
H-22a	0.8593	0.3692	0.5400	11.2
H-22b	0.8363	0.2366	0.5286	11.2
H-22c	0.9774	0.2820	0.5813	11.2
H-23a	0.5205	−0.3421	0.4621	12.6
H-23b	0.6981	−0.2967	0.4966	12.6
H-23c	0.5670	−0.2106	0.4602	12.6
H(OH)	0.9559	−0.4440	0.6859	10.5

[a]Estimated standard deviations of the significant figures are given in parentheses.
[b]The isotropic equivalent thermal parameter is given for anisotropic atoms.

rated by preparative tlc using the same solvent and eluting to afford white needles of **3** (7 mg, 0.000035%), mp 212–214°; $[\alpha]^{22}D$ −135° (*c* = 0.06, MeOH); uv λ max (log ε) (MeOH) 216 (4.55), 286.5 (3.72) nm; λ max (log ε) (MeOH/NaOH) 207 (4.77), 231.5 sh (4.45), 300 (3.68) nm; ir ν max (KBr) 3244, 1720, 1694, 1621, 1469, 1222, 1211, 1202, 1115, 832 cm^{-1}; ^{1}H-nmr see Table 1; ^{13}C-nmr see Table 2; ms *m/z* (rel. int.) $[M]^+$ 356 (2), 325 (4), 164 (74), 108 (100); cd Δε (MeOH) +16.20 (230), −3.89 (276).

11-HYDROXYHUMANTENINE [**5**].—The residue (210 mg) of fractions 43–44 of Column 2 was separated in the same way to afford white needles of **5** (8 mg, 0.00004%), mp 176–177°; $[\alpha]^{22}D$ −130° (*c* = 0.05, MeOH); uv λ max (log ε) (MeOH) 215 (4.40), 286 (3.49) nm, λ max (log ε) (MeOH/NaOH) 207 (4.54), 231 sh (4.31), 310 (3.51) nm; ir ν max (KBr) 1721, 1629, 1497, 1468, 1206, 1111 cm^{-1}; ^{1}H-nmr see Table 1; ^{13}C-nmr see Table 2; ms *m/z* (rel. int.) $[M]^+$ 370 (100), 339 (94), 178 (12), 122 (40); hrms 370.1889 for $C_{21}H_{26}N_2O_4$, calcd 370.1892; cd Δε (MeOH) +15.78 (237), −2.10 (276).

11-METHOXYHUMANTENINE [**7**] AND HUMANTENINE [**4**].—The residue (1.35 g) of fractions 28–32 of Column 1 was separated in the same way. The second band (R_f 0.75) afforded humantenine [**4**] as a yellow powder (400 mg, 0.002%), and the third band (R_f 0.70) gave **7** as a yellow powder (12 mg, 0.00006%): $[\alpha]^{22}D$ −146.5° (*c* = 0.06, MeOH); uv λ max (log ε) (MeOH) 217 (4.37), 285.5 (3.19) nm; ir ν max (KBr) 3463, 1630, 1499, 1216, 1177, 1117, 1075, 1070 cm^{-1}; ^{1}H-nmr see Table 1; ^{13}C-nmr see Table 2; ms *m/z* (rel. int.) $[M]^+$ 384 (86), 353 (100), 178 (25), 122 (84); cd Δε (nm) (MeOH) +7.80 (236), −2.60 (280).

For humantenine [**4**], the $[\alpha]D$, uv, ir, and ms were as described previously (15); ^{1}H-nmr see Table 1; ^{13}C-nmr see Table 2; cd Δε (MeOH) +32.18 (235), −8.58 (260), −7.50 (288).

RANKINIDINE [**2**] AND HUMANTENIRINE [**6**].—The residue (850 mg) of fractions 37–42 of Column 1 was separated in the same way to afford white needles of **2** (65 mg, 0.00033%) and white needles of **6** (150 mg, 0.00075%). The mp, $[\alpha]D$, uv, ir, ms, and some ^{1}H-nmr data of **2** and **6** were essentially the same as those published previously (15,18). For ^{13}C-nmr of **2** and **6** see Table 2. Cd of **2**: Δε (MeOH) +13.74 (230), −3.43 (260), −2.06 (285). Cd of **6**: Δε (MeOH) +20.02 (237), −4.27 (270).

SINGLE CRYSTAL X-RAY ANALYSIS OF 11-HYDROXYHUMANTENINE [**5**][3].—A crystal of approximate dimensions 0.30 × 0.35 × 0.40 mm was used for data collection. Crystal data: $C_{21}H_{26}N_2O_4 \cdot H_2O$, MW = 388.46, orthorhombic, space group $P2_12_12_1$, a = 7.809(2), b = 12.353(2), c = 21.158(4) Å, V = 2041.0(7) $Å^3$, Z = 4, D_c = 1.26 g/cm^3, μ (CuKα) = 7.02 cm^{-1}. The intensities of 1609 independent reflections with $2\theta \leq 114°$ were collected using 1° ω-scans, and after correction for Lorentz, polarization, and background effects, 1341 (83%) were judged observed ($|Fo| \geq 3\sigma(Fo)$). The structure was solved uneventfully, and hydrogen atoms were located on a ΔF-synthesis. The final refinement used anisotropic nonhydrogen atoms and fixed isotropic hydrogens. The final residual was 0.076 for the observed reflections, and the largest peak in the final ΔF-synthesis was 0.30 e/$Å^3$. The final atomic coordinates are given in Table 3.

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[3]Atomic coordinates for this structure have been deposited with the Cambridge Crystallographic Data Centre and can be obtained from Dr. Olga Kennard, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK.

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