A New Rearrangement in *Iboga* Alkaloids

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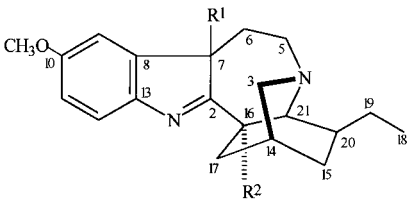
The hydroxyindolenine **2**, upon treatment with Ac_2O in pyridine, rearranged into the bridged 16-spiro compound **3**. Compound **3** can be considered to be a synthon of the carbocation at C(16) of ibogaine (**7**) since the solvolysis of **3** in EtOH/H_2O gave a mixture of the 16-ethoxy- and 16-hydroxyibogaine derivatives **5** and **6**, respectively.

Introduction. – The hydroxyindolenines and derivatives have proved to be versatile compounds in the chemistry of indole alkaloids. The treatment of iboga hydroxyindolenine alkaloids with methanolic hydrogen chloride [1] or sodium methoxide [2] gave the corresponding pseudoindoxyl, and the acetoxindolenines of the yohimbinoid alkaloids were used in the synthesis of oxindole derivatives [3]. In a previous work [4], we described the isomerization at the OH-substituted C(7)[1]) followed by decarbomethoxylation at C(16), in basic media, of the voacangine hydroxyindolenine (**1**), the major autoxidation product of voacangine (**4**) [5], to give the hydroxyindolenine **2**. Now we report on the rearrangement of the hydroxyindolenine **2** into the spiro-bridged compound **3** and that of **3** to give the 16-ethoxy and 16-hydroxy derivatives **5** and **6**, respectively, of ibogaine (= 10-methoxyibogamine; **7**)[1]).

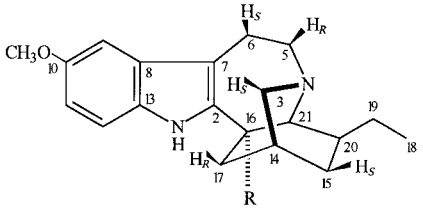
Results and Discussion. – When the hydroxyindolenine **2** was treated at room temperature with Ac_2O in pyridine, the rearranged compound **3** was obtained as the sole reaction product. The ^{1}H- and ^{13}C-NMR spectra (*Tables 1* and *2*) showed signals for the ethyl side chain (δ(H) 0.96 (*t*), 1.60 (*m*), 1.93 (*m*); δ(C) 12.8 (*q*), 28.9 (*t*)), an aromatic MeO group (δ(H) 3.86 (*s*); δ(C) 55.9 (*q*)), and a secondary-acetate group (δ(H) 2.04 (*s*), 4.51 (*s*); HMQC: δ(C) 81.9 (*d*); HMBC δ(C) 169.3 (*s*)). The presence of a secondary-acetate group in the molecule, together with a new C-signal (*s* at δ(C) 62.4) in the ^{13}C-NMR spectrum indicated that a rearrangement of the iboga skeleton had taken place. A broad signal at δ(H) 7.73 (*s*, 1 H, H–N(1)), together with the low-field C-signals, revealed the generation of the indole nucleus during the reaction, and permitted us to assign, among others, the signals of C(2), C(7), and C(8)[1]) (δ(C) 138.0 (*s*), 109.6 (*s*), and 130.8 (*s*), resp.) [6].

Taking into account the chemical shifts, the C-resonances δ(C) 50.9 (*t*; HMQC: δ(H) 2.61 and 3.17), 60.3 (*t*; δ(H) 3.12 and 2.66), and 62.4 (*s*) were ascribed to C-atoms bound to an N-atom of **3**. In the ^{1}H,^{1}H-COSY, an *ABMX* system for CH_2CH_2 was evident at δ(H) 2.76 and 2.73 (HMQC: δ(C) 21.6 (*t*)) and 2.61 and 3.17 (HMQC: δ(C) 50.9 (*t*)). Moreover, the following long-range connectivities corresponding to one-proton signals

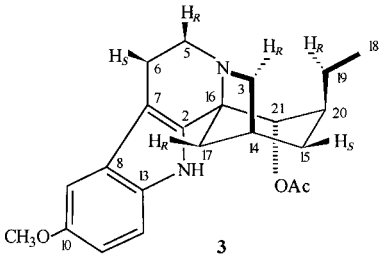
[1]) Trivial numbering according to *Formulae*; for systematic names, see *Exper. Part*. H_R and H_S are short forms of $H_{pro\text{-}R}$ and $H_{pro\text{-}S}$, respectively.



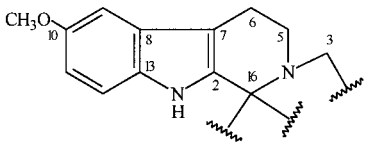
1 $R^1 = \beta$–OH , $R^2 = COOCH_3$
2 $R^1 = \alpha$–OH , $R^2 = H$
8 $R^1 = \alpha$–OAc , $R^2 = H$
14 $R^1 = \beta$–OAc , $R^2 = COOCH_3$



4 $R = COOCH_3$
5 $R = OCH_2CH_3$
6 $R = OH$
7 $R = H$
13 $R = OAc$



3



3a

Table 1. *^1H,^{13}C-HMQC and ^1H,^{13}C-HMBC-NMR Data of* **3**[a])[1])

	δ(H)	Correlated C-atom	
		HMQC	HMBC
H_R–C(3)	3.12 (*d*, *J* = 9.2)	60.3 (*t*)	C(15), C(16), C(17)
H_S–C(3)	2.66 (*dd*, *J* = 5.0, 9.2)	60.3 (*t*)	C(5), C(14), C(15)
H_R–C(5)	2.61 (*ddd*, *J* = 4.3, 10.1, 10.1)	50.9 (*t*)	C(3), C(7)
H_S–C(5)	3.17 (*ddd*, *J* = 3.7, 3.7, 10.3)	50.9 (*t*)	C(7), C(16)
H_R–C(6)	2.76 (*ddd*, *J* = 4.1, 14.0, 14.0)	21.6 (*t*)	C(2), C(5), C(7), C(8)
H_S–C(6)	2.73 (*ddd*, *J* = 3.7, 3.7, 14.0)	21.6 (*t*)	C(2), C(5), C(7), C(8)
H–C(9)	6.97 (*d*, *J* = 2.4)	100.6 (*d*)	C(7), C(10), C(11), C(13)
H–C(11)	6.80 (*dd*, *J* = 2.5, 8.7)	111.3 (*d*)	C(9), C(10), C(13)
H–C(12)	7.18 (*d*, *J* = 8.7)	111.0 (*d*)	C(8), C(10)
H–C(14)	2.47 (*ddd*, *J* = 4.2, 4.2, 8.4)	34.4 (*d*)	
H_R–C(15)	1.90 (*m*)[b])	30.5 (*t*)	C(3), C(19), C(20)
H_S–C(15)	1.58 (*m*)[b])	30.5 (*t*)	C(17), C(19), C(20), C(21)
H_R–C(17)	1.67 (*dd*, *J* = 4.6, 11.2)	35.1 (*t*)	C(2), C(14), C(15), C(16), C(21)
H_S–C(17)	2.25 (*d*, *J* = 11.0)	35.1 (*t*)	C(3), C(14), C(15), C(21)
Me–(18)	0.96 (*t*, *J* = 7.1)	12.8 (*q*)	C(19), C(20), C(21)
H_R–C(19)	1.93 (*m*)[b])	28.9 (*t*)	C(15), C(18), C(20), C(21)
H_S–C(19)	1.60 (*m*)[b])	28.9 (*t*)	C(15), C(18), C(20), C(21)
H–C(20)	1.62 (*m*)[b])	39.7 (*d*)	C(14), C(15), C(16), C(18), C(19), C(21)
H–C(21)	4.51 (*s*)	81.9 (*d*)	C(2), C(15), C(16), C(17), C(19), C(20), CO
MeO–C(10)	3.86 (*s*)	55.9 (*q*)	C(10)
Ac	2.04 (*s*)	21.6 (*q*)	CO
H–N(1)	7.73 (br. *s*)	–	C(2), C(7), C(8), C(13)

[a]) Chemical shifts in ppm rel. to $SiMe_4$ (= 0); coupling constants *J* in Hz. The *Hanson* system for prochirality is used to identify the protons [7]. [b]) Overlapped signals.

Table 2. *^{13}C-NMR* (125 MHz) *Assignments for Compounds* **3**–**7**[a])[1])

	3	**4**	**5**	**6**	**7**
C(2)	138.0	137.7	138.3	138.4	142.9
C(3)	60.3	51.6	49.6	48.6	50.0
C(5)	50.9	53.2	52.8	53.3	54.2
C(6)	21.6	22.2	22.4	21.5	20.7
C(7)	109.6	110.1	108.9	108.5	109.1
C(8)	130.8	129.2	129.3	129.2	129.7
C(9)	100.6	100.8	100.9	100.7	100.3
C(10)	153.9	154.0	153.8	153.9	
C(11)	111.2	111.9	111.5	111.4	110.8
C(12)	111.0	111.2	110.8	111.1	110.6
C(13)	126.7	130.7	130.5		130.0
C(14)	34.4	27.4	27.4	27.7	26.5
C(15)	30.5	32.1	32.3	31.6	32.0
C(16)	62.4	55.2	79.8	74.8	42.0
C(17)	35.1	36.5	42.4	43.0	34.2
C(18)	12.8	11.7	11.7	11.7	11.9
C(19)	28.8	26.8	26.6	27.1	27.8
C(20)	39.7	39.1	33.8	34.3	41.5
C(21)	81.9	57.5	58.3	63.3	57.5
MeO–C(10)	55.9	56.0	56.0	55.9	56.0
MeOO*C*–C(16)	–	175.8	–	–	–
*Me*OOC–C(16)	–	52.6	–	–	–
MeCH_2O–(16)	–	–	15.8	–	–
Me_3CH_2O–(16)	–	–	58.9	–	–
Ac	169.3, 21.6	–	–	–	–

[a]) Chemical shifts in ppm rel. to $SiMe_4$ (= 0); solvent $CDCl_3$.

were observed in the HMBC spectrum: δ(H) 2.76 and 2.73 with C(2) and C(8), δ(H) 3.17 with C(7) and 62.4 (*s*), δ(H) 3.12 with δ(C) 62.4 (*s*), and δ(H) 2.66 with 50.9 (*t*). These findings were in accord with the partial structure **3a** for the rearranged product and allowed us to assign the H- and C-resonances for CH_2(3), CH_2(5), CH_2(6), and C(16) (*Table 1*). The remaining C- and H-signals in the NMR spectra and homo- and hetero-correlations observed in the 2D spectra were in agreement with the proposed structure for **3**. The ^{1}H,^{1}H-COSY showed scalar correlations between H_S–C(3) (δ(H) 2.66) and H–C(14) (δ(H) 2.47) which in turn gave a one-bond correlation with the methine resonance at δ(C) 34.4, in the HMQC spectrum; H–C(14) was correlated to H_R–C(17) (δ(H) 1.67, δ(C) 35.1 (*t*)), H_S–C(15) (δ(H) 1.58, δ(C) 30.5 (*t*)), and H_R–C(15) (δ(H) 1.90, δ(C) 30.5 (*t*)); H_R–C(15) was correlated to H–C(20) (δ(H) 1.62, δ(C) 39.7 (*d*)), and H–C(20) to H_R–C(19) (δ(H) 1.60, δ(C) 28.9 (*t*)) and to H–C(21) (δ(H) 4.51, δ(C) 81.9 (*d*)). Additionally, three-bond connectivities were observed in the HMBC spectrum between H_R–C(3) and C(15) and C(17), between H_S–C(3) and C(15), and between both H_R–C(17) and H–C(21) and C(2). Furthermore, in the NOESY experiment, spatial correlations were detected between H–N(1) and the nonequivalent protons CH_2(17) as well as H–C(21). The cyclohexane ring must be in a chair conformation, possessing C(3) and C(19) in axial position, in view of the chemical shift of one of the nonequivalent protons CH_2(19) at δ(H) 1.93 (H_R–C(19); deshielding effect of the lone electron pair of the N-atom) and the NOE observed for H_R–C(3) and CH_2(19). Since H–C(21) also showed an NOE with H_R–C(19), the secondary-acetate group is also in axial position. The small coupling constant between the equatorial protons H–C(21) and H–C(20) observed in the ^{1}H,^{1}H-COSY revealed that the cyclohexane ring is in a slightly distorted chair conformation, due to the axial position of C(3), N(4), and C(19). The position of the methylene protons was mainly deduced from the NOEs and the W couplings observed in the NOESY and ^{1}H-COSY, respectively (*Table 3*).

Treatment of **3** with EtOH/H_2O at room temperature yielded compounds **5** ($C_{22}H_{30}N_2O_2$) and **6** ($C_{20}H_{26}N_2O_2$) as the sole reaction products. The analysis of their

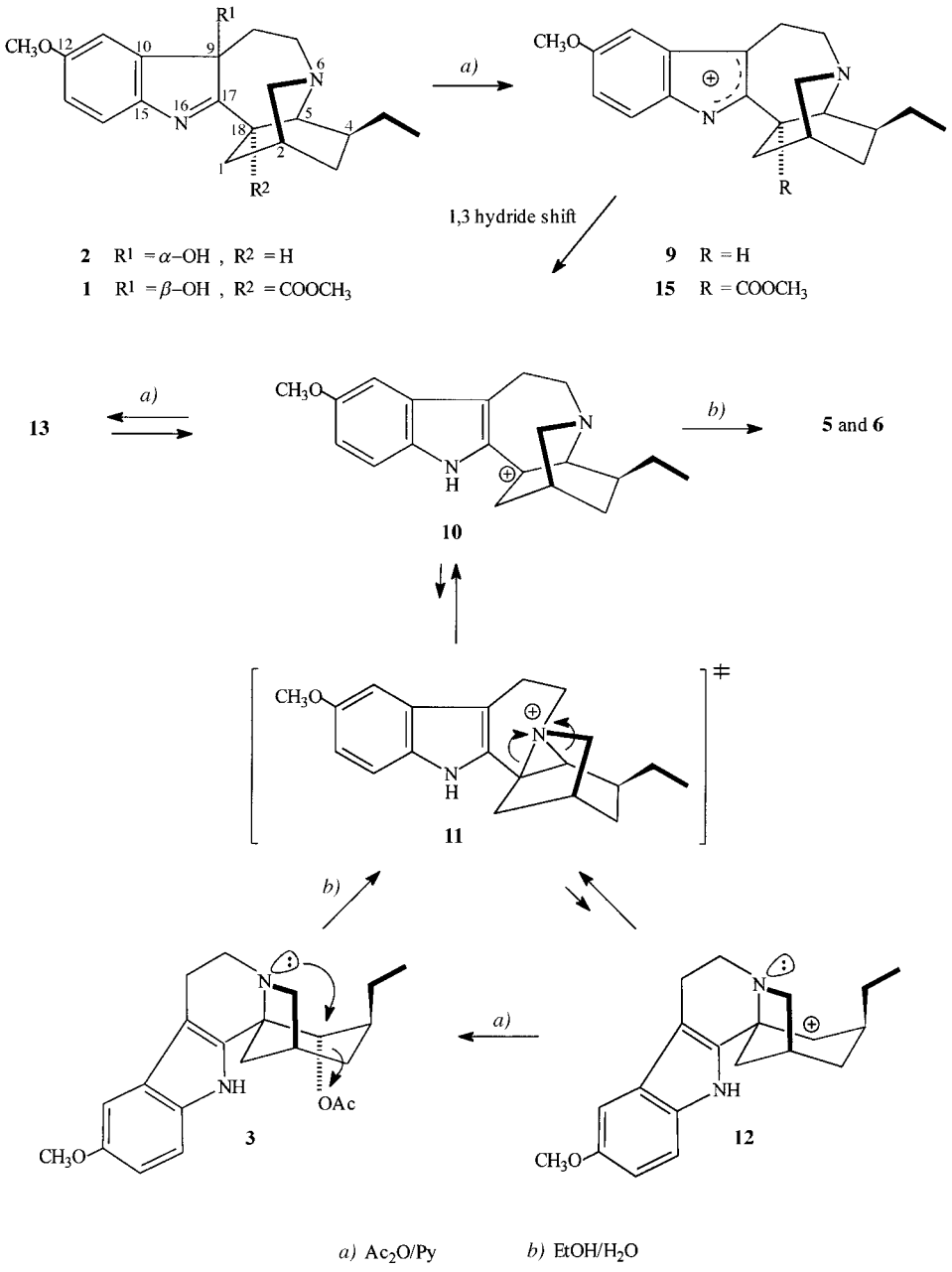
Table 3. *Scalar and Spatial Correlation of the Protons of* **3**[1])

	COSY	NOESY
H_R–C(3)	H_S–C(3), H_S–C(17)(W)	H_S–C(3), H–C(14), H_S–C(15), H_R–C(19), H_R–C(19), Me(18)
H_S–C(3)	H_R–C(3), H–C(14), H_R–C(15)(W)	H_R–C(3), H_R–C(5), H–C(14), H_R–C(17)
H_R–C(5)	H_S–C(5), H_R–C(6), H_S–C(6)	H_S–C(3), H_S–C(6), H_S–C(5), H_R–C(17)
H_S–C(5)	H_R–C(5), H_R–C(6), H_S–C(6)	H_R–C(5), H_R–C(6), H_S–C(6)
H_R–C(6)	H_R–C(5), H_S–C(5), H_S–C(6)	H_S–C(5), H_S–C(6)
H_S–C(6)	H_R–C(5), H_S–C(5), H_R–C(6)	H_R–C(5), H_S–C(5), H_R–C(6), H–C(9)
H–C(9)	H–C(11)	H_S–C(6), MeO–C(10)
H–C(11)	H–C(9), H–C(12)	H–C(12)
H–C(12)	H–C(11)	H–C(11), H–N(1)
H–C(14)	H_S–C(3), H_R–C(15), H_S–C(15), H_R–C(17), H_S–C(17) H–C(20)(W)	H_R–C(3), H_S–C(3), H_R–C(15), H_S–C(15), H_R–C(17), H_S–C(17)
H_R–C(15)	H–C(14), H–C(20), H_S–C(15)	H–C(14), H_S–C(15), H_S–C(17), H–C(20)
H_S–C(15)	H_R–C(15)	H_R–C(3), H–C(14), H_R–C(15), Me(18)
H_R–C(17)	H–C(14), H_S–C(17), H–C(21)(W)	H_S–C(3), H_R–C(5), H–C(14), H_S–C(17), H–N(1)
H_S–C(17)	H_R–C(3)(W), H_R–C(17)	H–C(14), H_R–C(15), H_R–C(17), H–C(20), H–N(1)
Me(18)	H_R–C(19), H_S–C(19)	H_R–C(3), H_S–C(15), H_R–C(19), H_S–C(19), H–C(20), H–C(21)
H_R–C(19)	MeC(18), H_S–C(19), H–C(20)	H_R–C(3), Me(18), H_S–C(19), H–C(20), H–C(21)
H_S–C(19)	Me(18), H_R–C(19), H–C(20)	H_R–C(3), Me(18), H_R–C(19), H–C(20), H–C(21)
H–C(20)	H–C(14)C(W), H_R–C(15), H_R–C(19), H_S–C(19), H–C(21)	H_S–C(17), H_R–C(19), H_S–C(19), H–C(21), Ac
H–C(21)	H_R–C(17)C(W), H–C(20)	Me(18), H_R–C(19), H–C(20), H–N(1)
MeO–C(10)	–	H–C(9), H–C(11)
Ac	–	H–C(20), H–C(21), H–N(1)
H–NC(1)	–	H–C(12), H_R–C(17), H_S–C(17), H–C(21)

[1]H-NMR spectra and the comparison of their [13]C-NMR data with those of voacangine (**4**) and ibogaine (**7**) [8] (*Table 2*) showed that **5** and **6** are 16-ethoxy- and 16-hydroxyibogaine, respectively.

The probable mechanism of formation of **3** from **2** and that of the solvolysis of **3** to give the ibogaine derivatives **5** and **6** is outlined in the *Scheme*. The delocalized cation **9**, produced by heterolysis of the non-isolated acetoxyindolenine **8** (see above), leads to the intermediate carbocation **10** by a 1,3-H shift. The intermediate **10** is in equilibrium with the rearranged carbocation **12** probably through the aziridinium transition state **11**, which is reached from both carbocations by the intramolecular attack of the lone electron pair of the N-atom. The anchimeric assistance by this lone electron pair also accounts for the easy solvolysis of **3** in EtOH/H_2O to afford **5** and **6** *via* the same transition state **11** and carbocation **10**. The fact that no products arising from solvent quenching of carbocation **12** were detected indicates that in the proposed equilibrium between **10** and **12**, the carbocation **10** is highly predominant. The sole formation of acetate **3** in the reaction of **2** with Ac_2O in pyridine could be explained by the facile

Scheme


a)
1,3 hydride shift
2 R1 = α–OH , R2 = H
1 R1 = β–OH , R2 = COOCH3
9 R = H
15 R = COOCH3
13
a)
b)
5 and 6
10
11
b)
a)
3
12
a) Ac2O/Py
b) EtOH/H2O

solvolysis of the non-isolated acetate **13** (see above) and the irreversibility of the pathway from **12** to **3** (*Scheme*).

On the other hand, treatment of voacangine hydroxyindolenine (**1**) under stronger conditions, *i.e.*, refluxing in Ac_2O/Py, provided the acetoxyindolenine **14** (see above) [5] as the sole reaction product. A delocalized cation **15** is possibly formed too, but no hydride shift is feasible in this case (see *Scheme*). The existence of an ion-pair between the acetate ion and **15** could account for the fact that the reaction proceeds with retention of configuration at C(7).

The MS of compounds of compounds **3**, **5**, and **6** display peaks at *m/z* 309, 308, 293, 279, 266, and 239 which, in contrast, are unnoticed in the MS of voacangine (**4**) [9] and ibogaine (**7**) [10]. These facts suggest that the fragmentation pathways of **3**, **5** and **6** are alike and that the molecular ion of **5** and **6** undergoes a radical rearrangement resembling that of the carbocation **10** (*Scheme*), initiated by homolytic cleavage of the C(16)–OR bond.

Since compound **3** is a synthon of carbocation **10**, other ibogaine derivatives substituted at C(16) could be prepared from **3** by selection of the suitable solvent and nucleophile.

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Experimental Part

1. *General*. Yields are given relative to reacted reagents. TLC: *Macherey-Nagel and Polygram-Alox-N* chromatoplates were used for anal. and prep. separations; detection by a UV lamp and with *Dragendorff* spray reagent. NMR: *Bruker-WP-200-SY* or *Bruker-AMX-500* spectrometers; in $CDCl_3$; δ values in ppm rel. to internal $SiMe_4$ (= 0 ppm); J values in Hz; DEPT, ^{1}H,^{1}H-COSY, HMQC, HMBC (J = 8 Hz), and NOESY (mixing time 500 ms) experiments with the pulse sequences given by *Bruker*, C-multiplicities by DEPT or HMQC data. Mass spectra (*m/z*; rel.%): *Micromass-Autospec* spectrometer at 70 eV.

2. *(1*R*,2*S*,4*R*,13b*S*)-2-Ethyl-2,3,4,5,7,8-hexahydro-10-methoxy-13*H*-4,13b-methano-1*H*-azepino[1′,2′: 1,2]pyrido-[3,4-*b*]indol-1-ol Acetate* (**3**). A mixture of **2** (4.6 mg), pyridine (0.5 ml), and Ac_2O (0.1 ml) was stirred at r.t. till disappearance of **2** (TLC, 8 d) and then evaporated. The residue was purified by prep. TLC (hexane/AcOEt 4:1): **3** (1.7 mg, 42%). ^{1}H-NMR (500 MHz) and ^{13}C-NMR (125 MHz): *Tables 1* and *2*, resp. EI-MS: 368 (20, M^+), 339 (4, $[M-Et]^+$), 325 (30, $[M-Ac]^+$), 309 (50, $[M-AcO]^+$), 308(47, $[M-AcOH]^+$), 293(5), 279(10), 266(54), 250(18), 239(100), 224(5), 149(6), 60(7). HR-EI-MS: 368.2186 ($C_{22}H_{28}N_2O_3^+$; calc. 368.2099), 325.1903 ($C_{20}H_{25}N_2O_2^+$; calc. 325.1903), 309.1999 ($C_{20}H_{25}N_2O^+$; calc. 309.1966), 308.1926 ($C_{20}H_{24}N_2O^+$; calc. 308.1888), 293.1578 ($C_{19}H_{21}N_2O^+$; calc. 293.1655), 279.1545 ($C_{18}H_{19}N_2O^+$; calc. 279.1497), 266.1427 ($C_{17}H_{18}N_2O^+$; calc. 266.1419), 250.1205 ($C_{17}H_{16}NO^+$; calc. 250.1231), 239.1200 ($C_{15}H_{15}N_2O^+$; calc. 239.1184).

3. *Compounds* **5** *and* **6** *from* **3**. A soln. of **3** (1.5 mg) in EtOH (3 ml) was left to stand at r.t. for three days and then evaporated. Anal. TLC revealed a mixture of two alkaloids of very different polarity in a ratio of *ca.* 1:1. The mixture was separated by prep. TLC (hexane/AcOEt 7:3): **5** (0.6 mg, 42%) and **6** (0.7 mg, 49%).

5-Ethoxy-12-methoxyibogamine (**5**). ^{1}H-NMR (500 MHz)[1]): 8.07 (br. *s*, H–N(1)); 7.21 (*d*, J = 8.6, H–C(12)); 6.94 (*d*, J = 2.4, H–C(9)); 6.84 (*dd*, J = 8.5, 2.4, H–C(11)); 3.87 (*s*, MeO–C(10)); 3.36 (*m*, H_R–C(5), H_A of MeCH_2–O–C(16)); 3.24 (*m*, H_S–C(5), H_S–C(6)); 3.15 (*m*, H_B of MeCH_2–O–C(16)); 3.00 (*s*, H–C(21)); 2.85 (*dt*, J = 8.4, 2.5, H_R–C(3)); 2.78 (*m*, H_R–C(6)); 2.72 (br. *d*, J = 8.4, H_S–C(3)); 1.99 (br. *m*, H–C(20)); 1.85 (*m*, H–C(14), CH_2(17), H_R–C(15)); 1.52 (*m*, CH_2(19)); 1.89 (*t*, J = 7.0, *Me*CH_2O–C(16)); 1.12 (br. *m*, H_S–C(15)); 0.94 (*t*, J = 7.4, Me(18)). ^{13}C-NMR (125 MHz): *Table 3*. EI-MS: 354 (25, M^+), 326 (23), 325 (100, $[M-Et]^+$), 309 (21), 308 (32, $[M-EtOH]^+$), 279 (7), 266 (45), 250 (14), 239 (13), 224 (5), 174 (27), 163 (5), 136 (6), 122 (5). HR-EI-MS: 354.2336 ($C_{22}H_{30}N_2O_2^+$; calc. 354.2307), 325.1936 ($C_{20}H_{25}N_2O_2^+$; calc. 325.1916), 308.1795 ($C_{20}H_{24}N_2O^+$; calc. 308.1888), 293.1642 ($C_{19}H_{21}N_2O^+$; calc. 293.16553), 279.1474 ($C_{18}H_{19}N_2O^+$; calc. 279.1497), 266.1491 ($C_{18}H_{20}NO^+$; calc. 266.1544), 250.1225 ($C_{17}H_{16}NO^+$; calc. 250.1231), 239.1164 ($C_{15}H_{15}N_2O^+$; calc. 239.1184).

12-Methoxyibogamin-5-ol (**6**). ^{1}H-NMR (500 MHz)[1]): 8.35 (br. *s*, H–N(1)); 7.18 (*d*, *J* = 8.7, H–C(12)); 6.89 (*d*, *J* = 2.4, H–C(9)); 6.78 (*dd*, *J* = 8.7, 2.4, H–C(11)); 3.83 (*s*, MeO–C(10)); 3.38 (*dq*, *J* = 11.5, 2.0, H_R–C(5)); 3.27 (*ddd*, *J* = 14.0, 14.0, 4.8, H_S–C(6)); 3.15 (*ddd*, *J* = 13.9, 13.9, 3.9, H_S–C(5)); 2.88 (*dt*, *J* = 8.9, 2.5, H_R–C(3)); 2.83 (*dt*, *J* = 8.9, 1.5, H_S–C(3)); 2.71 (*d*, *J* = 1.6 H–C(21)); 2.63 (*dq*, *J* = 14.5, 2.5, H_R–C(6)); 2.13 (br. *m*, H–C(20)); 1.97 (*dt*, *J* = 14.1, 2.9, H_R–C(17)); 1.91 (br. *s*, H–C(14)); 1.78 (*dt*, *J* = 13.8, 2.2, H_R–C(15)); 1.75 (*d*, *J* = 14.5, H_S–C(17)); 1.50 (*m*, CH_2(19)); 1.11 (*dm*, *J* = 9.7, H_S–C(15)); 0.88 (*t*, *J* = 7.4, Me(18)). NOESY (500 MHz)[1]): 2.88 (H_R–C(3)) → 1.11 (H_S–C(15)); 2.83 (H_S–C(3)) → 1.97 (H_R–C(17)) and 3.27 (H_S–C(6)); 3.15 (H_S–C(5)) → 2.71 (H–C(21)). ^{13}C-NMR (125 MHz) *Table 2*. EI-MS: 326 (19, M^+), 309 (25, $[M - OH]^+$), 308 (96, $[M - H_2O]^+$), 293 (30), 279 (30), 267 (24), 266 (97), 265 (46), 250 (38), 239 (100), 225 (12), 210 (10), 204 (7), 192 (9), 173 (13), 160 (8), 154 (4), 136 (16), 122 (10), 84 (39), 59 (25). HR-EI-MS: 326.2006 ($C_{20}H_{26}N_2O_2^+$; calc. 326.1994), 309.1924 ($C_{20}H_{25}N_2O^+$; calc. 309.1966), 308.1896 ($C_{20}H_{24}N_2O^+$; calc. 308.1888), 293.1670 ($C_{19}H_{21}N_2O^+$; calc. 293.1655), 279.1536 ($C_{18}H_{19}N_2O^+$; calc. 279.1497), 266.1565 ($C_{18}H_{20}NO^+$; calc. 266.1544), 250.1268 ($C_{17}H_{16}NO^+$; calc. 250.1231), 239.1217 ($C_{15}H_{15}N_2O^+$; calc. 239.1184), 225.1173 ($C_{15}H_{15}NO^+$; calc. 225.1153), 136.1149 ($C_9H_{14}N^+$; calc. 136.1126).

4. *9β-(Acetyloxy)-16,17-didehydro-9,17-dihydro-12-methoxyibogamine-18-carboxylic Acid Methyl Ester* (**14**). A soln. of **1** (3 mg) in pyridine (2 ml) and Ac_2O (0.1 ml) was refluxed for 2 h and then evaporated. TLC and ^{1}H-NMR: **1**/**14** [5] *ca.* 2:1.

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