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...ALKALOIDS FROM LEAVES AND ROOT BARK OF *ERVATAMIA HIRTA*

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Key Word Index—*Ervatamia hirta*; Apocynaceae; leaves; root bark; indole alkaloids; ^{1}H and ^{13}C NMR.

...ract—During chemical investigation of the leaves and root bark of *Ervatamia hirta*, 33 alkaloids were isolated. ...are new; six are the 'monomeric' alkaloids (*E*) 16-*epi*-normacusine B, (*E*) 16-*epi*-affinisine, *O*-acetyl-16-*epi*-...isine, affinisine-*N*(4)-oxide, dehydro-16-*epi*-affinisine, norfluorocurarine-*N*(4)-oxide, and the seventh is the ...dole 16-decarbomethoxyvoacamine-pseudoindoxyl. The known alkaloids are: (*E*) 16-*epi*-isositsirikine, β-yohim-...yohimbine, 19,20-dehydro-β-yohimbine, β-yohimbine-pseudoindoxyl, isositsirikine, 19,20-dihydroisositsirikine, ...himbine-oxindole, normacusine B, affinisine, vobasine, dregamine, tabernaemontanine, norfluorocurarine, 12-...roxynorfluorocurarine, apparicine, 3,14-dihydroellipticine, antirhine, voacristine, ibogaine, iboxygaine, ibo-...ine-hydroxyindolenine, iboluteine, 4',17,(17β)-dihydrotchibangensine, 16-decarbomethoxyvoacamine and 19,20-...dro-16-decarbomethoxyvoacamine. Structural elucidation of the new alkaloids is based on spectral data and ...ical correlations.

INTRODUCTION

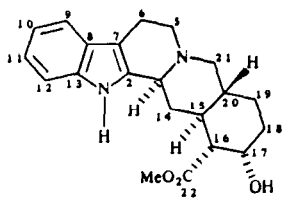
...part of our continuing research on the genus *Erva-*... [1, 2], we report our results on the alkaloid content ...*hirta* [3, 4], which is a tree 5–7 m tall from Malaysia. ...plant was included in the preparation of poisoned ...s and was used in traditional medicine for treat-... of ulcerations of the nose [5]. Material was col-...by T. Sévenet and J. R. Deverre at Trengganu ...ysia). This work is a part of a collaborative research ...am between C.N.R.S. and the University of Malaya ...7].

RESULTS AND DISCUSSION

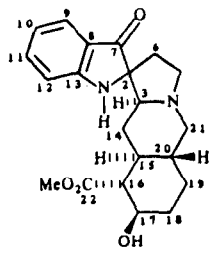
...tractions were conducted in the usual fashion and ...following alkaloid yields were obtained, 13.5 g kg^{-1} ...s) and 11.4 g kg^{-1} (root bark). Direct crystallization ...ethanol of the crude alkaloid mixture (AM) from the ...s afforded pure β-yohimbine (**1**) (69% AM). Five ...loids were isolated from the resulting mother liquors ...L) by means of column and prep. TLC chromato-...hy. They are (*E*) 16-*epi*-isositsirikine (**2**) (1.38% ML), ...mbine (**3**) (0.61% ML), 19,20-dehydro-β-yohimbine ...0% ML) and β-yohimbine-pseudoinodoxyl (**5**) ...% ML). The root bark crude alkaloid mixture ...ded together with **1** (29.6% AM), **2** (5.1% AM) and **3** ...% AM), 28 alkaloids: isositsirikine (**6**) (0.12% AM), ...-dihydroisositsirikine (**7**) (0.16% AM), β-yohimbine-...ole (**8**) (0.02% AM), normacusine B (**9**) (0.70% AM), ...16-*epi*-normacusine B (**10**) (0.50% AM), affinisine (**11**) ...% AM), affinisine-*N*(4)-oxide (**12**) (0.13% AM), (E) ...-*epi*-affinisine (**13**) (3.4% AM), *O*-acetyl-16-*epi*-affini-... (**14**) (0.14% AM), dehydro-16-*epi*-affinisine (**15**) ...6% AM), vobasine (**16**) (0.16% AM), dregamine (**17**) ...% AM), tabernaemontanine (**18**) (0.12% AM), norfluorocurarine (**19**) (9.6% AM), norfluorocurarine-*N*(4)-oxide (**20**) (0.10% AM), 12-hydroxynorfluorocurarine (**21**) (1.76% AM), apparicine (**22**) (0.01% AM), 3,14-dihydroellipticine (**23**) (0.06% AM), antirhine (**24**) (1.67% AM), voacristine (**25**) (0.05% AM), ibogaine (**26**) (2.17% AM), iboxygaine (**27**) (0.06% AM), iboxygaine-hydroxyindolenine (**28**) (0.04% AM), iboluteine (**29**) (0.22% AM), 4',17,(17β) dihydrotchibangensine (**30**) (0.07% AM), 16-decarbomethoxyvoacamine (**31**) (3.23% AM), 19,20-dihydro-16-decarbomethoxyvoacamine (**32**) (0.21% AM) and 16-decarbomethoxyvoacaminepseudoindoxyl (**33**) (0.30% AM).

Compounds **1**, **3**, **9**, **11**, **16–19**, **22–25**, **29** and **30** were identified by means of their spectral and co-TLC with reference samples. Alkaloids **2**, **4–8**, **21**, **26–28**, **31** and **32** were identified by comparison of their spectra with literature data. The novel isolation of **1**, **3–5**, **8**, **19**, **21**, **23**, **29** and **31** has provided the opportunity to obtain complete ^{1}H and ^{13}C NMR assignments (see Experimental) by means of 2D NMR experiments. The structures of the seven new alkaloids **10**, **12–15**, **20**, **23** have been established by spectroscopic methods. Chemical correlations have confirmed the structure of alkaloids **12**, **14**, **15**, **20**.

The five new alkaloids **10**, **12–15** possess a normacusine B-affinisine skeleton as shown by their ^{1}H NMR spectra [8], their UV spectra which display the three maxima of an indole chromophore, and their similar mass fragmentation (see Experimental). Compound **10** ([M]$^+$ at *m/z* 294) is a stereoisomer of normacusine B (**9**); compound **13** ([M]$^+$ at *m/z* 308) is a stereoisomer of affinisine **11**; compound **12** ([M]$^+$ at *m/z* 324 and same fragments) is an *N*(4)-oxide derivative of **11** or of a stereoisomer; compound **14** which gives a [M]$^+$ at *m/z* 350 and an IR absorption at 1730 and 1240 cm^{-1} is an *O*-acetyl derivative of **11** or of a stereoisomer; compound **15** ([M]$^+$ at *m/z* 306) is a dehydro derivative of **11**.



1 17-βOH
3 17-αOH
4 17-βOH, Δ^{19}



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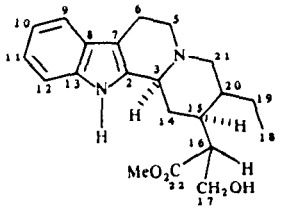

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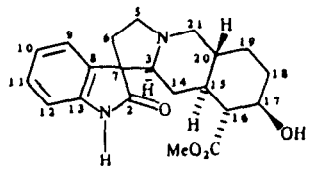

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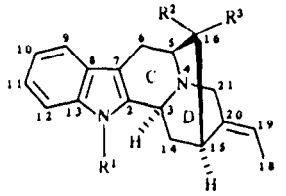
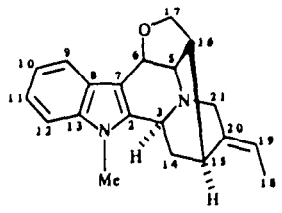


	R^1	R^2	R^3	
9	H	H	CH_2OH	
*10	H	CH_2OH	H	
11	Me	H	CH_2OH	
*12	Me	H	CH_2OH	N(4) → O
*13	Me	CH_2OH	H	
*14	Me	CH_2OAc	H	



*15

* New alkaloids

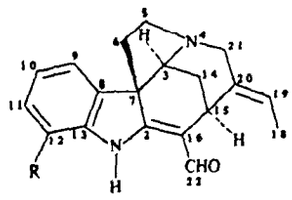
Complete structures of these compounds were elucidated by ^1H and ^{13}C NMR analysis.

Comparison of the chemical shift of H-5, H-6, H-14, H-16, H-17 of **10** and **13**, respectively, with those of the corresponding protons of **9** and **11** indicates that the isomerism occurs at C-16 [8,9] and that **10** and **13** have the 16*S* configuration, assuming that they belong to the '15αH' series. This is confirmed by the characteristic shielding of C-6, C-14 and C-17 of **10** and **13** compared to **9** and **11** [9,10]. The *E* geometry of the ethylidene side-chain of **10** and **13** is deduced from the observation of NOE between Me-18 and H-15. Additional proof is also provided by the chemical shifts of C-15 and C-21 of **9**–**11** and **13** that are consistent with an *E* geometry for the ethylidene side-chain [10]. Thus, **10** and **13** are 16-*epi*-normacusine B and 16-*epi*-affinisine, respectively. The geometry of the ethylidene group of koumidine, the *Z* isomer of **10**, has recently been revised [9, 11]. To the best of our knowledge, **10** has only been reported as a synthetic product [12].

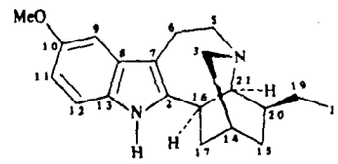
The parenthood of **14** with 16-*epi*-affinisine (**13**) is deduced from the similarity of their NMR spectral data (see Tables 1 and 2). The *O*-acetylation at C-17 is confirmed by the presence in the ^1H NMR spectrum of a three-proton singlet at δ 1.97, the downfield shift of the methylene protons H-17 and the presence in the ^{13}C NMR spectrum of the two carbons of the acetyl group (δ 20.9 and 170.4). The ^{13}C resonances of carbons C-15 and C-21 (δ 26.6 and 56.3) establish the *E* configuration of the ethylidene side-chain [10]. Acetylation of 16-*epi*-affinisine (see Experimental) gave a compound identical (TLC, IR, mass spectrum, ^1H NMR) to **14**.

The structure of **12** has been elucidated after comparison of its NMR spectra with those of **11**. In the deshielding of the signals of H-3, H-5, the two bridgehead and C-3, C-5, C-21 is characteristic of an *N*(4)-oxide derivative. This was demonstrated by conversion of (see Experimental) into a compound identical (TLC, ^1H NMR) with **12**.

Alkaloid **15** gave in its ^1H NMR spectrum a typical doublet for one proton (J = 7.6 Hz) at δ 5.6 assigned to the proton H-6 from 2D ^1H–^1H and ^1H–^{13}C heteronuclear experiments. Such a chemical shift is consistent with a hexacyclic structure related to a dehydrovoacheline type [13,14]. The deshielding of C-6 identified as a methine carbon (δ 71.4) and the chemical shifts of carbons C-5, C-17 and C-16 of **15** compared to those of 16-*epi*-affinisine (**13**) support the formation of a new bond between carbon C-6 and the oxygen atom located at C-17. The *E* geometry of the ethylidene side-chain



	R
19	H
*20	H : N(4)⋯→ O
21	OH



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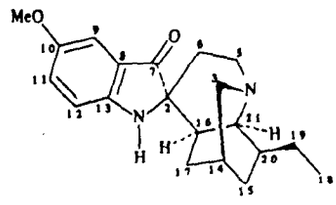

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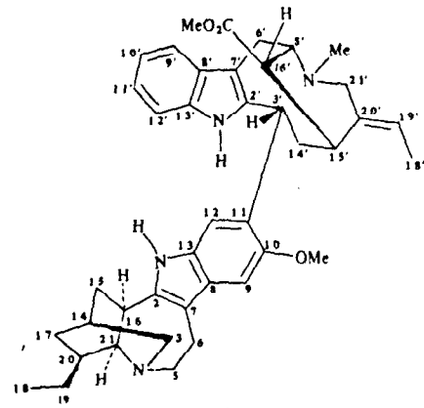

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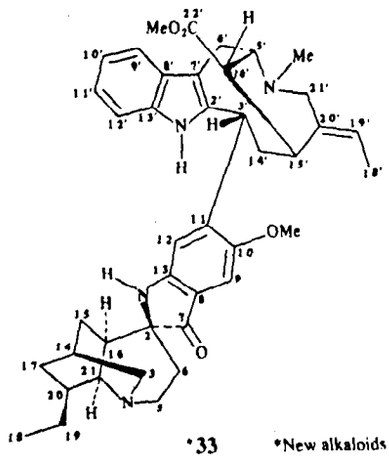

*33 *New alkaloids

...duced from the chemical shifts of C-15 and C-21 [10]. ...synthesis of **15** was achieved by oxidation of **13** (see ...perimental).

...kaloid **20** was identified from spectroscopic evidence. ...UV spectrum was identical with that of norfluorocura... (**19**) and the absorption band in the IR spectrum at ...0 cm^{-1} characterises the conjugated C=O. Its mass ...trum displayed a $[M]^+$ at m/z 308 (16 mu more than ... Compounds **19** and **20** also had an identical frag... (m/z 263, 249, 222, 208, 194, 180, 168, 121). ...parison of ^{1}H and ^{13}C NMR spectra of **19** and **20** ...cates that **20** is the *N*(4)-oxide derivative of **19**. In **20**, ... protons and carbons in the neighbourhood of *N*(4) were downfield shifted as in **12**. Oxidation of norfluorocurarine **19** led to an identical compound (TLC, UV, IR, mass spectrum, ^{1}H and ^{13}C NMR) with **20**.

The new bisindole alkaloid **33** (16-decarbomethoxyvoacaminepseudoindoxyl) possesses in solution an intense yellow-green fluorescent coloration which indicates a pseudoindoxyl chromophore. This was confirmed by the UV spectrum [absorptions at 228, 272 (sh), 294 (sh), 417 nm] and the absorption at 1660 cm^{-1} in the IR spectrum which displayed additional bands at 3360 cm^{-1} (NH/OH) and 1720 cm^{-1} (ester group). The mass spectrum of **33** showed a $[M]^+$ at m/z 662 analysing for $C_{41}H_{50}N_4O_4$ (16 mu more than 16-decarbomethoxy-

Table 1. ^{13}C NMR spectral data of alkaloids **10**, **12**–**15** and **20** (75 MHz, $CDCl_3$ and int. ref. $\delta = 77$).

C	10	12	13	14	15	20
2	136.1	134.5	138.4	138.5	143.3	164.8
3	49.9	65.1	51.9	48.7	47.6	78.6
5	52.3	69.0	51.9	51.8	59.6	70.2
6	22.1	23.9	22.4	23.0	71.4	41.4
7	104.9	102.1	105.1	104.7	103.7	55.5
8	125.9	126.5	126.0	126.1	126.2	133.7*
9	117.7	118.6	118.1	118.1	118.9	121.5
10	118.7	119.1*	118.7	118.8	119.7	122.9
11	121.1	121.5	120.8	120.9	121.3	129.2
12	110.9	108.8	108.6	108.6	108.9	111.0
13	136.4	137.5	137.2	137.3	137.4	142.3
14	26.6	32.8	26.4	26.6	27.4	28.1
15	25.9	26.0	26.0	26.6	27.1	29.6
16	41.8	43.1	42.1	39.4	38.9	111.3
17	60.1	63.0	60.7	63.2	64.8	—
18	12.3	12.6	12.7	12.7	12.9	14.0
19	114.5	119.3*	113.4	113.9	114.0	127.0
20	138.0	130.6	139.0	139.0	138.9	134.4*
21	55.5	70.9	56.3	56.3	56.0	74.6
22	—	—	—	—	—	188.3
N(Me)-1	—	29.4	29.0	29.1	29.1	—
OAc	—	—	—	170.4	—	—
				20.9		

*Interchangeable values in a same column.

voacamine, **31**) together with a low intensity peak at $[M+14]^+$ as observed in **31** [15]. Fragments of the iboluteinyl moiety are present at *m/z* 108, 122, 124, 136, 138, 150, 176 [16] and those of the vobasinyl moiety at *m/z* 122, 180, 182, 194 [17, 18]. The ^1H NMR spectrum of **33** was similar to that of **31** with the exception of the N-1 proton of the iboluteinyl part which was shielded upfield (Table 3) as expected for a pseudoindoxyl moiety. The ^{13}C NMR spectrum provides further evidence for this structure. Besides the carbons of the vobasinyl moiety, characteristic carbons of the iboluteinyl moiety are observed: C-2 at δ67.5 and C-7 at δ204.8. The substitution at C-11 was confirmed by the chemical shift variations of the aromatic carbons of **33** compared with those of iboluteine **29**. Identical variations occurred between **31** and ibogaine **26**. The stereochemistry of C-3 is fixed for hindrance reasons as described previously [19].

In conclusion, *E. hirta* possesses a high alkaloidal content and a great variety of alkaloids which belong to types I and III [20]. Among the 33 isolated alkaloids, seven are new: **10**, **12**–**15**, **20** and **33**. A striking feature of this plant is the presence of quasidimer (**30**) and yohimbine skeletons which are isolated for the frist time from the genus *Ervatamia* [21, 22]. The large amount of β-yohimbine in the leaves (70% of AM) is in agreement with the pharmacological activity which has been observed in the course of preliminary study of this species.

EXPERIMENTAL

General. ^1H and ^{13}C NMR were recorded in $CDCl_3$ at 300 and 75 MHz, respectively. Chemical shifts are reported in δ from TMS. Prep. TLC as performed on silica gel K6F Whatman and CC on silica gel 60 (70–230 mesh) Merck.

Plant material. E. hirta (Hook.f) King and Gamble was collected in September 1984 in Malaysia. A voucher specimen is kept at the herbarium of the Department of Phytochemistry, University of Malaya under number D-235.

Extraction. Dried powdered leaves (0.6 kg) were wetted with 50% NH_4OH, *macerated overnight in EtOAc, then lixiviated*. The lixiviate was extracted with 2% H_2SO_4. The aq. layer was basified with NH_4OH and extracted with $CHCl_3$. The $CHCl_3$ layers were dried (Na_2SO_4) and evapd *in vacuo* to give 8.1 g of crude alkaloid mixture (AM). Extraction of root bark (3.3 kg) performed according to the same process gave 37.5 g of AM.

Isolation. Rootbark AM was purified by CC on 2340 g silica gel packed in $CHCl_3$; 30 ml frs were collected. Elution was performed with $CHCl_3$ (3.9 l); $CHCl_3$–MeOH (99:1, 7.5 l), (99:1, 9.6 l), (19:1, 9.6 l), (9:1, 7.05 l), (4:1, 7.35 l), (1:1, 7.2 l) and MeOH (9.48 l). Alkaloid **1** was in frs 695–820, **2** in frs 876–1040, **3** in frs 561–644, **6** in frs 846–875, **7** in frs 536–549, **8** in frs 821–834, **9** in frs 1161–1337, **10** in frs 1045–1160, **11** in frs 645–724, **12** in frs 645–670, **13** in frs 536–644, **14** in frs 421–430, **15** in frs 390–420, **16** in frs 421–457, **17** in frs 431–457, **18** in frs 321–380, **19** in frs 536–670, **20** in frs 561–644, **21** in frs 971–1080, **22** in frs 645–670, **23** in frs 681–1044, **24** in frs 1391–1500, **25** in frs 266–320, **27** and **28** in frs 536–549, **29** in frs 1601–2056, **30** in frs 1771–1900, **31** and **32** in frs 645–724, and **33** in frs 1700–2056.

Alkaloids from leaves were isolated and sepd in a similar fashion. Alkaloid **1** was obtained by crystallization of crude AM from EtOH (yield 69%). The mother liquors of crystallization were purified by CC on 100 g silica gel packed in $CHCl_3$; 20 ml frs were collected. Elution was performed with $CHCl_3$ (1.3 l), $CHCl_3$–MeOH, (99:1, 140 ml), (49:1, 360 ml), (24:1, 600 ml), (23:2, 880 ml), (4:1, 340 ml) and MeOH (580 ml). Alkaloid **1** was in frs 100–120, **2** in frs 134–164, **3** in frs 98–115, **4** in frs 100–165 and **5** in frs 118–149.

(E) 16-*Epinormacusine B* (**10**). Ceric sulphate TLC (CR) green then pale yellow: R_f 0.18 ($CHCl_3$–MeOH, 9:1). $[\alpha]_D$ +7° (MeOH; *c* 0.25). UV λ_{max}^{MeOH} nm (log ε) 226 (4.41), 281 (3.71), 288 (3.61 sh), IR ν^{CHCl_3} cm^{-1}: 3220, 2920, 2840, 1450, 1310, 1280, 1160, 1020, 740. MS: *m/z* (rel. int.): 294 ($[M]^+$, 100), 293 (79), 278 (10), 277 (13), 263 (38), 249 (11), 195 (6), 182 (11), 169 (79), 168 (54), 156 (10), 144 (8), 130 (8); HRMS: $C_{19}H_{22}N_2O$ calcd 294.1732, found 294.1709. ^1H and ^{13}C NMR see Tables 1 and 2.

Affinisine-N(4)-*oxide* (**12**). CR TLC grey-purple then yellow-orange: R_f 0.10 ($CHCl_3$–MeOH, 9:1). $[\alpha]_D$: +3° (MeOH, *c* 0.5). UV λ_{max}^{MeOH} nm (log ε): 226 (4.51), 284 (3.77), 292 (3.71 sh). IR ν^{KBr} cm^{-1}: 3360, 2920, 1470, 1380, 1190, 1030, 740. MS: *m/z* (rel. int.): 324 ($[M]^+$, $C_{20}H_{24}N_2O_2$, 46), 308 (100), 307 (100), 293 (43), 291 (23), 277 (79), 263 (23), 249 (17), 235 (15), 221 (19), 196 (41), 183 (59), 182 (40), 170 (23), 168 (19), 154 (8). ^1H and ^{13}C NMR see Tables 1 and 2. Hemisynthesis from affinisine (**11**). To a soln of affinisine (23 mg, 0.07 mmol) in CH_2Cl_2 (2 ml), 19 mg (1.5 eq) *m*-chloroperbenzoic acid was added under magnetic stirring at 0°. After completion (TLC), the soln was cond in *in vacuo*. The residue was purified by prep. TLC ($CHCl_3$–MeOH, 9:1) and yielded affinisine-*N*(4)-oxide (**12**) (20 mg; yield 87%).

(E) 16-*Epiaffinisine* (**13**). CR TLC green then pale yellow: R_f 0.44 ($CHCl_3$–MeOH, 9:1); $[\alpha]_D$ −18° (MeOH; *c* 0.2). UV λ_{max}^{MeOH} nm (log ε): 229 (4.43), 286 (3.75), 293 (3.71 sh). IR ν^{KBr} cm^{-1}: 3360, 2940, 1470, 1380, 1040, 750. MS: *m/z* (rel. int.): 308 ($[M]^+$, 100), 307 (58), 293 (8), 291 (10), 277 (33), 263 (11), 249 (4), 196 (8), 183 (65), 182 (54), 168 (21), 157 (8), 154 (8); HRMS: $C_{20}H_{24}N_2O$ calcd 308.1888, found 308.1867. ^1H and ^{13}C NMR see Tables 1 and 2.

O-*Acetyl*-16-*epiaffinisine* (**14**). CR TLC green then pale yellow: R_f 0.64 ($CHCl_3$–MeOH, 9:1). $[\alpha]_D$ −14° (MeOH; *c* 0.5). UV λ_{max}^{MeOH} nm (log ε): 228 (4.52), 285 (3.81), 292 (3, 77 sh).

Table 2. ^{1}H NMR spectral data of alkaloids **10**, **12**–**15**, **20** (300 MHz, $CDCl_3$, residual $CHCl_3$ used as int. ref. $\delta = 7.27$)

H	10*	12	13	14	15	20
3	4.04 *dd* (9.0; 4.3)	4.43 *br d* (10.0)	4.07 *dd* (10.3; 3.1)	4.20 *dd* (10.2; 3.2)	4.09 *dd* (9.8; 4.0)	4.49 *br s*
5	3.46–3.56 *m*	3.03 *br dd* (4.5; 7.0)	3.31–3.42 *m*	3.56–3.64 *m*	3.72–3.87 *m*	3.78–3.89 *m*
	—	—	—	—	—	4.04–41.8 *m*
6	2.83–2.89 *m*	2.59 *d* (15.6)	2.75–2.84 *m*	2.91 *dd* (16.2; 1.1)	5.63 *d* (7.6)	2.51 *td* (13.0; 6.5)
	2.83–2.89 *m*	3.39 *dd* (15.6; 4.5)	2.75–2.84 *m*	3.02 *dd* (16.2; 5.6)	—	2.06 *br dd* (13.0; 6.8)
9	7.35 *br d* (7.2)	7.29 *br d* (7.1)	7.40 *br d* (7.0)	7.48 *br d* (7.7)	7.72 *dd* (7.7; 1.2)	7.65 *br d* (7.2)
10	6.97 *td* (7.2; 1.0)	7.04 *br t* (7.1)	7.08 *td* (7.0; 1.2)	7.09 *td* (7.7; 1.2)	7.15 *td* (7.7; 1.2)	7.05 *td* (7.2; 1.1)
11	7.03 *td* (7.2; 1.0)	7.19 *br t* (7.1)	7.18 *td* (7.0; 1.2)	7.18 *td* (7.7; 1.2)	7.22 *td* (7.7; 1.2)	7.26 *td* (7.2; 1.1)
12	7.22 *br d* (7.2)	7.26 *br d* (7.1)	7.27 *br d* (7.0)	7.28 *br d* (7.7)	7.30 *dd* (7.7; 1.2)	6.95 *br d* (7.2)
14	1.69–1.84 *m*	1.62 *br d* (12.0)	1.59–1.67 *m*	1.80 *dt* (13.1; 3.5)	1.81–1.98 *m*	1.45 *dt* (14.5; 1.4)
	1.69–1.84 *m*	2.19 *br dd* (12.0; 10.0)	1.79 *br dd* (12.7; 10.3)	1.86–2.0 *m*	1.81–1.98 *m*	2.96 *ddd* (14.5; 4.0, 2.0)
15	2.81 *q* (3.0)	2.52 *br s*	2.75–2.84 *m*	2.79 *q* (3.5)	2.84 *q* (3.1)	3.78–3.89 *m*
16	2.03–2.15 *m*	1.87 *br q* (7.0)	1.97–2.09 *m*	2.25–2.36 *m*	2.24–2.36 *m*	—
17	3.07 *dd* (10.8; 8.9)	3.13–3.28 *m*	3.07 *dd* (10.6; 8.8)	3.75 *dd* (11.3–8.8)	3.43 *t* (9.5)	—
	3.39 *dd* (10.8–6.3)	3.13–3.28 *m*	3.36 *dd* (10.6; 6.6)	4.07 *dd* (13.3–6.7)	3.72–3.87 *m*	
Me-18	1.55 *dt* (6.8; 1.9)	1.52 *br d* (6.7)	1.63 *dt* (6.8; 1.9)	1.65 *dt* (6.8; 2.0)	1.66 *dt* (6.8; 2.0)	1.67 *dt* (7.0; 1.0)
19	5.18 *br q* (6.8)	5.26 *br q* (6.7)	5.22 *br q* (6.8)	5.29 *qt* (6.8; 1.9)	5.33 *qt* (6.8; 2.0)	5.69 *qt* (7.0; 1.5)
21	3.46–3.56 *m*	3.88 *br d* (15.9)	3.56–3.62 *m*	3.68–3.73 *m*	3.72–3.87 *m*	4.04–4.18 *m*
	3.46–3.56 *m*	4.57 *br d* (15.9)	3.56–3.62 *m*	3.68–3.73 *m*	3.72–3.87 *m*	4.40 *br d* (14.0)
22	—	—	—	—	—	9.45 *s*
NH	9.45 *s*	—	—	—	—	10.22 *br s*
NMe	—	3.53 *s*	3.55 *s*	3.61 *s*	3.63 *s*	—
OAc	—	—	—	1.97 *s*	—	—

*Methanol-d_4 was added to favour solubilization.

cm^{-1}: 2920, 1730, 1460, 1240, 740. MS: *m/z* (rel. int.): 350 , 90), 349 (57), 291 (94), 277 (17), 263 (8), 249 (4), 209 (6), 196 183 (100), 182 (61), 168 (21), 157 (10), 154 (6); HRMS.: $_{20}N_2O_2$ calcd 350.1994, found 350.1997. ^{1}H and ^{13}C NMR Tables 1 and 2. *Hemisynthesis of* **14** *from* (E)16-*epiaffinisine* To a soln of **13** (20 mg, 0.06 mmol) in CH_2Cl_2 (10 ml), 2 ml $_2O$ and a catalytic amount of 4-dimethylaminopyridine added. The soln was stirred overnight then washed $CuSO_4$ soln, satd $NaHCO_3$ soln and H_2O). The organic was dried (Na_2SO_4) and evapd to dryness. *O*-Acetyl- affinisine (**14**) was purified by prep. TLC (Et_2O–MeOH, yield 43%.

-16-epiaffinisine (**15**). CR TLC violet, centre yellow: ($CHCl_3$–MeOH, 9:1). $[\alpha]_D$: +58.8° (MeOH; *c* 0.25). UV λ_{max}^{MeOH} nm (log ε): 224 (4.37), 281 (3.65), 290 (3.58 sh). IR ν^{CHCl_3} cm^{-1}: 2920, 2860, 1460, 1080, 1040, 990, 740. MS: *m/z* (rel. int.): 306 ([M]$^+$, 100), 305 (25), 291 (10), 289 (15), 277 (10), 275 (11), 249 (6), 196 (25), 183 (61), 182 (79), 168 (8); HRMS.: $C_{20}H_{22}N_2O$ calcd 306.1732, found 306.1718. ^{1}H and ^{13}C NMR see Tables 1 and 2. *Hemisynthesis of* **15** *from* (E)16-*epiaffinisine* (**13**). To a soln of **13** (40 mg, 0.13 mmol) in THF (3 ml), 59 mg of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone were added. After 1 hr reflux, the soln was concd *in vacuo*. The residue dissolved in CH_2Cl_2 was washed (satd $NaHCO_3$ soln). the organic phase dried (Na_2SO_4) and concd *in vacuo*, yielding **15** in 97% yield.

Norfluorocurarine-N(4)-*oxide* (**20**). CR TLC green then yellow: R_f: 0.17 ($CHCl_3$–MeOH, 22:3). $[\alpha]_D$ −690° (MeOH; *c* 1). UV λ_{max}^{MeOH} nm (log ε): 203 (4.30), 241 (3.92), 299 (3.53), 361 (4.13).

Table 3. ^1H and ^{13}C NMR spectral data of alkaloid 33 (300 MHz, ^1H frequency, residual $CHCl_3$ used as int. ref. δ 7.27)

Position	H	C		H	C
1	4.30 *br s*		1′	8.00 *br s*	
2	—	67.5	2′	—	136.1[b]
3	2.96 *br d* (11.2)	52.2	3′	5.05 *br d* (11.3)	38.2
	2.87–3.01 *m*				
5	2.38–2.68 *m*	48.2	5′	4.00 *br td* (8.1; 2.6)	60.0
	3.31–3.50 *m*				
6	1.13–1.23 *m*	22.7	6′	3.20 *dd* (14.6; 8.1)	19.8
	1.80–2.03 *m*			3.31–3.50 *m*	
7	—	204.8	7′	—	111.1
8	—	118.9[a]	8′	—	129.6
9	7.00 *s*	103.8	9′	7.50–7.57 *m*	117.5
10	—	154.9	10′	7.04–7.16 *m*	119.1[a]
11	—	145.7	11′	7.04–7.16 *m*	121.9
12	6.37 *br s*	113.0	12′	7.04–7.16 *m*	110.0
13	—	150.3	13′	—	135.9[b]
14	1.55–1.77 *m*	26.0	14′	1.80–2.03 *m*	35.3
				2.38–2.68 *m*	
15	1.07 *br d* (10.4)	32.7	15′	3.69–3.81 *m*	33.6
	1.55–1.77 *m*				
16	1.55–1.77 *m*	36.9	16′	2.38–2.68 *m*	46.4
17	1.31–1.50 *m*	30.0	—		
	1.55–1.77 *m*				
Me-18	0.91 *t* (7.0)	12.0	18′	1.68 *d* (5.7)	12.2
19	1.31–1.50 *m*	28.6	19′	5.35 *q* (6.7)	118.9[a]
	1.55–1.77 *m*				
20	1.31–1.50 *m*	39.4	20′		137.6
21	3.52 *br s*	48.2	21′	2.90 *d* (14.0)	52.2
				2.69–3.81 *m*	
			22′		171.5
OMe-11	3.88 *br s*	55.9			
			N′Me	2.59 *s*	42.3
			O′Me	2.46 *s*	49.8

[a,b] Interchangeable values.

IR ν^{CHCl_3} cm^{-1}: 3300, 2980, 2940, 1650, 1580, 1550, 1460, 1180, 1150, 740. MS: *m/z* (rel. int.): 308 ($[M]^+$, $C_{19}H_{20}N_2O_2$, 15), 293 (100), 292 (58), 290 (50), 263 (19), 249 (25), 222 (19), 208 (21), 194 (21), 180 (21), 168 (31), 121 (67). ^1H NMR see Tables 1 and 2.

Hemisynthesis of **20** *from* **19**. The procedure described for the prepn of **12** was applied to **19** (156 mg, 0.53 mmol). Compound **20** was isolated in 85% yield.

16-*Decarbomethoxyvoacamine-pseudoindoxyl* (**33**). CR TLC yellow: R_f: 0.30 ($CHCl_3$–MeOH, 47:3, vap NH_4OH). $[\alpha]_D$: −14° (MeOH; *c* 0.5). UV λ_{max}^{MeOH} nm (log ε): 228 (4.64), 272 (4.14 sh), 294 (3.95 sh), 417 (3.62). IR ν^{CHCl_3} cm^{-1}: 3360, 2920, 2860, 1720, 1660, 1620, 1480, 1220, 1030, 750. MS: *m/z* (rel. int.): 676 ($[M+14]^+$, 9), 662 ($[M]^+$, $C_{41}H_{50}N_4O_4$, 39), 630 (59), 603 (9), 482 (27), 469 (32), 454 (7), 352 (36), 308 (27), 278 (20), 249 (23), 247 (23), 225 (46), 195 (61), 194 (50), 182 (98), 180 (79), 176 (23), 150 (70), 149 (45), 138 (52), 136 (43), 124 (43), 122 (100), 108 (36). ^1H and ^{13}C NMR see Table 3.

β-Yohimbine (**1**). ^1H NMR (300 MHz, $CDCl_3$) δ: 7.82 (*br s*, N-H); 7.48 (*br d*, J = 7.4 Hz, H-9); 7.31 (*br d*, J = 7.4 Hz; H-12); 7.15 (*br t*, J = 7.4 Hz, H-11); 7.09 (*br t*, J = 7.4 Hz, H-10); 3.80–3.93 (*m*, H-17); 3.85 (*s*, OMe); 3.26 (*br d*, J = 10.9 Hz, H-3); 2.93–3.14 (*m*, H-5, H-6, H-21); 2.72 (*br d*, J = 15.3 Hz, H-6); 2.56–2.67 (*m*, H-5); 2.21 (*t*, J = 10.0 Hz, H-16); 2.06–2.19 (*m*, H-18, H-21); 1.94 (*br d*, J = 11.8 Hz, H-14); 1.65–1.81 (*m*, H-19); 1.36–1.60 (*m*, H-14, H-15, H-18, H-20); 1.11–1.28 (*m*, H-19).

Yohimbine (**3**). ^1H NMR (300 MHz, $CDCl_3$) δ: 8.16 (*br s*, N-H); 7.45 (*br d*, J = 7.0 Hz, H-9); 7.27 (*br d*, J = 7.0 Hz, H-12); 7.11 (*td*, J = 7.0; 1.0 Hz, H-11); 7.06 (*td*, J = 7.0; 1.0 Hz, H-10); 4.21 (*br s*, H-17); 3.78 (*s*, OMe), 3.28 (*br d*, J = 11.7 Hz, H-3); 2.94–3.10 (*m*, H-6); 2.90 (*dd*, J = 12.0; 2.0 Hz, H-21); 2.64–2.76 (*m*, H-6); 2.53–2.64 (*m*, H-5); 2.32 (*dd*, J = 11.5; 2.0 Hz, H-16); 2.19 (*dd*, J = 12.0; 9.0 Hz, H-21); 1.90–2.09 (*m*, H-14, H-18, H-19); 1.46–1.65 (*m*, H-18, H-19, H-20); 1.35–1.42 (*m*, H-15); 1.31 (*q*, J = 11.7 Hz, H-14).

19,20-*Dehydro-β-yohimbine* (**4**). ^1H NMR (300 MHz, $CDCl_3$) δ: 7.86 (*br s*, N-H); 7.46 (*br d*, J = 7.1 Hz, H-9); 7.31 (*br d*, J = 7.1 Hz, H-12); 7.14 (*td*, J = 7.1; 1.1 Hz, H-11); 7.08 (*td*, J = 7.1; 1.1 Hz, H-10); 5.56 (*dd*, J = 3.7; 1.6 Hz, H-19); 4.07 (*td*, J = 5.5 Hz, H-17); 3.9 (*s*, OMe); 3.46 (*d*, J = 12.6 Hz, H-21); 3.40 (*br d*, J = 11.8 Hz, H-3); 2.95–3.15 (*m*, H-5, H-6, H-21); 2.59–2.80 (*m*, H-5, H-6, H-15); 2.42–2.53 (*m*, H-18); 2.42 (*t*, J = 10.3 Hz, H-16); 2.20 (*ddd*, J = 12.0; 5.0; 2.5 Hz, H-14); 2.07–2.20 (*m*, H-18); 1.47 (*d*, J = 12.0 Hz, H-14). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 174.7 (C-21); 135.9 (C-13); 133.3 (C-2, C-20); 127.0 (C-8); 121.3 (C-11); 119.4 (C-10); 119.2[a] (C-19); 118.0 (C-9); 110.6 (C-12); 108.2 (C-7); 108.1 (C-17); 60.9 (C-3); 58.7 (C-16); 55.1 (C-21); 52.3[b] (OMe); 51.9 (C-5); 39.0[c] (C-14); 35.9[c] (C-15); 33.7[c] (C-18); 21.3 (C-6).

β-Yohimbine-pseudoindoxyl (**5**). ^1H NMR (300 MHz, $CDCl_3$) δ: 7.55 (*br d*, J = 7.1 Hz, H-9); 7.43 (*ddd*, J = 8.2; 7.1; 1.3 Hz, H-11); 6.83 (*br d*, J = 8.2 Hz, H-12); 6.76 (*br t*, J = 7.1 Hz,

[illegible] 5.15 (*sl*, $W_{1/2} \approx 7$ Hz, N-H); 3.78 (*td*, $J = 10.8$; 4.5 Hz, H-[illegible]); 3.55 (*s*, OMe); 3.18–3.26 (*m*, H-3); 3.08 (*dd*, $J = 11.0$; 2.4 Hz, [illegible]); 2.26–2.48 (*m*, H-14); 1.90–2.15 (*m*, H-14, H-16, H-18); 1.84 ([illegible] $J = 11.0$; 10.0 Hz, H-21); 1.67 (*br dd*, $J = 12.7$; 3.0 Hz, H-19); [illegible] $J = 12.8$; 3.9 Hz, H-18); 1.07–1.34 (*m*, H-15, H-19, H-20).

[illegible]*himbine-oxindole* (8). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.94 ([illegible]); 7.20 (*td*, $J = 7.5$; 0.8 Hz, H-11); 7.17 (*br d*, $J = 7.5$ Hz, H-[illegible]); [illegible] (*td*, $J = 7.5$; 0.8 Hz, H-10); 6.85 (*br d*, $J = 7.5$ Hz, H-12); [illegible] (*ddd*, $J = 11.1$; 10.3; 4.5 Hz, H-17); 3.60 (*s*, OMe); 3.31–3.41 ([illegible]); 3.23 (*dd*, $J = 10.8$; 3.7 Hz, H-21); 2.38–2.55 (*m*); 2.23 (*dd*, J [illegible]; 2.5 Hz, H-3); 2.17 (*t*, $J = 10.3$ Hz, H-16); 1.97–2.10 (*m*, H-[illegible]); 1.73 (*t*, $J = 10.8$ Hz, H-21); 1.68 (*dq*, $J = 12.9$; 3.4 Hz, H-19); [illegible]1.54 (*m*, 2H-14, H-15, H-18, H-19, H-20). ^{13}C NMR ([illegible] MHz, $CDCl_3$) δ: 181.0 (C-2); 174.7 (C-22); 140.6 (C-13); 133.2 ([illegible]); 128.0 (C-11); 123.1^a (C-9); 122.7^a (C-10); 109.4 (C-12); 74.1 ([illegible]); 72.4 (C-17); 58.4 (C-21); 57.3 (C-16); 55.7 (C-7); 54.4 (C-5); [illegible] (OMe); 39.2 (C-20); 41.9 (C-15); 34.7 (C-14); 34.0 (C-18); 29.5 ([illegible]); 27.8 (C-19).

[illegible]*rusine B* (9). ^{1}H NMR (300 MHz, $CDCl_3 + CD_3OD$ to [illegible] solubility) δ: 8.76 (*s*, N-H); 7.42 (*br d*, $J = 7.2$ Hz, H-9); 7.30 ([illegible] $J = 7.2$ Hz, H-12); 7.11 (*td*, $J = 7.2$; 1.2 Hz, H-11); 7.05 (*td*, J [illegible]; 1.2 Hz, H-10); 5.30 (*br q*, $J = 6.7$ Hz, H-19); 4.19 (*br d*, J [illegible] Hz, H-3); 3.42–3.58 (*m*, H_2-17, H_2-21); 3.08 (*dd*, $J = 15.5$; [illegible], H-6); 2.73–2.78 (*m*, H-15); 2.82 (*br dd*, $J = 7.6$; 5.2 Hz, H-5); [illegible] (*br d*, $J = 15.5$ Hz, H-6); 2.02 (*ddd*, $J = 12.6$; 10.1; 2.2 Hz, H-[illegible]); [illegible] (*br q*, $J = 7.6$ Hz, H-16); 1.72 (*ddd*, $J = 12.6$; 3.8; 2.4 Hz, [illegible]); 1.59 (*br d*, $J = 6.7$ Hz, Me-18). ^{13}C NMR (75 MHz, [illegible]) δ: 138.0 (C-2); 136.4 (C-13), 135.6 (C-20); 127.6 (C-8); [illegible] (C-11); 119.3 (C-10); 118.0 (C-9); 116.7 (C-19); 111.0 (C-12); [illegible] (C-7); 64.9 (C-17); 55.8 (C-21); 54.4 (C-5); 50.4 (C-3); 44.2 (C-[illegible]); [illegible] (C-14); 27.6 (C-15); 27.0 (C-6); 12.7 (C-18).

[illegible] (11). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.43 (*br d*, J [illegible] Hz, H-9); 7.28 (*br d*; $J = 7.0$ Hz, H-12); 7.18 (*td*, $J = 7.0$; [illegible] Hz, H-11); 7.08 (*td*, $J = 7.0$; 1.2 Hz, H-10); 5.38 (*br q*, J [illegible] Hz, H-19); 4.22 (*dd*, $J = 10.0$; 2.4 Hz, H-3); 3.63–3.43 (*m*, H_2-[illegible], H_2-21); 3.61 (*s*, N(Me)-1); 3.07 (*dd*, $J = 15.5$; 5.2 Hz, H-6); [illegible] (*m*, H-15, H-5); 2.63 (*br d*, $J = 15.4$ Hz, H-6); 2.07 (*ddd*, J [illegible]; 10.0; 2.0 Hz, H-14); 1.79 (*qd*, $J = 6.0$; 1.2 Hz, H-16); 1.64 ([illegible] $J = 12.2$; 3.8; 2.4 Hz, H-14); 1.62 (*dt*, $J = 6.8$; 2.0 Hz, Me-18). [illegible] NMR (75 MHz, $CDCl_3$) δ: 138.8 (C-2); 137.1 (C-13); 134.5 ([illegible]); 127.0 (C-8); 120.8 (C-11); 118.7 (C-10); 117.9 (C-9); 116.8 ([illegible]); 108.5 (C-12); 103.2 (C-7); 64.2 (C-17); 55.6 (C-21); 54.5 (C-[illegible]); [illegible] (C-3); 43.8 (C-16); 32.4 (C-14); 29.0 (N(Me)-1); 28.7 (C-6); [illegible] (C-15); 12.4 (C-18).

[illegible]*orocurarine* (19). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 10.35 ([illegible] N-H); 9.31 (*s*, H-22); 7.22 (*dl*, $J = 7.7$, H-9); 7.12 (*td*, $J = 7.7$; [illegible] Hz, H-11); 6.91 (*td*, $J = 7.7$; 1.3 Hz, H-10); 6.87 (*br d*, J [illegible] Hz, H-12); 5.34 (*qt*, $J = 6.9$; 2.3 Hz, H-19); 4.03 (*dt*, $J = 3.6$; [illegible] Hz, H-3); 3.94 (*dsx*, $J = 15.7$; 2.2 Hz, H-21); 3.62–3.68 (*m*, H-[illegible]); 3.25 (*td*, $J = 12.4$; 5.4 Hz, H-5); 3.00 (*dd*, $J = 12.4$; 6.6 Hz, H-5); [illegible] $J = 15.7$ Hz, H-21); 2.50 (*ddd*, $J = 13.5$; 4.0; 2.2, H-14); 2.32 ([illegible] $J = 12.4$; 6.6 Hz, H-6); 1.75 (*ddd*, $J = 12.4$; 5.4; 1.1 Hz, H-6); [illegible] $J = 6.9$; 1.9 Hz, Me-18); 1.17–1.25 (*m*, H-14). ^{13}C NMR. ([illegible] MHz, $CDCl_3$): 188.4 (C-22); 168.8 (C-2); 142.8 (C-13); 139.4 ([illegible]); 136.9 (C-8); 127.8 (C-11); 121.9 (C-10); 120.8 (C-9); 120.6 ([illegible]); 111.1 (C-16); 110.4 (C-12); 61.7 (C-3); 58.3 (C-7); 56.7^a (C-[illegible]); [illegible]^a (C-5); 46.4 (C-6); 31.2 (C-15); 30.8 (C-14); 12.9 (C-18).

[illegible]*ydroxynorfluorocurarine* (21). ^{1}H NMR (300 MHz, [illegible]) δ: 9.13 (*s*, H-22); 6.83 (*t*, $J = 7.3$ Hz, H-10); 6.78 (*dd*, J [illegible]; 1.8 Hz, H-11); 6.72 (*dd*, $J = 7.3$; 1.8 Hz, H-9); 5.40 (*br q*, J [illegible] Hz, H-19); 4.06 (*br s*, H-3); 3.95 (*br d*, $J = 15.6$ Hz, H-21); [illegible] (*br s*, H-15); 3.33 (*td*, $J = 12.7$; 5.2 Hz, H-5); 3.04 (*br dd*, [illegible]; 6.6 Hz, H-5); 2.95 (*d*, $J = 15.6$ Hz, H-21); 2.49 (*ddd*, [illegible]; 3.6; 2.2 Hz, H-14); 2.39 (*dt*, $J = 12.7$; 6.6 Hz, H-6); 1.80 (*br* [illegible] $J = 12.7$; 5.2 Hz, H-6); 1.54 (*d*, $J = 6.8$ Hz, Me-18); 1.24 (*br d*, J [illegible] Hz, H-14).

Iboluteine (29). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.12 (*dd*, $J = 8.8$; 2.6 Hz, H-11); 7.0 (*d*, $J = 2.6$ Hz, H-9); 6.80 (*d*, $J = 8.8$, H-12); 4.34 (*s*, N(H)-1); 3.78 (*s*, OMe-11); 3.55 (*ddd*, $J = 14.3$; 13.5; 3.7 Hz, H-5); 3.53 (*br s*, H-21); 3.02 (*br d*, $J = 11.2$ Hz, H-3); 2.77 (*br dd*, $J = 14.3$; 4.8 Hz, H-5); 2.70 (*dt*, $J = 11.2$; 2.7 Hz; H-3); 2.07 (*td*, $J = 13.5$; 5.3 Hz, H-6); 1.78–1.35 (*m*, H-6, H-14, H-15, H-16, H_2-17, H_2-19, H-20); 1.18–1.08 (*m*; H-15); 0.96 (*t*, $J = 7.1$ Hz, Me-18). ^{13}C NMR (75 MHz, $CDCl_3$): 204.7 (C-7); 154.8 (C-13); 153.1 (C-10); 127.3 (C-11); 120.3 (C-8); 113.8 (C-12); 104.5 (C-9); 67.2 (C-2); 55.6 (OMe-11); 52.0 (C-3); 48.5 (C-21); 48.2 (C-5); 38.9 (C-20); 36.6 (C-16); 32.3 (C-15); 28.6 (C-17); 28.4 (C-19); 25.7 (C-14); 22.6 (C-6); 11.9 (C-18).

Ibogaine (26). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.56 (*br s*, N(H)-1); 7.10 (*d*, $J = 8.6$ Hz, H-12); 6.92 (*d*, $J = 2.4$, H-9); 6.76 (*dd*, $J = 8.6$; 2.4 Hz, H-11); 3.85 (*s*, OMe-11); 3.40–3.25 (*m*, H-5, H-6); 3.12 (*ddd*, $J = 14.9$; 12.6; 1.2 Hz, H-5); 3.06 (*dt*, $J = 9.3$; 2.0 Hz, H-3); 2.97 (*dt*, $J = 9.3$; 2.7 Hz, H-3); 2.84 (*ddd*, $J = 12.2$; 4.1; 1.6 Hz, H-16); 2.82 (*br s*, H-21); 2.64–2.54 (*m*, H-6); 2.0 (*tt*, $J = 12.2$; 2.5; H-17); 1.86–1.72 (*m*, H-14, H-15); 1.66–1.38 (*m*, H-17, H_2-19, H-20); 1.24–1.15 (*m*, H-15); 0.89 (*t*, $J = 7.2$, Me-18). ^{13}C NMR (75 MHz, $CDCl_3$): 153.8 (C-10); 143.0 (C-2); 130.0 (C-8); 110.8 (C-12); 110.5 (C-11); 108.9 (C-7); 100.4 (C-9); 57.4 (C-21); 55.9 (OMe-11); 54.2 (C-5); 49.9 (C-3); 41.9 (C-20); 41.3 (C-16); 34.1 (C-17); 32.0 (C-15); 29.7 (C-13); 27.8 (C-19); 26.4 (C-14); 20.6 (C-6); 11.9 (C-18).

16-*Decarbomethoxyvoacamine* (31). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.76 (*br s*, N(H)-1′); 7.57 (*d*, $J = 7.4$ Hz, H-9′); 7.27 (*br s*, N(H)-1); 7.10–6.95 (*m*, H-10′, H-11′, H-12′); 6.92 (*s*, H-9); 6.61 (*br s*, H-12); 5.34 (*q*, $J = 6.5$ Hz, H-19′); 5.12 (*br s*, H-3′); 4.11–3.80 (*m*, H-5′); 4.00 (*br s*, OMe-11); 3.84–3.74 (*m*, H-15′); 3.68 (*br d*, $J = 13.7$ Hz, H-21′), 3.52–3.05 (*m*, H_2-5, H-6, H_2-6′); 2.99 (*br s*, H_2-3); 2.89 (*d*, $J = 13.7$ Hz, H-21′); 2.80–2.69 (*m*, H-16, H-16′, H-21); 2.66–2.51 (*m*, H-6); 2.58 (*s*, N(Me)-4′); 2.51–2.34 (*m*, H-14′); 2.48 (*s*, CO_2Me′); 2.07–1.86 (*m*, H-17, H-14′); 1.78 (*br s*, H-14, H-15); 1.70 (*d*, $J = 6.5$ Hz, Me-18′); 1.58–1.42 (*m*, H-17, H_2-19, H-20); 1.18 (*br d*, $J = 12.4$ Hz, H-15); 0.88 (*t*, $J = 7.0$ Hz, Me-18). ^{13}C NMR (75 MHz, $CDCl_3$): 171.3 (C-22′); 150.8 (C-10); 142.3 (C-2); 138.0^a (C-2′); 137.8^a (C-20′); 135.7 (C-13′); 129.6 (C-8′); 129.2^b (C-13); 128.6^b (C-11); 128.1 (C-8); 121.4 (C-11′); 118.8 (C-10′); 118.5 (C-19′); 117.2 (C-9′); 110.2 (C-7′, C-12); 109.8 (C-12′); 108.5 (C-7); 98.6 (C-9); 59.8 (C-5′); 57.5 (C-21); 55.9 (OMe-11); 54.1 (C-5); 52.3 (C-21′), 49.3 (OMe′); 48.9 (C-3); 46.8 (C-16′); 41.8 (C-20); 41.0 (C-16); 37.5 (C-3′); 36.1 (C-14′); 33.9 (C-17); 33.5 (C-15′); 31.8 (C-15); 27.7 (C-19); 26.2 (C-14); 20.6 (C-6); 19.4 (C-6′); 11.7 (C-18); 12.2 (C-18′).

19,20-*Dihydroisositsirikine* (7). CR TLC green: R_f: 0.72 (Me_2CO–MeOH, 23:2). UV λ_{max}^{MeOH} nm (log ε): 226, 282, 291. IR ν^{CHCl_3} cm^{-1}: 3360, 2940, 1710, 1450, 1430, 1220, 1160, 1060, 1050, 750. MS: m/z (rel. int.): 356 ([M]$^+$, 100), 355 (98), 341 (8), 299 (4), 253 (55), 251 (33), 225 (29), 197 (9), 184 (16), 170 (29), 156 (2). ^{1}H NMR (300 MHz, $CDCl_3$): 8.15 (*br s*, N-H); 7.46 (*br d*, $J = 7.0$ Hz, H-9); 7.33 (*br d*, $J = 7.0$ Hz, H-12); 7.15 (*td*, $J = 7.0$; 1.3 Hz, H-11); 7.09 (*td*, $J = 7.0$; 1.3 Hz, H-10); 4.03 (*dd*, $J = 11.0$; 7.9 Hz, H-17); 3.76 (*dd*, $J = 11.0$; 5.8 Hz, H-17); 3.68 (*s*, OMe); 2.95–3.20 (*m*, H-3, H-5, H-6, H-16, H-21); 2.67–2.80 (*m*, H-6); 2.50–2.61 (*m*, H-5); 2.20 (*br d*, $J = 11.9$ Hz, H-14′); 2.00 (*t*, $J = 11.0$, H-21); 1.60–1.85 (*m*, H-15, H-19, H-20); 1.45 (*q*, $J = 11.9$ Hz, H-14); 1.10–1.30 (*m*, H-19); 0.93 (*t*, $J = 7.4$ Hz, H-18). ^{13}C NMR (75 MHz, $CDCl_3$): 174.1 (C-22); 136.2^a (C-13); 134.2^a (C-2); 127.1 (C-8); 121.3 (C-11); 119.3 (C-10); 118.0 (C-9); 111.1 (C-12); 107.5 (C-7); 61.4 (C-17); 59.8 (C-21); 59.7 (C-3); 52.7 (C-5); 51.6 (OMe); 47.4 (C-16); 39.8 (C-15); 39.1 (C-20); 31.4 (C-14); 22.9 (C-19); 21.3 (C-6); 10.6 (C-18). $^{a-c}$Interchangeable values.

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