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FURTHER ALKALOIDS FROM *STRYCHNOS LONGICAUDATA* AND *STRYCHNOS NGOUNIENSIS*

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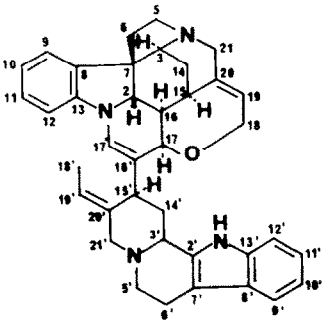
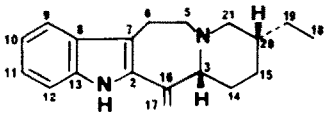
Abstract—Twenty four alkaloids have been isolated and identified from the root and stem barks of *Strychnos longicaudata* Gilg and *Strychnos ngouniensis* Pellegrin. Among these, 17 alkaloids are isolated for the first time; the novel bisindole series represented by longicaudatine includes now two other compounds: longicaudatines F and Y; besides ngouniensine, its epimer epingouniensine has been isolated along with two glucosyl-ngouniensines. Other new alkaloids include tubotaïwinal and several bases possessing the akuammicine skeleton.

As part of a chemotaxonomic study of *Strychnos* species from Zaire, we set out to study the alkaloidal composition of *S. longicaudata* Gilg and of *S. ngouniensis* Pellegr. In two separate communications, we have described longicaudatine **1**,[1] an ubiquitous base in the *Strychnos* realm, and ngouniensine **2**,[2] the first member of a hitherto unknown class of indole alkaloids. It is the purpose of this article to give a complete account of the other alkaloids of *S. longicaudata* and of *S. ngouniensis*.



1 longicaudatine



2 ngouniensine
(rel.config.)

Extractions follow the usual protocol which has been described elsewhere.[3] the two species are lianes and only the barks of the roots and of the trunk were investigated. Four extractions were carried out with the following yields (Table 1).

In all cases, complex mixtures were obtained and purifications were carried out by a combination of medium pressure liquid chromatography, thin layer chromatography and crystallization.

ALKALOIDS OF *STRYCHNOS LONGICAUDATA*

From the root bark of *S. longicaudata*, 6 alkaloids were isolated, while 11 were found in the stem bark (Table 2); 5 of them were present in both parts of the plant. For the sake of brevity, they will be described according to their structural type.

Table 1.

	Quantity investigated(g)	Weight of alkaloids(g)	Yield (g/kg)
S. longicaudata			
roots	170	3.1	18
stem	420	1.04	2.5
S. ngouniensis			
roots	230	1.6	7
stem	550	1.3	2.4

Table 2. Alkaloids of *S. longicaudata*

Dimers	MW	Occurence	Yield[a]
nor dihydrotoxiferine 3	552	root bark	3%
		stem bark	1%
bisnor C alkaloid H 4	568	root bark	1,5%
* longicaudatine 1	568	root bark	20%
		stem bark	13%
* longicaudatine Y 5	570	root bark	5%
		stem bark	2%
* longicaudatine F 6	586	root bark	6%
		stem bark	<1%
Monomers			
Wieland Gümlich aldehyde 7	310	root bark	4%
		stem bark	8%
Diaboline 8	352	stem bark	15%
* 1,2-dehydro desacetyl retuline 9	294	stem bark	2%
* N(1)-desacetyl 18-acetoxy isoretuline 11	354	stem bark	3%
N(1)-desacetyl 18-hydroxy isoretuline 12	312	stem bark	6%
* 23-hydroxy 2,16-dehydroretuline 13	352	stem bark	1%
Flavopeirerine 14	246	stem bark	<1%

a Yields refer to isolated material

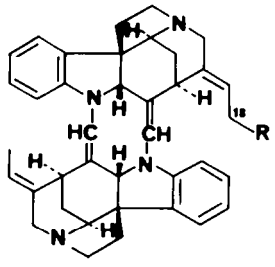
* New compounds encountered in this study

(a) *Bis-indole alkaloids*

Two types of bisindoles are found in *S. longicaudata*: the classical curare type exemplified by nordihydrotoxiferine **3**, and a novel type represented by longicaudatine **1**. Both series exhibit similar behaviour on TLC and give a blue color with ceric spray (longicaudatines are dark blue; toxiferines are purple). Their UV spectra possess maxima at the same wavelengths but with different intensities.

Nordihydrotoxiferine **3**. This alkaloid first isolated from *S. toxifera* by Karrer *et al.*[4] was later found to be a major constituent of *S. pseudoquina*[5]. It belongs to the curare type and is identified by its spectral properties.

Bis-nor C alkaloid H **4**. This alkaloid differs from **3** by 16 mass units, i.e. a primary alcohol on C-18. Although it has been confused in the past with longicaudatine,[1] all its physical properties correspond to 18-hydroxynordihydrotoxiferine **4**.



3 R=H nordihydrotoxiferine

4 R=OH bis-nor C alkaloid H

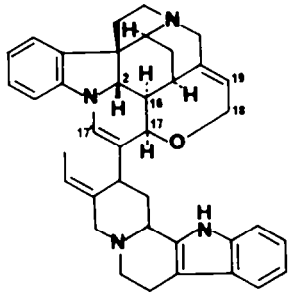
Longicaudatine **1**. It is the most abundant alkaloid of the root bark of *S. longicaudata*; its mass spectrum indicates that it is an isomer of bis nor C alkaloid H **4** ($M^{+\cdot}$ at 568.318, $C_{38}H_{40}N_4O$). The mass spectrum of longicaudatine shows two major fragments at *m/z* 250 and 318; the cluster of ions centered at 250 characterizes indoloquinolizidines bearing an unsaturated two-C side chain,[6] a feature which does not appear in the curare type alkaloids. The structure of longicaudatine was finally solved by a combination of ^{13}C NMR and of high field ^1H NMR spectroscopy.[1]

Longicaudatine Y **5**. This alkaloid possesses the same UV chromophore as longicaudatine and gives a blue color upon spraying with Ce–IV. Its mass spectrum displays a molecular ion at *m/z* 570 and fragments at *m/z* 522 ($M^{+\cdot}$-H_2O), 251, 250 and 249 (*vide supra*).

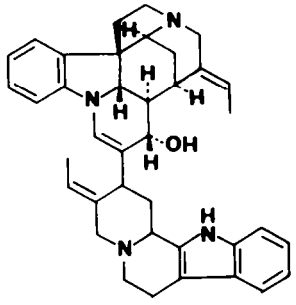
The IR spectrum shows NH or/and OH vibrations at 3480 and 3420 cm^{-1} but no CO absorptions are detectable. Structure of **5** mainly rests on the analysis of its 400 MHz ^1H NMR spectrum. Beside similarities with the spectrum of **1**, it shows signals for two ethylidene side chains; the triplet assigned to H-19 of **1** is replaced by a quartet at 5.5 ppm (J = 7 Hz), the singlet due to H-17′ appears at 6.3 ppm. Multiple irradiation experiments allow the identification of H-17 (d at 4.08 ppm, J = 10 Hz) and of H-2 (d at 3.25 ppm, J = 11 Hz); both are coupled to a multiplet situated at 1.68 ppm (H-16). These coupling constants indicate that **1** and **5** possess the same 2βH,16αH configuration; the stereochemistry of the O bound on C-17 is different.

Longicaudatine F **6**. This is the most polar of the longicaudatines and its IR, UV and MS are similar to those of **1**. The mass spectrum of **6** shows a weak molecular ion at *m/z* 586 and an intense ion at *m/z* 568 ($M^{+\cdot}$-H_2O); the usual cluster of ions centered at *m/z* 250 shows that no substitution has taken place on the indoloquinolizidine part of the molecule. Longicaudatine F displays in its ^{1}H NMR spectrum signals for a single ethylidene side-chain and for a C=CH–CH_2OH unit. As in **5**, a doublet appears at δ 4.28 ppm (J = 10 Hz), which is coupled to a high field multiplet (δ = 1.6 ppm, H-16). The signal corresponding to H-2 appears at 3 ppm in an entangled area and it is not possible to ascertain the relative stereochemistries of H-2 and of H-16; it is likely however than longicaudatine F is the 2βH,16αH isomer as for **1** and **5**. These data led us to the conclusion that longicaudatine F is 18-hydroxy-longicaudatine Y.

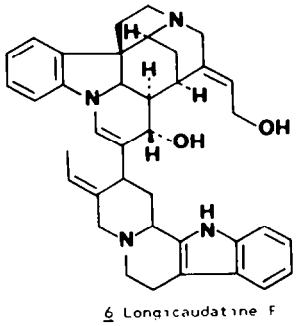
All three longicaudatines are characterized by the absence of Bohlmann bands in their IR spectra; although this has only been rigorously proved for longicaudatine **1** (^{13}C NMR), we suggest that they all possess a *cis* quinolizidine arrangement.



1 Longicaudatine



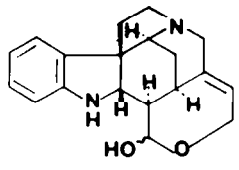
5 Longicaudatine Y



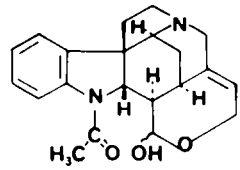
6 Longicaudatine F

(b) *Monomeric indole alkaloids*

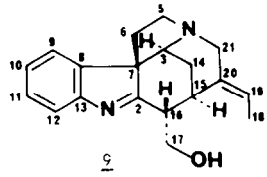
Wieland–Gümlich aldehyde **7**. Also known as caracurin VII,[7] this alkaloid is the only monomer found in the root bark *S. longicaudata*. It is recognized by its well-known mass spectrum[8] and its ^{1}H NMR spectrum shows that it exists as a hemiketal. It is accompanied in the stem bark by its N-acetyl derivative, *diaboline* **8**. Compounds **7** and **8** were identified by comparison with authentic samples.



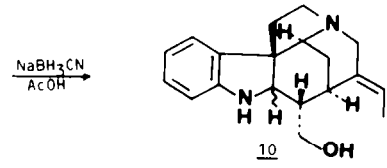
7 Wieland-Gümlich aldehyde



8 diaboline



9



10

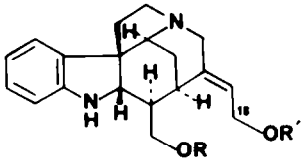
1,2-*Dehydrodesacetyl–retuline* **9**. The formula of this alkaloid is $C_{19}H_{22}N_2O$ as shown by high resolution mass spectrometry (294.1740). The main fragmentation in the MS, the loss of 31 mu suggests the presence of a primary alcohol. An indolenine chromophore is indicated by the UV. absorptions at 232 and 287 nm; $NaBH_3CN$–AcOH reduction transforms it into an indoline **10** (UV max at 214, 258 and 295 nm). The structure 1,2-dehydrodesacetyl–retuline or 1,2-dehydroakuammicinol is proposed for **9** after analysis of the 400 MHz ^{1}H NMR spectrum. In this spectrum, all the high field protons of the molecule give rise to separated resonances which were identified by extensive decoupling experiments (Table 3). The observation of a 4 Hz coupling constant between H-16 and H-15 favors a 16βH configuration.[9]

N(1)-*Desacetyl* 18-*acetoxyisoretuline* **11**. This alkaloid is a dihydroindole (UV max at 218, 246 and 300 nm); its molecular ion (*m/z* 354) corresponds to a molecular formula of $C_{21}H_{26}N_2O_3$. The presence of an acetate unit in **11** was deduced from the ^{1}H NMR spectrum (3-proton singlet at 2.03 ppm), in the IR spectrum (1730, 1230 cm^{-1}) and in the mass spectrum (losses of 43, 59, 60 and 73 mu). The 400 MHz ^{1}H NMR spectrum of **11** (Table 4) was analyzed by multiple irradiation experiments; most protons of the molecule are thus identified and these data lead to structure N(1)-desacetyl 18-acetoxyisoretuline for **11**. The isoretuline series for **11** is proposed on the basis

Table 3. 400 MHz ^{1}H NMR spectrum of **9** ($CDCl_3$)

	δ(ppm)	shape	J(Hz)		δ(ppm)	shape	J(Hz)
H-3	3.85	bs	W1/2:8	H-14	2.43	ddd	13,3,2
H-5	3.15	ddd	15,8,2	-	2.13	ddd	13,4,2
-	2.65	ddd	15,10,7	H-15	3.33	bs	W1/2=10
H-6	3.36	ddd	12,10,2	H-16	4.57	q	4
-	2.18	m	12,8,7	H-17	4.35	dd	13,4
H-9	7.56	m		-	4.00	dd	13,4
H-10				H-18	1.61	dd	7,2
H-11	7.12	m		H-19	5.37	dq	1.5,7
H-12	7.73	m		H-21	2.56	d	13
				-	1.33	bd	13

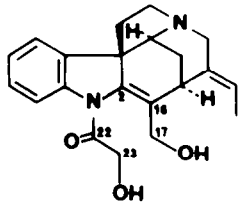
of a 10 Hz coupling constant observed between H-2 and H-16.[9] Compound **11** is an isomer of N(1) desacetyl-17-acetoxy-18-hydroxyisoretuline **11a** isolated from *S. henningsii*.[10] These two compounds proved to be different (TLC, NMR, IR) but both are hydrolyzed to Wieland–Gümlich diol **12**[11] (TLC, NMR, IR, UV, MS). Location of the acetate at C-18 in **11** causes a deshielding of the acetate bearing methylene ($\delta > 4.5$ ppm in **11**; $\delta < 4.2$ ppm in **11a**).



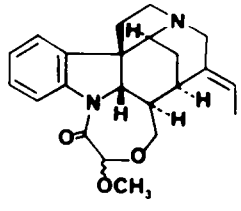
11 R=H R'=Ac
11a R=Ac R'=H
12 R=R'=H

N(1)-*Desacetyl* 18-*hydroxyisoretuline* **12**. This compound is the alcohol corresponding to acetate **11**; it is also present in *S. henningsii*.[10]

23-*Hydroxy* 2,16-*dehydroretuline* **13**. This alkaloid is an isomer of diaboline ($M^{+\cdot}$ 352, $C_{21}H_{24}N_2O_3$). The indole N in **13** is acylated as shown by the IR spectrum (1650 cm^{-1}), by the UV spectrum (λ max at 255, 283 and 292 nm) and by the ^{1}H NMR spectrum which shows a deshielded aromatic proton at 8.32 ppm. Structure **13** is proposed to account for the ^{1}H NMR spectrum (400 MHz, Table 5) which shows signals for an unsubstituted ethylidene side chain and two AB systems between 4 and 5 ppm. One of these systems is attributed to an allylic CH_2OH and the other to a hydroxyacetamide moiety. This alkaloid belongs to the tsilanine[12] family and its chromophore has previously been encountered among the alkaloids of *S. henningsii*.[13]



13



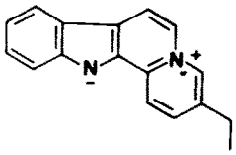
tsilanine

Table 4. Partial 400 MHz ^{1}H NMR spectrum of **11** ($CDCl_3$)

	δ(ppm)	shape	J(Hz)		δ(ppm)	shape	J(Hz)
H-2	3.35	d	10	H-12	7.05	m	
H-3	3.50	bs	-	H-15	2.8	bs	
H-5	3.17	ddd	13,10,8	H-16	1.89	m	
-	2.8	m	-	H_2-17	3.56	d	7
H-6	2.46	dt	13,8	H-18	4.70	dd	14,7
-	1.95	ddd	13,10,3	-	4.53	dd	14,7
H-9	6.63	d	7	H-19	5.56	dt	2,7
H-10	7.05	m	-	H-21	3.45	d	13
H-11	6.76	t	7	-	3.02	bd	13

Table 5. Partial 400 MHz ^{1}H NMR spectrum of **13** ($CDCl_3$)

	δ(ppm)	shape	J(Hz)		δ(ppm)	shape	J(Hz)
H-3	3.50	bs	W1/2:7	H-17	4.83	d	9
H-5	3.12	m		-	4.48	d	9
or/and H-6	2.83	m		H-18	1.63	d	7
-	2.45	m		H-19	5.62	bq	7
H-9,10,11	7.20	m		H-21	3.36	d	12
H-12	8.32	d	8	H-23	4.72	d	17
H-15	3.01	bs	W1/2 : 9	-	4.27	d	17



14 flavopeirerine

Flavopeirerine **14**. This is the most polar of the alkaloids of the stem bark of *S. longicaudata*; it is characterized by an extended UV chromophore (λ max 227, 247, 293, 343 and 390 nm). It has previously been found in *Geissospermum laeve*[14] and in *S. melinoniana*.[15]

As in all African *Strychnos* so far studied, the alkaloids of *S. longicaudata* belong to type I of the Le Men–Taylor classification.[16] Subtype α (geissoschizine), as defined by Robinson,[17] is present in flavopeirerine and in a moiety of the longicaudatine dimers. All other alkaloids belong to subtype β (strychnine) and among these seven bear an O on C-18; they all have the 16αH configuration of strychnine except for **9** where this center may be equilibrated under mild alkaline conditions.

The longicaudatine dimers are presumably formed by an aldol condensation between geissoschizal and an alkaloid of the type Iβ whose C-17 is at the oxidation level of an aldehyde. Despite the weak basicity of the aniline N, an enamine of geissoschizal may be envisaged for the C–C bond formation step. The three longicaudatines which have been isolated are the result of the condensation of geissoschizal and Wieland–Gümlich aldehyde (**1** and **6**) or of geissoschizal and desoxy Wieland–Gümlich aldehyde (**5**, Scheme I).

In the initial C–C bond formation, the configuration of the OH group dictates the final ring closure: if it is β oriented (strychnine configuration) a seventh ring is formed by elimination of water between the two alcohols at C-17 and C-18. If the configuration of the alcohol is α the ring closure is made more difficult and diol **6** is obtained.

Desoxy Wieland Gümlich aldehyde, although present in dimers **4** and **5** has not been found among the alkaloids of *S. longicaudata*.

ALKALOIDS OF *STRYCHNOS NGOUNIENSIS*

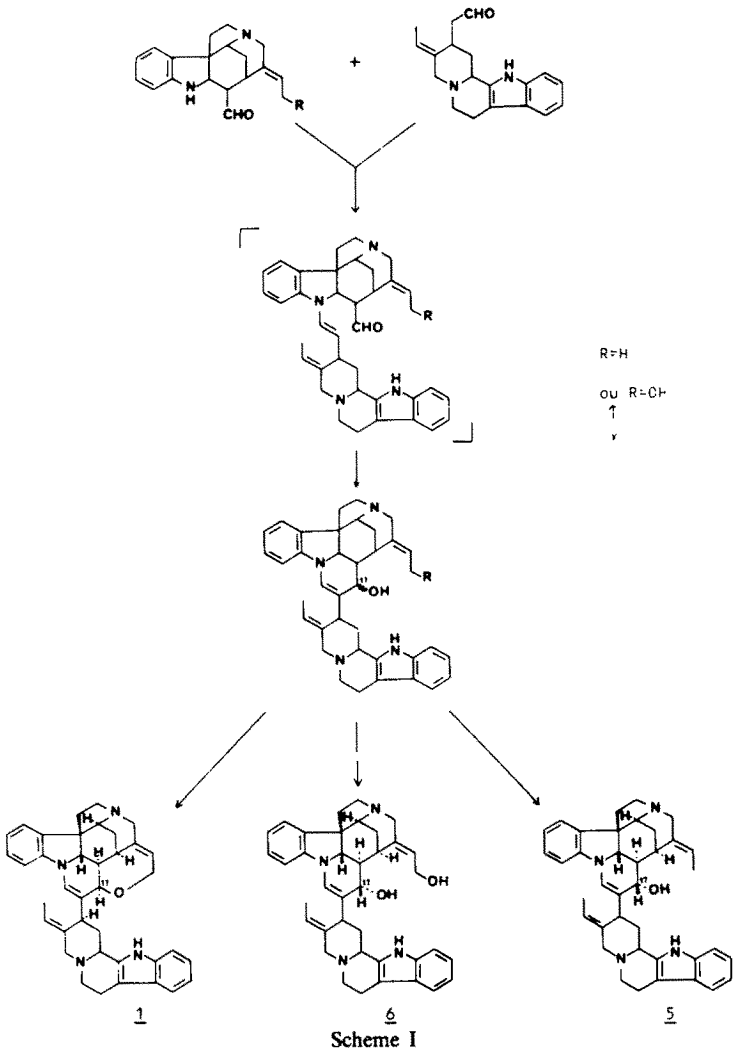
Ten alkaloids were isolated and identified in the bark of the roots of *S. ngouniensis* (Table 6); among them, the most abundant are ngouniensine **2** and congeners, **19**, **20** and **21**. In the stem bark, 11 alkaloids were identified and particularly longicaudatine **1**, the major alkaloid of *S. longicaudata*.

(a) *Dimers and quasidimers*

Longicaudatine **1**. This alkaloid is identified by its spectral properties and by comparison with an authentic sample. It is mainly present in the stem bark and no trace of the other longicaudatines are found in the plant.

4′,17-Dihydrotchibangensines **15**, **16**. These two isomeric bases show the typical mass spectrum fragmentation of the "quasidimeric" alkaloids, i.e. a molecular ion at *m/z* 436 and fragments at 265, 252, 251, 250, 185 and 171. Compounds **15** and **16** are identified to be the reduction products of tchibangensine, the major alkaloid of *S. tchibangensis*[18] (=5′,6′ dihydrousambarensine). The configuration of their C-3 and C-15 carbons rests on their high field ^{1}H NMR spectra, ^{13}C NMR spectra (Table 7) and on a partial synthesis from geissoschizine;[19] configuration of their C-17 carbons is a result of the comparison of their CD spectra with those of ochrolifuanines C and D.[20] Compounds **15** and **16** have recently been identified among the alkaloids of *Aspidosperma marcgravianum*.[21]

10′-Hydroxy 4′,17-dihydrotchibangensines **17**, **18**. These alkaloids have an indole chromophore (UV) and lack CO bands in their IR spectra. Their mass spectra show a molecular ion at *m/z* 452.256, analyzing for $C_{29}H_{32}N_4O$ with fragmentation to ions at *m/z* 252 and 201. Their ^{1}H NMR spectra (400 MHz) present close similarities to those of **15** and **16**: they are superimposable in the upfield region but only 7 protons are noted in the aromatic part. These data suggest that **17** and **18** are hydroxylated dihydrotchibangensines. The OH is located on the tetrahydrocarbazole moiety to account for the mass spectrum fragmentation and more precisely on C-10′ or C-11′ to explain the ABX pattern of the NMR spectrum of the 3 remaining aromatic protons (J = 8 Hz, J′ = 2 Hz). Final location of the OH on C-10′ is proposed in order to justify the chemical shifts of the aromatic carbons of **17** and **18** and more precisely of C-12′ (112 ppm), a C which is expected



Scheme I

Table 6. Alkaloids of *S. ngouniensis*

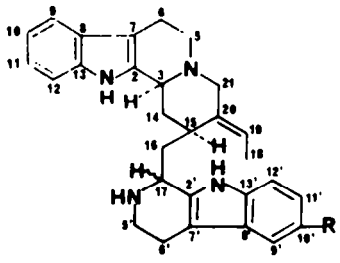
	MW	Occurence	Yield[a]
Dimers and quasidimers			
* longicaudatine 1	568	stem bark	10%
		root bark	<1%
* 4',17-dihydro 17α-tchibangensine 15	436	stem bark	<1%
* 4',17-dihydro 17β-tchibangensine 16	436	root bark	9%
		stem bark	3%
* 10'-hydroxy 4',17-dihydro 17α-tchibangensine 17	452	stem bark	8%
		root bark	8%
* 10'-hydroxy 4',17-dihydro 17β-tchibangensine 18	452	root bark	10%
		stem bark	8%
Monomers			
* ngouniensine 2	280	stem bark	15%
		root bark	24%
* epi-ngouniensine 19	280	stem bark	3%
		root bark	3%
* glucosylngouniensine 20	458	root bark	2%
* epi-glucosylngouniensine 21	458	root bark	0.5%
nor fluorocurarine 22	292	stem bark	1.5%
* 18-hydroxy nor fluorocurarine 23	308	stem bark	1%
* 18-acetoxy nor fluorocurarine 24	350	stem bark	0.5%
* tubotaiwinal 25	294	stem bark	7%
		root bark	14%

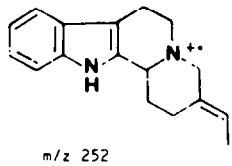
a Yields refer to isolated material

to be found below 100 ppm when an OH is located on C-11'.

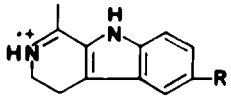
(b) *The monomers*

Ngouniensine **2**, *epi-ngouniensine* **19**. Ngouniensine





m/z 252



m/z 201 R=OH

m/z 185 R=H

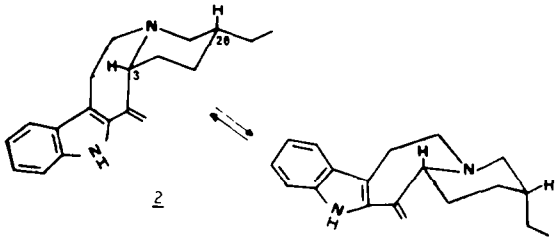
15	R=H	17αH
16	R=H	17βH
17	R=OH	17αH
18	R=OH	17βH

Table 7. ^{13}C NMR spectra of **15**, **16**, **17** and **18**

	15 ($CDCl_3$)	17 (CD_3OD)	16 ($CDCl_3$)	18 (CD_3OD)
2	136.0[b]	138.9[b]	135.6[b]	138.1[b]
3	53.3	53.4	53.3	55.3
5	51.3	52.6	51.0	52.3
6	18.3	19.1	17.9	20.7
7	108.2[c]	109.1[c]	108.1[c]	109.1[c]
8	127.4	129.9[d]	127.9[d]	130.0[d]
9	117.8[a]	119.3[a]	118.0[a]	119.3[a]
10	121,4[a]	123.9[a]	121.8[a]	123.8[a]
11	119.2[a]	120.6[a]	119.8[a]	120.5[a]
12	111.3	112.5	111.2	112.4[e]
13	136.5[b]	138.4[b]	137.5[b]	138.1[b]
14	33.3	35.3	29.3	33.0
15	30.9	33.0	29.8	31.7
16	37.8	39.4	37.5	40.3
17	51.3	52.6	49.7	52.3
18	13.0	14.1	12.6	14.0
19	121.4[a]	122.9[a]	119.8[a]	122.5[a]
20	134.5[b]	133.1[b]	135.0[b]	132.9[b]
21	54.0	55.1	53.3	56.5
2'	137.5[b]	138.2[b]	135.4[b]	139.3[b]
5'	42.1	43.7	41.2	44.0
6'	22.4	23.7	22.5	23.9
7'	106.9[c]	108.2[c]	107.5[c]	108.7[c]
8'	127.4	129.1[d]	127.1[c]	129.4[d]
9'	117.8	112.8	117.8	112.4[e]
10'	121.4[a]	151.7	121.8[a]	151.9
11'	119.2[a]	113.0	119.8	113.1[e]
12'	111.3	112.8	111.2	112.9[e]
13'	136.1[b]	135,0[b]	135.8[b]	135.3[b]

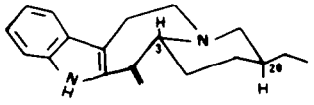
a,b,c... values within the same column may be interchanged.

is the most unusual base of *S. ngouniensis* since it is the first alkaloid containing a C-16 to C-3 bond.[2] After the structure of **2** was elucidated, another alkaloid **19** was found possessing properties similar to those of **2**: its mass spectrum is superimposable on the mass spectrum of ngouniensine except for some intensities; its UV spectrum shows maxima at 227 and 305, with a shoulder at 223 nm. The two singlets attributed to the exomethylene protons appear in the ^{1}H NMR spectrum at 5.35 and 5.5 ppm but the congested high field region does not lend itself to analysis. Integrity of the ngouniensine skeleton in **19** is demonstrated by the ^{13}C NMR spectrum in which all the carbons are found at expected δ values with the expected multiplicities (Table 8). The discrepancies between some chemical shifts of **2** and **19** reflect configurational as well as conformational differences. Ngouniensine is the *cis* isomer (3βH, 20βH, relative configuration), which exists in an equilibrium between two chair forms. Epingouniensine is the *trans* isomer, which is rigidly locked in a single chair conformation. In **19**, the substituents bound on C-20 and C-3 are equatorial and they neither create nor are prone to γ-shielding effects. The absolute configurations of **2** and **19** have not yet been determined.



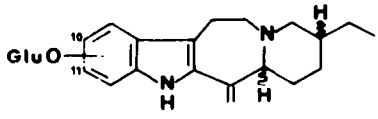
2

2

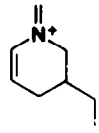


19

Glucosylngouniensines **20, 21**. The most polar alkaloids of *S. ngouniensis* (eluted with MeOH) are water-soluble compounds which possess UV spectra similar to those of **2** and **19**. Mass spectra of **20** and **21** show molecular ions at *m/z* 458 and fragments at 296, 295, 281 and 124. The peak at *m/z* 124, also present in ngouniensine, corresponds to the fragmentation of the piperidine D ring. The ion at *m/z* 296 is due to the loss of a sugar residue (M-162, $C_6H_{10}O_5$); further loss of a Me residue yields a peak at *m/z* 281. All the protons of the C and D rings of ngouniensine are observable on the 400 MHz ^{1}H NMR spectrum of **20**, and among these the exomethylene protons appear at 5.27 and 5.52 ppm. Between 3 and 4 ppm, there appear several protons with the characteristic lineshapes of a glucose residue and at 4.9 ppm a doublet (J = 9 Hz) is assigned to the anomeric proton. Location of the sugar residue at C-10 or C-11 is proposed to explain the ABX pattern, which is observed for the remaining three aromatic protons of **20** (J = 7 Hz, J′ = 2 Hz). Compound **21** is an isomer of **20** and paucity of material has not allowed any more accurate determination.



20, 21



m/z 124

Norfluorocurarine **22**. This alkaloid possesses a characteristic UV spectrum (λmax at 230, 292, 302, 365 nm) and a well known mass spectrum.[22] It is accompanied in *S. ngouniensis* by three alkaloids possessing the same UV chromophore. All three are vinylogous amides as shown by their IR spectra (1645, 1610, 1590, 1560 cm^{-1}) and by their ^{1}H NMR

Table 8. ^{13}C NMR spectra of **2** and of **19**

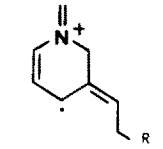
	Ngouniensine 2	Epi-Ngouniensine 19		Ngouniensine 2	Epi-Ngouniensine 19
C-2	142.2	143.2	C-13	135.7	135.7
C-3	62.3	67.8	C-14	27.8[b]	31.0[a]
C-5	56.4[a]	55.8	C-15	26.0[b]	27.1[a]
C-6	22.5	22.2	C-16	135.7	135.7
C-7	115.2	114.3	C-17	112.1	112.0
C-8	128.9	128.8	C-18	11.7	11.3
C-9	118.7	118.5	C-19	29.1	32.7
C-10	122.5	122.3	C-20	37.7	38.1
C-11	119.4	119.3	C-21	55.2[a]	61.8
C-12	110.7	110.7			

a,b these assignments could be interchanged

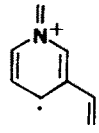
spectra (CHO at 9.3 ppm; NH at 10.3 ppm). They are:

(a) 18-*Hydroxynorfluorocurarine* **23**

Compound **23** is a hydroxylated analogue of norfluorocurarine **22**. The O is located at C-18 as seen from the absence of a Me doublet in the ^{1}H NMR spectrum; H-19 is a triplet at 5.5 ppm and the 18-CH_2 resonates as a doublet at 4.2 ppm. As a consequence of this substitution the ions corresponding to the piperidine ring are shifted from *m/z* 121 to *m/z* 119 and 137.



R=H m/z 121
R=OH m/z 137
R=OAc m/z 169



m/z 119

(b) 18-*Acetoxynorfluorocurarine* **24**

An acetate unit is detected in **24** in its IR spectrum (1735, 1230 cm^{-1}) and in its ^{1}H NMR spectrum (3-proton singlet at 2.0 ppm).

Mild alkaline hydrolysis of **24** yields **23**, which allows one to propose the structure 18-acetoxy-norfluorocurarine for **24**.

(c) *Tubotaïwinal* **25**

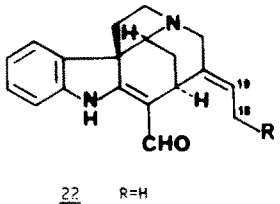
The molecular weight of this alkaloid has been determined by high resolution mass spectroscopy (*m/z*: 294.1723, $C_{19}H_{22}N_2O$); it corresponds to a 19,20-dihydronorfluorocurarine **26**. This structure is partly supported by the ^{13}C NMR spectrum, which shows at high field signals for 3CH, $5CH_2$ and $1CH_3$.

The observation of the aminomethylene carbons, however, is better explained by a tubotaïwine-type structure (Table 9 54.5 and 44.8 ppm). The presence of the Et chain in the C ring causes a deshielding of C-21 and C-15 and a shielding of C-3 and C-14. Comparison of the ^{13}C spectra of **25** and of tubotaïwine[23] indicates that **25** belongs to the tubotaïwine series and not to the dihydro-condylocarpine series.

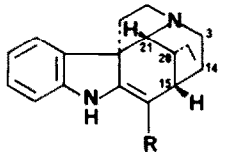
CONCLUSION

Unlike *S. longicaudata*, *S. ngouniensis* does not contain any toxiferine-like dimers; it contains however the two other types of bisindoles found in the *Strychnos* species: longicaudatine and usambarensine. As far as monomers are concerned, *S. ngouniensis* seems to have a propensity to manufacture type I alkaloids possessing an aldehyde function at C-17; these aldehydes belong to the akuammicine or condylocarpine series. Remarkably, *S. ngouniensis* is the source of the novel ngouniensine-type alkaloids, i.e. indoles in which the C-16 atom has slipped from C-15 to C-3.

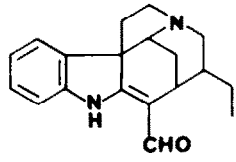
The study of the alkaloidal content of *S. longicaudata* and of *S. ngouniensis* has allowed the iso-



22 R=H
23 R=OH
24 R=OAc



tubotaïwine R=CO_2Me
25 tubotaïwinal R=CHO



26

Table 9. ^{13}C NMR spectra of tubotaïwine and tubotaïwinal **25**

	25	Tubotaïwine		25	Tubotaïwine
C-2	172.1	170.3	C-13	143.1	143.6
C-3	44.8	43.6	C-14	29.8	28.5
C-5	54.5	53.7	C-15	32.1	30.6
C-6	44.1	45.2	C-16	106.5	95.7
C-7	55.9	54.8	C-17	190.1	168.8
C-8	137.4	136.7	C-18	11.1	11.6
C-9	122.3	121.2	C-19	23.7	23.6
C-10	120.0	119.6	C-20	41.3	40.9
C-11	127.6	127.4	C-21	66.3	65.5
C-12	110.7	109.8	OCH_3		51.2

lation of 24 different alkaloids, among which 17 had not been encountered before. As a consequence of this work, a third type of *Strychnos* dimer and a novel type of monomer have been added to the list of natural indole alkaloids. It is hoped that this may contribute to the chemotaxonomic classification of the *Strychnos* species. The discovery of new materials, whose biological properties are being investigated, creates a challenge for synthetic organic chemists.

EXPERIMENTAL

General. Plant material was collected by one of us (C.D.) in Zaire and identified by H. Breyne. A herbarium specimen is deposited in the Brussels National Gardens under Nos HB 3435 (*S. ngouniensis*), HB 3824 (*S. longicaudata*).

M.ps are uncorrected. Rotations were determined on a Perkin–Elmer 141 automatic polarimeter. ^{1}H NMR were measured at 60 MHz with a Bruker WP60 spectrometer or at 400 MHz with a prototype built at the Institut d'Electronique Fondamentale, Université de Paris Sud, Orsay. ^{13}C NMR were obtained at 15 MHz on a Bruker WP60 or at 22 MHz on a JEOLCO FX90Q. TMS is the internal standard. Chromatographic columns were packed with Merck H60 Sigel. Prep. TLC plates were Merck 60F-254. Colour reactions (CR) were obtained by spraying plates with a solution of Ce(IV)$(NH_4)_2SO_4$.

Typical extraction procedure. S. ngouniensis root bark. Finely ground root bark (230 g) is wetted with 140 ml of conc NH_4OH half diluted in water and lixiviated overnight by means of 16 l of EtOAc. Completeness of the extraction is verified by the Valser Mayer test. The organic soln was extracted by 2% H_2SO_4aq; the acid layer was separated, alkalinized with NH_4OH and extracted by $CHCl_3$. The $CHCl_3$ soln was washed with water, dried over Na_2SO_4 and evaporated *in vacuo*; one obtains 1.6 g of crude alkaloid mixture (A.M.), yield is 7 g/kg.

Separation of the alkaloids. A preliminary separation was obtained by medium pressure liquid chromatography (Jobin–Yvon chromatospac-10 bar). Fractions are further purified by prep. TLC or crystallization. Table 10(a)–(d) sums up these operations.

New alkaloids. Longicaudatine **1** (CR blue m.p. > 350° (dec.); $(\alpha)_D = +141°$ ($c = 0.5$; $CHCl_3$); UV λ_{max}^{EtOH} 223 (log ϵ 4.66), 270 (sh), 284 (4.28), 290 (4.26), 307 (sh, 3.97) nm; $\lambda_{max}^{EtOH+HClO_4}$: 223, 268, 280, 290, 300 (sh); IR ($CHCl_3$) cm^{-1}: 3420, 2900, 1630, 1600, 1480, 740; MS *m/z* (rel. int.): 568 (100), 552 (10), 539 (10), 398 (10), 318 (5), 284 (M^{++}, 10), 251 (25), 250 (60), 249 (50), 235 (10), 171 (20), 144 (15); for ^{1}H and ^{13}C NMR see Ref. 1.

Longicaudatine Y **5** (CR blue); amorphous; $(\alpha)_D = +328°$ ($c = 0.4$; MeOH); UV λ_{max}^{MeOH}: 226, 285, 290 (s); IR (KBr) cm^{-1}: 3480, 3420, 3150, 3050, 2800, 2750, 1630, 1600, 1475, 1450; MS *m/z* (rel. int.): 570 (M^+, 1), 552 (6), 320 (85), 302 (90), 251, 250, 249, 235; ^{1}H NMR (400 MHz, $CDCl_3$): 7.8 (s, NH), 7.4 (d, 7 Hz, 1H), 7.25 (d, 7 Hz, 1H), 7.05 (m, 4H), 6.71 (t, 7 Hz, 1H), 6.53 (d, 7 Hz, 1H), 6.3 (s, H-17′), 5.56 (q, 7 Hz, H-19′), 5.5 (q, 7 Hz, H-19), 4.08 (d, 10 Hz, H-17), 3.78 (d, 14 Hz, H-21′), 3.75 (dd; 10, 4 Hz, 1H), 3.68 (dd, 11, 4 Hz, 1H), 3.60 (d, 15 Hz, H-21), 3.58 (bs, 1H, H-3 or H-3′), 3.30 (d, 14 Hz, H-21′), 3.25 (d, 11 Hz, H-2), 3.10 (bs, 1H, H-15′), 1.74 (d, 7 Hz, CH_3-18), 1.68 (m, 1H, H-16), 1.65 (d, 7 Hz, CH_3-18′).

Longicaudatine F **6** (CR blue); amorphous; $(\alpha)_D = +268°$ ($c = 0.6$; MeOH); UV λ_{max}^{MeOH}: 223, 283, 290, 310 (sh); IR ($CHCl_3$): 3300, 3050, 1630, 1605, 1480, 1460 cm^{-1}; MS *m/z* (rel. int.): 586 (2), 568 (80), 552, 551, 550, 318 (10), 251, 250 (100), 249 (95); ^{1}H NMR (400 MHz, $CDCl_3$): 8.8 (s, NH), 7.4 (d, 7 Hz, 1H), 7.3 (d, 7 Hz, 1H), 7.05 (m, 4H), 6.8 (t, 7Hz, 1H), 6.5 (d, 7 Hz,), 6.2 (s, 1H, H-17) 5.86 (t, 6 Hz, H-19), 5.62 (q, 7 Hz, H-19), 4.35 (dd, 11, 8 Hz, H-18), 4.28 (d, 10 Hz, H-17), 3.9 (m, H-18), 1.63 (d, 7 Hz, CH_3-18′).

1,2-*Dehydrodesacetylretuline* **9** (CR yellow); $(\alpha)_D = +127°$ ($c = 0.67$; $CHCl_3$); UV λ_{max}^{EtOH} 232, 287; IR ($CHCl_3$) cm^{-1}: 3380 (br sh), 1640, 1610, 1450; MS *m/z* (rel. int.): 294 ($M^{+\cdot}$ 80), 279 (5), 277 (2), 264 (35), 263 (100), 239 (180); high resolutions MS tr *m/z* 294, 1740 ($C_{19}H_{22}N_2O$; Calc. 294.1730), 263, 1567 ($C_{18}H_{19}N_2$; Calc. 263.159); ^{1}H NMR: see text.

N(1)*Desacetyl*-18-*acetoxyisoretuline* **11** (CR orange: then grey-purple); $(\alpha)_D = -31°$ ($c = 0.55$; $CHCl_3$); UV λ_{max}^{EtOH} 218, 246, 300 nm; IR ($CHCl_3$) cm^{-1}: 3380, 1730, 1605, 1480, 1460, 1230; MS *m/z* (rel. int.): 354 ($M^{+\cdot}$ 85), 337 (10), 323 (5), 311 (10), 309 (10), 295 (50), 294 (60), 281, 263, 224 (95), 164, 144 (100), 143, 134, 130; ^{1}H NMR: see text.

N(1)*Desacetyl*-18-*hydroxyisoretuline* **12** (CR orange); $(\alpha)_D = -25°$ ($c = 0.3$; MeOH); UV λ_{max}^{EtOH}: 215, 247, 298 nm; IR ($CHCl_3$) cm^{-1}: 3340, 1610, 1490, 1470, 1050, 990; MS *m/z* (rel. int.): 312 ($M^{+\cdot}$ 30), 294 (40), 281, 267, 251, 249, 182 (100), 180, 144 (70), 143, 131, 130.

23-*Hydroxy*-2,16-*dehydroretuline* **13** (CR colorless); UV λ_{max}^{EtOH}: 218, 255, 283, 293 nm; IR ($CHCl_3$) cm^{-1}: 3380, 1660, 1650, 1600, 1485, 1460, 1400, 1060; MS *m/z* (rel. int.) 352 (50), 337, 326, 323, 309 (40), 295, 279, 202, 167, 164.

4′,17-*Dihydro*-17α-*tchibangensine* **15** (CR yellow); $(\alpha)_D = -11°$ ($c = 1$; EtOH); UV λ_{max}^{EtOH} (log ϵ): 226 (4.73), 283 (4.16), 290 (4.1); IR ($CHCl_3$) cm^{-1}: 3480, 3260–3200, 1460, 1450; MS *m/z* (rel. int.), 436 (8), 306 (2), 252 (50), 251,. 250, 249 (30), 235, 223, 185 (100), 171, 144, 130; ^{1}H NMR (60 MHz, $CDCl_3$): 7.8 (s, NH), 5.5 (dq, 2, 7 Hz), 4.2 (bs), 1.6 (dd, 3H, 7, 2 Hz).

4′,17-*Dihydro*-17β-*tchibangensine* **16** (CR yellow); $(\alpha)_D = +40°$ ($c = 0.5$; EtOH); UV λ_{max}^{EtOH} (log ϵ): 226 (4.78), 284 (4.18), 291 (4.11); IR ($CHCl_3$) cm^{-1}: 3420, 3200, 3060, 2750, 1460, 1450; MS *m/z* (rel. int.): 436 (10), 265, 252 (50), 251, 249, 235, 223, 185 (100), 171, 144; ^{1}H NMR (400 MHz, $CDCl_3$): 8.05 (NH), 7.6 (d, 7 Hz), 7.4 (dd, 7, 2 Hz), 7.3 (m, 2H), 7.04 (m, 3H), 6.82 (NH), 6.78 (dd, 7, 2 Hz), 5.4 (bq, 7 Hz), 4.36 (bs, W1/2 = 10 Hz, H-3), 4.18 (d, 12 Hz, H-17),

Table 10(a). Separation of the alkaloids of *S. longicaudata*—roots. The alkaloid mixture (4.8 g) was fractionated under gravity on an alumina column (150 g). 20 fractions were collected (vol: 120 ml), which are further purified by crystallization and prep. TLC

fractions	eluent	weight(mg)	alkaloids isolated
2	$CHCl_3$	1 500	1, 3
3	"	340	1
4	"	140	1, 5, 6
5-6	"	80	5, 7
7	"	20	7
8-12	$CHCl_3$-MeOH:49-1	100	4, 7
13	"	370	6, 7
14	"	670	4, 6, 7
15-20	"	600	6, 7

Table 10(b). Stem bark. A.M. (1.04 g) is chromatographed on 200 g Sigel; fractions (25 ml) are pooled after TLC

fractions	eluent	mg	alkaloids isolated
110 - 135	$CHCl_3$-MeOH 99-1	180	2
184 - 219	" 49-1	13	19
220 - 240	" "	13	19, 24
295 - 327	" 19-1	23	22
328 - 414	" "	130	25
496 - 585	" 9-1	160	1
604 - 618	" 4-1	42	16
696 - 760	MeOH	170	15, 17, 18

Table 10(c). Stem bark. Separation of the alkaloids of *S. ngouniensis*

fractions	eluent	mg	alkaloids isolated
325 - 390	$CHCl_3$ - MeOH 19-1	90	3, 9, 11, 13
410 - 422	" 9-1	70	1
423 - 493	" "	250	1, 8
494 - 541	" 4-1	60	1, 5, 7, 8, 14
542 - 565	" "	60	7
566 - 582	" "	50	6, 7
583 - 645	" 1-1	80	6, 12

Table 10(d). Root bark. A.M. (1.6 g) is chromatographed in 200 g Sigel

fractions	eluent	mg	alkaloids isolated
114 - 141	$CHCl_3$-MeOH 99-1	360	2
164 - 222	" "	55	19
260 - 383	" 49-1	260	25
525 - 575	" 3-1	130	1, 16
576 - 640	" "	220	16, 17, 18
640 - 700	MeOH	200	18, 20, 21

3.65 (d, 13 Hz, H-21), 2.94 (d, 13 Hz, H-21), 1.68 (t, 13 Hz), 1.6 (dd, 7, 2 Hz, CH_3-18), 1.16 (t, 12 Hz); ^{13}C NMR: see text.

10′-Hydroxy-4′,17-dihydro-17α-tchibangensine **17** (CR grey yellow); $(\alpha)_D = 0°$ ($c = 0.5$; EtOH); UV λ_{max}^{MeOH} ($\log \epsilon$): 227 (4.58), 284 (4.1), 292 (4.02); IR (KBr) cm^{-1}: 3420, 3300, 2910, 1620, 1590; MS *m/z* (rel. int.): 452 (5), 252 (80), 251 (55), 250 (50), 249 (80), 248, 247 (50), 201 (100), 187, 171, 144; high resolution MS: 452.2561 ($C_{29}H_{32}N_4O$ Calc: 452.255), 201.1024 ($C_{12}H_{13}N_2O$ Calc: 201.1028), 200.0946 ($C_{12}H_{12}N_2O$ Calc: 200.0939); ^1H NMR (400 MHz, $CDCl_3$–CD_3OD: 4–1): 7.28 (d, 7 Hz), 7.11 (d, 7 Hz), 6.89 (m, 2H), 6.72 (d, 8 Hz), 6.58 (d, 2 Hz), 6.42 (dd, 8, 2 Hz), 5.35 (q, 7 Hz), 4.08 (bt, 5 Hz), 3.55 (bd, 10 Hz), 1.30 (d, 7 Hz, 3H).

10′-Hydroxy-4′,17-dihydro-17β-tchibangensine **18** (CR yellow); $(\alpha)_D = +47°$ ($c = 0.5$; EtOH); UV λ_{max}^{MeOH} ($\log \epsilon$) nm: 225 (4.36), 282 (3.84), 291 (3.75); IR ($CHCl_3$) cm^{-1}: 3420, 2910, 1620, 1590; MS *m/z* (rel. int.): 452 ($M^{+\cdot}$ 10), 265, 252 (60), 251, 250, 249, 201 (100), 187, 171, 144; ^1H NMR (400 MHz, $CDCl_3$–CD_3OD:20–1): 7.51 (d, 7 Hz), 7.28 (d, 7 Hz), 7.16 (m, 2H), 6.74 (d, 2 Hz), 6.62 (d, 8 Hz), 6.57 (dd, 8, 2 Hz), 5.36 (q, 7 Hz), 4.22 (bt, 5 Hz), 4.13 (bd, 11 Hz), 3.63 (bd, 13 Hz), 2.92 (d, 13 Hz), 1.72 (t, 11 Hz), 1.57 (d, 3H, 7 Hz), 1.18 (t, 10 Hz).

Ngouniensine **2** (CR yellow); $(\alpha)_D = -44°$ ($c = 1$; $CHCl_3$), $-89°$ ($c = 0$, 7; MeOH); UV λ_{max}^{MeOH} ($\log \epsilon$)nm: 220 (4.17), 230 (4.18), 307 (4.13); IR ($CHCl_3$) cm^{-1}: 3420, 3290, 1630, 1610, 1460, 1320, 1210; MS *m/z* (rel. int.): 280 ($M^{+\cdot}$ 100), 279 (30), 265 (25), 251 (25), 168 (45), 135 (35), 124 (80), 122 (30); for ^1H and ^{13}C NMR see Ref 2.

Epi-ngouniensine **19** (CR yellow); $(\alpha)_D = -32°$ ($c = 0.5$; MeOH); UV λ_{max}^{MeOH} ($\log \epsilon$) nm: 223 (sh,), 228 (4.17), 305 (4.08); IR ($CHCl_3$) cm^{-1}: 3240, 1620, 1450, 1320, 1230, 1210; MS *m/z* (rel. int.): 280 ($M^{+\cdot}$ 100), 279 (30), 265 (25), 251 (20), 169 (30), 168 (60), 135 (60), 124 (80), 122 (35); ^1H NMR (60 MHz, $CDCl_3$): 8.1 (s, NH), 5.5 (bs, 1H), 5.35 (s, 1H), 2.4 (t, 15 Hz), 0.85 (m, 3H); ^{13}C NMR see text.

Glucosyl ngouniensine **20** (CR yellow); $(\alpha)_D = -107°$ ($c = 0.26$; MeOH); UV λ_{max}^{MeOH} ($\log \epsilon$) nm: 217 (4.29), 242 (4.21), 302 (4.18); IR (KBr) cm^{-1}: 3400, 1610, 1580, 1500, 1070, 1030; MS *m/z* (rel. int.): 458 ($M^{+\cdot}$ 20), 296 (100), 295 (60), 281 (35), 267, 184, 124 (90), 122 (10); ^1H NMR (400 MHz, CD_3OD–$CDCl_3$: 1–1): 6.83 (m, 2H), 6.49 (d, 7 Hz), 5.52 (s), 5.27 (s), 4.50 (d, 10 Hz), 3.81 (bt, 5 Hz), 3.75 (dd, 12, 2 Hz), 3.63 (dd, 12, 4 Hz), 3.47 (t, 8 Hz), 0.80 (t, 7 Hz, 3H).

Glucosyl epingouniensine **21** (CR yellow); $(\alpha)_D = -80°$ ($c = 0.29$; MeOH); UV λ_{max}^{MeOH} ($\log \epsilon$) nm: 223 (4.25), 307 (4.13); IR (KBr) cm^{-1}: 3400, 1620, 1450, 1190, 1070, 1030; MS *m/z* (rel. int.): 458 ($M^{+\cdot}$ 10), 296 (100), 295 (40), 281 (75), 124 (70); ^1H NMR (400 MHz, CD_3OD): 7.0 (m, 2H), 6.8 (d, 7 Hz), 5.55 (bs), 5.26 (bs), 4.66 (d, 8 Hz), 3.78 (bt, 5 Hz), 0.75 (t, 7 Hz, 3H).

18-*Hydroxynorfluorocurarine* **23** (CR: grey then red); $(\alpha)_D = -280°$ ($c = 0.3$; MeOH); UV λ_{max}^{MeOH} nm: 228, 280, 292, 365; IR ($CHCl_3$) cm^{-1}: 3300, 1650, 1610, 1580, 1550, 1450, 1370; MS *m/z* (rel. int.): 308 ($M^{+\cdot}$ 40), 290 (20), 277 (20), 247, 234, 180, 156, 137 (100), 119 (30); ^1H NMR (60 MHz, $CDCl_3$): 10.25 (s, NH), 9.3 (s, H-17), 5.3 (t, 7 Hz), 4.2 (d, 2H).

18-*Acetoxynorfluorocurarine* **24** (CR: blue green); UV λ_{max}^{MeOH} nm: 213, 245, 290, 302, 365; IR ($CHCl_3$) cm^{-1}: 3300, 1735, 1640, 1610, 1590, 1560, 1460, 1230; MS *m/z* (rel. int.): 350 ($M^{+\cdot}$ 60), 307, 290 (50), 277, 261, 247, 234 (40), 179, 171, 168, 119 (100); ^1H NMR (60 MHz, $CDCl_3$): 10.25 (s, NH), 9.3 (s, H-17), 5.4 (t, 7 Hz), 4.6 (m, 2H), 2.05 (s, 3H).

(+)*Tubotaïwinal* **25** (CR: yellow then purple); $(\alpha)_D$: $+894°$ ($c = 1.17$; $CHCl_3$); $(\alpha)_D = +613°$ ($c = 1.2$; MeOH); UV λ_{max}^{MeOH} ($\log \epsilon$) nm: 210 (4.0), 245 (3.89), 254 (3.85), 300 (3.55), 368 (4.14); IR ($CHCl_3$) cm^{-1}: 3300, 2730, 1645, 1610, 1590, 1560, 1460, 1200, 1165, 1120, 1110; MS *m/z* (rel. int.): 294 (20), 279, 265, 237, 211, 210, 182, 168, 95 (90), 71 (100); high resolution MS: 294.1723 ($C_{19}H_{22}N_2O$: Calc 294.1716); 237.1141 ($C_{16}H_{15}NO$: Calc 237.1130); ^1H NMR (60 MHz, $CDCl_3$): 10.2 (s, NH), 9.2 (s, H-17), 3.9 (bs, 1H), 0.7 (bs, 5H).

Saponification of **11** (**11**→**12**) (*typical procedure*). Acetate **11** (10 mg) was dissolved in 2 ml MeOH and 0.5 ml 2N NaOH in H_2O was added. The mixture was refluxed during 2hr, then poured into 50 ml H_2O. Extraction with $CHCl_3$ (3 × 10 ml), drying of the organic layer (Na_2SO_4), filtration and evaporation yielded 6 mg of a gum showing one spot on TLC. This compound was identical in all respects to Wieland–Gümlich diol **12** (TLC, IR, UV, MS, NMR).

Reduction of indolenine **9** (**9**→**10**). Indolenine **9** (4 mg) was dissolved in 0.5 ml AcOH and 10 mg $NaBH_3CN$ was added in small portions over 1 hr. After 4 hr stirring at room temp, the AcOH was neutralized with NaOH aq and the suspension was extracted with $CHCl_3$ (3 × 5 ml). The organic layer was washed with brine, dried over Na_2SO_4 and evaporated, providing 2 mg of a more polar compound. UV: λmax (MeOH): 214, 258, 295 nm; IR ($CHCl_3$): 3400, 1610 cm^{-1}; MS *m/z* (rel. int.): 296 (30), 281, 279, 265 (100), 144, 135, 130, 122, 107.

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